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Synthesis, characterization and reactions of complexes containing new ligands with carbon-phosphorus multiple bonds

Wayde Vincent Konze

Iowa State University

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Synthesis, characterization and reactions of complexes containing new ligands with carbon-phosphorus multiple bonds

by

Wayde Vincent Konze

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry
Major Professor: Robert J. Angelici

Iowa State University
Ames, Iowa
1997
This is to certify that the Doctoral dissertation of

Wayde Vincent Konze

has met the thesis requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

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For the Graduate College
To my family, who have given me love, life and the comfort of a milestone from which I may always know how far I have come and how far there is yet to go:

Rebecca Ann, Nicolette Amber and
Joseph Allen Konze
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ABBREVIATIONS

Mes*, 2,4,6-tri-tert-butylbenzene
Mes, 2,4,6-tri-methylbenzene
xyl, 2,6-dimethylbenzene
COD, 1,5-cyclooctadiene
Cp, \( \eta^1 \)-C\(_5\)H\(_5\) ligand
Cp*, \( \eta^5 \)-C\(_5\)Me\(_5\) ligand
Me, -CH\(_3\) group
Et, -CH\(_2\)CH\(_3\)
i-Pr, -CH(CH\(_3\))\(_2\)
t-Bu, -C(CH\(_3\))\(_3\)
Ph, -C\(_6\)H\(_5\) group
Cy, -C\(_6\)H\(_11\) group
Bn, -CH\(_2\)Ph
dppm, Ph\(_2\)PCH\(_2\)PPh\(_2\)
dppe, Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\)
dba, dibenzylideneacetone
GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains three papers in the format required for journal publication, describing the research I performed at Iowa State University. Preceding these papers is a literature review of π-complexation of carbon-phosphorus double and triple bonds. In the literature review as well as the papers, the literature citations, schemes, tables and figures pertain only to the chapters in which they appear. After the final paper is a general summary.

Literature Review

Introduction

The field of carbon-phosphorus multiply bonded compounds has seen remarkable growth in a relatively short period of time. These compounds violate the outdated "double bond rule" which stated that 4th and 5th row main group elements should not be capable of forming multiple bonds. This reluctance to take part in multiple bond formation is a manifestation of the inert s-pair effect in higher main group elements; the s-orbitals are contracted due to the greater nuclear charge and this spatial inequity between the s and p-orbitals makes the formation of hybrid orbitals less favored, even though the energy differences between the s and p-orbitals in 4th and 5th row main group elements are comparable to those in second row elements. Although C=P π-bonds are calculated to be 22.3 kcal/mol less stable than C=C π-bonds, Becker was able to isolate the first example of a stable phosphaalkene compound in 1976 by incorporating bulky R-groups on the carbon and phosphorus atoms in order to kinetically stabilize the reactive C=P double bond. Since this discovery, many examples of stable phosphaalkene and other interesting C=P containing...
compounds have been reported and the coordination chemistry of these compounds has developed at a very rapid pace. Theoretical calculations and photoelectron studies on MeP=CH$_2$ have shown that the HOMO consists mainly of the C=P $\pi$-orbital and that the LUMO consists mainly of the relatively low lying C=P $\pi^*$ orbital. Consequently, compounds containing C-P multiple bonds have shown a rich olefin-like $\eta^1$-coordination chemistry. In fact, complexes containing C-P multiple bond analogs of almost all C-C multiple bond ligands are known, including phosphaalkenes, phosphaalkynes, phosphaallyls, phosphaallenes, phosphabutadienes, phosphacycloprenes, phosphacyclobutadienes, phosphacyclopentadienyls and phosphaaranes. All of these C-P multiple bond ligands exhibit the ability to coordinate to metals through the C-P $\pi$-system, and offer the additional coordination site of the phosphorus lone pair as well. The $^{31}$P NMR spectroscopy of these ligands has proven useful for structure elucidation and bonding explanations and is a very important diagnostic tool. Although these $\pi$-bonded C-P multiple bond ligands are in many cases analogous to their carbon counterparts, they also exhibit important differences which have allowed them to become more than just phosphorus analogs of common ligands. Unlike commonly tetravalent carbon, phosphorus is able to form mono, di, tri, tetra, penta and hexavalent compounds, which has allowed for the coordination of several C-P multiple bond ligands that have no analogs in carbon chemistry.

This review covers structure and bonding aspects of $\pi$-complexes of carbon-phosphorus unsaturated ligands in the literature through the middle of 1997.

$\eta^2$-Phosphaalkene (R$_2$C=PR) Complexes

Both $ab\ initiio$ STO/3G calculations and photoelectron spectroscopic results on phosphaalkenes indicate that the $\sigma$-phosphorus lone pair and the C=P $\pi$-orbitals are very close in energy, with the $\pi$-orbital as the HOMO in the parent compound CH$_2$=PH. These results suggest that phosphaalkenes should be capable of coordination either $\eta^1$ through the C=P
double bond or η¹ through the phosphorus lone pair, both of which have been accomplished in practice; there are several examples of complexes containing η¹-P coordinated or η²-C=P coordinated phosphaalkenes, as well as mixed, η¹, η²-coordinated phosphaalkenes.⁸,¹⁰ There are also a few examples of cluster-stabilized phosphaalkenes with the phosphaalkene bridging between several metals.⁸,¹⁰ The majority of these complexes have been prepared by displacing weakly coordinating ligands on a transition metal complex with stable phosphaalkene ligands. Both steric and electronic factors determine whether the phosphaalkene ligands will coordinate η¹ or η² to a transition metal complex; electron-rich metal centers are better able to donate into the π* orbital and thus favor η²-coordination, while complexes containing bulky ancillary ligands tend to prefer η¹-coordination to avoid interaction with the often bulky R-groups on the C=P carbon atom.

In the phosphaalkene complex Pt(PPh₃)₂(P(Mes)=CPh₂), both η¹ and η² forms of the phosphaalkene ligand were present and an equilibrium was established (eq 1) between these two forms. At low temperatures the η²-coordinated complex was prevalent, while at higher temperatures and in the solid state the η¹-coordinated complex was more favored; the structure of the η¹ complex was determined by X-ray diffraction studies.¹² Both calculations and equilibrium studies found that the η²-coordinated form was more stable (smaller enthalpy), but the difference was small (~4 kcal/mol).¹¹ When the PPh₃ ligands were replaced with PCy₃ (tricyclohexyl phosphine) groups, only the η¹-phosphaalkene complex was observed with no evidence of the η²-form,¹³ evidently because the greater steric bulk in the PCy₃ ligands favors the less crowded η¹-form. However, when Pt(PPh₃)₂ was coordinated to the phosphaalkene (9-fluorenylidene)C=P(xyl) (xyl = 2,6 dimethylphenyl), only the η²-phosphaalkene complex
was present in both the solid state and in solution. In this complex, the two aryl rings on the C=P carbon are forced into one plane, which allows the Pt\((\text{PPh}_3)_2\) fragment to coordinate the C=P double bond with little steric interaction.

As mentioned, electronic factors also play a role in determining the coordination mode of phosphaalkene ligands; \(\text{Ni}(\text{CO})_4\) reacted with \(\text{Ph}_2\text{C}=\text{P}(\text{xyl})\) to form the \(\eta^1\)-phosphaalkene complex \((\text{CO})_3\text{Ni}[\eta^1-(\text{xyl})\text{P}=\text{CPh}_2]\), while the same phosphaalkene coordinated in \(\eta^2\)-fashion to the 2,2'-bipyridyl-nickel fragment. An explanation for this difference is that the CO ligands in the former are strongly \(\pi\)-accepting, which reduces the ability of nickel to backbond into the \(\pi^*\) orbital of an \(\eta^2\)-phosphaalkene ligand, but favors the \(\eta^1\)-coordination through the phosphorus lone pair in which more electron density is donated to the \(\text{Ni}(\text{CO})_3\) fragment. However, when the better \(\sigma\)-donor ligand 2,2'-bipyridyl is present on nickel, the \(\eta^2\)-form of the phosphaalkene becomes more stable. A similar effect was found in complexes of platinum, where the phosphaalkene \(\text{Ph}_2\text{C}=\text{P}(\text{xyl})\) coordinated \(\eta^1\) to the Pt(COD) fragment, but \(\eta^2\) to the Pt(triphos) fragment, with the triphos ligand acting as a bidentate ligand instead of the usual tridentate form to accommodate the phosphaalkene ligand. Again, the more \(\pi\)-accepting COD ligand favors \(\eta^1\)-coordination, while the better \(\sigma\)-donating triphos ligand favors \(\eta^2\)-coordination. However, there are also examples of \(\eta^2\)-coordinated phosphaalkenes in which
the ancillary ligands are all strongly \( \pi \)-accepting. For instance, \( \text{Ni(CO)}_4 \) reacted with two equivalents of \( (\text{SiMe}_3)_2\text{C} = \text{PCl} \) to generate \( (\text{CO})\text{Ni}[\eta^2-\text{C(SiMe}_3)_2 = \text{PCl}]_2 \), in which two phosphaalkene ligands are coordinated \( \eta^2 \) to the \( \text{Ni(CO)} \) fragment.\(^{10}\) Also, in the reactions of \( \text{Fe}_2(\text{CO})_9 \) with either \( \text{H}_2\text{C} = \text{PMes}^* \) or \( (\text{H})(\text{t-Bu})\text{C} = \text{P(} \text{t-Bu}) \), mixtures of the \( \eta^1\)-P and \( \eta^2\)-\( \text{C} = \text{P} \) complexes were afforded (eq 2).\(^{17}\) Treatment in both cases (eq 2) with another equivalent of \( \text{Fe}_2(\text{CO})_9 \) resulted in formation of the \( \eta^1\), \( \eta^1\)-coordinated phosphaalkene complexes which were structurally characterized.\(^{17}\)

The \( \pi \)-complexation of the \( \text{C}=\text{P} \) bond in phosphaalkenes is analogous to the \( \eta^2 \)-coordination of olefins and has also been described\(^{11}\) by the Dewar-Chatt-Duncanson model in which the \( \pi \)-orbital (HOMO) donates to the transition metal fragment with a synergistic back bonding from the metal fragment to the \( \pi^* \)-orbital (LUMO). This causes a lengthening of the \( \text{C}-\text{P} \) bond distance that is on the order of the lengthening of the \( \text{C}-\text{C} \) bond distance in coordinated olefins; a comparison of \( \text{C}-\text{P} \) bond lengths in free phosphaalkenes (typically about 1.67 Å)\(^{10}\) with the \( \text{C}-\text{P} \) bond lengths in the complexes \( (\text{Me}_3\text{P})_2\text{Ni}[\eta^2\text{C(SiMe}_3)_2 = \text{PCl}] \) and \( (\text{Ph}_3\text{P})_2\text{Pt}[\eta^2\text{C(} \text{9-fluorenylidene}) = \text{P(xy1})] \) (1.773(8) Å and 1.832(6) Å, respectively) shows that the phosphaalkene \( \text{C}=\text{P} \) bonds are lengthened to almost a typical \( \text{C}=\text{P} \) single bond length (1.82-1.87 Å).\(^{15}\) Also, the \( ^{31}\text{P} \) NMR chemical shift of the \( \text{C}=\text{P} \) phosphorus atom in \( \eta^2 \)-coordinated phosphaalkene complexes is far upfield from that in free phosphaalkenes, analogous to the upfield shifts found in the \( ^{13}\text{C} \) NMR of \( \eta^2 \)-coordinated olefins. For instance, the \( ^{31}\text{P} \) chemical shift of the \( \text{C}=\text{P} \) phosphorus in \( (\text{Me}_3\text{P})_2\text{Ni}[\eta^2\text{C(SiMe}_3)_2 = \text{PCl}] \) is \( \delta \) 23.4 ppm, 380 ppm upfield from the free
phosphaalkene \((\text{Me}_2\text{Si})_2\text{C} = \text{PC}(\text{H})(\text{SiMe}_3)\) at \(\delta 404\) ppm,\(^{18}\) while an upfield shift of 266 ppm is found for the \(\text{C} = \text{P}\) phosphorus atom in \((\text{Ph}_3\text{P})_2\text{Pt}[\eta^2-\text{Ph}_2\text{C} = \text{PMes}]\) relative to free \(\text{Ph}_2\text{C} = \text{PMes}\).\(^{11}\) Another distinguishing \(^{31}\text{P}\) NMR feature of \(\eta^2\)-coordinated phosphaalkenes is the extremely small \(J_{\text{PP}}\) coupling constants that are found when the coordinating metal contains an NMR active nucleus. An illustrative example is the difference between the \(\eta^1\) and \(\eta^2\) coordinated phosphaalkene complexes \((\text{Ph}_3\text{P})_2\text{Pt}[\eta^1-\text{P(Mes)} = \text{CPh}_2]\) and \((\text{Ph}_3\text{P})_2\text{Pt}[\eta^2-\text{Ph}_2\text{C} = \text{PMes}]\); the \(\eta^1\)-phosphaalkene complex has \(J_{\text{PP}} = 4960\) Hz, while the \(\eta^2\)-complex of the same phosphaalkene has \(J_{\text{PP}} = 500\) Hz.\(^{11}\) The former is a typical one bond P-Pt coupling constant in three-coordinate platinum phosphine complexes, while the latter is extremely small, indicating the small amount of s-character present in the Pt-P bond. This is a manifestation of the "inert s-pair" effect found in 3rd and 4th row main group elements in which the s-pair of electrons is reluctant to take part in hybridization, causing the \(\text{C} = \text{P}\) double bond to contain very little phosphorus s-character, while the phosphorus lone pair contains mainly s-character.

\(\eta^1\)-Phosphaalkyne (R-\(\text{C} = \text{P}\)) Complexes

Photoelectron spectroscopic studies\(^{20,21}\) on a series of phosphaalkynes has shown that the HOMO is of the \(\pi\)-type and the \(\pi-\pi\) separation is greater than in corresponding nitriles (R-\(\text{C} = \text{N}\)), indicating that \(\eta^2\)-coordination of the \(\text{C} = \text{P}\) bond should be preferred over \(\eta^1\)-coordination through the phosphorus lone-pair. This contrasts with the known propensity of nitriles to coordinate \(\eta^1\) through the nitrogen lone pair. These calculations are consistent with the fact that only a few examples of \(\eta^1\)-P coordinated phosphaalkynes are known, while the vast majority of these complexes are either \(\eta^1\)-coordinated through the \(\text{C} = \text{P}\) bond to a single metal fragment or bridged \(\mu-\eta^1\), \(\eta^2\) between two metals.

The first examples of mononuclear \(\eta^2\)-coordinated phosphaalkynes were prepared by reacting (eq 3) zerovalent platinum complexes with \(t\text{-Bu-}\text{C} = \text{P}\) to form \((\text{R}_3\text{P})_2\text{Pt}(\eta^2-\text{t-BuC} = \text{P})\)
The structure of $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^3\text{-t-BuC}≡\text{P})$ was determined by an X-ray diffraction study which showed that the C-P bond length (1.672(17) Å) was much longer than that (1.536(2) Å) in free t-BuCsP.\textsuperscript{22} The C-P distances in $\eta^3$-coordinated phosphaalkynes are similar to those found in typical phosphaalkenes, which is consistent with back-bonding into the $\pi^*$ orbitals in R-C≡P by electron rich metal fragments. Similar increases in C-C bond lengths have been reported in $\eta^3$-coordinated alkyne complexes as well, indicating a similar type of bonding in these species. The $^{31}\text{P}$ NMR spectrum of $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^3\text{-t-BuC}≡\text{P})$ exhibits a signal at δ 82.1 ppm that is far downfield from that of t-BuCsP at δ -69.2 ppm, consistent with the C≡P double-bond-like character, and the value of $^1J_{pp} = 62$ Hz is the smallest one-bond Pt-P coupling constant yet recorded.\textsuperscript{22} As in the $\eta^3$-phosphaalkene complexes, this small coupling constant is due to the low s-character on phosphorus in the C≡P bond. More recently, the complex $(\text{Ph}_3\text{P})_2\text{Pt}[\eta^3\text{-}(\text{i-Pr,N})\text{C}≡\text{P}]$ was prepared, which showed similar $^{31}\text{P}$ NMR properties to the t-BuCsP complexes.\textsuperscript{23}

The reactions (eq 4) of $\text{Cp}_2\text{M}(\text{PMe}_3)_2$ (M = Ti, Zr) with t-BuCsP resulted in the $\eta^2$-coordinated phosphaalkyne complexes $\text{Cp}_2\text{M}(\text{PMe}_3)[\eta^2\text{-t-BuC}≡\text{P}]$ (M = Ti, Zr) by displacement of one $\text{PMe}_3$ ligand.\textsuperscript{24} The structure of the titanium complex was determined by X-ray diffraction and revealed a C-P distance of 1.634 Å, which is lengthened from the free phosphaalkyne but not as much as in the platinum complex. The $^{31}\text{P}$ NMR of the titanium and zirconium complexes exhibited signals for the phosphaalkyne phosphorus atoms at δ 122.7
ppm and δ 196.9 ppm, respectively, which are even farther downfield than that of the platinum phosphaalkyne complex. The titanium and zirconium complexes also exhibited $^{13}$C NMR chemical shifts for the C≡P carbon atoms at δ 298.6 ppm and δ 310.7 ppm, respectively, which are far downfield in the region of metal-carbene or metal-acyl complexes. Interestingly, these compounds reacted (eq 5) with BEt₃ to remove the PMe₃ ligand and generate a titanium dimer

and a zirconium trimer in which the t-BuC≡P ligands were coordinated $\eta^1, \eta^2$ through both the C≡P triple bond and the phosphorus lone pair.

Several dinuclear phosphaalkyne complexes have been prepared in which the phosphaalkynes are bridged $\mu$-perpendicular-$\eta^1, \eta^2$ to two metals forming complexes with a tetrahedral $M_2CP$ core where the R-C≡P ligand acts as a four-electron donor to the two metals. These compounds are similar to $\mu$-$\eta^2, \eta^2$-bridged alkynes and have been prepared similarly by reacting R-C≡P with dimeric metal complexes containing metal-metal single, double or triple bonds. The majority of these complexes contain the readily available
phosphaalkyne t-BuC≡P; complexes thus obtained with R = t-Bu include L_nM[μ_2-η^2, η^2-(t-Bu)C≡P]ML' \_n'; L_nM = ML' = Co(CO)_3; L_nM = ML' = NiCp; L_nM = ML' = Mo(Cp)(CO)_2; L_nM = (CO)_3Co, ML' = NiCp; L_nM = Cp(CO)_2Mo, ML' = W(Cp)(CO)_2. With the dicobalt metal system, the complexes (CO)_3Co[μ_2-η^2, η^2-RC≡P]Co(CO)_3 with R = N(i-Pr)_2, Me, Ph and SiMe_3 have also been prepared, although the complexes with R = Me, Ph and SiMe_3 were not formed by reacting R-C≡P with the dimeric metal complex, but rather were formed by the dechlorination of R-CCl_2-PCl_2 with Co_2(CO)_8. The crystal structure of (Cp)(CO)_2Mo[μ_2-η^2, η^2-(t-Bu)C≡P]Mo(Cp)(CO)_2 exhibited a phosphaalkyne C-P bond length (1.719 Å) that was quite a bit longer than those in mononuclear η^2-bonded phosphaalkyne complexes, but not quite as long as a C-P single bond (1.82-1.87 Å). There are also some recent examples of μ_2-η^2, η^2-phosphaalkyne complexes containing bridging ancillary ligands, e.g., Fe_2(CO)_4(μ-CO)(μ-dppm)(μ-η^2, η^2-t-BuC≡P) and Co_2(CO)_4(μ-η^2, η^2-t-BuC≡P)(μ-Ph_2PNHPh_2-P,P') \); the structure of both of these complexes were determined by X-ray diffraction studies and showed similar C-P bond lengths to those in other μ_2-η^2, η^2-phosphaalkyne complexes. There is also an example of a dinuclear, μ-perpendicular-η^2, η^2-bridging phosphaalkyne complex Cl_2Pt(μ-dppm)_2(μ-t-BuC≡P) which was formed by reacting (eq 6) the Pt-Pt bonded dimer Cl_2Pt(μ-dppm)_2 with t-BuC≡P. In

\[
\text{R-CCl}_2\text{PCl}_2 + [\text{Co}_2(\text{CO})_8] \rightarrow (\text{OC})_3\text{Co} \rightarrow \text{Co(CO)_3}
\]

(R = Me, Ph, Me_3Si)
this complex, the phosphaalkyne donates one electron to each Pt center and is perhaps best viewed as a C,P-dimetallaphosphaalkene.34

Recently, mononuclear \( \eta^2 \)-complexes of phosphaalkynes acting as four-electron donors have been described.35,36 Although none have been structurally characterized because of the tendency to react further to form 1,3-diphosphacyclobutadiene complexes, these compounds represent a new class of phosphaalkyne complexes which are related to \( \eta^2 \)-(4e) alkyne and nitrile complexes. In the complex [WF(C₆H₄CH₂NMeCH₂CH₂NMe₂)(CO)(t-BuC=P)],36 the \(^{31}\text{P} \) NMR chemical shift of the phosphaalkyne phosphorus atom (δ 452.4 ppm) is far downfield, even more so than in \( \mu-\eta^2 \), \( \eta^2 \)-phosphaalkynes, and the \(^{13}\text{C} \) NMR spectrum showed a similar downfield signal for the phosphaalkyne carbon at δ 315.2 ppm. The large \( ^1J_{\text{CP}} \) value of 117.7 Hz is much larger than that in the free phosphaalkyne \( (^1J_{\text{CP}} = 38.5 \text{ Hz}) \) which is also indicative of the \( \eta^2 \)-(4e) coordination mode.36 These complexes underwent interesting coupling reactions35,36 with phosphaalkynes and CO, which do not occur in the related \( \eta^2 \)-(4e) nitrile complexes whose chemistry is dominated by ready dissociation of the nitrile ligand.

A great deal of work has been recently devoted to the functionalization of coordinated phosphaalkyne ligands by dimerization into \( \eta^4 \)-diphosphacyclobutadiene complexes and by trimerization into \( \eta^6 \)-triphosphaarene complexes. Also, phosphaalkynes have been functionalized into \( \eta^5 \)-coordinated phosphacyclopentadienyl complexes having various numbers of phosphorus substituents. The chemistry of these ligands is quite well-developed, but is outside the scope of this review. However, several reviews7-9 have been written on these fascinating new C=P multiply bonded ligands.
In contrast to $\lambda^3$-phosphaalkynes ($R-C=\overset{\text{+}}{\text{P}}$) which possess a triple bond, $\lambda^5$-phosphaalkynes must be regarded as a mixture of three resonance structures including a phosphorus-vinyl ylide (A), a phosphino-carbene (B) and a $\lambda^5$-phosphaalkyne (C). From ab initio calculations on the parent compound HCPH$_2$, the carbon-phosphorus overlap population is larger than in the isomeric phosphaalkene H$_2$CPH, and the calculated bond length was rather short (1.61 Å), indicating a strong contribution from resonance form C. A series of these free $\lambda^5$-phosphaalkynes was prepared, but no X-ray structures were reported. Although direct complexation of a free $\lambda^5$-phosphaalkyne has not yet been accomplished, a few examples of complexes containing $\eta^2$-$\lambda^5$-phosphaalkynes were prepared by other methods. When the tungsten carbene complex (CO)$_4$[(Me)(H)(Ph)P]W(=C(NEt$_2$)(PMePh) was heated (eq 7), the phosphine ligand was removed with concomitant rearrangement of the carbene ligand from $\eta^1$-$\text{C}$ to $\eta^2$-$\text{C}$, P forming (CO)$_4$W[$\eta^2$-C(NEt$_2$)=P(Ph)(Me)]. The structure of this compound was determined by X-ray diffraction studies to exhibit an $\eta^1$-$\lambda^5$-phosphaalkyne ligand acting as a four-electron donor. Recently, a series of these complexes were prepared in a different manner (eq 8) by treating molybdenum and tungsten carbyne complexes of the type
Cp(CO)$_2$M=CR' with PR$_2$Cl and NaBPh$_4$ to form [CpM(CO)$_2$($\eta^2$-C(R')=P(R'))](BPh$_4$) (M = Mo, W), or with PMe$_3$ followed by PR$_2$Cl and NaBPh$_4$ to generate [CpM(CO)(PMe$_3$)$_2$($\eta^2$-C(R')=P(R'))](BPh$_4$) (M = W).\textsuperscript{40-42} Although no crystal structures were determined in this system, spectroscopic properties were consistent with the presence of $\eta^2$-$\lambda^2$-phosphaalkyne ligands in the metal complexes.

A different method of preparing $\eta^2$-$\lambda^2$-phosphaalkyne complexes involved the double intramolecular C-H bond activation of a coordinated PMe$_3$ ligand in early transition metal complexes to generate ($\eta^2$-(H)C=PMMe$_2$) ligands. When Cp*$^\text{TaCl}_4$ was reacted (eq 9) with metallic sodium in neat PMe$_3$, the complex Cp*($\eta^2$-PMe$_3$)$_2$Ta[$\eta^2$-(H)C=PMMe$_2$] formed in good yield, where the two hydride ligands originated from a PMe$_3$ ligand to form the $\eta^2$-$\lambda^2$-phosphaalkyne complex.\textsuperscript{43} Interestingly, if this complex was reacted with CO or H$_2$, the hydride ligands migrated back to the HC=PMMe$_2$ ligand to form Cp*$^\text{Ta(PMMe$_3$)$_2$}(CO)$_2$ or Cp*$^\text{Ta(PMMe$_3$)$_2(H)$_2$}$, respectively. However, when treated with MeX (X = Cl, Br) or CHCl$_3$, the HC=PMMe$_2$ ligand remained intact. Similar to eq 9, if TaCl$_5$ was treated with sodium in neat PMe$_3$, the complex (Me$_3$P)$_2$Ta[$\eta^2$-(H)C=PMMe$_2$] resulted which was further reacted with butadiene to generate the complex (Me$_3$P)$_2$(Cl)Ta($\eta^2$-C$_2$H$_4$][$\eta^2$-(H)C=PMMe$_2$], the structure of which was determined by X-ray diffraction studies.\textsuperscript{44}
A more recent example of an \( \eta^2-\lambda^5 \)-phosphaalkyne complex involved the functionalization of a coordinated \( \lambda^1 \)-phosphaalkyne complex. When the \( \eta^2 \)-vinyl complex \( \text{Cp}(\text{Ph}_3\text{P})(\text{Br})\text{Re}[=\text{C(Ph)CH(Ph)}] \) was reacted (eq 10) with t-BuCsP and HBF\(_4\)•OEt\(_2\), the vinyl ligand was protonated and removed as \( \text{trans} \)-stilbene, and the complex \( \text{Cp}(\text{Ph}_3\text{P})(\text{Br})\text{Re}[\text{t-BuC}==\text{P}] \) formed; the structure of this complex was determined by X-ray diffraction studies to contain an \( \eta^2-\lambda^5 \)-phosphaalkyne with a short C-P bond (1.699(7) Å).\(^{45}\) This complex formed presumably by protonation of an \( \eta^2-\lambda^1 \)-phosphaalkyne intermediate followed by oxygen transfer and conversion of BF\(_4\)^- to BF\(_3\), although detailed mechanistic information was not obtained. In all of the \( \eta^2-\lambda^5 \)-phosphaalkyne complexes that were characterized by X-ray analysis, the metal-carbon distances were within the range for metal-carbon double bonds, indicating a strong contribution from a phosphino-carbene resonance form (D). However, the C-P distances (1.683-1.807 Å) are considerably shorter than that expected for a C-P single bond (1.82-1.87 Å), indicating a substantial contribution from an \( \eta^2-\lambda^5 \)-phosphaalkyne resonance form (E). The NMR properties of these complexes are also characteristic, exhibiting downfield \( ^{13} \text{C} \) NMR chemical shifts for the C=P carbon (δ 170-287 ppm) and upfield \( ^{31} \text{P} \) NMR chemical shifts for the C=P phosphorus (δ -62 to -153 ppm). Also, a few examples of cluster-stabilized \( \eta^2-\lambda^5 \)-phosphaalkyne osmium complexes have been prepared.\(^{46}\)
\( \eta^2 \)-Phosphaallene (R, C=C=PR) and Diphosphaallene (RP=C=PR) Complexes

Only a few examples of mono- and diphosphaallene metal complexes are known. Ab initio calculations on HP=C=PH have shown that the two sets of \( \sigma \)-phosphorus lone pair (\( n \)) orbitals and the C=P \( \pi \)-orbitals are similar in energy and act as the quasi-degenerate HOMOs; similar calculations on HP=C=CH\(_2\) showed that the C=P \( \pi \)-orbital is the HOMO. In accord with these findings, the complexes (PR\(_3\))\(_2\)M(\( \eta^1 \)-Mes*P=C=PMes*) (M = Ni, R = Ph; M = Pd, R = Ph, Et; M = Pt, R = Ph) have been prepared, in which one of the C=P bonds is \( \eta^2 \)-coordinated to the transition metal. The structure of (PEt\(_3\))\(_2\)Pd(\( \eta^2 \)-Mes*P=C=PMes*) was determined by X-ray diffraction and showed that the \( \eta^2 \)-ligated C=P bond length (1.73(3) Å) is slightly longer than that in the non-coordinated C=P bond (1.67(3) Å). Interestingly, in the \( \eta^2 \)-monophosphaallene Pt(0) complexes (PR\(_3\))\(_2\)Pt(\( \eta^1 \)-Mes*P=C=CPt\(_2\)), the metal coordinates through the C=P bond rather than the C=C bond, indicating the propensity of C=P bonds to participate in \( \pi \)-bonding to transition metals. When metal carbonyl fragments (e.g., W(CO)\(_5\) and Ni(CO)\(_3\)) were coordinated to mono- and di-phosphaallenes, \( \eta^1 \)-ligation through the phosphorus lone pair took place. This is analogous to the situation in phosphaalkenes in which \( \pi \)-accepting ancillary ligands favor \( \eta^1 \)-P over \( \eta^1 \)-C=P coordination. There are also a few examples of cluster-stabilized phosphaallene complexes.

More recently, the first examples of \( \eta^1 \)-coordinated 2-phosphaallene complexes (PR\(_3\))(Cl)M(\( \eta^2 \)-C(SiMe\(_3\))\(_2\)=P=C(SiMe\(_3\))\(_2\)) (M = Pt, Ni) were reported from the reactions of...
The structure of the nickel compound with \( \text{PR}_3 = \text{PET} \) was determined from X-ray diffraction studies and showed that the \((\text{SiMe}_3)_2\text{C}=\text{P}\text{C}(\text{SiMe}_3)_2\) ligand was coordinated through one of the \(\text{C}=\text{P}\) bonds, acting as a three-electron donor to the \(\text{Ni}(\text{PET})\text{Cl}\) fragment. The \(\eta^2\)-coordinated \(\text{C}=\text{P}\) bond length (1.732(7) Å) was longer than that in the non-coordinated \(\text{C}=\text{P}\) bond (1.663(8) Å), consistent with the lengthening of \(\eta^2\)-coordinated \(\text{C}=\text{P}\) bonds in other phosphaallene systems.

\(\eta^1\)-1-Phosphaallyl (\(\text{RP}-\text{CR}=\text{CR}_2\)) and 1,3-Diphosphaallyl (\(\text{RP}-\text{CR}=\text{PR}\)) Complexes

Similar to allyl compounds which contain a delocalized \(\pi\)-system and tend to coordinate \(\eta^3\) to transition metal fragments, phosphaallyl and diphosphaallyl compounds (where \(\text{PR}\) groups are substituted for \(\text{CR}_2\) groups in an allyl) have also been found to contain delocalized \(\pi\)-systems and can coordinate in an \(\eta^1\)-fashion. There is only one known example of an \(\eta^1\)-coordinated monophosphaallyl complex, Cp(CO)Fe[\(\eta^1\)-\(\text{CH}_2\text{CHPPh}\)]W(CO)\(_5\), which was additionally \(\eta^1\)-coordinated through the phosphorus lone pair to a W(CO)\(_5\) fragment.\(^{54,55}\) NMR studies of this complex showed that the W-P-CH=CH\(_2\) moiety is planar, and the P-C=C unit is \(\eta^3\)-coordinated to the Cp(CO)Fe fragment. In contrast, there are several known examples of \(\eta^3\)-coordinated 1,3-diphosphaallyl complexes. These complexes were first prepared by reacting (eq 11) Na[Co(CO)\(_4\)] with the chlorophosphino-substituted 1,3-diphosphapropene compound Mes*P=CH-P(Cl)(Mes*) to form (CO)\(_3\)Co[\(\eta^3\)].
diphosphaallyl.\textsuperscript{56} The X-ray-determined structure showed a planar arrangement of the PCP-skeleton and the C(1) atoms of the aryl moieties: the three atoms of the PCP triad are coordinated to cobalt.\textsuperscript{56} The C-P bond lengths were both very similar and intermediate between single and double C-P bonds, further supporting the delocalized bonding. Similarly, K[CpNi(CO)] and Na\textsubscript{2}[Fe(CO)\textsubscript{4}] were reacted with Mes*P=CH-P(Cl)(Mes*) to form CpNi[\eta\textsuperscript{1}-diphosphaallyl]\textsuperscript{57} and [(CO)\textsubscript{3}Fe(\eta\textsuperscript{1}-diphosphaallyl)]\textsuperscript{58}\textsuperscript{58} respectively. The diphosphaallyl complex of iron was also formed by reacting the diphosphaallyl anion [Mes*P=CH-P(Mes*)]Li with Fe(CO)\textsubscript{5} or by reacting (eq 12) the \eta\textsuperscript{1},\eta\textsuperscript{2}-diphosphapropene complex (CO)\textsubscript{3}Fe[\eta\textsuperscript{1},\eta\textsuperscript{2}-P(Mes*)=CH-PMes*] with n-BuLi.\textsuperscript{58} This \eta\textsuperscript{1},\eta\textsuperscript{2}-
diphosphapropene complex was then regenerated (eq 12) by protonating the \( \eta^1 \)-diphosphaallyl complex with HCl. When the \( \eta^1 \)-diphosphaallyl complex of iron was reacted with nickelocene (eq 13), a new type of complex was obtained which, in addition to the \( \eta^3 \)-coordination of the Fe\((\text{CO})_3\) group, contained a NiCp fragment coordinated to both of the lone pairs of the diphosphaallyl ligand.\(^{59}\) The X-ray determined structure showed a planar diphosphaallyl fragment that is still \( \eta^1 \)-coordinated to iron, and the Ni-P distances were very similar to those in related nickel phosphine complexes.

More recently, a series of \( \eta^1 \)-diphosphaallyl complexes have been prepared (eq 14) by reacting anionic metal complexes with diphosphirane compounds.\(^{60}\) Some of these reactions also produced intermediate \( \eta^1 \)-P bound diphosphaallyl complexes, which were characterized by NMR spectroscopy. All of the X-ray structures of these diphosphaallyl complexes exhibit planar PCP units that have very similar C-P bond lengths that are intermediate between single and double bond lengths, indicative of the delocalization in these complexes.
\( \eta^4\text{-Phosphabutadiene} \ (RP=C(R)-C(R)=CR_2) \) and \( \text{Diphosphabutadiene} \ (RP=C(R)-C(R)=PR) \) Complexes

By analogy with the many \( \eta^4\)-butadiene complexes that are known to involve delocalized \( \pi \)-bonds within the planar C\(_4\) skeleton of the ligand, a variety of phosphorus-substituted analogs have been investigated as ligands. A few examples of \( \eta^1\)-coordinated tungsten 1-phosphabutadienes are known of the type \((CO)_4W(\eta^1\cdot RP=C(R)-C(R)=CR_2)\); although no structures have been reported, NMR evidence suggests planar, delocalized PCCC frameworks in these complexes.\(^6\) There is also an example of an \( \eta^4\)-coordinated 1-phospha-4-metallabutadiene complex that was formed (eq 15) by insertion of an alkyne into one of the Fe-

\[ \text{Fe}_3(CO)_{10}PR + \text{PhC}=\text{CH} \rightarrow \begin{array}{c}
\text{Ph} \\
\text{C} \\
\text{Fe} \\
\text{Fe(CO)}_4 \\
\hline
\text{H} \\
\text{C} \\
\text{P} \\
\text{R} \\
\hline
\text{OC} \\
\text{OC} \\
\text{OC}
\end{array} \]  

(eq 15)

P bonds of the phosphinidene complex \([\text{Fe}_3(CO)_{10}PR] \ (R = p\text{-MeOC}_6\text{H}_4)\).\(^6\) The structure of this complex exhibited a nearly planar FeCCP moiety that is \( \eta^1\)-coordinated to an Fe(CO)\(_3\) fragment. There have been two recent examples of \( \eta^4\)-coordinated 2-phosphabutadiene complexes, both of which contain a W(CO)\(_5\) fragment coordinated to the phosphabutadiene phosphorus lone pair and were characterized by X-ray diffraction studies. When the \( \eta^1\cdot2\)-phosphabutadiene tungsten complex \((CO)_5W[\eta^1\cdot(SiMe_3)C=P-C(OEt)=C(H)Ph] \) was reacted (eq 16) with Fe\(_2\)(CO)\(_9\), an \( \eta^1\), \( \eta^4\cdot2\)-phosphabutadiene complex resulted, in which the CPCC
moiety is almost planar and only partially delocalized with C-P distances of 1.754(8) Å and 1.814(8) Å, indicating partial C=P-C=C character in the phosphabutadiene ligand. In contrast, full delocalization occurs in the \( \eta^1, \eta^1 \)-2-phosphabutadiene complex \([\text{(CO)}_3\text{Fe} \{\eta^1-\text{CHMe}_2(\text{H})\text{C}=\text{P}-\text{C}(\text{H})=\text{P}(\text{H})\text{Ph}[\text{W(CO)}_5]\}]\), where the C-P distances of 1.753(4) Å and 1.743(4) Å are the same within error, and the CPCC skeleton is planar.

There are a few examples of \( \eta^1 \)-coordinated 1,3-diphosphabutadiene complexes, which tend to exhibit planar PCPC skeletons as in monophosphabutadiene complexes. These have been prepared by reacting 1,3-diphosphabutadienes with transition-metal carbonyl complexes. In the reaction (eq 17) of Mes\(^*\)P=C(OSiMe\(_3\))P=CO(OSiMe\(_3\))t-Bu with Fe\(_2\)(CO)\(_9\), the \( \eta^1 \)-coordinated 1,3-diphosphabutadiene complex \([\text{(CO)}_3\text{Fe} \{\ eta^1-\text{Mes}^*\text{P}=\text{C(OSiMe}_3\text{)}\text{P}=\text{C(OSiMe}_3\text{)}\text{t-Bu}\}]\) formed, but a reaction with the same 1,3-diphosphabutadiene and Ni(CO)\(_4\) resulted in formation of the \( \eta^1 \)-P coordinated complex. The \(^{31}\text{P} \) NMR spectra of these complexes showed peaks at \( \delta \) -14.5 and -62.5 ppm in the former and at \( \delta \) 179.8 and 138.3 ppm in the latter; the upfield shift of the signals in the \( \eta^1 \)-complex is typical of the large upfield shifts seen in side-on bound C=P compounds. There is also a report of an interesting \( \eta^1 \)-coordinated 1,3-diphospha-4-metallabutadiene complex that was prepared (eq 18) by
reacting a tungsten phosphinidene complex with Fe$_2$(CO)$_9$.

The structure of this complex, determined by X-ray diffraction studies, exhibits a nearly planar arrangement of the W-P-C-P framework and the two P-C bonds were the same within error, supporting the view that this is a delocalized heterobutadiene complex.

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NICKEL COMPLEXES CONTAINING NEW CARBON-PHOSPHORUS UNSATURATED LIGANDS: FIRST EXAMPLES OF PHOSPHAVINYLDENE-PHOSPHORANE \([R_3P=C=PR']\) AND PHOSPHAVINYL PHOSPHONIUM \([C(H)(PR_3)=P(R')\]^+\) LIGANDS

Wayde V. Konze, Victor G. Young, Jr.*, and Robert J. Angelici*

Abstract

Oxidative addition reactions of \(\text{Cl}_2C=PN(SiMe_3)_2\) with 1:2 \(\text{Ni}(\text{COD})_2/\text{PPh}_3\), \(\text{Ni}(\text{PPh}_3)_4\) or \((\text{Ph}_3\text{P})_2\text{Ni}(\text{C}_2\text{H}_4)\) initially yields the phosphavinyl phosphonium complex \(\text{Cl}(\text{Ph}_3\text{P})\text{Ni}[\mu-\eta^2-\text{C}(\text{Cl})(\text{PPh}_3)=\text{PN}(\text{SiMe}_3)_2]\) (IIa). Addition of another equivalent of \(\text{Ni}(0)\) reagent to IIa results in the formation of the novel, dinuclear, phosphavinylidene-phosphorane complex \(\text{Ni}_2\text{Cl}_2(\text{PPh}_3)_2[\mu-\eta^2-\eta^2-\text{C}(\text{PPh}_3)=\text{PN}(\text{SiMe}_3)_2]\) (IIa). The structure of IIa was established by X-ray diffraction and contains a \(\text{Ph}_3\text{P}=\text{C}=\text{PR}'\) ligand bridged between two 4-coordinate, planar nickel atoms in a butterfly arrangement with a Ni-Ni distance that is too long for significant bonding interaction. The \(\text{Ph}_3\text{P}=\text{C}=\text{PR}'\) ligand, which may be viewed as a phosphavinylidene (=C=PR) ligand with a phosphine donor substituent, acts as a six-electron donor to the two nickel atoms. This contrasts with the known diphosphaallene compounds of the types \(R_3P=C=PR_3\) and \(RP=C=PR\) which act as two-electron donor ligands. When the reaction of the \(\text{Ni}(0)\) reagent is performed with \(\text{Cl}_2C=\text{PMes}^*\) (\(\text{Mes}^*=2,4,6\)-tri-\text{tert}-\text{butyl}phenyl), the mononuclear phosphonio-phosphavinyl complex \(\text{Cl}(\text{Ph}_3\text{P})\text{Ni}[\eta^2-\text{C}(\text{H})(\text{PPh}_3)=\text{P}(\text{Mes}^*)]\) (Va) forms. The structure of Va was established by X-ray diffraction and contains a \([\text{C}(\text{H})(\text{PR}_3)=\text{P}(\text{R}')]\) ligand which acts as a three-electron donor to the \(\text{Ni}(\text{PPh}_3)_2\text{Cl}\) fragment. This structure also exhibits a puckered, boat-shaped supermesityl ring. Both IIa and Va
exhibit labile PPh₃ groups on nickel which are easily substituted with PEt₃, but the carbon-bound PPh₃ groups could not be substituted with PEt₃.

† X-Ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, MN 55455

Introduction

Many recent advances have been made in the coordination chemistry of ligands containing carbon-phosphorus multiple bonds. There are numerous examples of phosphorus analogues of common unsaturated organic ligands which exhibit rich coordination chemistries due in part to the presence of the phosphorus lone electron pair. Examples of η¹- through η⁶-coordinated phosphorus-substituted hydrocarbon ligands are known; representative examples include phosphaalkenes (A), phosphaalkynes (B), diphosphaallenes (C), diphosphaallyls (D), phosphacyclobutadienes (E), phosphacyclopentadienyls (F) and phosphabenzenes (G).

\[
\begin{align*}
\text{(A)} & \quad \text{(B)} & \quad \text{(C)} & \quad \text{(D)} \\
\begin{array}{c}
\text{M} \\
\text{C} \equiv \text{P}
\end{array} & \begin{array}{c}
\text{M} \\
\text{C} \equiv \text{P}
\end{array} & \begin{array}{c}
\text{M} \\
\text{P} \equiv \text{C} \equiv \text{P}
\end{array} & \begin{array}{c}
\text{M} \\
\text{P} \equiv \text{C}
\end{array}
\end{align*}
\]

The coordination chemistry of phosphaalkenes (A) and phosphaalkynes (B) has been reviewed,¹ as has the coordination chemistry of the cyclic phosphorus-substituted compounds of types E-G.² However, the coordination chemistry of diphosphaallenes (C) and diphosphaallyls (D) is much less developed.³ Phosphorus ylides (R'₂C=PR₃), which are the tetracoordinate (σ⁴) phosphorus analogs of phosphaalkenes, have been studied a great deal with respect to their utility in the Wittig reaction and have been studied to a lesser extent as ligands in transition metal complexes.⁴ Interestingly, the coordination chemistry of ylides, which is
mainly limited to \( \eta^1 \)-C-coordination\(^4 \) is dramatically different than that of phosphaalkenes. There are also examples of \( \sigma^4 \)-phosphorus analogs of diphosphaallenes, i.e. \((R_3P=C=PR_3)^5\) and diphosphaallyls, i.e. \([(R_3P)HC=PR_3]^+ \).\(^6\) as well as mixed \( \sigma^3, \sigma^4 \)-diphosphaallyls \([(R_3P)HC=PR']^+.\(^7-10\) However, there are no examples of mixed \( \sigma^3, \sigma^4 \)-diphosphaallenes \((R_3P=C=PR')\). Of these \( \sigma^4 \)-diphosphaallene and diphosphaallyl compounds, only the \( \sigma^4 \)-diphosphaallenes \((R_3P=C=PR_3)\) have been investigated as ligands,\(^11\) exhibiting a preferential \( \eta^1 \)-C-coordination as in the \( R'_3C=PR_3 \) compounds due to the strongly carbanionic character of the ylidic carbon.\(^4\) The dramatic differences imparted by the \( \sigma^4 \)-phosphorus should give these compounds interesting ligation properties that contrast with their \( \sigma^2 \)-phosphorus counterparts, particularly in the case of the mixed \( \sigma^3, \sigma^4 \)-diphosphaallyls \([(R_3P)HC=PR']^+ \) and \( \sigma^3, \sigma^4 \)-diphosphaallenes \((R_3P=C=PR')\) in which comparisons of bonding properties can be made directly between the \( \sigma^2 \) and \( \sigma^4 \) phosphorus atoms.

We recently succeeded in preparing the first example of a coordinated isocyaphide, \((:C=PR)\) ligand by oxidative addition of the C-X bond in the phosphavinyi complex (1) (eq 1) to generate a diplatinum complex \( [(Cl)(Et_3P)Pt(\mu-C=PR)Pt(PEt_3)_2(Cl)] \) (2) containing a semi-

\[
Pt(PEt_3)_4 + Cl_2C=PR \\
(R = Mes*, 2,4,6-tri-tert-butylbenzene)
\]

bridging \( :C=PR \) group.\(^12\) More recently, Weber and coworkers reported the synthesis (eq 2) of a diiron complex containing a symmetrically-bridged \( :C=PR \) ligand (3) by a different route.\(^13\)
We also reported an expanded study of the syntheses and reactions of the phosphavinyl compounds \( X(R',P)M[C=PR] \) (\( M = Pt, Pd; X = Cl, Br; R' = Ph, Et; R = 2,4,6-tri-tert-butylphenyl \))\(^{14}\) in order to assess the general usefulness of these starting materials for the preparation of complexes containing \(:C=PR\) ligands according to eq 1. However, this approach was limited by the tendency of the R-group to migrate from phosphorus to carbon thereby forming the phosphaalkyne (\( R-C=P \), \( R = 2,4,6\)-tri-tert-butylphenyl). A detailed study of this migration in the case of \( R' = Et \) showed that it proceeds through a novel bicyclic intermediate (eq 3).\(^{14}\) Rearrangement of the \( 2,4,6\)-tri-tert-butylphenyl R-group from \( Pt(PEt_3)_4 + X_2C=PR \)

\[
\text{Pt}(PEt_3)_4 + X_2C=PR
\]

\[
\xrightarrow{X, PEt_3, Et_3P, X, R, X=Cl, Br, R=2,4,6\text{-tri-tert-butylphenyl}}
\]

\[
R-C=P + \text{trans-}X_2Pt(PEt_3)_2
\]

phosphorus to carbon has also been reported in the conversion of \( Li(Cl)C=PR \) to \( LiCl \) and \( R-C=P \)\(^{15\text{-}18\text{}}\) and in the reaction of \( Pd(PPh_3)_4 \) with \( Cl_2C=PR \) to give \( Cl_2Pd(PPh_3)_2 \) and \( R-C=P \).\(^{19}\)

In order to probe the generality of eq 1 for the synthesis of other complexes containing \(:C=PR\) ligands, we explore in the present paper reactions of \( Cl_2C=PR \) with \( Ni(0) \) complexes. We chose \( Cl_2C=PR \) reactants with non-aromatic R groups in order to circumvent R-group rearrangement (eq 3). During the course of these studies, we isolated the first example of a mixed \( \sigma^-, \sigma^t\)-diphosphaallene, or phosphavinyldiene-phosphorane ligand, which is bridged...
between two nickel atoms in a butterfly arrangement with the R₃P=C=PR' ligand acting as a six-electron donor as in H. This ligand may be considered as a triphenylphosphine donor-stabilized phosphavinylidene ligand. Phosphavinylidene ligands can also be called

\[
\text{PR₃C=PR'} \quad \text{(H)}
\]

isocyaphides (C≡PR) and are phosphorus analogs of isocyanides (C≡NR). Since there are no examples of donor stabilized isocyanide R₃P=C=NR, carbonyl R₃P=C=O or thiocarbonyl R₃P=C=S ligands, the formation of the PPh₃-stabilized :C=PR ligand in H illustrates that phosphorus analogs of isocyanides offer unique differences in bonding with respect to their well-studied isoelectronic analogs. We have also isolated the first example of a coordinated σ\(^3\), σ\(^1\)-dipphosphaallyl, or phosphavinyl phosphonium ligand, which is coordinated η\(^2\) to a nickel atom with the \((R₃P)(H)C=PR'\) ligand acting as a three electron donor as in I. The preparations of complexes of types H and I will be discussed, along with likely pathways of formation and chemical reactivity. Structure and bonding in these new ligands will also be discussed.

**Experimental Section**

**General Procedure.** All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled over sodium benzophenone ketyl, while hexanes and toluene were distilled over CaH₂. Acetone was distilled over anhydrous MgSO₄.

The \(^1\)H NMR spectra of compounds were recorded in \(C₆D₆\) solvent unless otherwise specified using a Varian VXR 300-MHz spectrometer with TMS (δ 0.00 ppm) as the internal
standard. The $^{31}$P{H} and $^{31}$P NMR spectra were recorded on a Bruker AC 200-MHz spectrometer using 85% H$_3$PO$_4$ (δ 0.00 ppm) as the external standard. The $^{13}$C{H} and $^{13}$C NMR spectra were recorded on a Bruker DRX 400-MHz spectrometer using CDCl$_3$ as the internal standard. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The compounds Ni(COD)$_2$, $^{20}$ (PPh$_3$)$_2$Ni(C$_2$H$_4$)$_2$, $^{21}$ Ni(PPh$_3$)$_4$, $^{22}$ Cl$_2$C=PN(SiMe$_3$)$_2$, $^{23}$ Cl$_2$C=PMes* $^{24}$ and Br$_2$C=PMes* $^{25}$ were prepared by literature methods. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh$_3$, which was recrystallized from MeOH.

**Preparation of Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ-η$^2$-η$^2$-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIA) through Intermediate Cl(Ph$_3$P)Ni[η$^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIA).**

**Method A.** To a cooled (-50°C) slurry of Ni(COD)$_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of PPh$_3$ (0.954 g, 3.64 mmol) and Cl$_2$C=PN(SiMe$_3$)$_2$ (0.249 g, 0.909 mmol) in toluene (10 mL). The dark red solution was allowed to warm slowly with stirring. A $^{31}$P{H} NMR spectrum taken when the reaction had reached -20°C after about 20 min showed IIa as an intermediate, with no traces of IIIa. When the solution reached room temperature after about one hour, IIa had converted almost completely to IIIa. The solution was filtered and the solvent was removed under vacuum to yield a red-green oily solid. The residue was treated with 25 mL of Et$_2$O, and the flask was placed in a sonicating bath for 15 min to break up the solids. The dark green precipitate was collected on a medium porosity fritted glass filter and washed with 3x5 mL portions of Et$_2$O and dried under vacuum. The solids were extracted with 25 mL of toluene, and after reducing the extract to one-fourth of its volume under vacuum, dark green crystals of IIIa (0.735 g, 69%) were obtained by slowly cooling the solution to -78°C.

**Method B.** To a cooled (-50°C) slurry of Ni(PPh$_3$)$_2$ (0.500 g, 0.451 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of Cl$_2$C=PN(SiMe$_3$)$_2$ (0.0619 g, 0.226 mmol) in
toluene (5 mL). After warming to room temperature with stirring over the course of an hour, the reaction mixture was worked up as above.

**Method C.** To a cooled (-50°C) slurry of \((\text{Ph}_3\text{P})_2\text{Ni}(\text{C}_2\text{H}_4)\) (0.500 g, 0.818 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of \(\text{Cl}_2\text{C}═\text{PN(SiMe}_3\text{)}_2\) (0.112 g, 0.409 mmol) in toluene (5 mL). After warming to room temperature with stirring over the course of an hour, the reaction mixture was worked up as above to yield 0.369 g of \(\text{IIla}(74\%)\).

\[ {^3}\text{P}^\{^1\text{H}\} \text{NMR (toluene, -50°C) (see Scheme 1 for atom labels) for \(\text{IIla}: \ \delta(P(x)) 103.7 \text{ (dd, } 2^J_{\text{P(x)P(b)}} = 60.5 \text{ Hz, } 2^J_{\text{P(x)P(a)}} = 24.7 \text{ Hz}), \delta(P(a)) 22.4 \text{ (d, } 2^J_{\text{P(a)P(b)}} = 24.7 \text{ Hz), } \delta(P(b)) 19.0 \text{ (d, } 2^J_{\text{P(b)P(x)}} = 60.5 \text{ Hz). For \(\text{IIla}: \ \delta(P(x)) 38.0 \text{ (dt, } 2^J_{\text{P(a)P(x)}} = 57.8 \text{ Hz, } 2^J_{\text{P(b)P(x)}} = 41.2 \text{ Hz), } \delta(P(a)) 22.3 \text{ (d, } 2^J_{\text{P(a)P(x)}} = 57.8 \text{ Hz), } \delta(P(b)) 20.0 \text{ (d, } 2^J_{\text{P(b)P(x)}} = 41.2 \text{ Hz). Anal. Calcd for } \text{C}_{61}\text{H}_{63}\text{Cl}_2\text{N}_3\text{i}_3\text{P}_5\text{Si}_2(\text{IIla}): \ C, 62.17; \ H, 5.39; \ N, 1.19. Found: } \ C, 62.08; \ H, 5.44; \ N, 1.25.\]

**Reaction of \(\text{Ni(COD)}_2, \text{PEt}_3\text{ and Cl}_2\text{C}═\text{PN(SiMe}_3\text{)}_2; \text{Characterization of Cl(ET}_2\text{P})_2\text{Ni}[\text{C(Cl)}═\text{PN(SiMe}_3\text{)}_2]\) (\(\text{Ib}\)).** This reaction was carried out as in Method A above. The reagents used were \(\text{Ni(COD)}_2\) (0.100 g, 0.364 mmol), \(\text{PEt}_3\) (0.0859 g, 0.728 mmol) and \(\text{Cl}_2\text{C}═\text{PN(SiMe}_3\text{)}_2\) (0.0498 g, 0.182 mmol) in toluene (10 mL). After reaching room temperature in about 1 h, a \(^{31}\text{P}\{^1\text{H}\} \text{NMR showed \(\text{Ib}\) as the main product. Compound \(\text{Ib}\) decomposed into non-isolable products after one day in solution and was characterized by \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectroscopy as discussed in the Results.}\)

\[ {^3}\text{P}^\{^1\text{H}\} \text{NMR (toluene) (see Scheme 1 for atom labels): } \delta(P(x)) 221.7 \text{ (t, } 3^J_{\text{P(x)P(a)}} = 27.5 \text{ Hz), } \delta(P(a)) 27.7 \text{ (d, } 3^J_{\text{P(a)P(b)}} = 27.5 \text{ Hz).} \]

**Conversion of \(\text{Ni}_2\text{Cl}_2(\text{PPh}_3)_2[\mu_2\cdot\eta^2\cdot\eta^2\cdot\text{C(PPh}_3)═\text{PN(SiMe}_3\text{)}_2]\) (\(\text{IIla}\)) to \(\text{Ni}_2\text{Cl}_2(\text{PEt}_3)_2[\mu_2\cdot\eta^2\cdot\eta^2\cdot\text{C(PPh}_3)═\text{PN(SiMe}_3\text{)}_2]\) (\(\text{IV}\)).** To a cooled (-78°C) THF (5 mL) solution of \(\text{IIla}\) (0.0500 g, 0.0424 mmol) was added \(\text{PEt}_3\) (0.0151 g, 0.128 mmol). After warming to -40°C in 15 min with stirring, a \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum showed that \(\text{IV}\) formed in essentially quantitative yield. Compound \(\text{IV}\) decomposed into non-isolable products after one day in solution and was characterized by \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectroscopy as discussed in the} \)
Results. $^{31}$P{‘H} NMR (THF, -40°C) (see Scheme 2 for atom labels): $\delta$ (P(x)) 39.5 (dt, $^2 J_{P(3)P(2)} = 54.3$ Hz, $^2 J_{P(3)P(1)} = 49.9$ Hz), $\delta$(P(a)) 20.3 (dt, $^2 J_{P(3)P(1)} = 54.3$ Hz, $^2 J_{P(3)P(2)} = 5.5$ Hz), $\delta$(P(b)) 10.9 (dd, $^2 J_{P(3)P(1)} = 49.9$ Hz, $^2 J_{P(3)P(2)} = 5.5$ Hz).

Preparation of Cl(PPh$_3$)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (Mes* = 2,4,6-tri-tert-butylphenyl) (Va). Method A. To a cooled (-50°C) slurry of Ni(COD)$_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of PPh$_3$ (0.954 g, 3.64 mmol) and Cl$_2$C=PMes* (0.294 g, 0.909 mmol) in toluene (10 mL). After warming slowly to room temperature with stirring, the dark red solution was filtered and the solvent was removed under vacuum. The deep red residue was dissolved in acetone (25 mL) and the acetone solution was reduced to one-fourth of its volume under vacuum and cooled to -78°C to precipitate a mixture of dark red crystals of Va and yellow solids of Ni(PPh$_3$)$_3$Cl. The solids were isolated with a filter cannula and washed with 3 x 10 mL portions of acetone at 0°C to remove the Ni(PPh$_3$)$_3$Cl as a yellow solution. The remaining red solids were dissolved in a mixture of toluene (2 mL) and hexanes (6 mL) and cooled slowly to -78°C to form red crystals of Va which were isolated and dried under vacuum (0.387 g, 49% based on Cl$_2$C=PMes*).

Method B. To a cooled (-50°C) slurry of Ni(PPh$_3$)$_3$ (0.500 g, 0.451 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of Cl$_2$C=PMes* (0.0729 g, 0.226 mmol) in toluene (5 mL). After warming slowly to room temperature with stirring, the reaction mixture was worked up as above.

Method C. To a cooled (-50°C) slurry of (Ph$_3$P)$_2$Ni(C$_2$H$_4$) (0.500 g, 0.818 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of Cl$_2$C=PMes* (0.132 g, 0.409 mmol) in toluene (5 mL). After warming slowly to room temperature with stirring, the reaction mixture was worked up as above to yield 0.121 g of Va (34% based on Cl$_2$C=PMes*).

$^{31}$P{‘H} NMR (toluene) (see eq 4 for atom labels): $\delta$(P(a)) 25.5 (d, $^2 J_{P(3)P(2)} = 33.1$ Hz), $\delta$(P(x)) 21.6 (dd, $^2 J_{P(3)P(1)} = 33.1$ Hz, $^2 J_{P(3)P(2)} = 82.5$ Hz), $\delta$(P(b)) 17.8 (d, $^2 J_{P(3)P(1)} = 82.5$ Hz).

Anal. Calcd for C$_{55}$H$_{50}$ClNi$_3$P$_5$ (Va): C, 72.74; H, 6.66. Found: C, 72.60; H, 6.42.
**Preparation of Br(PPh$_3$)Ni[η$^-$-C(H)(PPh$_3$)=P(Mes*)] (Vb).** To a cooled (-50°C) slurry of Ni(COD)$_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (-50°C) solution of PPh$_3$ (0.954 g, 3.64 mmol) and Br$_2$C=PMes* (0.375 g, 0.909 mmol) in toluene (10 mL). After warming slowly to room temperature with stirring, the dark red solution was filtered and the solvent was reduced to 5 mL under vacuum. The deep red solution was treated with hexanes (40 mL), filtered, and crystals of Vb (0.295 g, 35% based on Br$_2$C=PMes*) were obtained by cooling the filtrate slowly to -78°C. $^3$P{H} NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 26.2 (d, $^2$J$_{P(a)Sp(a)}$ = 30.2 Hz), δ(P(x)) 23.1 (dd, $^2$J$_{P(x)Sp(x)}$ = 30.2 Hz, $^2$J$_{P(x)Sp(b)}$ = 85.2 Hz), δ(P(b)) 19.2 (d, $^2$J$_{P(b)Sp(a)}$ = 85.2 Hz).

**Preparation of Br(Cy$_3$P)Ni[η$^-$-C(H)(PCy$_3$)=P(Mes*)] (Vc).** This reaction was carried out as in the preparation of Vb above. The reagents used were Ni(COD)$_2$ (0.200 g, 0.727 mmol), tricyclohexylphosphine (PCy$_3$) (0.408 g, 1.45 mmol) and Br$_2$C=PMes* (0.150 g, 0.364 mmol) in toluene (10 mL). After warming slowly to room temperature with stirring, the lilac-colored solution was filtered. Compound Vc could not be isolated pure as it decomposed during attempted crystallization and was characterized by $^3$P{H} NMR spectroscopy as discussed in the Results. $^3$P{H} NMR (toluene): δ(P(b)) 32.2 (d, $^2$J$_{P(b)Sp(b)}$ = 55.0 Hz), δ(P(a)) 30.1 (d, $^2$J$_{P(a)Sp(a)}$ = 16.5 Hz), δ(P(x)) 5.6 (dd, $^2$J$_{P(x)Sp(b)}$ = 55.0 Hz, $^2$J$_{P(x)Sp(a)}$ = 16.5 Hz).

**$^{13}$C Labeling Studies of Cl(Ph$_3$P)Ni[η$^-$-C(H)(PPh$_3$)=P(Mes*)] (Va).** The compound Cl$_2$C=PMes* was prepared by substituting labeled $^{13}$CCl$_4$ for CCl$_4$ in the literature preparation. This compound was then used to prepare Cl(Ph$_3$P)Ni[η$^-$-$^{13}$C(H)(PPh$_3$)=P(Mes*)] by using the procedure in Method A above. $^3$P{H} NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 25.5 (dd, $^2$J$_{P(a)Sp(a)}$ = 33.1 Hz, $^2$J$_{CP}$ = 30.7 Hz), δ(P(x)) 21.6 (ddd, $^2$J$_{P(x)Sp(a)}$ = 33.1 Hz, $^2$J$_{P(x)Sp(b)}$ = 82.5 Hz, $^1$J$_{CP}$ = 93.5 Hz), δ(P(b)) 17.8 (dd, $^2$J$_{P(b)Sp(a)}$ = 82.5 Hz, $^1$J$_{CP}$ = 57.2 Hz). $^{13}$C{H} NMR (toluene): δ(C=P) 24.3 (ddd, $^1$J$_{CP(a)}$ = 93.5 Hz, $^1$J$_{CP(b)}$ = 57.2 Hz, $^2$J$_{CP(a)}$ = 30.7 Hz).
Hz). $^{13}$C NMR (toluene): $\delta$(C=P) 24.3 (ddddd, $^1J_{CP}$ = 145.8 Hz, $^1J_{CP(A)} = 93.5$ Hz, $^1J_{CP(B)} = 57.2$ Hz, $^2J_{CP(A)} = 30.71$ Hz).

Conversion of Br(Ph$_3$P)Ni[η$^2$-C(H)(PPh$_3$)=P(Mes*)] (Vb) to Br(Et$_3$P)Ni[η$^2$-C(H)(PPh$_3$)=P(Mes*)] (VI). To a THF solution of compound Vb (0.050 g, 0.0545 mmol) in an NMR tube was added one equivalent of PEt$_3$ (8 µL) at room temperature. Compound Vb was converted immediately and completely to compound VI, which was characterized by $^{31}$P{ $^1$H} NMR spectroscopy as described in the Results section. Addition of two more equivalents of PEt$_3$ (16 µL) did not cause further change. $^{31}$P{ $^1$H} NMR (THF) (see Scheme 2 for atom labels): $\delta$(P(x)) 22.5 (dd, $^2J_{PxPb}$ = 30.2 Hz, $^2J_{PxPb}$ = 90.5 Hz), $\delta$(P(a)) 18.5 (d, $^2J_{PaPb}$ = 90.5 Hz), $\delta$(P(b)) -5.5 (d, $^2J_{PbPb}$ = 30.2 Hz).

X-ray Crystallographic Study of Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ$_2$-η$^2$:η$^2$-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIA) Diffraction-quality crystals of IIIa were obtained by recrystallization from toluene at -78°C. Data collection and reduction information are given in Table 1. A dark green crystal of IIIa was mounted on a glass fiber for data collection. Cell constants were determined from a set of 25 reflections found by a random search routine. The data were corrected for Lorentz and polarization effects. A correction based on nonlinear decay in the three standard reflections was applied to the data. An absorption correction based on a series of ψ-scans using the semiempirical method was applied. The space group P1 was unambiguously determined by intensity statistics. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. One toluene molecule is disordered over two partially occupied sites. The phenyl groups of the triphenylphosphines were used as a model to restrain C-C interatomic distances within both unique toluene solvent molecules. A secondary crystallite was
unavoidably attached to the specimen used for data collection. An unsuccessful attempt was made to determine its orientation so a twin law could be applied. However, eight reflections which had $F_o^2 >> F_c^2$ were removed from the least-squares refinement, reducing R1 by about 2%. Selected bond distances and bond angles are given in Table 2.

**X-ray Crystallographic Study of Cl(Ph,P)Ni[η^2-C(H)(PPh₃)=P(Mes*)] (Va).** Diffraction-quality crystals of Va were obtained by recrystallization at -78°C in acetone. Data collection and reduction information are given in Table 1. A dark red crystal of Va was mounted on a glass fiber for data collection. An initial set of cell constants was calculated from 50 reflections taken from three sets of 20 frames. Final cell constants were calculated from a set of 4943 strong reflections taken during the data collection. The space group P1 was unambiguously determined by systematic absences and intensity statistics. A hemisphere-type data collection was employed in which a randomly oriented region of space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.87 Å. Three major swaths of frames were collected with 0.30° steps in $\omega$, providing a high degree of redundancy. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms, except for the C=P hydrogen atom (H(1)), which was refined as an independent atom. PLATON/SQUEEZE was used to remove the effects of the disordered toluene solvent molecule on the data. This solvent void was approximately 216.4 Å³ or 8.6% of the total volume. A total of 41.1 electrons were located in the disordered void, and the refinement improved by 1.1% after applying the program. Selected bond distances and bond angles are given in Table 3.
Results

Reactions of Ni(0) Complexes with Cl₂C=PN(SiMe₃)₂. The reactions (Scheme 1) of one-half equivalent of Cl₂C=PN(SiMe₃)₂ with 1:2 Ni(COD)₂/PPh₃, Ni(PPh₃)₄ or (Ph₃P)₂Ni(C₂H₄) in toluene at -78°C produce Ni₂Cl₂(PPh₃)₂[R₂-n':Tl'-C(PPh₃)=PN(SiMe₃)₂] (Iia) in 69-74% yield. The reaction with (Ph₃P)₂Ni(C₂H₄) (Method C) is preferred because it produces fewer impurities and gives slightly higher yields. Low temperature (-30°C) ³¹P NMR monitoring shows complex IIa as the only observable intermediate in these reactions. A 1:1 stoichiometric reaction of (Ph₃P)₂Ni(C₂H₄) with Cl₂C=PN(SiMe₃)₂ quantitatively forms IIa at -30°C. However, complex IIa could not be isolated and decomposes to unidentified products in solution at room temperature. Formation of IIIa occurs upon addition of another equivalent of (Ph₃P)₂Ni(C₂H₄) to the solution of IIa at 0°C. In this reaction, the remaining C-Cl bond in IIa is oxidatively added to (Ph₃P)₂Ni(C₂H₄), resulting in the formation of IIIa. Complex IIIa is oxygen sensitive in the solid state and in solution but does not react with water; it is thermally sensitive and decomposes when heated above 30°C.
Compounds IIa and IIIa were characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; the structure of IIIa was established by X-ray diffraction studies. The $^{31}\text{P}$ NMR spectrum of IIIa was collected at -50°C, as signal broadening occurred at room temperature. Excess PPh$_3$ present in solution enhanced this broadening, and at room temperature the signal for free PPh$_3$ disappeared. This is most likely due to phosphine exchange, although detailed studies were not carried out. Compound IIIa exhibits a $^{31}\text{P}$ NMR spectrum that is consistent with the structural data. A proton-coupled $^{31}\text{P}$ NMR spectrum shows the peak at $\delta$ 38.0 as a sharp doublet of triplets, which allows assignment of this peak to the C=PR phosphorus P(x), while the other two peaks are broadened due to coupling with phenyl protons and are assigned as PPh$_3$ groups. The characteristic doublet-of-triplets splitting pattern for P(x) allows for unambiguous assignments of the peaks; the doublet arises from splitting by the carbon-bound phosphine P(a) at $\delta$ 22.3 with $^3J = 57.8$ Hz, and the triplet is caused by the two equivalent nickel phosphines P(b) at $\delta$ 20.0 with $^2J = 41.2$ Hz. Although it is not possible to compare the $^{31}\text{P}$ NMR properties of IIIa with uncoordinated R$_3$P=C=PR ligands since they are unknown, some comparisons with similar compounds can be made. The chemical shift of $\delta$ 38.0 for P(x) in IIIa is significantly upfield from that of the phosphaalkene Cl$_2$C=PN(SiMe$_3$)$_2$ ($\delta$ 251.7 ppm) and the phosphavinyl phosphonium salt [(Ph$_3$P)(H)C=PN(i-Pr)$_2$]$^+$ ($\delta$ 303.5 ppm for C=P)$.^2^3$ This is consistent with similar dramatic upfield shifts which occur upon $\eta^2$-coordination of C=P double bonds; for example, Ni(PMe$_5$)$_2[\eta^2-(\text{Me}_3\text{Si})_2\text{C}\equiv\text{PCH(SiMe}_3)_2]$ ($\delta$ 23.4 ppm for C=P) is 380 ppm upfield from the free phosphaalkene (Me$_3$Si)$_2$C=PCH(SiMe$_3$)$_2$ ($\delta$ 404 ppm).$^2^8$ The coupling constant of $^2J = 57.8$ Hz between the C=P phosphorus P(x) and the carbon-bound phosphine P(a) in IIIa is smaller than values found for free phosphavinyl phosphonium salts, e.g., $^2J_{p,p} = 124.6$ Hz in [(Ph$_3$P)(H)C=PN(i-Pr)$_2$]$^+$, which also contains an R$_3$P-C=PR linkage.$^7$ However, in IIIa, the C=P phosphorus P(x) has sp$^1$-like character, which allows for less s-character in the bonding to carbon and would then result in a smaller coupling constant between P(x) and P(a). An even smaller $^2J_{p,p}$ value of 10.9 Hz was reported.
in the $\eta^1$-diphosphaallene complex \([(\text{Ph}_3\text{P})_2\text{Pt}(\eta^1-\text{R}P=\text{C}PR)]^2\) (R = tri-tert-butylbenzene) which contains an RP=\text{C}PR unit with one of the C=\text{P} bonds coordinated. The coupling constant of $^2J = 41.2$ Hz in IIIa between the C=\text{P} phosphorus P(x) and the two equivalent nickel phosphines P(b) that are located \text{cis} to P(x) is slightly larger than the coupling constant of $^2J_{p,p} = 28.6$ Hz between P(x) and the PMe$_3$ group that is \text{cis} to it in Ni(PMe$_3$)$_2[\eta^1$-(Me$_3$Si)$_2\text{C}P\text{CH(SiMe}_3)_2]$, most likely because the P(x) lone pair is involved in bonding to the nickel atoms in IIIa, which allows for more s-character from phosphorus in the P(x)-Ni bonds.

The $^{31}$P NMR spectrum of IIa is similar to that of the analogous compound Va (eq 4). The peak at $\delta$ 103.7 ppm is assigned to the C=\text{PR} phosphorus P(x), since a proton-coupled $^{31}$P NMR spectrum showed this peak as a sharp doublet of doublets, while the peaks at $\delta$ 22.4 and 19.0 ppm were broadened by proton coupling, indicative of PPh$_3$ groups. The peak for P(x) in IIa is 82.1 ppm downfield from the corresponding peak for P(x) in Va. This may be partially due to the different R-group on phosphorus or the proton on the carbon in Va instead of a chloride in IIa. However, a comparison of the $^{31}$P NMR spectra of two phosphaalkenes with different substituents that correspond to the different C- and P-substituents in IIa and Va, Cl$_2$C=PN(SiMe$_3$)$_2$ ($\delta$ 251.7 ppm)$^{23}$ and (Cl)(H)C=PMes* ($\delta$ 245 ppm)$^{30}$, shows that changes in these particular substituents do not necessarily impart large changes on the $^{31}$P NMR chemical shifts. A better explanation for the large differences in chemical shifts between IIa and Va is that the configuration around the C=\text{P} bond in IIa (Z) is different than that which was determined by X-ray diffraction for Va (E). It is well documented that the $E$ and $Z$ configurations of phosphaalkenes can have a large effect on the $^{31}$P chemical shift of the C=\text{P} phosphorus, although it is not possible to predict the relative shifts of the isomers.$^{31}$ An illustrative example is the phosphaalkene compound \([(\text{Ph})(\text{Me},\text{Si})\text{N})\text{C(Ph)=P(Ph)}\), in which the $E$ isomer has a chemical shift of $\delta$ 225 ppm and the $Z$ isomer is at $\delta$ 144 ppm.$^{32}$ Further evidence for the different configurations in IIa and Va is the appreciably smaller value of
$^{2}J_{P(C)} = 60.5$ Hz in IIa than that ($^{2}J_{P(C)} = 82.5$ Hz) in Va. According to the cis-rule in phosphaalkenes, substituents that are located cis to the phosphorus lone pair show larger couplings to the C=P phosphorus atom as is the case in the $E$ configuration in Va. The value of $^{2}J_{P(C)}$ in IIa (60.5 Hz) is also quite similar to that in IIIa (57.8 Hz), in which the carbon-bound PPh$_3$ group and the N(SiMe$_3$)$_2$ group are arranged in a $Z$ configuration as well.

In contrast to the reactions above with triphenylphosphine as the ligand, when a 1:2 Ni(COD)$_2$/PMe$_3$ mixture was reacted with Cl$_2$C=PN(SiMe$_3$)$_2$, complex Ib formed (Scheme 1). This compound did not react further to form the triethylphosphine analogs of IIa or IIIa, even when two equivalents of the Ni(0) reagent were added. However, all attempts to isolate Ib resulted in decomposition to unidentified products. The $^{31}$P NMR spectrum of compound Ib, $\delta$ 221.7 (t, $^{3}J_{P} = 27.5$ Hz, C=P-R), 27.7 (d, $^{3}J_{P} = 27.5$ Hz, Ni-PMe$_3$), is quite characteristic of a phosphavinyl structure (Scheme 1), and is very similar to that of a platinum analog Cl(Et$_3$P)$_2$Pt[C(Cl)=P(Mes*)], $\delta$ 234.2 (t, $^{3}J_{P} = 24.7$ Hz, C=P-R), 15.0 (d, $^{3}J_{P} = 24.7$ Hz, Pt-PMe$_3$) that was characterized previously by X-ray diffraction studies.

Reactions of Ni(0) Complexes with X$_2$C=PMes$^*$ (X=Cl, Br). The reactions (eq 4) of one-half equivalent of X$_2$C=PMes$^*$ (X = Cl, Br) with 1:2 Ni(COD)$_2$/PPh$_3$, Ni(PPh$_3$)$_2$ or (Ph$_3$P)$_2$Ni(C$_2$H$_4$) in toluene at $-78^\circ$C produce X(Ph$_3$P)Ni[=C(H)(PPh$_3$)=P(Mes$^*$)], (Va X = Cl; Vb X = Br) in moderate yields, along with a roughly equimolar amount of Ni(PPh$_3$)$_2$X. This Ni(I) compound was characterized by X-ray diffraction studies as the acetone solvate (Ph$_3$P)$_2$ClNi*(Me$_2$C=O), but the structure of a toluene solvate of the same compound was reported previously. The preparation of Va using Ni(COD)$_2$ and PPh$_3$ (Method A) is preferred because of the higher yield. The 2:1 metal complex to X$_2$C=PMes$^*$ stoichiometry is necessary to optimize the yield of product. When only one equivalent of metal complex is added, unreacted X$_2$C=PMes$^*$ remains in solution, while all of the Ni(0) reagent is consumed. Compounds Va and Vb are moderately air stable in the solid state, but air sensitive in solution. A similar reaction of 1:2
Ni(COD)₂/tricyclohexylphosphine (PCy₃) with one half equivalent of Br₃C=PMes* gave an analogous product (Vc), which was characterized by its ³¹P NMR spectrum.

\[
\text{Ni(PR₃)₂L + X₂C=PMes*} \rightarrow \text{Va-Vc}
\]

Compounds Va-Vc were characterized by ³¹P{¹H} NMR spectroscopy; the structure of Va was established by X-ray diffraction studies. A preliminary X-ray-determined structure for Vb was also obtained and showed that it was isostructural with Va. However, due to disordered solvent molecules, the final refinement was unacceptable for publication.

Compound Va exhibits a ³¹P NMR spectrum that is consistent with the structural data. The signal at δ 21.6 is assigned to P(x) based on a proton-coupled ³¹P spectrum which showed this peak as a sharp doublet of doublets, while the peaks at δ 25.5, assigned to P(a), and 17.8, assigned to P(b), were broadened due to phenyl proton couplings. The chemical shift of P(x) is significantly upfield from that in Cl₂C=PMes* (232.0 ppm)²⁴ and also significantly upfield from P(x) in the related complex IIA (103.7 ppm). The greater upfield shift of P(x) in Va, along with the larger ²Jₚ(x)ₚ(a) coupling constant of 82.5 relative to that in IIA (²Jₚ(x)ₚ(a) = 60.5) is indicative of the E configuration in Va, with the ylidic phosphine group being cis to the C=P phosphorus lone pair. The peak at δ 17.8 is assigned to P(b) and shows a cis- ²Jₚ(b)ₚ(x) = 33.1 Hz, which is similar to the cis- ²Jₚ(b)ₚ(x) = 24.7 Hz found in IIA, and the cis- ²Jₚ(b)ₚ(x) = 28.6 Hz found in the η²-phosphaalkene complex Ni(PMe₃)₂[η²-(Me₂Si)₂C=PCH(SiMe₃)₂].²⁸ The signal for the proton on the C=P carbon atom in Va is obscured by PPh₃ protons in the ¹H NMR spectrum, and the presence of this proton was deduced indirectly from the ¹H-coupled ¹³C NMR spectrum of ¹³C-labeled Va, [Cl(Ph₃P)Ni[η²-¹³C(H)(PPh₃)]=P(Mes*)]. The
measured $J_{\text{CH}}$ of 145.8 Hz is typical of one-bond sp$^2$ C-H coupling constants and is similar to $J_{\text{CH}} = 148.4$ Hz of the sp$^2$ carbon atom in MeCH=C(Me)$_2$.$^{35}$ The use of labeled Va also allowed for the elucidation of C-P coupling constants and unambiguous assignment of the signals in the $^{31}$P NMR spectrum. The $J_{\text{CP}(a)}$ value of 93.5 Hz is similar to $J_{\text{CP}(a)} = 86.9$ Hz found in (Me$_3$Si)$_2$C=PMes*,$^{36}$ and to $J_{\text{CP}(a)} = 92.5$ Hz found in the phosphonvinyl phosphonium salt [(Ph$_3$P)(H)C=PN(i-Pr)$_2$]$^+$.$^7$ The $J_{\text{CP}(a)}$ value of 57.2 Hz is similar to that $J_{\text{CP}(P)} = 52$ Hz found in the phosphonium salt (Ph$_3$P*CH$_3$)$_2$.$^5$ and is roughly intermediate between C-P coupling constants$^{37}$ in free (e.g., $J_{\text{CP}(P)} = 100.7$ Hz in Ph$_3$P=CH$_2$) and $\eta^1$ C-coordinated (e.g., $J_{\text{CP}(P)} = 26.1$ Hz in (CO)$_3$Ni(CH$_2$PPh$_3$)) phosphorus ylides. Both $J_{\text{CP}(a)}$ and $J_{\text{CP}(P)}$ are larger than the two-bond C-P coupling constant $J_{\text{CPb}} = 30.7$ Hz between the Ni-PPh$_3$ phosphorus and the C=P carbon. The $^{31}$P NMR spectra of Vb and Ve are very similar to that of Va; the peaks for P(x) at $\delta$ 26.19 for Vb and $\delta$ 5.64 for Ve are again split into doublets of doublets and do not show any signal broadening in the proton-coupled $^{31}$P NMR spectra.

**Phosphine Substitution Reactions of IIIa and Vb.** Compound IIIa reacts with two equivalents of triethylphosphine at $-40^\circ$C to generate Ni$_2$Cl$_2$(PEt$_3$)$_2[\mu_2-\eta^2;\eta^2$-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IV) in which the PPh$_3$ groups on nickel have been substituted by PEt$_3$ (Scheme 2). However, Compound IV decomposes in solution at $-25^\circ$C after one day and
could not be isolated. Substitution of the carbon-bound PPh₃ group was not observed, even when three equivalents of PEt₃ were added and the solution was warmed to room temperature. Compound IV was identified by the similarity of its $^{31}$P NMR spectrum to that of IIIa. The chemical shifts for P(x) at δ 39.5 and P(a) at δ 20.3 are quite similar to those in IIIa, 38.0 and 22.3, respectively. However, the chemical shift for P(b) is now at δ 10.9, 9.1 ppm upfield from P(b) in IIIa, which indicates that the nickel-coordinated PPh₃ groups have been substituted by PEt₃. The coupling constants, $J_{P(\text{a})(P\text{a})} = 54.3$ Hz and $J_{P(\text{b})(P\text{a})} = 49.9$ Hz in IV, are similar to those in IIIa, $J_{P(\text{a})(P\text{a})} = 57.8$ Hz and $J_{P(\text{b})(P\text{a})} = 41.2$ Hz, indicating that the geometry of the molecule is the same.

Since compound IIIa can be viewed as a triphenylphosphine-donor stabilized phosphavinyldene (Ph₃P=C=PR), an attempt was made to remove the carbon-bound phosphine-donor group to generate the parent phosphavinyldene complex. This was done by reacting IIIa with 9-BBN dimer (9, 9'-bi-borabicyclo[3.3.1]nonane), which is a known phosphine sponge reagent. However, no phosphavinyldene compounds were isolated, as the reaction results in complete decomposition of the complex with no isolable products.
Evidently, the carbon-bound PPh$_3$ group in IIIa is much more difficult to substitute or remove than the nickel-bound PPh$_3$ ligands, which precludes the formation of a phosphavinyldiene complex from IIIa.

Compound Vb reacts with one equivalent of triethylphosphine at room temperature to generate Br(Et$_3$P)Ni[η$^2$:C(H)(PPh$_3$)=PMes$^*$] (VI), in which the PPh$_3$ group on nickel has been substituted by PEt$_3$ (Scheme 2). Substitution of the carbon-bound PPh$_3$ group did not occur, even when two more equivalents of PEt$_3$ were added at room temperature. The $^{31}$P NMR spectrum of VI shows very similar splittings and chemical shifts to those of Vb. The chemical shifts for P(x) at δ 22.5 and P(a) at δ 18.5 are very similar to those in Vb, 23.1 and 19.2, respectively. However, the chemical shift for P(b) is now at δ -5.5, 31.7 ppm upfield from P(b) in Vb, which demonstrates that the nickel-coordinated PPh$_3$ group has been substituted by PEt$_3$. The coupling constants, $^2J_{P(x)P(a)} = 90.5$ Hz and $^2J_{P(b)P(a)} = 30.2$ Hz, are similar to those in Vb, $^2J_{P(x)P(a)} = 85.2$ Hz and $^2J_{P(b)P(a)} = 30.2$ Hz, indicating that the geometry of the molecule is the same.

Discussion

Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ-η$^2$:C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIA). Compound IIIa contains the first example of a phosphavinyldiene phosphorane (R$_3$P=C=PR) ligand, or phosphine donor stabilized phosphavinyldiene, which acts as a six-electron donor to the two nickel atoms in IIIa. Since there are no known examples of related isoelectronic R$_3$P=C=O, R$_3$P=C=NR or R$_3$P=C=S compounds in the chemistry of carbonyl, isocyanide or thiocarbonyl ligands, the formation of the R$_3$P=C=PR ligand in IIIa illustrates a new type of bonding capability in phosphavinylenes (:C=PR) that is not accessible with the more thoroughly studied, isoelectronic C=O, C=NR and C=S ligands. There are some examples of free$^{39}$ and coordinated$^{40,41}$ vinylidene phosphoranes R$_3$P=C=CR$_2$, which are carbon analogs of R$_3$P=C=PR. However, these compounds are only known to coordinate η$^1$ through the ylidic
carbon as two electron donor ligands. The phosphine-donor-stabilized phosphavinylidene ligand in **IIIa** is not formed simply by PPh₃ attack on a phosphavinylidene complex as compound **IIa** was observed as an intermediate in the reaction. A likely mechanism for the formation of compounds **IIa** and **IIIa** is outlined in Scheme 3. The first step in Scheme 3 involves the oxidative addition of a C-Cl bond from Cl₂C=PN(SiMe₃)₂ to the Ni(0) reagent. The product of this addition is the phosphavinyli intermediate **Ia**, which could not be observed in variable temperature NMR experiments from -50°C to -30°C; at -30°C, compound **IIa** begins to form. However, when triethylphosphine is used in this reaction, the phosphavinyli compound Cl(Et₃P)₂Ni[C(Cl)=PN(SiMe₃)₂] (**Ib**) forms and was characterized by ³¹P NMR spectroscopy as discussed in the Results section, which indirectly supports **Ia** as an intermediate. It is not clear why compound **Ib** does not go on to form triethylphosphine analogs of **IIa** and **IIIa**. Assuming **Ia** is an intermediate, it must rapidly isomerize to compound **IIa**, which was characterized by low temperature ³¹P NMR spectroscopy as discussed in the Results section.
The step involving rearrangement of Ia to IIa is similar to the intramolecular 1,2 shift of PMe₃ in an η¹-vinyl nickel complex (eq 5) to form an η¹-vinyl phosphonium compound.\(^{42}\)

\[
\begin{align*}
\text{Cl} & \text{Ni} & \text{PMe₃} & \text{COR} \\
\text{Me₃P} & \text{Ph} & \text{C} & = & \text{C} & \text{H} & \text{R} = \text{CH₂CMe₂Ph} \\
\text{Cl} & \text{Ni} & \text{PMe₃} & \text{COR} \\
\text{Me₃P} & \text{Ph} & \text{C} & = & \text{C} & \text{H} & \text{R} = \text{CH₃, 5b: R=CH₂SiMe₃,} \\
& & & & & & \\
5c: R=CH₂CMe₃, 5d: R=CH₂CMe₂Ph, \\
& & & & & & \\
5e: R=CH₂C₆H₄-ο-Me \\
\end{align*}
\]

In the structurally characterized η¹-vinyl complex \((\text{Me₃P})₂\text{ClNi[PhC=CH(COCH₂SiMe₃)]} \) (5b), the geometry around nickel is planar with a weak Ni-O interaction (Ni-O = 2.535(7) Å). It is interesting to note that the rearrangement to the η²-vinyl phosphonium compound in eq 5 was not general, and only in the case of \(R = \text{CH₂CMe₂Ph} \) did the 1,2 PMe₃ shift occur to form \((\text{Me₃P})₂\text{ClNi[η²-(Ph)(Me₃P)C=CH(COCH₂CMe₂Ph)]} \) (6d).\(^{42}\) A similar reaction was found in a series of Mo and W η¹-vinyl compounds which react with PMe₃ to generate η²-vinyl phosphonium compounds.\(^{43}\) These η²-vinyl phosphonium ligands may be considered as carbon analogs of the η²-phosphavinyl phosphonium ligands in compounds IIa and Va.

Although no mechanisms were postulated in these transformations, the reactions give precedent for the rearrangement of Ia to IIa, and this isomerization can be rationalized by proposing (Scheme 3) the rearrangement of the η¹-phosphavinyl (Ia) to an η²-phosphavinyl intermediate (Ia', Ia''), which is then attacked by PPh₃ at the carbon atom to generate IIa. Vinyl, acyl and iminoacyl ligands are all known to exhibit both η¹ and η² coordination, and there are some examples of coordinated iminoacyl compounds\(^{44}\) which undergo transformation from η¹ to η² coordination with concomitant loss of a phosphine ligand as in the rearrangement of Ia to Ia'. Ia'' in Scheme 3. Structural, spectroscopic and chemical studies of η²-vinyl\(^{45,46}\) and η²-acyl ligands\(^{47,48}\) suggest some influence of a carbene-like resonance form, similar to that (Ia'') proposed in Scheme 3. Since the attack of phosphines on carbene ligands is well known,\(^{49}\)
the attack of PPh₃ on the carbene-like intermediate \( \text{Ia}'' \) to generate \( \text{IIa} \) (Scheme 3) is reasonable. Further precedent for the postulated attack of PPh₃ on an \( \eta^2 \)-phosphavinyl complex is a reaction (eq 6) involving PPh₃ attack on an \( \eta^2 \)-vinyl intermediate.⁵⁰ There are

\[
\begin{align*}
\text{Os(NH₃)₅}^{3+} & \rightarrow \text{PPh₃} \\
\text{Os(NH₃)₅}^{2+} & \rightarrow \text{PPh₃}
\end{align*}
\]

also a few examples of phosphine attack on related \( \eta^2 \)-acyl ligands⁵¹-⁵³ (eq 7). A plausible explanation for the ease of nucleophilic attack by PPh₃ on the \( \eta^2 \)-phosphavinyl ligand (Ia', Ia'') in Scheme 3 is that the carbene-phosphido resonance structure (Ia'') is favored more than the alkyl-phosphine resonance form (Ia') because of the known instability of C=P double bonds,⁵⁴ which gives more carbene-like character to this intermediate and favors PPh₃ attack. This carbene-like resonance structure in the \( \eta^2 \)-phosphavinyl ligand (Ia'') is preceded by the X-ray structure of a similar \( \eta^2 \)-phosphavinyl complex of tungsten Cp(CO)₂W[\( \eta^2 \)-C(Ph)=PPh{W(CO)₅}] which contained a W-C bond length (1.954(8) Å) that is typical of a W=C double bond.⁵⁵ When another equivalent of the Ni(0) reagent is added to compound IIa at 0°C, compound IIIa is formed almost quantitatively. This reaction entails oxidative addition of the C-Cl bond in IIa to the Ni(0) reagent with subsequent loss of one equivalent of PPh₃ and the formation of dinuclear IIIa. It should be noted that in the Z-configuration which is postulated for IIa (see Results section), the second equivalent of Ni(0) is sterically able to access the open side of the C=P bond to undergo oxidative addition and form the dinuclear complex IIIa. Thus, the reaction pathway outlined in Scheme 3 reasonably accounts for the formation of IIa and IIIa.
Cl(Ph₃P)Ni[η²-C(H)(PPh₃)=P(Mes*)] Va. The reactions of Ni(0) complexes with Cl₂C=PN(SiMe₃)T (Scheme 1) and Cl₂C=PMes* (eq 4) occur under the same mild conditions but give quite different products. In an effort to understand why different R groups in the phosphaalkenes (Cl₂C=PR) lead to different products, one might assume that both reactions proceed by a phosphavinylic phosphonium intermediate such as Ila. As discussed above, the reaction of this intermediate with Ni(0) reagents for R = N(SiMe₃)₂ leads to the dinuclear IIIa (Scheme 3), but when R is the more bulky supermesityl group, oxidative addition across the C-Cl bond in the phosphavinylic phosphonium intermediate does not occur. Instead, the Ni(0) reagent abstracts a Cl atom from this intermediate to generate the Ni(I) compounds Ni(PPh₃)₃Cl, which was isolated from the reaction, and Ni(PR₃)(X)[C(PR₃)=PMes*], which abstracts an H atom to form compound Va. The formation of Ni(I) species from reaction of the Ni(II) phosphavinylic phosphonium intermediate with the Ni(0) reagent is somewhat similar to the known reaction of Ni(PPh₃)₄ with Ni(PPh₃)₂Cl₂ to generate two equivalents of Ni(PPh₃)₃Cl. Unfortunately, the reaction pathway could not be verified as no intermediates could be detected in variable temperature (-50°C to 20°C) ³¹P NMR studies. In an attempt to identify the source of the H atom in the C(H)(PPh₃)=PMes* ligand, an experiment was carried out in a dry box in which Ni(PPh₃)₄ (0.0903 mmol) was dissolved in distilled C₆D₆ (3 mL, no H₂O present in ¹H NMR) in a flask (dried at 150°C for 3 d) and reacted with Cl₂¹³C=PMes* (0.0451 mmol). Compound Va formed, but the proton coupled ¹³C NMR spectrum showed the same multiplet (ddd) for the C=P carbon as observed when the reaction was performed in non-deuterated toluene; no broadening was detected due to deuterium incorporation. Thus, the H atom in the C(H)(PPh₃)=PMes* ligand does not originate from the solvent. The phosphavinylic phosphonium ligands C(H)(PR₃)=PMes* in Va-c are the first examples of this type of ligand.

Structure and Bonding in Ni₂Cl₂(PPh₃)₂[μ-η²:η¹-C(PPh₃)=PN(SiMe₃)₂] (IIIa). Thermal ellipsoid drawings (Figures 1 and 2) of complex IIIa show that the nickel
atoms are both in planar environments defined by the PPh₃, Cl, and Ph₃P=C=PR ligands (sum of angles around nickel atoms are 360.2° for Ni(2) and 362.6° for Ni(1)). The dinuclear complex exhibits a “butterfly” geometry, with a long Ni-Ni distance (2.966(7) Å) that is outside the range of a typical Ni-Ni single bond (2.4-2.7 Å). This Ni-Ni distance in IIIa (Table 2) is longer than that in dinuclear nickel complexes in which a Ni-Ni bonding interaction has been excluded, e.g., d(Ni-Ni) = 2.908(3) Å in \([\{(Et_2PCH_2)_2Ni\}_2(\mu,n^2-P=P)\] , which is a dinuclear complex with a similar butterfly geometry containing a bridging P=PR unit, and d(Ni-Ni) = 2.874(2) Å in the A-frame complex \([Ni_2(\mu-C=CH_2)(dppe)_2Br_2]\). The C(1)-P(1) distance in IIIa (1.707(7) Å) indicates some double bond character, as it is more similar to a typical C=P double bond as found in Cl_3C=PN(SiMe_3)_2 (1.685(2) Å) than to that (1.773(8) Å) of the side-on π-bound phosphaalkene in Ni(PMe_3)_2[I-n-(Me_3Si)_2CHP=C(SiMe_3)_2]. The C(1)-P(2) distance (1.709(7) Å) is very similar to the C(1)-P(1) distance, and is intermediate between typical ylide C-P bond lengths, e.g. 1.661(8) Å in Ph_3P=CH_2, and C-coordinated ylide C-P bond lengths, e.g. 1.745(8) Å in (CO)_3Ni[(H)(Me)C=PCy_3]. The C(1)-P(2) distance indicates more ylidic (C*-P*) than phosphonium (C-P*) character in the bond, as it is significantly shorter than the C-PPh₃ distance (1.798(14) Å) found in the phosphavinyl phosphonium salt \([(Ph,P)(H)C=PN(i-Pr)_2)(BF_4)\]. The Ni(1)-P(1) and Ni(2)-P(1) distances (2.133(2) Å and 2.103(2) Å, respectively) are much shorter than the nickel-phosphine (Ni(1)-P(3) and Ni(2)-P(4)) distances (2.202(2) Å and 2.195(2) Å, respectively) and are also shorter than the Ni-P (phosphaalkene) distance (2.239(2) Å) found in Ni(PMe_3)_2[I-n^2-(Me_3Si)_2CHP=C(SiMe_3)_2]. The nitrogen atom of the N(SiMe₃)₂ group is in a planar environment, which is generally preferred for this group in other structures.

The structure of IIIa (Fig. 1) suggests that the novel phosphavinylidene-phosphorane ligand (R,P=C=PR) is a six-electron donor, providing two electrons from the ylide carbon, two from the C=P double bond and two from the lone pair on phosphorus as shown in L. As
mentioned, this ligand can also be considered the first example of a mixed $\sigma^2, \sigma^4$-diphosphaallene, and has much different coordinating abilities than the known $\sigma^4, \sigma^4$-diphosphaallenes $^{11}$ (J) and $\sigma^2, \sigma^2$-diphosphaallenes $^{3}$ (K) which have only been coordinated as two-electron donor ligands through the ylidic carbon in J and through one of the C=P double bonds in K. The $R_3P=C=PR$ in L ligand is drawn as the ylide rather than ylene form, which is a more appropriate representation as ab initio calculations have shown that the short C-PR$_3$ bond lengths found in ylides are more due to strong electrostatic attraction between the anionic carbon and the cationic phosphorus $R_2C^-PR_3^+$ than to a true ylene form $R_2C=PR_3$ with a C=P double bond.$^{63,64}$ A more appropriate comparison of the bridging phosphavinyldene-phosphorane ligand L is with diimino (M), iminophosphine (N), diphosphene (O) and disulfur (P) ligands.$^{65}$ These ligands are isolobal with L, when L is drawn in the ylide form, and have the capability of donating two electrons from each lone pair and two electrons from the double bond for a total of six electrons, as for L. These ligands are quite different than $\mu_2:\pi^2,\pi^2$-alkynes which can only donate four electrons to two metal atoms in a dimer. All four of the ligand types M-P have been coordinated as six-electron donor ligands in the iron dimers 7-10.$^{65-67}$ The tetrahedrane dimers 7-10 are closely related to IIIa, although they contain
metal-metal bonds to give an eighteen electron count, while in IIIa the two nickel atoms have a total of sixteen valence electrons each and no metal-metal bond is needed. The bonding in IIIa may be expressed by three resonance structures which are presented in Scheme 4. Resonance structure (a) may be viewed as a metalla-ylide-phosphido structure, where the phosphorus atom is covalently bonded to one nickel atom and the phosphorus lone pair donates two electrons to the other nickel fragment; the carbon atom is also covalently bonded to one nickel atom and the ylide carbon lone pair donates two electrons to the other nickel fragment. Both of the nickel atoms are then Ni(II), with the R3P=C=PR group acting as a six-electron donor overall. This is quite similar to the bonding in the related dimers 7-10. The short Ni(1)-P(1) and Ni(2)-P(1) bond lengths support a contribution from this phosphido-type of resonance form, and the short C(1)-P(2) bond length is explained by the electrostatic attraction
between the adjacent charges on the cationic P(2) and anionic C(1) in this resonance form.

Resonance structures (b) and (c) are formulated as zwitterionic structures where the minus charge is located on the nickel atom that is bound \( \eta^2 \) to the C=P double bond, while the other nickel atom coordinates to the R3P=C=PR ligand as an \( \eta^2 \)-phosphavinyl (three electron donor) ligand. In structures b and c, the anionic nickel atom is formally Ni(0), while the neutral nickel atom is formally Ni(II). Here the R3P=C=PR group acts as a five-electron donor ligand. The short C(1)-P(1) bond length suggests some contribution from these two resonance structures.

**Structure and Bonding in Cl(Ph3P)Ni[\eta^2-C(H)(PPPh3)=P(Mes*)] (Va).**

The structural drawing (Figure 3) of complex Va shows that the nickel atom is in a planar environment defined by the PPh3, Cl, and [C(H)(PPPh3)=PR] ligands (sum of angles around the nickel atom is 359.3°). The carbon-bound PPh3 and the Mes* groups are situated in a *trans* arrangement across the C(1)-P(1) bond. The H, PPh3, and Mes* groups are bent back from planarity in the C(H)(PPPh3)=PMes* unit, indicating a pyramidalization at C(1) and P(1). This is seen in both the dihedral angle of C(11)-P(1)-C(1)-P(2) = -123.1(3)° and in the sum of angles around C(1) = 343.5°. This indicates that C(1) is roughly intermediate between sp\(^2\) and sp\(^3\) hybridization, which is similar to structural features of \( \eta^2 \)-coordinated olefins and phosphaalkenes.\(^{28}\) The C-P distances can be compared with those found in the phosphavinyl phosphonium salt \([(Ph3P)(H)C=PN(i-Pr2)](BF4)\),\(^7\) which is a cationic analog of the C(H)(PPPh3)=PMes* ligand in Va, differing only in the R-group on phosphorus. The C(1)-P(1) distance in Va (1.796(5) Å) is much longer than the analogous C=P distance found in \[(Ph3P)(H)C=PN(i-Pr2)](BF4) (1.684(14) Å). This is consistent with the lengthening of C=P bonds which occurs upon \( \eta^2 \)-coordination of phosphaalkenes, and in fact the C(1)-P(1) distance in Va (1.796(5) Å) is quite similar to the C=P distance (1.773(8) Å) in the \( \eta^2 \)-phosphaalkene complex Ni(PMe3)\(_2[\eta^2-(Me3Si)\(_2\)CHP=C(SiMe3)\(_2\)].\(^{28}\) The C(1)-P(2) distance (1.742(5) Å), although shorter than the C(1)-P(1) distance, is longer than a typical ylide C-P
bond length, e.g., 1.661(8) Å in Ph3P=CH2,61 but shorter than the corresponding Ph3P-C bond (1.798(14) Å) in [(PPh3)(H)C=PN(i-Pr2)](BF4). The Ni-C(1) distance in Va (1.977(5) Å) is the same within error as the Ni-C distances (1.97(1) and 1.95(2) Å) in the related \( \eta^2 \)-vinyl phosphonium compound (Me3P)2ClNi[\( \eta^2 \)-PhC=CH(COCH2CMe2Ph)] (6d, eq 5).42 The Ni-P(1) distance in Va (2.1793(13) Å) is the same within error as the Ni-P(3) distance (2.1783(14) Å) which suggests the lack of participation of a Ni-P(1) phosphido-like resonance structure as observed in IIIa.

Compound Va is the first example of a complex containing a coordinated phosphavinyl phosphonium ligand. A few examples of uncoordinated phosphavinyl phosphonium salts [(R3P)RC=PR]*7-10 have been reported in the literature and the structure of [(PPh3)(H)C=PN(i-Pr2)](BF4) was determined by X-ray diffraction.7 The NMR spectra of these compounds, along with the X-ray evidence, suggest that there is a contribution from both resonance forms d and e in Scheme 5, and these compounds have also been referred to as \( \sigma^2 \), \( \sigma^4 \)-diphosphaallyl cations (resonance form f).10 However, we find no evidence for allyl-like behavior in the (Ph3P)(H)C=PMes* ligand which is bound \( \eta^2 \) through the C(1)-P(1) bond in Va as opposed to \( \eta^3 \) through the P(2)-C(1)-P(1) allyl-like unit as in compounds of the type (R3P)(X)Ni[\( \eta^3 \)-allyl]. There are a few examples of \( \eta^3 \)-coordinated \( \sigma^2 \), \( \sigma^4 \)-diphosphaallyl ligands,68-71 but the (Ph3P)(H)C=PMes* group in Va is best viewed as a phosphavinyl phosphonium ligand. Since it is generally accepted that the short bond lengths found in ylide C-P bonds are caused by an electrostatic interaction and not a genuine \( \pi \)-bond, and there are no structurally characterized examples of \( \eta^3 \)-C=PR, coordinated ylide compounds, the \( \eta^3 \)-
coordination of the \((\text{Ph}_3\text{P})(\text{H})\text{C} = \text{PMes}^*\) ligand in \(\text{Va}\) is unlikely, and further supports the lack of \(\pi\)-bonding in ylides.

The bonding in compound \(\text{Va}\) may be described as a mixture of two resonance structures as shown in Scheme 6. Resonance form \(g\) can be viewed as an ylide-phosphido structure with a dative two electron donation from \(\text{C}(1)\) and a covalent, phosphido-type bond between \(\text{P}(1)\) and nickel. Here the \((\text{Ph}_3\text{P})(\text{H})\text{C} = \text{PMes}^*\) ligand donates three electrons to the thirteen-electron nickel fragment, which is formally \(\text{Ni}(II)\). Resonance form \(h\) can be viewed as an \(\eta^2\)-phosphavinyl phosphonium cation \((1+)\) coordinated to a formally \(\text{Ni}(0)\) metal fragment. This is a zwitterionic structure with the minus charge located on nickel and the \(\text{C} = \text{P}\) double bond acting as a two-electron donor. The somewhat short \(\text{C}(1)-\text{P}(2)\) distance found in \(\text{Va}\) suggests a contribution from form \(g\) in Scheme 6. However, the \(\text{Ni}-\text{P}(1)\) distance is typical of \(\text{Ni}\)-phosphine bonds, and is not indicative of a phosphido structure, suggesting more of a contribution from resonance form \(h\). Unlike structure \(\text{IIIa}\), the \(\text{C} = \text{P}\) phosphorus lone pair is unavailable for bonding in this structure, as it is pointing down and away from the metal center. The resonance structures in Scheme 6 are quite similar to those postulated for the related \(\eta^1\)-vinyl phosphonium compound \((\text{Me}_3\text{P})_2\text{ClNi}[\eta^1-(\text{Ph})(\text{Me}_3\text{P})\text{C} = \text{CH}(\text{COCH}_2\text{CMe}_2\text{Ph})]\) \((6d, eq \text{5})\).
The structure of Va exhibits an interesting feature in that it contains a somewhat distorted, boat-shaped supermesityl ring with the P(1) atom located 1.09 Å out of the plane of the carbon atoms in the arene ring. This is most likely a steric effect, as compound Va is quite bulky and the supermesityl ring is forced to bend back away from the nickel-bound P(1) atom in order to alleviate steric strain, with a concomitant puckering of the ring. Calculations have shown that in very bulky substituted-phenyl rings in which the substituents are forced to bend out of the plane of the ring, a similar puckering of the aromatic ring occurs in order to maintain the greatest amount of delocalization in the ring, and such distortions were calculated to be favorable with much of the electron delocalization (aromaticity) of the ring remaining. In other sterically encumbered supermesityl systems, a similar puckering of the ring is observed (Table 4). The cell coordinates and atomic positions for the compounds in Table 4 were obtained from the literature references and entered into CSC Chem 3D Plus™ (Version 3.1.1, Cambridge Scientific Computing) in order to ascertain the deviation from planarity in the rings. The first column of data represents the average deviation from planarity of the six carbon atoms making up the Mes* ring in the given compound, while the second data column gives the distance that the P or In atom is displaced out of the average plane defined by the six ring carbon atoms of the supermesityl ring. As can be seen in Table 4, all of these compounds show similar distortions as those in Va to varying degrees and the most sterically crowded systems seem to show the greatest distortions. In the iron-coordinated diphosphene complex Cp(CO)₂FeP=PMes* (12), in which there is no steric interference between the Mes* group and the rest of the complex, there is no deviation from planarity in the ring and the phosphorus atom is only 0.123 Å out of the plane of the ring. However, when the P=P bond is η¹-coordinated to the bulky Pt(PPh₃)₂ moiety in Pt(PPh₃)₂[η¹-Cp(CO)₂FeP=PMes*] (13), the Mes* ring becomes puckered with an average deviation from planarity in the ring C-atoms of 0.040 Å, and the phosphorus atom is situated 0.562 Å out of the average plane of the ring. The compound In(Mes*)₂Br (11) exhibits a structure that is perhaps the most sterically
bulky of all of the structures that were examined, containing two Mes* groups attached to the same atom. Correspondingly, this structure exhibits the greatest deviation of the heteroatom out of the average plane of the ring (1.44 Å), but its average deviation from planarity in the ring (0.057 Å) is similar to that of compounds 1 (0.061 Å), 2 (0.052 Å) and Va (0.073 Å). Thus, puckering of the ring and bending out of the plane of the P(1) atom in Va are most likely caused by steric congestion in the molecule, and this type of distortion is similar to that observed in other sterically bulky compounds containing Mes* rings.

Summary

Oxidative addition reactions of Ni(0)-PPh3 reagents with Cl2C=PN(SiMe3)2 results in formation of the first example of a phosphavinyldene phosphorane ligand (Ph3P=C=PR'), which may also be viewed as a σ2, σ4-diphosphaallene, coordinated as a six-electron donor ligand in the dinuclear nickel butterfly dimer Ni2Cl2(PPh3)2[μ2-η2:η2-C(PPh3)=PN(SiMe3)]=PN(SiMe3)2 (IIIa) (Scheme 1, Fig. 1). A phosphavinyldene phosphonium intermediate Cl(Ph3P)Ni[η2-C(Cl)(PPh3)=PN(SiMe3)] (IIa) was identified in this reaction and most likely results from PPh3 attack on an η2-phosphavinyldene intermediate that reacts like an electrophilic carbene (Scheme 3). The Ph3P=C=PR' ligand in IIIa is isovalb with diimine (RN=NR), iminophosphine (RN=PR), diphosgene (RP=PR) and disulfur (RS=SR) ligands, which also act as dibridging six-electron donors. A similar reaction using PEt3 instead of PPh3 resulted in formation of the η1-phosphavinyldene compound Cl(Et3P)2Ni[η1-C(Cl)=PN(SiMe3)] (Ib). In contrast, when the same Ni(0)-PPh3 reagents are reacted with X2C=PMes* (X = Cl, Br; Mes*=2,4,6-tri-2-butylbenzene), the phosphavinyldene phosphonium compounds X(Ph3P)Ni[η2-C(H)(PPh3)=P(Mes*)] (Va,b) form along with Ni(PPh3)3X (eq 4). A similar reaction using PCy3 instead of PPh3 formed an unstable PCy3 analog (Vc) of Va. The difference in reactivity between Cl2C=PN(SiMe3)2 and Cl2C=PMes* with Ni(0) reagents is likely due to the greater steric bulk of the Mes* group which prevents the formation of a dimer analogous to IIIa.
Compound Va is the first example of a metal complex containing a phosphavinyldiphosphonium ligand (C(H)(PPh₃)=PMes*), which may also be viewed as an π²-coordinated σ², σ⁴-diphosphaallyl ligand coordinated as a three-electron donor (Scheme 6). This compound also exhibits a somewhat distorted supermesityl ring, which is likely due to steric constraints in the molecule and has been observed in other bulky supermesityl-containing compounds.

Acknowledgment

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References


(26) SHELXTL-Plus V5.0. Siemens Industrial Automation Inc., Madison, WI.


(49) Kreissl, F. R. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, 1983, pp 156-159.


Table 1. Crystal and Data Collection Parameters for Ni₂Cl₂(PPh₃)₂[μ-η²:η²-C(PPh₃)=PN(SiMe₃)J (IIIA) and Cl(Ph₃P)Ni[η²-C(H)(PPh₃)=P(Mes*)] (Va).

<table>
<thead>
<tr>
<th>Formula</th>
<th>IIIa</th>
<th>Va</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{75} \text{H}</em>{79} \text{Cl}<em>{12} \text{Ni}</em>{2} \text{P}<em>{3} \text{Si}</em>{2} )</td>
<td>( \text{C}<em>{58.50} \text{H}</em>{54} \text{ClNiP}_{3} )</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{P} \bar{I} )</td>
<td>( \text{P} \bar{I} )</td>
</tr>
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<td>10.904(2)</td>
<td>10.7005(8)</td>
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<tr>
<td>( b, \text{ Å} )</td>
<td>17.073(3)</td>
<td>12.968(1)</td>
</tr>
<tr>
<td>( c, \text{ Å} )</td>
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<td>74.537(1)</td>
</tr>
<tr>
<td>( \beta, \text{ deg} )</td>
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<td>83.690(1)</td>
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<tr>
<td>( \gamma, \text{ deg} )</td>
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<td>68.106(1)</td>
</tr>
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<td>( V, \text{ Å}^3 )</td>
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<td>2525.1(4)</td>
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<tr>
<td>( Z )</td>
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<td>2</td>
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<tr>
<td>( d_{\text{calc}}, \text{ g/cm}^3 )</td>
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<td>1.255</td>
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<td>Crystal size, mm</td>
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<td>( \mu, \text{ mm}^{-1} )</td>
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<td>Temp, K</td>
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<td>173(2)</td>
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<td>Scan method</td>
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<td>Area Detector, ( \omega )-frames</td>
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<td>7384</td>
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<td></td>
<td>IIIa</td>
<td>Va</td>
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<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>with I &gt; 2σ (I)</td>
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<td>5879</td>
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<td>613</td>
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<tr>
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<td>0.0622</td>
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<tr>
<td>R_w b (I &gt; 2σ (I))</td>
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<td>0.1378</td>
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<tr>
<td>quality of fit indicator^c</td>
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<td>1.090</td>
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<tr>
<td>largest peak, e/Å^3</td>
<td>0.642</td>
<td>0.610</td>
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^aR = Σ||F_o|-|F_c||/Σ|F_o|.  
^bR_w = [Σw(|F_o|-|F_c|)^2/Σw|F_o|^2]^{1/2}; w = 1/σ^2(|F_o|).  
^cQuality-of-fit =

[Σw(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}. 
Table 2. Selected Bond Distances (Å) and Angles (deg) for Ni$_2$Cl$_2$(PPh$_3$)$_2$[$\mu$-$\eta^2$-$\eta^2$]-C(PPh$_3$)PN(SiMe$_3$)$_2$ (IIIa).

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Ni(1)-Ni(2)</th>
<th>2.966(7)</th>
<th>Ni(2)-C(1)</th>
<th>2.036(7)</th>
<th>C(1)-P(2)</th>
<th>1.709(7)</th>
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<tr>
<td>Ni(1)-C(1)</td>
<td>1.983(7)</td>
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<td>Ni(2)-P(1)</td>
<td>2.103(2)</td>
<td>P(1)-N(1)</td>
<td>1.684(6)</td>
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<tr>
<td>Ni(1)-P(1)</td>
<td>2.133(2)</td>
<td>Ni(2)-P(4)</td>
<td>2.195(2)</td>
<td>N(1)-Si(1)</td>
<td>1.773(6)</td>
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<tr>
<td>Ni(1)-P(3)</td>
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<td>2.205(2)</td>
<td>N(1)-Si(2)</td>
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<td>C(1)-P(1)</td>
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<table>
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<tr>
<th>Bond Angles (deg)</th>
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<tr>
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<tr>
<td>C(1)-Ni(1)-P(3)</td>
<td>158.1(2)</td>
<td>C(1)-Ni(2)-Cl(2)</td>
<td>104.2(2)</td>
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<tr>
<td>C(1)-Ni(1)-Cl(1)</td>
<td>101.5(2)</td>
<td>P(1)-Ni(2)-Cl(2)</td>
<td>152.57(9)</td>
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<tr>
<td>P(1)-Ni(1)-Cl(1)</td>
<td>147.54(10)</td>
<td>P(4)-Ni(2)-Cl(2)</td>
<td>93.41(8)</td>
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<tr>
<td>P(3)-Ni(1)-Cl(1)</td>
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<td>P(1)-N(1)-Si(1)</td>
<td>121.7(3)</td>
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<td>P(1)-Ni(1)-P(3)</td>
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<td>C(1)-Ni(2)-P(1)</td>
<td>48.7(2)</td>
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*Numbers in parentheses are estimated standard deviations in the least significant digits.*
Table 3. Selected Bond Distances (Å) and Angles (deg) for Cl(Ph₃P)Ni[η²-C(H)(PPh₃)=P(Mes*)] (Va).

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>C(1)-P(1)</th>
<th>1.796(5)</th>
<th>Ni-Cl</th>
<th>2.2338(12)</th>
<th>C(13)-C(14)</th>
<th>1.389(6)</th>
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<tbody>
<tr>
<td>C(1)-P(2)</td>
<td>1.742(5)</td>
<td></td>
<td>P(1)-C(11)</td>
<td>1.892(4)</td>
<td>C(14)-C(15)</td>
<td>1.391(6)</td>
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<tr>
<td>Ni-C(1)</td>
<td>1.977(5)</td>
<td></td>
<td>C(1)-H(1)</td>
<td>0.86(4)</td>
<td>C(15)-C(16)</td>
<td>1.394(6)</td>
</tr>
<tr>
<td>Ni-P(1)</td>
<td>2.1793(13)</td>
<td>C(11)-C(12)</td>
<td>1.421(6)</td>
<td>C(16)-C(11)</td>
<td>1.432(6)</td>
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<tr>
<td>Ni-P(3)</td>
<td>2.1783(14)</td>
<td>C(12)-C(13)</td>
<td>1.393(6)</td>
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</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
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<tbody>
<tr>
<td>P(1)-C(1)-P(2)</td>
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<td>C(1)-Ni-P(1)</td>
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<td>C(1)-Ni-P(3)</td>
</tr>
<tr>
<td>C(1)-Ni-Cl</td>
</tr>
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<td>P(1)-Ni-P(3)</td>
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<td>P(1)-Ni-Cl</td>
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<tr>
<td>P(3)-Ni-Cl</td>
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*Numbers in parentheses are estimated standard deviations in the least significant digits.*
Table 4. Deviations From Planarity in Supermesityl Rings.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C Atom(^a) Deviation (Å)</th>
<th>P (or In) Deviation(^b) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PEt(_3))(_2)Cl[(Cl)C=P(Mes(*)] (1)(^c)</td>
<td>0.061</td>
<td>0.668</td>
</tr>
<tr>
<td>(Et(_3)P)(_2)ClPt[(\mu-(C=P(Mes(*)])Pt(PEt(_3))Cl (2)(^d)</td>
<td>0.052</td>
<td>0.499</td>
</tr>
<tr>
<td>Cl(Ph(_3)P)Ni[(\eta^2-C(H)(PPh(_3))=P(Mes(*))] (Va)(^e)</td>
<td>0.073</td>
<td>1.09</td>
</tr>
<tr>
<td>In(Mes(*))(_2)Br (11)(^f)</td>
<td>0.057</td>
<td>1.44</td>
</tr>
<tr>
<td>Cp(CO)(_2)FeP=P(Mes(*) (12)(^g)</td>
<td>0.000</td>
<td>0.123</td>
</tr>
<tr>
<td>Pt(PPh(_3))(_2[\eta^2-Cp(CO)(_2)FeP=P(Mes(*)] (13)(^h)</td>
<td>0.040</td>
<td>0.562</td>
</tr>
</tbody>
</table>

\(^a\) Average deviation of ring C atoms from ring plane.

\(^b\) Deviation of P (or In) from average carbon ring plane.

\(^c\) Ref. 12.

\(^d\) Ref. 12.

\(^e\) This work.

\(^f\) Ref. 75.

\(^g\) Ref. 73.

\(^h\) Ref. 74.
Figure Captions

**Figure 1.** Thermal ellipsoid drawing of Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ$_3$-η$^2$-η$^2$-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIa)

**Figure 2.** Thermal ellipsoid drawing of Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ$_3$-η$^2$-η$^2$-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIa) with phenyl and methyl groups removed.

**Figure 3.** Thermal ellipsoid drawing of Cl(PPh$_3$)Ni[η$^2$-C(H)(PPh$_3$)=P(Mes*)] (Va)
Figure 1.
Figure 2.
Figure 3.
The oxidative addition reaction of $\text{Pd(PPh}_3)_4$ with $\text{Cl}_2\text{C}=\text{PN(SiMe}_3)_2$ forms the phosphavinyl phosphonium complex $\text{Cl(Ph}_3\text{P)}\text{Pd(}\eta^1\text{-C}^\text{(Cl)}\text{(PPh}_3)_2\text{)=PN(SiMe}_3)_2\text{]}$ (IIa) which results from $\text{PPh}_3$ migration from Pd to carbon in the $\eta^1$-phosphavinyl intermediate trans-$\text{Cl(Ph}_3\text{P)}\text{Pd}[\text{C}^\text{(Cl)}\text{=}\text{PN(SiMe}_3)_2\text{]}$ (IIa). The reaction of $\text{Pd(dba)(dppe)}$ with $\text{Cl}_2\text{C}=\text{PN(SiMe}_3)_2$ forms the $\eta^1$-phosphavinyl complex $\text{cis-Cl(dppe)}\text{Pd}[\text{C}^\text{(Cl)}\text{=}\text{PN(SiMe}_3)_2\text{]}$ (VI), which does not undergo phosphine migration. Compound IIIa undergoes substitution of the chloride ligand by $\text{PPh}_3$ or $\text{MeCN}$ in the presence of $\text{KPF}_6$ to generate $[(\text{Ph}_3\text{P})_2\text{Pd(}\eta^1\text{-C}^\text{(Cl)}\text{(PPh}_3)_2\text{)=PN(SiMe}_3)_2\text{]}] \text{(IV)}$ or $[(\text{Ph}_3\text{P})(\text{MeCN})\text{Pd(}\eta^1\text{-C}^\text{(Cl)}\text{(PPh}_3)_2\text{)=PN(SiMe}_3)_2\text{]}] \text{(PF}_6\text{)} $ (V), respectively; the structure of V was determined by X-ray diffraction studies. The reaction of $\text{Pd(PEt}_3)_4$ with $\text{Cl}_2\text{C}=\text{PN(SiMe}_3)_2$ forms the $\eta^1$-phosphavinyl complex trans-$\text{Cl(PEt}_3)_2\text{Pd}[\text{C}^\text{(Cl)}\text{=}\text{PN(SiMe}_3)_2\text{]}$ (IIb), which does not undergo PEt$_3$ migration. When two equivalents of $\text{Pd(PEt}_3)_4$ are reacted with $\text{Cl}_2\text{C}=\text{PN(SiMe}_3)_2$ the phosphonio-methylene(imino)metallophosphorane complex $\text{Pd(PEt}_3)_2(\text{Cl}[\mu-\eta^1;\eta^2-\text{C(SiMe}_3)_2](\text{PEt}_3)_2\text{)=PN(PEt}_3)_2\text{]}$ (VIIa-b) forms as a 1:1 isomeric mixture. Compound VIIa-b reacts with $\text{MeI}$ or $\text{NaI}$ to generate $\text{Pd(PEt}_3)_2(\text{I}[\mu-\eta^1;\eta^2-\text{C(SiMe}_3)_2]$.
C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)Pd(PEt$_3$)I (VIIa-b) and reacts with traces of water to generate Cl(Et$_3$P)Pd[$\eta^2$-C(SiMe$_3$)(PEt$_3$)=P(=O)NH(SiMe$_3$)] (IX). The structure of VIIb was partially determined, and the structure of IX was determined by X-ray diffraction studies. Compounds VIIa-b, VIIa-b and IX exhibit the first examples of coordinated methylene(imino, oxo)phosphorane ligands.

† X-Ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, MN 55455

**Introduction**

Carbon-phosphorus multiply-bonded ligands have received much attention recently because of the rich coordination chemistry that they afford. In particular, the C=\(\text{P}\) double bonds in several different types of ligands have been found to exhibit a preferential \(\eta^2\)-coordination mode in many transition metal complexes. Several examples of \(\eta^2\)-coordinated phosphaalkenes are known,\(^1\)-\(^4\) and there are examples of \(\eta^3\)-coordinated diphosphaallyl complexes,\(^5\)-\(^8\) in which two bonds having C=P double bond character are coordinated; in addition, a few examples of \(\eta^3\)-coordinated diphosphaallenes have been reported.\(^9\) There are also examples of cyclic phosphorus-substituted ligands including \(\eta^4\)-phosphacyclobutadienes, \(\eta^4\)-phosphacyclopentadienyls and \(\eta^6\)-phosphabenzenes in which delocalized rings containing C=P double bonds are coordinated to transition metal complexes.\(^10\) The propensity for \(\eta^2\)-coordination of C=P double bonds is especially evident in phosphallenes (A) which coordinate through the C=P double bond in preference to the C=C double bond.\(^11,\)\(^12\) In view of the
many different coordination compounds with ligands containing C=P double bonds, it is
interesting that there are none of methylene(oxo)phosphoranes \(R_2C=P(=O)R\) (B) or
methylene(imino)phosphoranes \(R_2C=P(=NR)R\) (C). These compounds are included in a
recent review\(^1\) of three-coordinate pentavalent phosphorus compounds (\(\sigma^3\lambda^5\)-phosphoranes)
and constitute an area of recently increased study. In these methylene(oxo,
imino)phosphoranes, the C=P double bond should allow for \(\eta^2\)-coordination to a transition
metal, although such complexes have not been previously discussed.

We recently succeeded in preparing the first example of a coordinated isocyaphide
\((:C=PR)\) ligand by oxidative addition of the C-X bond in the phosphavinyl complex (1) (eq 1)
to generate a diplatinum complex \([\text{Cl}(\text{Et}_3\text{P})\text{Pt}(\mu-C=PR)\text{Pt}(\text{PEt}_3)_2(\text{Cl})]\) (2) containing a semi-
bridging \(\text{C}=\text{PR}\) group.\(^1\)\(^4\) A series of phosphavinyl compounds \(X(R'\text{P})_2\text{M}[\text{C}(=\text{PR})X]\)
\[
\text{Pt}(\text{PEt}_3)_4 + \text{Cl}_2\text{C}=\text{PR} \\
(\text{R} = \text{Mes}^*, 2,4,6\text{-tri-tert-butylbenzene})
\]
\[
(1)
\]
\[
(2)
\]
\(\text{M} = \text{Pt}, \text{Pd}; \ X = \text{Cl}, \text{Br}; \ R' = \text{Ph}, \text{Et}; \ R = 2,4,6\text{-tri-tert-butylbenzene})\) analogous to (1) were
prepared and in all cases exhibited a novel R-group migration from phosphorus to carbon to
generate Mes\(^*\)C=P and M(\(PR'_3\))\(_2\)X\(_2\).\(^1\)\(^5\) Romanenko and coworkers\(^1\)\(^6\) reported the reaction of
\(\text{Pd}(\text{PPh}_3)_4\) with \(\text{Cl}_2\text{C}=\text{PMes}^*\) which resulted in the formation of Mes\(^*\)C=P and \(\text{Pd}(\text{PPh}_3)_2\text{Cl}_2\)
with no observable intermediates (eq 2). The Mes\(^*\) group rearrangement in these reactions
\[
\text{Pd}(\text{PPh}_3)_4 + \text{Cl}_2\text{C}=\text{PMes}^* \rightarrow \text{Mes}^*\text{C}=\text{P} + \text{Pd}(\text{PPh}_3)_2\text{Cl}_2 \quad (2)
\]
\(\text{Mes}^* = 2,4,6\text{-tri-tert-butylbenzene})\) prompted us to attempt similar oxidative addition reactions between dihalophosphaalkenes
containing non-aromatic R-groups and low-valent transition metals. In the course of these
studies, we have prepared\(^\text{17}\) (eq 3) and structurally characterized the first example of a complex (4) containing a phosphavinyldene phosphorane \((\text{Ph}_3\text{P} = \text{C} = \text{PR})\) ligand, which forms from an intermediate phosphavinylnyl phosphonium complex (3) which was not isolated. In a similar reaction\(^\text{17}\) (eq 4) with \(\text{Mes}^*\) as the R-group, we were able to isolate and structurally characterize the first example of a complex (5) containing a phosphavinylnyl phosphonium ligand. In these reactions, the R-group migration from phosphorus to carbon was avoided and an interesting \(\text{PPh}_3\) migration to the \(\text{C}=\text{P}\) carbon afforded the new ligands. The reactions in eq 3-4 were postulated to involve \(\eta^1\)-phosphavinylnyl intermediates similar to that (1) in eq 1, which then rearranged to \(\eta^2\)-phosphavinylnyl complexes having carbene-like character which facilitated the attack of \(\text{PPh}_3\) on the \(\text{C}=\text{P}\) carbon atoms.\(^\text{17}\)

In our continuing studies of oxidative addition reactions of dihalophosphaalkenes with low valent transition metal complexes, we explore in the present paper reactions of \(\text{Cl}_2\text{C}=\text{PN(SiMe}_3)_2\) with Pd(0) complexes. During the course of these studies, we isolated a stable phosphavinylnyl phosphonium complex that is the palladium analog of the unstable nickel complex (3) (eq 3) and explored ligand substitution reactions to generate a series of these complexes with \(\eta^1-\langle \text{R}_4\text{P}\rangle(\text{Cl})\text{C}=\text{PR}\) ligands acting as three electron donors (D). We have also
isolated the first example of a complex with a phosphonio-
methylene(imino)metallophosphorane ligand \( \eta^2 \)-coordinated to one palladium center and \( \eta^1 \)- to another in a dinuclear complex (E). This new ligand results from a 1,3-SiMe\(_3\) migration from nitrogen to carbon and was further functionalized by a hydrolysis reaction into the first example of a phosphonio-methylene(oxo)phosphorane ligand, which is \( \eta^2 \)-coordinated to a palladium atom with the \((R_jP)(Me_3Si)C=P(=O)NSiMe_3\) ligand acting as a three-electron donor (F). The ligands in E and F represent the first examples of transition metal-coordinated methylene(imino)phosphoranes and methylene(oxo)phosphoranes, respectively. Although these ligands contain phosphonio substituents on the C=P carbon atoms, their \( \eta^2 \)-coordination through the C=P double bond opens up the possibility of coordinating other members of this well known class of \( \sigma^3\lambda^5 \)-phosphoranes.

The preparations of complexes of types D, E and F are discussed, along with substitution reactions, likely pathways of formation and chemical reactivity. Structure and bonding in the complexes containing these new ligands are also examined.

**Experimental Section**

**General Procedure.** All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. Solvents were reagent grade and dried by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et\(_2\)O) were distilled over sodium benzophenone ketyl, while hexanes, toluene
and dichloromethane were distilled over CaH₂. Acetonitrile was distilled over anhydrous MgSO₄.

The ¹H NMR spectra of compounds were recorded on a Varian VXR 300-MHz spectrometer with TMS (δ 0.00 ppm) as the internal standard. The ³¹P{¹H} and ³¹P NMR spectra were recorded on a Bruker AC 200-MHz spectrometer using 85% H₃PO₄ (δ 0.00 ppm) as the external standard. The ¹³C{¹H} and ¹³C NMR spectra were recorded on a Bruker DRX 400-MHz spectrometer using CDCl₃ as the internal standard. Electrospray mass spectra were recorded on a Finnigan TSQ 700 spectrometer using CH₂Cl₂ as solvent. FAB mass spectra were recorded on a Kratos MS 50 spectrometer using THF as solvent. The compounds Pd(dppe)(dba), Pd(PPh₃)₂(dba), Pd(PPh₃)₃, Pd(P₂Et₃)₂, and Cl₂C=PN(SiMe₃)₂ were prepared by literature methods. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh₃, which was recrystallized from MeOH.

Preparation of Cl(Ph₃P)Pd[η²-C(Cl)(PPh₃)=PN(SiMe₃)₂] (IIa) through Intermediates (Ph₃P)₂Pd[η²-C(Cl)₂=PN(SiMe₃)₂] (Ia) and trans-Cl(Ph₃P)₂Pd[η²-C(Cl)=PN(SiMe₃)₂] (IIa). To a cooled (-50°C) slurry of Pd(PPh₃)₄ (1.00 g, 0.865 mmol) in CH₂Cl₂ (20 mL) was added Cl₂C=PN(SiMe₃)₂ (0.261 g, 0.952 mmol). The initially light yellow solution was warmed slowly with stirring. A ³¹P{¹H} NMR spectrum taken after the initial addition (-50°C) showed Ia as the only intermediate. After the solution was allowed to warm slowly to 0°C, the color turned dark red. A ³¹P{¹H} NMR spectrum was taken (0°C) and showed traces of Ia along with IIa as the main product. When the solution reached room temperature after about 1 h, IIa had converted almost completely to IIIa, along with formation of Pd(PPh₃)₂Cl₂ (characterized by comparison of its ³¹P NMR spectrum with that of an authentic sample). The solution was filtered and the solvent was removed under vacuum from the filtrate to yield a red oily solid. The residue was treated with 25 mL of THF, the red solution was filtered to remove Pd(PPh₃)₂Cl₂ and the filtrate was reduced to 2 mL. After adding 20 mL of hexanes and cooling to 0°C, a light yellow precipitate
formed which was collected on a medium porosity fritted glass filter, washed with 3x5 mL portions of hexanes and dried under vacuum to give analytically pure \( \text{IIa} \) (0.580 g, 74% based on Pd). \(^{31}\text{P}\left( ^1\text{H}\right)\text{NMR } (\text{CH}_2\text{Cl}_2)\) (see Scheme 1 for atom labels) for \( \text{IIa} \), -50°C: \( \delta(\text{P}(\text{x})) 41.8 \text{ (dd, } ^2J_{\text{P}(\text{a})\text{P}(\text{x})} = 35.3 \text{ Hz, } ^2J_{\text{P}(\text{a})\text{P}(\text{b})} = 23.4 \text{ Hz)}, \delta(\text{P}(\text{a})) 25.8 \text{ (d, } ^2J_{\text{P}(\text{b})\text{P}(\text{a})} = 23.4 \text{ Hz), } \delta(\text{P}(\text{b})) 21.3 \text{ (d, } ^2J_{\text{P}(\text{a})\text{P}(\text{b})} = 35.3 \text{ Hz). For } \text{IIa}, \text{ 0°C: } \delta(\text{P}(\text{a})) 213.9 \text{ (t, } ^3J_{\text{P}(\text{a})\text{P}(\text{a})} = 50.1 \text{ Hz), } \delta(\text{P}(\text{a})) 22.3 \text{ (d, } ^2J_{\text{P}(\text{a})\text{P}(\text{a})} = 50.1 \text{ Hz). For } \text{IIa}, \text{ 25°C: } \delta(\text{P}(\text{a})) 124.4 \text{ (d, } ^2J_{\text{P}(\text{a})\text{P}(\text{a})} = 91.4 \text{ Hz), } \delta(\text{P}(\text{a})) 25.8 \text{ (dd, } ^3J_{\text{P}(\text{a})\text{P}(\text{a})} = 91.4 \text{ Hz, } ^3J_{\text{P}(\text{a})\text{P}(\text{b})} = 10.1 \text{ Hz), } \delta(\text{P}(\text{b})) 21.3 \text{ (d, } ^3J_{\text{P}(\text{b})\text{P}(\text{a})} = 10.1 \text{ Hz). Electrospray MS (for } \text{IIa): } m/e 870 \text{ (M}^+\text{Cl), 608 (M}^+\text{Cl+PPh}_3).\) Anal. Calcd for C\(_{45}\)H\(_{45}\)Cl\(_2\)N\(_2\)P\(_3\)Pd\(_5\)Si\(_2\): C, 57.05; H, 5.34; N, 1.55. Found: C, 56.75; H, 5.46; N, 1.68.

**Preparation of** \([\text{(Ph}_3\text{P)}_2\text{Pd}(\eta^1\text{-C(Cl)(PPh}_3)\text{)=PN(SiMe}_3)_2\text{]} (\text{PF}_6)\) (IV).

**Method A.** To a cooled (-50°C), stirred slurry of Pd(PPh\(_3\))\(_4\) (1.00 g, 0.865 mmol) in CH\(_2\)Cl\(_2\) (20 mL) was added Cl\(_2\)C=PN(SiMe\(_3\))\(_2\) (0.261 g, 0.952 mmol) and KPF\(_6\) (0.319 g, 1.73 mmol). The initially light yellow solution turned red upon warming slowly to room temperature with stirring over a period of about 1 h. The solution was filtered, the filtrate was reduced to 5 mL, and 25 mL of hexanes was added to form a yellow precipitate, which was collected on a medium porosity fritted glass filter and washed with 3x10 mL portions of Et\(_2\)O to yield 0.715 g of crude product. A \(^{31}\text{P}\) NMR spectrum (in CH\(_2\)Cl\(_2\)) showed that this precipitate contained almost pure IV, with a small amount (5%) of [Pd(PPh\(_3\))\(_2\)Cl] (PF\(_6\)) (characterized by comparison of its \(^{31}\text{P}\) NMR spectrum with literature values\(^{23}\)) Further attempts to purify compound IV resulted in decomposition with formation of [Pd(PPh\(_3\))\(_2\)Cl] (PF\(_6\)) and unidentifiable products.

**Method B.** To a solution of Cl(Ph\(_3\)P)Pd[\(\eta^1\text{-C(Cl)(PPh}_3)\text{)=PN(SiMe}_3)_2\text{]} (\text{IIIa}) (0.100 g, 0.110 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added PPh\(_3\) (0.0318 g, 0.121 mmol) and KPF\(_6\) (0.0223 g, 0.121 mmol). After stirring for 30 min the solution was filtered, the filtrate was reduced to 5 mL, and 25 mL of hexanes was added to form a yellow precipitate, which was collected on a medium porosity fritted glass filter and washed with 3x10 mL portions of Et\(_2\)O.
A $^{31}$P NMR spectrum in CH$_2$Cl$_2$ showed that this precipitate contained IV with a small amount of [Pd(PPh$_3$)$_3$Cl] ($PF_g$) impurity which could not be separated. $^{31}$P{${}^1$H} NMR (CD$_2$Cl$_2$, 0°C) (see Scheme 2 for atom labels): $\delta$(P(x)) 118.2 (ddd, $^2J_{P(x)P(a)} = 123.6$ Hz, $^2J_{P(x)P(c)} = 32.5$ Hz, $^2J_{P(x)P(b)} = 5.1$ Hz), $\delta$(P(a)) 25.1 (ddd, $^2J_{P(a)P(c)} = 123.6$ Hz, $^3J_{P(a)P(b)} = 20.1$ Hz, $^3J_{P(a)P(c)} = 20.6$ Hz), $\delta$(P(b)) 17.4 (ddd, $^2J_{P(b)P(c)} = 120.1$ Hz, $^3J_{P(b)P(b)} = 11.9$ Hz, $^3J_{P(b)P(c)} = 5.1$ Hz), $\delta$(P(c)) 13.8 (ddd, $^2J_{P(c)P(a)} = 32.5$ Hz, $^3J_{P(c)P(b)} = 20.6$ Hz, $^3J_{P(c)P(c)} = 11.9$ Hz), $\delta$(PF$_6$) -144 (sept., $^1J_{PF} = 709.1$ Hz). Electrospray MS: m/e 870 (M$^-$-PPh$_3$), 608 (M$^-$-Cl+PPh$_3$).

**Preparation of [(Ph$_3$P)(MeCN)Pd(η$^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] ($PF_g$) (V).**

**Method A.** To a cooled (-30°C), stirred slurry of Pd(PPh$_3$)$_4$ (1.00 g, 0.865 mmol) in MeCN (30 mL) was added Cl$_2$C=PN(SiMe$_3$)$_2$ (0.261 g, 0.952 mmol) and KPF$_6$ (0.319 g, 1.73 mmol). The initially light yellow solution turned red upon warming slowly to room temperature with stirring over a period of about 1 h. The solution was filtered, the filtrate was reduced to 5 mL and a mixture of 15 mL hexanes and 15 mL Et$_2$O was added with stirring. The resulting red precipitate was collected by filter cannula, redissolved in minimal MeCN, filtered and cooled slowly to -30°C. After approximately 3 days at -30°C, compound V separated from the solution as clear crystals (0.445 g, 49%).

**Method B.** To a stirred solution of Cl(Ph$_3$P)Pd[η$^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIA) (0.500 g, 0.552 mmol) in MeCN (20 mL) at room temperature was added KPF$_6$ (0.112 g, 0.608 mmol). The solution was stirred for 15 min and filtered over Celite to remove KCl. The filtrate was reduced to 3 mL and a mixture of 15 mL hexanes and 15 mL Et$_2$O was added with stirring. The resulting red precipitate was collected by filter cannula and redissolved in minimal MeCN; the solution was then filtered and cooled slowly to -30°C. After approximately 3 days at -30°C, compound V was separated from the solution as light yellow crystals (0.357 g, 61%). $^1$H NMR (CD$_2$Cl$_2$, 25°C): $\delta$ 7.1-7.7 (30H, PPh$_3$), 1.66 (s, 3H, MeCN), 0.15 (s, 18H, N(SiMe$_3$)$_2$). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 25°C) (see Scheme 2 for atom labels): $\delta$(P(x)) 132.8 (d, $^2J_{P(x)P(a)} = 97.0$ Hz), $\delta$(P(a)) 28.0 (dd, $^2J_{P(a)P(b)} = 97.0$ Hz, $^1J_{P(a)P(c)} = 6.4$ Hz), $\delta$(P(b))
21.1 (d, \( ^1J_{Pb}(Pc)=6.4\) Hz), \( \delta(PF_6)\) -144 (sept., \( ^1J_{PF}=709.5\) Hz). Electrospray MS: \( m/e\) 870 (M\(^+-\)MeCN), 608 (M\(^+-\)(MeCN+PPh\(_3\))). Anal. Calcd for C\(_{45}\)H\(_{55}\)Cl\(_2\)F\(_5\)N\(_2\)P\(_4\)Pd\(_2\)Si\(_2\): C, 51.19; H, 4.87; N, 2.65. Found: C, 50.90; H, 4.85; N, 2.66.

**Conversion of \([(Ph_3P)(MeCN)Pd(\eta^2-C(Cl)(PPh_3)=PN(SiMe_3)2)] (PF_6) (V) to Cl(Ph_3P)Pd[\eta^2-C(Cl)(PPh_3)=PN(SiMe_3)2] (IIIa).** To a stirred solution of \([(Ph_3P)(MeCN)Pd(\eta^2-C(Cl)(PPh_3)=PN(SiMe_3)2)] (PF_6) (V) (0.100 g, 0.0947 mmol) in CH\(_2\)Cl\(_2\) (10 mL) at 25°C was added (Ph\(_3\))\(_3\)N\(^-\)Cr (PPNCl) (0.109 g, 0.189 mmol). After stirring for 5 min, a \( ^3P \) NMR spectrum showed quantitative conversion to Cl(Ph\(_3\)P)Pd[\( \eta^2-C(Cl)(PPh_3)=PN(SiMe_3)2\)] (IIla).

**Preparation of cK-Cl(dppe)Pd[\( \eta^2-C(Cl)=PN(SiMe_3)2\)] (VI).** To a solution of Pd(dppe)(dba) (1.00 g, 1.35 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was added Cl\(_2\)C=PN(SiMe\(_3\))\(_2\) (0.371 g, 1.35 mmol). The color turned from dark orange to light yellow immediately after the addition. After stirring for 5 min, the solution was filtered and the solvent was removed from the filtrate under vacuum to yield a light yellow oily-solid residue. The residue was stirred vigorously with 20 mL Et\(_2\)O to produce a yellow precipitate which was collected on a medium porosity fritted glass filter. The precipitate was washed with 2x10 mL Et\(_2\)O, followed by 3x5 mL MeCN to give pure VI (0.745 g, 71%). \( ^3P \{ ^1H \} \) NMR (CD\(_2\)Cl\(_2\), 25°C) (see eq 5 for atom labels): \( \delta(P(a))\) 230.1 (dd, \( ^1J_{P(a)P(b)} = 41.8\) Hz, \( ^3J_{P(a)P(b)} = 29.9\) Hz), \( \delta(P(b))\) 55.8 (dd, \( ^3J_{P(a)P(b)} = 29.9\) Hz, \( ^1J_{P(a)P(b)} = 22.1\) Hz).

**Preparation of trans-CI(Et\(_3\)P)\(_2\)Pd[\( \eta^2-C(Cl)=PN(SiMe_3)2\)] (IIb) through Intermediate (Et\(_3\)P)\(_2\)Pd[\( \eta^2-C(Cl)=PN(SiMe_3)2\)] (IIb).** To a stirred solution of Pd(PPEt\(_3\))\(_2\) (1.35 g, 2.93 mmol) in hexanes (20 mL) at 0°C was added dropwise Cl\(_2\)C=PN(SiMe\(_3\))\(_2\) (0.803 g, 2.93 mmol). The color changed from orange to almost colorless during the addition. A \( ^3P \) NMR spectrum taken after 5 min of stirring at 0°C showed quantitative formation of (Et\(_3\)P)\(_2\)Pd[\( \eta^2-C(Cl)=PN(SiMe_3)2\)] (IIb). The solution was allowed to warm slowly to room temperature and stirred for 1 h. A \( ^3P \) NMR spectrum showed that all
of IIb had converted to trans-Cl(Et₃P)₂Pd[C(Cl)=PN(SiMe₃)₂] (IIb). The solution was reduced to 5 mL under vacuum, filtered, and cooled slowly to -78°C to form colorless crystals of IIb. Compound IIb melts at 10°C and could not be isolated in pure form as it contains small amounts of Pd(PEt₃)₂Cl₂ (characterized by comparison of its ³¹P NMR spectrum with an authentic sample).

³¹P{¹H} NMR (hexanes) (see Scheme 3 for atom labels); for IIb, 0°C: δ(P(x)) 38.0 (dd, ²Jₚ(ₚₜ,ₚₜ) = 38.5 Hz, ²Jₚ(ₚₜ,ₚₐ) = 24.8 Hz), δ(P(a)) 5.5 (dd, ²Jₚ(ₚₜ,ₚₚₜ) = 24.8 Hz, ²Jₚ(ₚₚₜ,ₚₚₜ) = 5.5 Hz), δ(P(b)) 4.0 (dd, ²Jₚ(ₚₚₜ,ₚₚₜ) = 38.5 Hz, ²Jₚ(ₚₚₜ,ₚₚₜ) = 5.5 Hz). For IIb, 25°C: δ(P(x)) 223.8 (t, ³Jₚ(ₚₚₜ,ₚₚₜ) = 33.4 Hz), δ(P(a)) 16.1 (d, ³Jₚ(ₚₚₜ,ₚₚₜ) = 33.4 Hz). ¹³C{¹H} NMR (hexanes); for IIb, 25°C: δ(C=PR) 191.0 (dt, ¹Jₚ(ₚₚₜ,ₚₚₜ) = 135.1 Hz, ²Jₚ(ₚₚₜ,ₚₚₜ) = 9.6 Hz).

**Synthesis of Pd(PEt₃)(Cl)[µ-η¹:η²]**

C(SiMe₃)(PEt₃)=P=N(SiMe₃)]Pd(PEt₃)Cl (VIIa-b) through Intermediate (Et₃P)₂Pd[η¹-C(Cl)₂=PN(SiMe₃)₂] (Ib). To a stirred solution of Pd(PEt₃)₃ (1.58 g, 3.43 mmol) in hexanes (25 mL) at 0°C was added dropwise Cl₂C=PN(SiMe₃)₂ (0.470 g, 1.71 mmol). The color remained orange during the addition. A ³¹P NMR spectrum taken after 5 min of stirring at 0°C showed a mixture of (Et₃P)₂Pd[η¹-C(Cl)₂=PN(SiMe₃)₂] (Ib) and unreacted Pd(0). The solution was warmed quickly to room temperature and stirred for 15 min during which time the color turned red. Stirring was then stopped, and the flask was allowed to sit at room temperature overnight to form crystals of Pd(PEt₃)(Cl)[µ-η¹:η²].

C(SiMe₃)(PEt₃)=P=N(SiMe₃)]Pd(PEt₃)Cl (VIIa-b). The filtrate was removed by cannula and the crystals were washed with 3x5 mL hexanes and dried under vacuum to give pure VIIa-b (0.824 g, 57%). ³¹P{¹H} NMR (THF) (see Scheme 3 for atom labels); for VIIa: δ(P(x)) 194.9 (dd, ²Jₚ(ₚₚₚ,ₚₚₚ) = 18.0 Hz, ²Jₚ(ₚₚₚ,ₚₚₚ) = 8.3 Hz), δ(P(a)) 38.2 (dd, ²Jₚ(ₚₚₚ,ₚₚₚ) = 18.0 Hz, ³Jₚ(ₚₚₚ,ₚₚₚ) = 5.5 Hz), δ(P(b)) 27.2 (dd, ³Jₚ(ₚₚₚ,ₚₚₚ) = 63.3 Hz, ²Jₚ(ₚₚₚ,ₚₚₚ) = 8.3 Hz, ³Jₚ(ₚₚₚ,ₚₚₚ) = 5.5 Hz), δ(P(c)) 16.2 (d, ³Jₚ(ₚₚₚ,ₚₚₚ) = 63.3 Hz). For VIIb: δ(P(x)) 182.2 (dd, ²Jₚ(ₚₚₚ,ₚₚₚ) = 16.8 Hz, ²Jₚ(ₚₚₚ,ₚₚₚ) = 5.5 Hz, ²Jₚ(ₚₚₚ,ₚₚₚ) = 5.5 Hz, ³Jₚ(ₚₚₚ,ₚₚₚ) = 16.5 Hz), δ(P(a)) 31.3 (dd, ²Jₚ(ₚₚₚ,ₚₚₚ) = 16.8 Hz, ³Jₚ(ₚₚₚ,ₚₚₚ) = 16.5 Hz), δ(P(b)) 26.0
(dd, $^3J_{P(b)P(c)} = 55.0$ Hz, $^3J_{P(b)P(a)} = 16.5$ Hz, $^3J_{P(b)P(x)} = 5.5$ Hz), $^3J_{P(c)P(b)} = 55.0$ Hz, $^2J_{P(c)P(x)} = 5.5$ Hz). Anal. Calcd for C$_{25}$H$_{53}$CUN$_2$P$_4$Pd$_2$Si$_2$ (mixture of VIIa and VIIb) C, 35.68; H, 7.55; N, 1.66. Found: C, 35.20; H, 7.31; N, 1.49.

**Synthesis of Pd(PEt$_3$)(Cl)[µ-η$^1$:η$^2$-C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)I (VIIIa-b).** To a stirred solution of Pd(PEt$_3$)(Cl)[µ-η$^1$:η$^2$-C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)Cl (VIIa-b) (0.200 g, 0.238 mmol) in THF (10 mL) was added MeI (0.101 g, 0.713 mmol). After stirring for 24 hours at room temperature, the color had changed from orange to deep red. The solvent was removed under vacuum and the red, oily residue was taken up in 35 mL Et$_2$O. The solution was filtered quickly, and the filtrate was cooled slowly to -30°C to form red crystals. A $^3$P NMR spectrum showed the red crystals to be composed of approximately 90% VIIlb and 10% VIIla. Yield: (0.0635 g, 24%). $^3$P{¹H} NMR (THF) (see Scheme 4 for atom labels) (for VIIla): $\delta$(P(x)) 196.8 (d, $^2J_{P(c)P(x)} = 18.3$ Hz), $\delta$(P(a)) 37.2 (dd, $^3J_{P(b)P(x)} = 18.3$ Hz, $^3J_{P(b)P(b)} = 7.0$ Hz), $\delta$(P(b)) 21.5 (dd, $^3J_{P(b)P(c)} = 71.1$ Hz, $^3J_{P(b)P(x)} = 7.0$ Hz), $\delta$(P(c)) 17.4 (d, $^3J_{P(c)P(x)} = 71.1$ Hz); (for VIIlb): $\delta$(P(x)) 183.9 (d, $^2J_{P(b)P(x)} = 17.2$ Hz), $\delta$(P(a)) 30.7 (dd, $^3J_{P(b)P(a)} = 17.2$ Hz, $^3J_{P(b)P(b)} = 15.1$ Hz), $\delta$(P(b)) 19.8 (dd, $^3J_{P(b)P(c)} = 61.0$ Hz, $^3J_{P(b)P(x)} = 15.1$ Hz), $\delta$(P(c)) 13.1 (d, $^3J_{P(c)P(x)} = 61.0$ Hz).

**Preparation of Cl(Et$_3$P)Pd[η$^2$-C(SiMe$_3$)(PEt$_3$)=P(=O)NH(SiMe$_3$)] (IX).** To a stirred solution of Pd(PEt$_3$)(Cl)[µ-η$^1$:η$^2$-C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)Cl (VIIa-b) (0.100 g, 0.118 mmol) in THF (10 mL) was added deionized, degassed H$_2$O (4.28 mL, 0.238 mmol). After stirring for 5 min at room temperature, the color had changed from orange to dark orange. The solvent was reduced to 5 mL and 25 mL of Et$_2$O was added with stirring. The solution was filtered, and the filtrate was cooled slowly to -78°C to form yellow crystals. The crystals were isolated by removing the mother liquor with a cannula and washing with 3x5 mL hexanes at 0°C to yield pure IX (0.058 g, 82%). $^3$P{¹H} NMR (THF) (see Scheme 4 for atom labels) $\delta$(P(x)) 80.0 (d, $^2J_{P(x)P(b)} = 11.0$ Hz), $\delta$(P(a)) 37.1 (d, $^2J_{P(a)P(b)} = 8.3$ Hz), $\delta$(P(b))
24.2 (dd, $^2J_{Ph,Pd} = 8.3$ Hz, $^2J_{Ph,Pd} = 11.0$ Hz). FABMS: m/e 598 (M$^+\cdot$H), 561 (M$^+\cdot$(H+Cl)), 338 (M$^+\cdot$(H+Cl+Pd+PET$_3$)).

**X-ray Crystallographic Analyses of [(Ph$_3$P)(MeCN)Pd($\eta^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (V) and Cl(Et$_3$P)Pd[$\eta^2$-C(SiMe$_3$)(PET$_3$)=P(=O)NH(SiMe$_3$)] (IX).** Diffraction-quality crystals of V were obtained by recrystallization from acetonitrile at -30°C; crystals of IX were obtained from Et$_2$O at -30°C. Data collection and reduction information are given in Table 1. A colorless crystal of V and a yellow plate-like crystal of IX were mounted on glass fibers for data collection. Initial sets of cell constants were calculated from reflections taken from three sets of 20 frames, oriented such that orthogonal wedges of reciprocal space were surveyed to produce orientation matrices determined from 91 reflections in V and 114 in IX. Final cell constants were calculated from a set of 6961 strong reflections in V and 5673 in IX taken during the data collections. Hemisphere-type data collections were employed in both structure determinations in which randomly oriented regions of space were surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in $\omega$. The space group C2/c was unambiguously determined in V, and Fdd2 in IX by systematic absences and intensity statistics. Successful direct methods solutions were calculated which provided most non-hydrogen atoms from the E-maps. Several full-matrix least squares / difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. The structure of V contained three acetonitrile solvent molecules, and the PF$_6$ anion was split between two sites with 0.50:0.50 site occupancy, with one of the sites showing disorder. 102 restraints were used altogether. The structure of IX contained one Et$_2$O solvent molecule which was disordered on a two-fold axis. Several ethyl groups were also disordered,
and 260 total restraints were used. Selected bond distances and bond angles for V and IX are given in Tables 2 and 3.

Results

Reactions of PPh$_3$ or dppe Complexes of Pd(0) with Cl$_2$C=PN(SiMe$_3$)$_2$.

The reaction (Scheme 1) of Pd(PPh$_3$)$_4$ with 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ at -50°C in CH$_2$Cl$_2$ results in the formation of the phosphavinyl phosphonium compound Cl(Ph$_3$P)Pd[η$^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIa). Variable temperature (-50°C to 25°C) $^{31}$P NMR monitoring of the reaction solution shows two intermediates (Scheme 1). At -50°C, the only species present is the η$^2$-phosphaalkene complex (PPh$_3$)$_2$Pd[η$^2$-C(Cl)$_2$]=PN(SiMe$_3$)$_2$ (Ia) and free PPh$_3$. Upon warming to 0°C, Ia undergoes oxidative addition of one of the C-Cl bonds to form the phosphavinyl compound trans-Cl(Ph$_3$P)$_2$Pd(C(Cl)=PN(SiMe$_3$)$_2$] (IIa). After the solution reaches room temperature and is stirred for 3 hours, compound IIIa is the only product, along with a small amount of Pd(PPh$_3$)$_2$Cl$_2$. When the reaction is carried out with only two equivalents of PPh$_3$ using Pd(dba)(PPh$_3$)$_2$ and 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ in CH$_2$Cl$_2$, compound IIIa forms at the same temperature in the same amount of time.
However, if less polar solvents (e.g., THF, hexanes, toluene) are used, Ia still forms but decomposes to unidentified products instead of isomerizing to IIa and IIIa.

Compounds Ia, IIa and IIIa were characterized by their $^{31}$P and $^{31}$P{^1H} NMR spectra; compound IIIa was further characterized by elemental analysis and electrospray mass spectroscopy. Compound IIIa is air stable in the solid state, but air sensitive in solution. The peaks corresponding to P(x) in the $^{31}$P NMR for compounds Ia, IIa and IIIa are conveniently assigned by proton-coupled $^{31}$P NMR, in which the P(x) signal remains sharp, while the PPh$_3$ signals are broadened dramatically by the phenyl protons. The assignment of Ia as an $\eta^3$-coordinated phosphaalkene is consistent with the chemical shift for P(x) at $\delta$ 41.8 which is 210 ppm upfield from Cl$_2$C=PN(SiMe$_3$)$_2$. This is similar to the upfield shift of 266 ppm found for the P(x) phosphorus atom in $(\text{Ph}_3\text{P})_2\text{Pt}[\eta^3-$Ph$_2$C=PMes$]$ relative to free Ph$_2$C=PMes. The peak for P(x) in Ia is split into a doublet of doublets ($^2J_{P(x)P(b)} = 35.3$ Hz, $^2J_{P(x)P(a)} = 23.4$ Hz) by the two inequivalent PPh$_3$ groups on Pd, which is also consistent with the proposed $\eta^3$-structure. In IIa, the chemical shift ($\delta$ 213.9) for P(x) is 172 ppm downfield from that in Ia in the region (200-350 ppm) typical of uncoordinated C=P double bond compounds and is now split into a triplet ($^3J_{P(x)P(a)} = 50.1$ Hz) by the two equivalent PPh$_3$ groups on Pd. This is consistent with the proposed trans-phosphavinyl structure of IIa and is quite similar to the $^{31}$P NMR spectra ($\delta$ 223-243 ppm, $^3J_{pp} = 25-43$ Hz) of a series of trans-phosphavinyl compounds of the type X(\text{Et$_3$P})$_2\text{M}[\text{C(X)}=\text{PMes*}]$ (X = Cl, Br; M = Pd, Pt; Mes* = tri-tert-butylphenyl). In compound IIIa, where a PPh$_3$ group has migrated from palladium to the C=P carbon atom, the chemical shift of P(x) is $\delta$ 124.4 ppm, which is far upfield from P(x) in uncoordinated phosphavinyl phosphonium cations (e.g., in $[(\text{Ph}_3\text{P})(\text{H})\text{C}=\text{PN(i-Pr)$_2$}]$ (BF$_4$), $\delta$ 303.5), consistent with the $\eta^3$-coordinated structure in Scheme 1. The peak for P(x) in IIIa is split into a doublet with a large coupling constant ($^2J_{P(x)P(a)} = 91.4$ Hz) by the carbon-bound PPh$_3$ group. This is analogous to the large $^2J_{pp}$ coupling constants found in the uncoordinated phosphavinyl phosphonium cations (e.g., in $[(\text{Ph}_3\text{P})(\text{H})\text{C}=\text{PNiPr$_3$}]$ (BF$_4$), $^2J_{pp} = 124.6$
Further evidence for the structure of IIIa is the similarity of its $^{31}$P NMR spectrum (see Experimental) to that of the cationic MeCN analog \([(\text{Ph}_3P)(\text{MeCN})\text{Pd}(\eta^2-C(\text{Cl})=\text{PN(SiMe}_3)_2))\] (PF$_6$) (V), which was characterized by X-ray diffraction.

The reaction (eq 5) of Pd(dppe)(dba) with one equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ in CH$_2$Cl$_2$ at room temperature results in the formation of cis-Cl(dppe)Pd[C(Cl)=PN(SiMe$_3$)$_2$] (VI). This compound contains a chelating phosphine and did not rearrange further to form a phosphavinyl phosphonium compound as in the formation of IIIa. The $^{31}$P NMR spectrum of VI exhibits a signal for P(x) at $\delta = 230.1$ ppm which is split into a doublet of doublets ($^3J_{\text{P(x)P(b)}} = 41.8$ Hz, $^3J_{\text{P(x)P(a)}} = 29.9$ Hz) by the two inequivalent phosphorus atoms in the chelating dppe ligand. The chemical shifts and coupling constants are quite similar to those in the previously characterized cis-Cl(Ph$_3$P)$_2$Pt[C(Cl)=PMes$^*$] (P(x): $\delta = 234.6$ dd, $^3J_{\text{P(x)P(b)}} = 45.4$ Hz, $^3J_{\text{P(x)P(a)}} = 22.5$ Hz).\(^{15}\)

**Substitution Reactions of Cl(Ph$_3$P)Pd[\eta^2-C(\text{Cl})(\text{PPh}_3)=\text{PN(SiMe}_3)_2)] (IIIa).** The reaction (Scheme 2) of Cl(Ph$_3$P)Pd[\eta^2-C(\text{Cl})(\text{PPh}_3)=\text{PN(SiMe}_3)_2)] (IIIa) with 1.1 equivalent of PPh$_3$ and 2 equivalents of KPF$_6$ in CH$_2$Cl$_2$ at room temperature results in the...
substitution of the Cl' ligand by PPh$_3$ to form the cationic complex \([(\text{Ph}_3\text{P})_2\text{Pd}(\eta^2-\text{C}(\text{Cl})=\text{PN}((\text{SiMe}_3)_2)])\] (PF$_6$) (IV) along with a small amount of \([\text{Pd}(\text{PPh}_3)_3\text{Cl}](\text{PF}_6)^{23}\) which could not be separated. Compound IV was also prepared by the addition of 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ and 2 equivalents of KPF$_6$ to a cooled (-50°C) solution of Pd(Ph$_3$)$_4$ in CH$_2$Cl$_2$. When compound IV is dissolved in MeCN at room temperature, one of the PPh$_3$ ligands is substituted by MeCN to form \([(\text{Ph}_3\text{P})(\text{MeCN})\text{Pd}(\eta^2-\text{C}(\text{Cl})=\text{PN}((\text{SiMe}_3)_2)])\] (PF$_6$) (V). Compound V was also prepared by the addition of 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ and 2 equivalents of KPF$_6$ to a cooled (-30°C) solution of Pd(Ph$_3$)$_4$ in MeCN, but is best prepared by substitution of the Cl' ligand in Cl(Ph$_3$P)Pd[\(\eta^2\cdot\text{C}(\text{Cl})=(\text{PPh}_3)=\text{PN}((\text{SiMe}_3)_2)]\) (IIIa) with MeCN, in the presence of KPF$_6$. When compound V is isolated and dissolved in CD$_2$Cl$_2$, its $^1$H NMR spectrum shows a signal for the coordinated MeCN ligand. However, when V is dissolved in CD$_3$CN, the signal for the coordinated MeCN group disappears, indicating that the coordinated MeCN ligand undergoes exchange with the CD$_3$CN solvent. When compound V is treated with PPNCl at room temperature, the MeCN ligand is immediately displaced by Cl' to form compound IIIa.
Compound V is air sensitive in solution, but only slightly air sensitive in the solid state. These substitution reactions are summarized in Scheme 2.

Compound IV was characterized by \(^{31}\)P NMR spectroscopy and electrospray mass spectroscopy, while compound V was characterized by \(^1\)H NMR and \(^{31}\)P spectroscopy, electrospray mass spectroscopy, elemental analysis and X-ray diffraction studies. The peaks corresponding to \(\text{P(x)}\) in the \(^{31}\)P NMR spectra of compounds IV and V are conveniently assigned from their proton-coupled \(^{31}\)P NMR, in which the \(\text{P(x)}\) signals are sharp, but the \(\text{PPh}_3\) signals are broadened dramatically by the phenyl protons. The chemical shifts of \(\text{P(x)}\) in IV (\(\delta 118.2\)) and V (\(\delta 132.8\)) are similar to that for \(\text{P(x)}\) in IIIa (\(\delta 124.4\)) which is consistent with an \(\eta^2\)-coordinated phosphavinyl phosphonium ligand in all of these complexes. As also found for IIIa, compounds IV and V both show characteristically large \(^2J_{\text{P(x)P(c1)}}\) coupling constants (123.6 Hz in IV and 97.0 Hz in V) between the phosphonium substituent and the C=P phosphorus atom. In IV, the signal for \(\text{P(x)}\) is also split into a doublet of doublets by \(\text{P(b)}\) (\(^2J_{\text{P(x)P(b)}} = 5.1\) Hz) and \(\text{P(c)}\) (\(^2J_{\text{P(x)P(c)}} = 32.5\) Hz); the larger value for \(^2J_{\text{P(x)P(c)}}\) is consistent with \(\text{PPh}_3\) being situated trans to \(\text{P(x)}\).27,28 The MeCN ligand in V exhibits a signal in the \(^1\)H NMR spectrum at 1.66 ppm which is 0.28 ppm upfield of free MeCN (\(\delta 1.94\)) and similar to other N-coordinated MeCN ligands.29

Reactions of \(\text{Pd(PEt}_3\text{)}_3\) with \(\text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2\). The reaction (Scheme 3) of \(\text{Pd(PEt}_3\text{)}_3\) with one equivalent of \(\text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2\) in hexanes at 0°C results in the formation of the \(\text{PEt}_3\) analog of IIa, \(\text{trans-C(}\text{Et}_3\text{P})_2\text{Pd}[\text{C(Cl)}=\text{PN(SiMe}_3\text{)}_2]\) (IIb). Low temperature \((0°C)\) \(^{31}\)P NMR monitoring of the reaction shows the \(\text{PEt}_3\) analog of Ia, \((\text{Et}_3\text{P})_2\text{Pd}[^{\eta^2-\text{C(Cl)}}=\text{PN(SiMe}_3\text{)}_2]\) (Ib) as the only observable intermediate in the reaction. When the solution reaches room temperature and is allowed to stir for 1 hour, one of the C-Cl bonds in compound Ib undergoes oxidative addition to Pd to form IIb along with a small amount of \(\text{Pd(PEt}_3\text{)}_2\text{Cl}_2\).
When Pd(PEt₃)₃ is reacted (Scheme 3) with one-half equivalent of Cl₂C=PN(SiMe₃)₂ in hexanes at 0°C, ³¹P NMR monitoring of the reaction solution again shows Ib as an intermediate along with free Pd(PEt₃)₃. However, upon warming the solution to room temperature and stirring for 30 min, orange crystals of the 1:1 isomeric mixture of Pd(PEt₃)(Cl)[μ-η¹:η²-C(SiMe₃)(PEt₃)=P=N(SiMe₃)]Pd(PEt₃)Cl (VIIa-b) begin to form. After sitting overnight, the crystals of VIIa-b are isolated and the remaining filtrate contains a small amount of dissolved VIIa-b along with IIb, which forms as a by-product. In order to determine whether IIb is an intermediate that forms before VIIa-b, a sample of IIb was dissolved in hexanes and one equivalent of Pd(PEt₃)₃ was added; no reaction was evident after several hours of stirring at room temperature, which strongly suggests that IIb is not a precursor to VIIa-b.

Compounds Ib and IIb were characterized by ³¹P NMR spectroscopy; the spectra of these compounds were quite similar to those of Ia and IIa (see Experimental) and assignments of the peaks were made in a similar manner (see results of IIIa). The 1:1 mixture of isomers VIIa-b was characterized by ³¹P NMR spectroscopy and elemental analysis as well as by the
similarity of the spectra of VIIa-b to those of VIIIa-b (see Experimental); the structure of VIIIb was determined by a partially successful X-ray diffraction study. The peaks corresponding to P(x) in the 31P NMR of compounds VIIa-b are conveniently assigned by proton-coupled 31P NMR spectroscopy which shows that the P(x) signal remains sharp, while the PEt₃ signals are broadened dramatically by the ethyl protons. A 31P-31P COSY experiment was undertaken which showed that the very complex 31P NMR spectrum of VIIa-b results from the presence of two isomers as opposed to a large palladium cluster; it also allowed for the assignment of the P-P coupling constants. The exact nature of the different isomers in VIIa-b could not be determined but is likely due to E/Z isomers around the P=N double bond. E/Z isomers are known in iminophosphines (RN=PR)³₀ and imino(methylene)phosphoranes (RN=P(R)=CR₂)³¹ and the chemical shift difference in P(x) between VIIa (δ 194.9) and VIIb (δ 182.2) is similar to the difference found in the E/Z isomers around the P=N double bond in Me₃SiN=P[N(SiMe₃)₂]=C(H)Me (δ 105.5, 98.1).³² However, because of the complexity of the molecule this assignment of the isomers must be regarded as tentative. The chemical shifts of P(x) in VIIa and VIIb may be compared with that in the uncoordinated imino(phosphoranylidemethyl)phosphane compound [(Me₃N)₃P(Me₃Si)C=P=N(SiMe₃) (δ 407.5 (C=P=N)),³³ which differs from the ligand in VIIa-b only by the P(Me₃N)₃ group on carbon instead of a PPh₃ group; the upfield shifts of P(x) in VIIa-b are indicative of η²-coordination of the C=P double bond; such shifts are also known to occur upon η²-coordination of phosphaalkenes.¹⁻⁴

**Reactions of Pd(PEt₃)(Cl)[μ-η¹:η²-]**

C(SiMe₃)(PEt₃)=P=N(SiMe₃)Pd(PEt₃)Cl (VIIa-b). When the isomeric mixture of VIIa-b is reacted (Scheme 4) with three equivalents of MeI in THF at room temperature for 24 hours under anhydrous conditions, the color of the solution turns dark red and the only
products are the iodide-substituted analogs (both isomers) of $\text{VIIIa-b}$. Pd(P$\text{Et}_3$)(I)[μ-$\eta^1$-$\eta^2$-C(SiMe$_3$)$_2$(P$\text{Et}_3$)=P=N(SiMe$_3$)]Pd(P$\text{Et}_3$)I ($\text{VIIIa-b}$). Presumably, MeCl gas is liberated during this halide exchange reaction. A similar reaction using three equivalents of NaI resulted in the formation of $\text{VIIa-b}$ in only 5 minutes, but the product was contaminated with Cl(Et$_3$P)P[η$^2$-C(SiMe$_3$)$_2$(P$\text{Et}_3$)=P(=O)NH(SiMe$_3$)] (IX) which forms when $\text{VIIa-b}$ is exposed to traces of water, even though the NaI was heated under vacuum for several hours to remove water. When the isomeric mixture of $\text{VIIa-b}$ is crystallized from Et$_2$O, isomer $\text{VIIib}$ crystallizes preferentially, although some of $\text{VIIia}$ is also present in the crystals. Compounds $\text{VIIa-b}$ were characterized by $^{31}$P NMR spectroscopy and the structure of compound $\text{VIIib}$ was partially determined by X-ray diffraction studies. Although the refinement of the structure of $\text{VIIib}$ is not suitable for publication (final R factor 9%), the connectivity of the molecule was unambiguously determined. The $^{31}$P NMR spectrum of $\text{VIIa-b}$ is consistent with the structure obtained for $\text{VIIib}$, and assignments were made as in the very similar compounds $\text{VIIa-b}$ (see results of $\text{VIIa-b}$).

When a pure sample of $\text{VIIa-b}$ is reacted (Scheme 4) with two equivalents of degassed, deionized H$_2$O in THF at room temperature, the color darkens immediately and the $^{31}$P NMR spectrum shows the formation of the phosphonio-methylene(oxo)phosphorane compound IX along with two singlets that are most likely due to palladium phosphine complexes. Although these by-products were not identified, they were easily separated from
Compound IX was characterized by $^{31}$P NMR spectroscopy, FAB mass spectroscopy and the structure was determined by X-ray diffraction. The peak corresponding to P(x) at δ 80.0 in the $^{31}$P NMR spectrum of IX is readily assigned by the proton-coupled $^{31}$P NMR spectrum, in which the P(x) signal remains sharp, while the PEt$_3$ signals at δ 37.1 and 24.2 are broadened dramatically by coupling to the ethyl protons. In IX, the chemical shift of P(x) at δ 80.0 is upfield from the two known methylene(oxo)phosphoranes, Mes*P(=O)=CR(SiMe$_3$) (R = Ph, δ 153.7; R = SiMe$_3$, δ 161.1), which are somewhat related to the ligand in IX, but without a phosphonio substituent on the C=P carbon. This upfield shift is consistent with the upfield shifts found in $\eta^2$-coordinated phosphaalkene compounds. As in compounds VIIa-b and VIIIa-b, the coupling constants between the PEt$_3$ groups and the P(x) atom in IX are quite small ($^2J_{P(x)PEt_3} = 11.0$ Hz, $^2J_{P(x)PPh_3} = 0$ Hz), much smaller than the large coupling constant found in IIIa ($^2J_{P(x)PPh_3} = 91.4$ Hz). This is most likely due to the pentavalent nature of the P(x) atom in VIIa-b, VIIIa-b and IX, which allows for less phosphorus s-character in the bonding and results in smaller coupling constants.

Discussion

Cl(Ph$_3$P)Pd[\eta^2-C(Ph$_3$)Pd(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIla), [(Ph$_3$P)$_2$Pd(\eta^2-C(Ph$_3$)Pd(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (IV) and [(Ph$_3$P)(MeCN)Pd(\eta^2-C(Ph$_3$)Pd(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (V). In contrast to the reaction (eq 2) of Pd(PPh$_3$)$_4$ with Cl$_2$C=PMes* (Mes* = 2,4,6-tri-tert-butylphenyl) which results in the migration of the Mes* group to carbon to form Mes*-C=P and Pd(PPh$_3$)$_2$Cl$_2$ with no observed intermediates, the reaction of Pd(PPh$_3$)$_4$ with Cl$_2$C=PN(SiMe$_3$)$_2$ results in the formation of the $\eta^2$-coordinated phosphavinyld phosphonium compound Cl(Ph$_3$P)Pd[\eta^2-C(Ph$_3$)Pd(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIla) via intermediates (Ph$_3$P)$_2$Pd[\eta^2-C(Ph$_3$)Pd(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIa) and trans-Cl(Ph$_3$P)$_2$Pd(C(Ph$_3$)=PN(SiMe$_3$)$_2$] (IIla). This is analogous to the reported reaction of an $\eta^1$-vinyl complex of palladium which rearranged upon heating to an $\eta^2$-vinyl phosphonium.
complex.\textsuperscript{35} We previously obtained a nickel analog (3) of III\textsubscript{a} in a reaction (eq 3) of Ni(PPh\textsubscript{3})\textsubscript{4} with Cl\textsubscript{2}C=PN(SiMe\textsubscript{3})\textsubscript{2}, but in that case the product was unstable and reacted further with another equivalent of Ni(PPh\textsubscript{3})\textsubscript{4} to generate the dinuclear phosphavinyldene phosphorane complex (4).\textsuperscript{17} However, compound III\textsubscript{a} is air stable and does not react with Pd(PPh\textsubscript{3})\textsubscript{4}.

The isomerization reaction of II\textsubscript{a} to III\textsubscript{a} can be rationalized by proposing (Scheme 5) the rearrangement of the $\eta^1$-phosphavinyll (II\textsubscript{a}) to an $\eta^2$-phosphavinyll (II\textsubscript{a'} and II\textsubscript{a''}) intermediate which is attacked by PPh\textsubscript{3} to form the phosphavinyll phosphonium complex III\textsubscript{a}.

![Scheme 5](image)

The carbene-phosphido resonance structure (II\textsubscript{a''}) is probably more favored than the alkylphosphine resonance form (II\textsubscript{a'}) because the high energy C=P double bond\textsuperscript{36} is avoided; the electrophilic nature of the carbene-like carbon atom provides the driving force for nucleophilic attack by the PPh\textsubscript{3} group to form III\textsubscript{a}. This carbene-like resonance structure in the $\eta^2$-phosphavinyll ligand (II\textsubscript{a''}) is preceded by the X-ray structure of a similar $\eta^2$-phosphavinyll complex of tungsten Cp(CO)\textsubscript{2}W[\text{C(Ph)=PPh(W(CO)\textsubscript{5})}] which contained a W-C bond length (1.954(8) Å) that is typical of a W=C double bond.\textsuperscript{37} A similar mechanism for this phosphine migration was proposed previously for the formation of the nickel analog (3, eq 3) of III\textsubscript{a}.\textsuperscript{17}

When Cl\textsubscript{2}C=PN(SiMe\textsubscript{3})\textsubscript{2} is reacted with Pd(dba)(PPh\textsubscript{3})\textsubscript{2}, the formation of III\textsubscript{a} occurs quantitatively under the same conditions in the same amount of time. In this case there is no excess PPh\textsubscript{3} present in the reaction, which suggests that the PPh\textsubscript{3} that attacks the C=P carbon atom in II\textsubscript{a''} must have dissociated from palladium. Since dissociative mechanisms in square
planar group 10 complexes are very rare, the most likely mechanism is an associative mechanism where the C=P phosphorus lone pair attacks above the square plane in IIa with loss of a PPh$_3$ ligand to generate IIa' and IIa''. When Pd(dba)(dppe) is used as the Pd(0) reagent, the reaction (eq 5) stops at the phosphavinyl compound cis-Cl(dppe)Pd[C(Cl)=PN(SiMe$_3$)$_2$] (VI). Here, dissociation of one P-donor of the chelating phosphine ligand is more difficult and an analog of IIIa does not form. Compound VI does not react with PPh$_3$ and KPF$_6$ to generate an analog of IV containing a dppe ligand in place of the two PPh$_3$ ligands on palladium, presumably because the chelating phosphine and chloride ligands in VI are not displaced easily enough to form an $\eta^2$-phosphavinyl intermediate.

The chloride ligand in compound IIIa is easily substituted (Scheme 2) by neutral ligands upon addition of KPF$_6$; stirring in MeCN results in formation of the cationic phosphavinyl phosphonium complex $[(\text{Ph}_3\text{P})(\text{MeCN})\text{Pd}(\eta^2-\text{C(Cl)}(\text{PPh}_3)=\text{PN(SiMe}_3)\text{)}_2)]\text{(PF}_6\text{)}$ (V), while addition of PPh$_3$ leads to $[(\text{Ph}_3\text{P})_2\text{Pd}(\eta^2-\text{C(Cl)}(\text{PPh}_3)=\text{PN(SiMe}_3)\text{)}_2)]\text{(PF}_6\text{)}$ (IV). One of the palladium-coordinated PPh$_3$ ligands in IV is replaced by stirring in MeCN to generate V; the MeCN ligand in V is displaced by CD$_3$CN by stirring in CD$_3$CN, or by PPh$_3$ to generate IV, or by Cl$^-$ to generate IIIa. Thus, each of the compounds IIIa, IV and V contain a labile ligand on palladium, which is evident in the electrospray mass spectra which show the same highest molecular ion peak at $m/e$ 870 corresponding to the fragment $(\text{Ph}_3\text{P})\text{Pd}(\eta^2-\text{C(Cl)}(\text{PPh}_3)=\text{PN(SiMe}_3)\text{)}_2)]^+$, generated by the loss of Cl$^-$, PPh$_3$ and MeCN from IIIa, IV and V, respectively.

**X-ray Crystal Structure of $[(\text{Ph}_3\text{P})(\text{MeCN})\text{Pd}(\eta^2-\text{C(Cl)}(\text{PPh}_3)=\text{PN(SiMe}_3)\text{)}_2)]\text{(PF}_6\text{)}$ (V).** A thermal ellipsoid drawing of V (Figure 1) shows that the palladium atom is in a planar environment as defined by the coordinating atoms of the PPh$_3$, MeCN, and [C(Cl)(PPh$_3$)=PR] ligands; the sum of angles around the palladium atom is 359.9°. The [C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] ligand is coordinated $\eta^2$ to palladium through the C(1) and P(1) atoms, with the Cl, PPh$_3$ and N(SiMe$_3$) groups bent back from planarity in
the \([\text{C(Cl)(PPh}_3]_{\text{PN(SiMe}_3)J}\) ligand; the sum of angles around \(C(1)\) involving \(P(1), P(3)\) and \(\text{Cl}(1)\) of 347.4° indicates that \(C(1)\) is roughly intermediate between \(\text{sp}^2\) (360°) and \(\text{sp}^3\) (328.5°) hybridization, which is similar to structural features of \(\eta^2\)-coordinated olefins and phosphaalkenes (e.g., in \(\text{Ni(PMe}_3)_2[\eta^2-(\text{Me}_3\text{Si})_2\text{CHP=C(SiMe}_3)_2]\), the sum of angles around the \(C=\text{P}\) carbon is 343.5°).^ The structure of \(V\) is similar to that of the nickel \(\eta^2\)-phosphavinyl phosphonium complex \(\text{Cl(Ph}_3\text{P)Ni[\eta^2-C(H)(PPh}_3]=\text{PMes}^*]\) (5, eq 4).^\(^1\)\(^7\) The \(C(1)-P(1)\) distance in \(V\) (1.802(4) Å) is the same within error as that in the nickel complex \(\text{Cl(Ph}_3\text{P)Ni[\eta^2-C(H)(PPh}_3]=\text{PMes}^*]\) (5) (1.796(5) Å);^\(^1\)\(^7\) both of these distances are much longer than the corresponding \(C=\text{P}\) distance in the free phosphavinyl phosphonium salt \([(\text{PPh}_3)(\text{H})\text{C=PN(\text{i-Pr})}_2]\)(\(\text{BF}_4\)_2 (1.684(14) Å),^\(^2\)\(^6\) which is consistent with \(\eta^2\)-coordination of the phosphavinyl phosphonium ligand and is similar to the lengthening of \(C=\text{P}\) bonds which occurs upon \(\eta^2\)-coordination of phosphaalkenes.\(^1\)\(^4\) The \(C(1)-P(2)\) distance in \(V\) (1.771(4) Å) is slightly longer than the \(C-P\text{Ph}_3\) distance in \(\text{Cl(Ph}_3\text{P)Ni[\eta^2-C(H)(PPh}_3]=\text{PMes}^*]\) (5) (1.742(5) Å); both of these distances are much longer than typical ylide \(C-P\) bond lengths, e.g., 1.661(8) Å in \(\text{Ph}_3\text{P}=\text{CH}_2\)_3,^\(^3\)\(^8\) but are shorter than the phosphonium-type \(C-P\text{Ph}_3\) distance in \([(\text{PPh}_3)(\text{H})\text{C=PN(\text{i-Pr})}_2]\)(\(\text{BF}_4\)_2 (1.798(14) Å), indicating that there is more phosphonium (\(C-P^*\)) than ylidic (\(C-P^*\)) character in the \(C-P\text{Ph}_3\) bond in \(V\). The \(\text{Pd-P}(1)\) distance in \(V\) (2.2688(11) Å) is significantly shorter than the \(\text{Pd-P}(3)\) distance (2.3449(11)). The bonding in \(V\) may be described as a mixture of two resonance structures (Scheme 6), analogous to those.

**Scheme 6**

\[
\begin{align*}
&(a) \quad \text{MeCN} \quad \text{Ph}_3\text{P} \quad \text{Cl} \quad \text{Pd} \quad \text{Ph}_3\text{P} \quad \text{N(SiMe}_3)_2 \quad \text{MeCN} \quad \text{Ph}_3\text{P} \\
&(b) \quad \text{N(SiMe}_3)_2 \\
&\text{Ph}_3\text{P} \quad \text{Cl} \quad \text{Pd} \quad \text{Ph}_3\text{P} \quad \text{N(SiMe}_3)_2
\end{align*}
\]
proposed for the bonding in Cl(Ph3P)Ni[\eta^2-C(H)(PPh3)=PMes*] (5).\textsuperscript{17} Resonance form a is an ylide-phosphido structure with a dative two electron donation from C(1) and a phosphido-type covalent bond between P(1) and palladium, where the [C(Cl)(PPh3)=PN(SiMe3)\textsubscript{2}] group donates three electrons to the thirteen electron cationic metal fragment (Ph3P)(MeCN)Pd'^\textsuperscript{+}. Resonance form b is an \eta^2-phosphavinyl phosphonium cation (1+) which donates two electrons to a formally Pd(0) metal fragment. The somewhat long C(1)-P(2) distance argues for a contribution from form b, where the PPh\textsubscript{3} group on carbon has more phosphonium than ylide character, while the short Pd-P(1) distance argues for a contribution from form a with some Pd-P phosphido-character.

\[ \text{Pd(PEt}_3\text{)(Cl)}[\mu-\eta^1:\eta^2-C(SiMe}_3\text{)(PEt}_3\text{)=P=N(SiMe}_3\text{)]Pd(PEt}_3\text{Cl (VIIa-b)} \]

and \[ \text{Pd(PEt}_3\text{)(I)}[\mu-\eta^1:\eta^2-C(SiMe}_3\text{)(PEt}_3\text{)=P=N(SiMe}_3\text{)]Pd(PEt}_3\text{I (VIIa-b)} \].

The reaction of Pd(PEt\textsubscript{3})\textsubscript{3} with one equivalent of Cl\textsubscript{2}C=PN(SiMe\textsubscript{3})\textsubscript{2} (Scheme 3) in hexanes or CH\textsubscript{2}Cl\textsubscript{2} resulted in the formation of trans-Cl(Et\textsubscript{3}P\textsubscript{2})\textsubscript{Pd}[C(Cl)=PN(SiMe\textsubscript{3})\textsubscript{2}] (II\textsubscript{b}) through the intermediate (Et\textsubscript{3}P\textsubscript{2})\textsubscript{Pd}[\eta^2-C(Cl)=PN(SiMe\textsubscript{3})\textsubscript{2}] (II\textsubscript{b}), as occurred in the reaction (Scheme 1) involving Pd(PPh\textsubscript{3})\textsubscript{4}. However, II\textsubscript{b} did not undergo PEt\textsubscript{3} migration from Pd to the C=P carbon, as in the PPh\textsubscript{3} case, to form a PEt\textsubscript{3} analog of III\textsubscript{a}, even after stirring overnight followed by refluxing in hexanes for 4 h. A possible explanation is that the weaker coordinating ability of PPh\textsubscript{3} as compared with PEt\textsubscript{3} allows the dissociation of PPh\textsubscript{3} which results in the formation of III\textsubscript{a}; on the other hand, the PEt\textsubscript{3} ligands in II\textsubscript{b} are so strongly bound that formation of the \eta^2-phosphavinyl intermediate analogous to II\textsubscript{a}', II\textsubscript{a}'' (Scheme 5) is unfavorable.

When the reaction of Pd(PEt\textsubscript{3})\textsubscript{3} is carried out with only one-half equivalent of Cl\textsubscript{2}C=PN(SiMe\textsubscript{3})\textsubscript{2} (Scheme 3) and warmed to room temperature, the reaction takes a different route forming the dimeric complex Pd(PEt\textsubscript{3})(Cl)[\mu-\eta^1:\eta^2-
C(SiMe\textsubscript{3})(PEt\textsubscript{3})=P=N(SiMe\textsubscript{3})]Pd(PEt\textsubscript{3})Cl (VII\textsubscript{a-b}), in which a PEt\textsubscript{3} group and an SiMe\textsubscript{3} group have migrated to the C=P carbon atom. This reaction again goes through intermediate
Ib, and a small amount of IIb forms as a by-product. As mentioned in the Results, compound IIb is apparently not an intermediate in the formation of VIIa-b. Evidently, when two equivalents of Pd(PEt₃)₃ are used in this reaction, Ib reacts with Pd(PEt₃)₃ to form VIIa-b before undergoing oxidative addition to form IIb. When the reaction of Pd(PEt₃)₃ with one-half equivalent of Cl₂C=PN(SiMe₃)₂ is carried out and kept at -30°C for one week as opposed to warming to room temperature above, the oxidative addition reaction prevails and compound IIb forms along with unreacted Pd(PEt₃)₃, with no formation of VIIa-b. Although Ib was the only observable intermediate in ³¹P NMR spectra recorded during the formation of VIIa-b, a plausible intermediate to explain its formation (Scheme 7) is the dinuclear phosphavinylidene phosphorane complex Pd₂Cl₂(PET₃)₃[μ₂-η²:η²-C(PET₃)=PN(SiMe₃)₂] (VII). Intermediate VII is analogous to the nickel complex Ni₂Cl₂(PPh₃)₂[μ₂-η²:η²-C(PPh₃)=PN(SiMe₃)₂] (4, eq 3) that was previously characterized by X-ray diffraction studies. This intermediate must isomerize quickly to VIIa-b by undergoing a 1,3 SiMe₃ migration from nitrogen to carbon, a process that is well documented in the chemistry of phosphaalkenes and amino methylene phosphoranes, and has also been proposed to occur (eq 6) in the formation of an imino(phosphorylidene)methylene)phosphine (7) from a phosphavinylidene phosphorane intermediate (6). The proposed intermediate (6) is the same as the ligand in VII, but with a
(Me₂N)₃P⁺CH₂PCl₂ + 3 NaN₃SiMe₃

(6)

(Me₂N)₃P⁺P—C=NSiMe₃

(7)

P(Me₂N)₃ group on carbon instead of PPh₃; and compound 7, which was characterized by an X-ray diffraction study, is analogous to the ligand in VIIa-b, thus supporting VII as a reasonable intermediate that undergoes 1,3 SiMe₃ migration to form VIIa-b.

The isomeric mixture VIIa-b reacts (Scheme 4) with MeI or NaI to form the iodide-substituted isomeric mixture VIIIa-b. The structure of VIIIb was determined by X-ray diffraction studies, but the final refinement was unacceptable for publication. However, the connectivity was unambiguously determined and the bond lengths and angles were reasonable with respect to related structures. Because of the similarity of their ³¹P NMR spectra, compounds VIIa-b and VIIIa-b are very likely isostructural. The (Et₃P)(Me₃Si)C=P=NSiMe₃ ligand in VIIa-b and VIIIa-b is best described as an η²-coordinated phosphonio-methylene(imino)metalloporphorane ligand (c), which is a zwitterionic structure with the positive charge on the phosphonium PEt₃ group and the minus charge on Pd(2). Both palladium atoms are then formally (+1) with Pd(2) bonded covalently to the C=P phosphorus, and Pd(1) bonded η¹ to the C=P double bond. If the phosphonium
(PEt₃)⁺ and [(X)(PEt₃)Pd(2)]⁻ groups are mentally replaced with R-groups, this complex is then analogous to an η²-coordinated methylene(imino)phosphorane. Compounds VIIa-b and VIIIa-b are the first to contain a phosphonio-methylene(imino)metallophosphorane ligand; they are also the first examples of complexes with an η² methylene(imino)phosphorane ligand, in general. An analog, [(Me₂N)₃P(Me₃Si)C=P=N(SiMe₃)] (7, eq 6), of the free ligand (Ph₃P)(Me₃Si)C=P=N(SiMe₃) in VIIa-b and VIIIa-b, except possessing a P(NMe₂)₃ group on the C=P carbon instead of PPh₃ is known, but no attempts to coordinate it to a transition metal complex were reported. In light of the fact that the (Ph₃P)(Me₃Si)C=P=N(SiMe₃) group has been coordinated for the first time in VIIa-b and VIIIa-b, it seems reasonable that the coordination chemistry of these types of ligands could be explored further, as the P=N bond and the lone pair electrons on nitrogen are also available for bonding. It is also reasonable to assume that the well known class of methylene(imino)phosphoranes (R²C=P(=NR)R) should show interesting coordination properties, especially with respect to coordination of the C=P double bond as in VIIa-b and VIIIa-b.

Cl(Et₃P)Pd[η²-C(SiMe₃)(PEt₃)=P(=O)NH(SiMe₃)] (IX). The isomeric mixture of dimeric VIIa-b undergoes hydrolysis with even traces of water (Scheme 4) to form one isomer of the mononuclear compound Cl(Et₃P)Pd[η²-(SiMe₃)(PEt₃)=P(=O)NH(SiMe₃)] (IX). This is analogous to the known hydrolysis reaction (eq 7) of methylene(imino)phosphoranes (R²C=P(=NR)R). In the formation of IX, the oxygen from

\[
\begin{align*}
\text{Mes} & \quad \text{P} \quad \text{N} \quad \text{Ph} \\
\text{CPh₂} & \quad \text{H₂O} \quad \xrightarrow{} \quad \text{Mes} \quad \text{P} \quad \text{O} \quad \text{NH} \quad \text{Ph} \\
& \quad \text{CHPh₂}
\end{align*}
\]

(7)

the water adds to the phosphorus and a hydrogen adds to the nitrogen. The second hydrogen from the water presumably leaves with the Pd(PEt₃)Cl fragment, but the complex that forms was not isolated.
X-Ray Crystal Structure of Cl(Et₃P)Pd[η⁴-C(SiMe₃)P(=0)NH(SiMe₃)] (IX). The structure of IX exhibits an η¹-coordinated phosphonio-methylene(oxo)phosphorane (Et₃P)(Me₃Si)C=P(=O)NH(SiMe₃) ligand. The ORTEP drawing of IX (Figure 2) shows that the palladium atom is in a planar environment defined by the donor atoms of the PEt₃, Cl, and (Et₃P)(Me₃Si)C=P(=O)NH(SiMe₃) ligands; the sum of angles around the palladium atom is 360.2°. In contrast to the one structurally characterized methylene(oxo)phosphorane compound [(SiMe₃)(Ph)C=P(=0)Mes*]⁴¹ which has a trigonal planar geometry at phosphorus, the η¹-coordinated ligand in IX contains a pyramidalized C=P phosphorus atom (sum of angles around P(1) involving O(1), C(1) and N(1) is 342.3°). However, the sum of angles around C(1) involving P(1), P(2) and Si(2) is 357.3°, which suggests that C(1) is close to sp² hybridization. This contrasts with η²-phosphaalkenes in which both the carbon and phosphorus are pyramidalized to roughly between sp² and sp³ hybridization. The C(1)-P(1) distance in IX (1.787(6) Å) is much longer than the C=P distance in [(Me₃Si)(Ph)C=P(=0)Mes*] (1.657(4) Å), which is indicative of η¹-coordination of the phosphonio-methylene(oxo)phosphorane ligand and is consistent with the lengthening of C=P bonds which occurs upon η¹-coordination of phosphaalkenes.¹⁻⁴ The P=O distance in IX (1.489(4) Å) is similar to that in [(Me₃Si)(Ph)C=P(=O)Mes*] (1.458(3) Å). The C(1)-P(2) distance in IX (1.744(5) Å) is similar to the C-PPh₃ distance in Cl(PPh₃)Ni[η²-C(H)(PPh₃)=PMes*] (1.742(5) Å);¹⁷ both of these distances are much longer than typical ylide C-P bond lengths, e.g., 1.661(8) Å in Ph₃P=CH₂,³⁸ but are shorter than the phosphonium C-PPh₃ distance in [(PPh₃)(H)C=PN(t-Pr)₃](BF₄) (1.798(14) Å),²⁶ suggesting that the C(1)-P(2) bond in IX has more phosphonium (C-P⁺) than ylidic (C-P⁻) character. The Pd-P(1) distance in IX (2.1696(13) Å) is significantly shorter than the Pd-P(3) distance (2.270(2) Å).

The bonding in IX may be described as a mixture of two resonance structures as shown in Scheme 8. Resonance form d is an ylide-phosphido structure with a dative two-
electron donation from C(1) and a phosphido-type covalent bond between P(1) and palladium, where the \((\text{Et}_3\text{P})(\text{Me}_3\text{Si})\text{C}=\text{P}(=\text{O})\text{NH(}\text{SiMe}_5)\) group acts as a three electron donor to the thirteen electron Pd(PEt₃)Cl fragment. Resonance form e is a zwitterionic structure, where the minus charge is located on palladium, with the \(\eta^2\)-phosphonio-methylene(oxo)phosphorane cation \((1^+)\) donating two electrons to a formally Pd(0) metal fragment. The somewhat long \(\text{C}(1)-\text{P}(2)\) distance argues for a contribution from form e, where the PPh₃ group on carbon has more phosphonium than ylide character, while the short Pd-P(1) distance argues for a contribution from form d with some Pd-P phosphido-character. Although only two stable methylene(oxo)phosphoranes are known, quite a few have been postulated as intermediates and characterized by trapping experiments. Coordination of the phosphonio-methylene(oxo)phosphorane ligand in IX suggests that these compounds should have the ability to coordinate through the C=P bond in other transition metal complexes, and may be a way of stabilizing these reactive compounds for further study.

\section*{Conclusion}

In contrast to the reactions of Pt(PR₃)₄ or Pd(PR₃)₄ with Cl₂C=PMes* which result in the rearrangement of the aromatic Mes* group from phosphorus to carbon to generate Mes*-C=P via phosphavinyll intermediates, the reactions of Pd(0) reagents with
Cl$_2$C=PN(SiMe$_3$)$_2$ resulted in the formation of complexes containing new carbon-phosphorus multiply-bonded ligands. The reaction (Scheme 1) of Pd(PPh$_3$)$_4$, with Cl$_2$C=PN(SiMe$_3$)$_2$ formed the phosphavinyl phosphonium complex Cl(Ph$_3$P)Pd[$\eta^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIa) via the $\eta^2$-phosaalkene (Ph$_3$P)$_2$Pd[$\eta^2$-C(Cl)$_2$]=PN(SiMe$_3$)$_2$] (Ia) and the $\eta^1$-phosphavinyl trans Cl(Ph$_3$P)$_2$Pd[C(Cl)=PN(SiMe$_3$)$_2$] (IIa). The labile chloride ligand on palladium in IIa was substituted (Scheme 2) by PPh$_3$ or MeCN in the presence of KPF$_6$ to generate [(Ph$_3$P)$_2$Pd[$\eta^2$-C(Cl)](PPh$_3$)=PN(SiMe$_3$)$_2$] (PF$_6$) (IV) or [(Ph$_3$P)(MeCN)Pd[$\eta^2$-C(Cl)](PPh$_3$)=PN(SiMe$_3$)$_2$] (PF$_6$) (V), respectively. The structure of V was determined by X-ray diffraction studies which confirmed the $\eta^2$-coordination of the C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$ ligand. When Pd(PEt$_3$)$_3$, instead of Pd(PPh$_3$)$_4$ was reacted (Scheme 3) with Cl$_2$C=PN(SiMe$_3$)$_2$, the phosphavinyl complex trans-Cl(PEt$_3$)$_2$Pd[C(Cl)=PN(SiMe$_3$)$_2$] (IIb) formed but did not rearrange to form a phosphavinyl phosphonium complex analogous to IIa. However, when two equivalents of Pd(PEt$_3$)$_2$ were reacted (Scheme 3) with Cl$_2$C=PN(SiMe$_3$)$_2$, the novel, dimeric phosphonio-methylene(imino)metalophosphorane complex Pd(PEt$_3$)(Cl)[µ-$\eta^1$-$\eta^2$-(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)Cl (VIIa-b) formed as a mixture of two isomers; its formation involved migration of a SiMe$_3$ group from nitrogen to carbon and a PEt$_3$ group from palladium to the C=P carbon. The chloride ligands in VIIa-b were substituted by iodide using MeI or NaI to generate Pd(PEt$_3$)(I)[µ-$\eta^1$-$\eta^2$-C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)I (VIIia-b); the structure of VIIiba was partially determined by X-ray diffraction studies. Compound VIIa-b also undergoes hydrolysis with traces of water to form the phosphonio-methylene(oxo)phosphorane complex Cl(PEt$_3$Pd[$\eta^2$-C(SiMe$_3$)](PEt$_3$)=P(=O)NH(SiMe$_3$)] (IX); the structure of which was determined by X-ray diffraction studies. The ligands in VIIa-b, VIIa-b and IX represent the first examples of coordinated methylene(imino, oxo)phosphorane ligands.
The results for Pd(0) obtained herein may be compared with those from reactions of Ni(0) and Pt(0) reagents with \( \text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2 \), which in some cases gave much different results (Scheme 9). When \( \text{M(PEt}_3\text{)}_4 \) was reacted with \( \text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2 \), phosphavinyl complexes were observed with \( \text{M} = \text{Pd, Pt and Ni}, \) and there was no evidence for PEt, migration to carbon. However, when \( \text{M(PPPh}_3\text{)}_4 \) was reacted with \( \text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2 \), only in the case of \( \text{M} = \text{Pd} \) was a phosphavinyl complex observed (Scheme 1), which underwent PPh, rearrangement upon warming to form a phosphavinyl phosphonium complex. In the case of \( \text{M} = \text{Ni} \), a phosphavinyl intermediate was postulated, but only the phosphavinyl phosphonium complex (3, eq 3) was observed. Compound 3 was not isolated, but reacted with another equivalent of \( \text{Ni(PPPh}_3\text{)}_4 \) to generate the novel dinuclear phosphavinylidene phosphorane complex (4, eq 3). In all of the reactions with \( \text{Cl}_2\text{C}=\text{PN(SiMe}_3\text{)}_2 \), there is no R-group rearrangement from phosphorus to carbon as in the reactions with \( \text{Cl}_2\text{C}=\text{PMes}^* \). Evidently, the presence of PPh, ligands favors the formation of the phosphavinyl phosphonium complexes, while PEt, tends to stabilize the phosphavinyl complexes.
Acknowledgment

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research through grant 27360-AC3.

References


(24) SHELXTL-Plus V5.0, Siemens Industrial Automation Inc., Madison, WI.


Table 1. Crystal and Data Collection Parameters for [(Ph$_3$P)(MeCN)Pd(η$^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_J$ (V)) and Cl(Et$_3$P)Pd(η$^2$-C(SiMe$_3$)(PEt$_3$)=P(=O)NH(SiMe$_3$)) (IX).

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$^aR = \Sigma|F_o|-|F_c|\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. $^c$Quality of fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$. 
Table 2. Selected Bond Distances (Å) and Angles (deg) for [(Ph$_3$P)(MeCN)Pd($\eta^2$-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (V).

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| Numbers in parentheses are estimated standard deviations in the least significant digits.
Table 3. Selected Bond Distances (Å) and Angles (deg) for \( \text{Cl(Et}_2\text{P)}\text{Pd}[\eta^2-\text{C(SiMe}_3\text{)(PEt}_3\text{)=P(=O)NH(SiMe}_3\text{)}] \) (IX).

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Numbers in parentheses are estimated standard deviations in the least significant digits.
Figure Captions

**Figure 1.** Thermal ellipsoid drawing of [(Ph₃P)(MeCN)Pd(η²-C(Cl)(PPh₃)=PN(SiMe₃)₂)] (PF₆) (V).

**Figure 2.** Thermal ellipsoid drawing of Cl(Et₃P)Pd[η²-C(SiMe₃)(PET₃)=P(=O)NH(SiMe₃)] (IX).
Figure 1.
Figure 2.
FUNCTIONALIZATION OF $\eta^1$, $\eta^2$-BRIDGING CYAPHIDE ($C\equiv P$) LIGANDS: TRINUCLEAR $\eta^1$, $\eta^1$, $\eta^2$-BRIDGING CYAPHIDE AND DINUCLEAR BRIDGING ISOCYAPHIDE ($C\equiv PR$) COMPLEXES OF PLATINUM

A paper to be submitted to Organometallics

Wayde V. Konze, Victor G. Young, Jr., and Robert J. Angelici*

Abstract

The oxidative addition reaction of Pt(PEt$_3$)$_2$ with Cl$_2$C=PN(SiMe$_3$)$_2$ at low temperature (-50°C) forms the $\eta^1$-phosphavinyl complex cis-Cl(PEt$_3$)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] (Ia) which isomerizes to the trans-isomer (Ib) upon warming to 0°C; the structure of Ib was determined by X-ray diffraction studies. Complex Ib reacts with Pt(PEt$_3$)$_2$Cl$_2$ in the presence of three equivalents of sodium-benzophenone to generate the $\eta^1$, $\eta^2$-cyaphide-bridged dimer Cl(PEt$_3$)$_2$Pt($\mu$-$\eta^1$, $\eta^2$-$C\equiv P$)Pt(PEt$_3$)$_2$ (II) in good yield, providing a much simpler and higher yield preparation of II which was synthesized and characterized previously by a more circuitous route. Compound II reacts with one-half equivalent of [Cl$_2$Pt(PEt$_3$)$_2$] or with one equivalent of W(CO)$_5$(THF) to generate the trinuclear metal-cyaphide complexes Cl(PEt$_3$)$_2$Pt[$\mu$-$\eta^1$, $\eta^1$, $\eta^2$-$C\equiv P$]Pt(PEt$_3$)$_2$ (III) and Cl(PEt$_3$)$_2$Pt[$\mu$-$\eta^1$, $\eta^1$, $\eta^2$-$C\equiv P$]W(CO)$_5$(IV), respectively, in which the lone pair of electrons on the C≡P phosphorus atom is coordinated to a Pt(PEt$_3$)(Cl)$_2$ fragment in the former and a W(CO)$_5$ fragment in the latter; the structure of IV was determined by X-ray diffraction studies.

Compound II also reacts with MeI to form the methyl isocyaphide complex (Cl)(Et$_3$P)Pt($\mu$-$C\equiv P$Me)Pt(PEt$_3$)$_2$(IVc) in which the cyaphide (C≡P) ligand has been converted to a methyl isocyaphide (C≡PMe) ligand in a semi-bridging coordination mode. When compound II is reacted with MeOTf, the product is the cationic isocyaphide complex [(Cl)(Et$_3$P)$_2$Pt($\mu$-$\eta^1$, $\eta^2$-$C\equiv P$)Me]Cl (IIC) which was characterized by X-ray diffraction studies.
C≡PMe)Pt(PEt₃)₂[OTf] (Va), which is likely coordinated in an η¹, η²-bridging mode. Compound Va reacts with NaI to form Vc, which suggests that Va forms as an intermediate before Vc in the reaction of II with MeI.

† X-Ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, MN 55455

Introduction

Studies involving phosphorus analogs of common organic ligands have evolved at a very rapid pace recently, and coordination compounds of C-P analogs of almost all C-C multiple bond ligands are now known, including phosphaalkenes, phosphaalkynes, phosphaallyls, phosphaallenes, phosphabutadienes, phosphacycloprenes, phosphacyclobutadienes, phosphacyclopentadienyls and phosphaarenes.¹⁻⁶ However, phosphorus analogs of the well studied cyanide (C≡N⁻) and isocyanide (C≡NR) ligands have been limited.⁷⁻⁹ These phosphorus compounds have been calculated to be high energy species; the heat of formation in C≡P⁻ (cyaphide anion) is calculated to be ca. 40 kcal/mol less exothermic than that of C≡N⁻,¹⁰ and C≡PH (isocyaphide) is calculated to be 85 kcal/mol less stable than its isomer H-C≡P (phosphaalkyne).¹¹ Nevertheless, we recently succeeded in preparing the first example of a coordinated isocyaphide ligand by oxidative addition of the C-Cl bond in the phosphavinyl complex (1) (eq 1) to generate a diplatinum complex [(Cl)(Et₃P)Pt(μ-C≡PR)Pt(PEt₃)₂(Cl)] (2),
Pt(PEt₃)₄ + Cl₂C=PR
(R = Mes*, 2,4,6-tri-tert-butylbenzene)

in which the isocyaphide ligand exhibits a semi-bridging coordination mode. However, this preparation was limited by the few examples of dichlorophosphaalkenes available and by the bulky R-groups that are incorporated in these reagents. More recently, Weber and coworkers reported the synthesis (eq 2) of some diiron complexes containing symmetrically-bridged isocyaphide ligands (3) by a different route. In these reactions, the isocyaphide products were only prepared with bulky R-groups on phosphorus. We also obtained the first example of a cyaphide complex (Et₃P)₂ClPt(C≡P) (4) from a reaction (eq 3) of the phosphavinyln complex (1) with Pd(PEt₃)₄, in which the Mes* group was transferred from phosphorus to palladium forming (Et₃P)₂(Cl)Pd(Mes*) as a side product. Compound 4 could only be characterized by NMR, but reacted (eq 3) with Pt(PEt₃)₄ to generate the η¹, η²-cyaphide dimer Cl(Et₃P)₂Pt(μ-η¹, η²-C≡P)Pt(PEt₃)₂ (II), which was characterized by X-ray diffraction studies.
We describe in the present paper a high yield preparation of complex II utilizing a one-step reaction from the phosphavinyi complex trans-Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ib), which has much different reactivity than the analogous phosphavinyi complex trans-Cl(Et₃P)₂Pt[C(Cl)=PMe*] (I). We also investigate further functionalization of the cyaphide ligand in complex II by virtue of the accessible lone pair of electrons on the C=P phosphorus atom. During the course of these studies, we have isolated the first examples of trinuclear metal-cyaphide compounds (A) that were formed by coordinating the C=P phosphorus atom in II to other transition metal fragments. We have also found that the cyaphide ligand in II can be easily converted to an alkyl isocyaphide ligand by using various alkylating agents, constituting the first examples of cyaphide-isocyaphide conversions and demonstrating that isocyaphide ligands with less bulky alkyl R-groups can be stabilized on transition metals.

Results and Discussion

**Synthesis of trans-Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ib).** The reaction (eq 4) of Pt(PEt₃)₄ with Cl₂C=PN(SiMe₃)₂ in THF or hexanes at -50°C immediately and quantitatively forms the η¹-phosphavinyi complex cis-Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ia) by oxidative
addition of one of the C-Cl bonds; upon warming the solution to 0°C, the cis-isomer completely rearranges to the trans-isomer (Ib). Some formation of Pt(PEt$_3$)$_2$Cl$_2$ also occurs during this reaction. This cis-trans isomerization is quite similar to that in the analogous phosphavinyl complex Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] in which both the cis- and trans-isomers were isolated and characterized. The structure and $^{31}$P NMR spectrum of Ib are very similar to those of trans-Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] (I), but they differ in reactivity. For instance, compound I rearranges to Mes*C≡P and Pt(PEt$_3$)$_2$Cl$_2$ after 24 h in THF at room temperature, whereas Ib is stable in THF for weeks at room temperature, although a small amount of Pt(PEt$_3$)$_2$Cl$_2$ does form in this time. Further, compound I undergoes a second C-Cl oxidative addition reaction (eq I) with Pt(PEt$_3$)$_4$ in 24 h at room temperature to form the isocyaphide complex [(Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl)] (2); a similar reaction between Ib and Pt(PEt$_3$)$_4$ does not form the N(SiMe$_3$)$_2$ analog of compound 2, but results in decomposition to a complex mixture of unidentified products.

Compounds Ia and Ib were characterized by their $^{31}$P and $^{31}$P{ $^1$H} NMR spectra. The signals corresponding to P(x) in the $^{31}$P NMR spectra of Ia and Ib were assigned by their characteristic downfield chemical shifts of 225.1 and 222.3 ppm, respectively, and by their proton-coupled $^{31}$P NMR spectra in which these signals do not show any proton coupling, while the signals corresponding to the PEt$_3$ groups are greatly broadened. The P(x) peak in Ia is split into a doublet of doublets ($^3$$J_{P(x),P(x)}$ = 8.3 Hz, $^3$$J_{P(x),P(Et)}$ = 33.0 Hz) by the two inequivalent PEt$_3$ groups and exhibits platinum satellites with $^3$$J_{P(x),Pt}$ = 410 Hz. The P(x) peak in Ib is split
into a triplet ($^3J_{Pt,P(a)} = 20.0$ Hz) by the two equivalent PEt$_3$ groups and exhibits a larger $^{195}$Pt-P coupling constant ($^3J_{Pt,P} = 676$ Hz) than in $\text{Ia}$. In $\text{Ia}$, the PEt$_3$ ligand that is \textit{trans} to the C(Cl)=PN(SiMe$_3$)$_2$ group is assigned to P(b) at $\delta$ 10.1 ppm and the \textit{cis} PEt$_3$ ligand is assigned to P(a) at $\delta$ 5.6 ppm based on the larger coupling constant $^3J_{Pt,P(b)} = 33.0$ Hz between P(x) in the C(Cl)=PN(SiMe$_3$)$_2$ group and the trans PEt$_3$ group P(b). These $^{31}$P NMR data are analogous to those obtained for \textit{cis-Cl}($\text{Et}_3\text{P}$)$_2\text{Pt}[\text{C(Cl)}=\text{PMes*}]$ (5(P(x)): 224.0 (dd, $^3J_{Pt,P} = 12.3$ Hz, $^3J_{Pt,P(b)} = 46.3$ Hz, $^3J_{Pt,P(a)} = 365.4$ Hz) and \textit{trans-Cl}($\text{Et}_3\text{P}$)$_2\text{Pt}[\text{C(Cl)}=\text{PMes*}]$ (1) (6(P(x)): 223.3 (t, $^3J_{Pt,P} = 25.2$ Hz, $^3J_{Pt,P(a)} = 657.7$ Hz) which indicates that the compounds are isostructural and that the N(SiMe$_3$)$_2$ group does not impart dramatic differences in the bonding compared with the Mes* group. However, in order to more thoroughly compare the bonding properties in these complexes, the structure of $\text{Ib}$ was determined by X-ray diffraction studies and compared with the previously determined structure of compound 1.\textsuperscript{12}

\textbf{X-ray Crystal Structure of \textit{trans-Cl}($\text{Et}_3\text{P}$)$_2\text{Pt}[\text{C(Cl)}=\text{PN(SiMe$_3$)$_2$}]$ (Ib). A thermal ellipsoid drawing of $\text{Ib}$ (Figure 1) shows that the complex is isostructural with the previously characterized compound \textit{trans-Cl}($\text{Et}_3\text{P}$)$_2\text{Pt}[\text{C(Cl)}=\text{PMes*}]$ (1). The platinum atom is in a square-planar environment as defined by the two PEt$_3$, Cl, and [C(Cl)=PR] ligands; the sum of angles around the platinum atom is 360.0°. The C(1)-P(1) distance of 1.690(7) Å is marginally longer than that (1.678(5) Å) in compound 1 and is the same within error as the Pt-C distance (1.685(2) Å) in the free phosphaalkene Cl$_2$C=PN(SiMe$_3$)$_2$.\textsuperscript{13} The Pt-C(1) distance in $\text{Ib}$ (1.990(7) Å) is slightly shorter than the corresponding distance (2.013 (4) Å) in 1.\textsuperscript{12} The nitrogen atom in $\text{Ib}$ is in a trigonal planar environment, and the P(1)-N(1)-Si(1)-Si(2) plane is almost orthogonal (96.4°) to the plane defined by Pt, Cl(1), C(1), P(1) and N(1). This orthogonality rules out any conjugative effects from the nitrogen lone pair; in a series of X-ray determined structures of phosphaalkenes containing NR$_2$ groups on phosphorus, orthogonal NR$_2$ groups were found to show no conjugative effects with the C=P double bond.\textsuperscript{14} If the [C(Cl)=PR] ligands in 1 and $\text{Ib}$ were significantly different, the bond lengths
between platinum and the \textit{trans} ligands (Cl(2)) would be affected by this difference. However, the Pt-Cl(2) length in Ib (2.373(2) \textAA) is the same within error as that (2.377(2) \textAA) in 1. Thus, a comparison of the structures of 1 and Ib indicate that the N(SiMe$_3$)$_2$ and Mes* groups show similar structural effects in phosphavinyl complexes of the type \textit{trans}-Cl(Et$_3$P)$_2$Pt(C(Cl)=PR).

\textbf{Preparation of Cl(Et$_3$P)$_2$Pt(\(\mu\)-\(\eta^1\), \(\eta^2\)-C=\textit{P})Pt(PEt$_3$)$_2$ (II).} The reaction (eq 5) of 1.05 equivalents of \textit{trans}-Cl(Et$_3$P)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] (lb) and 1 equivalent of Pt(PEt$_3$)$_2$Cl$_2$ with 3 equivalents of a dropwise added 0.2 M solution of sodium benzophenone ketyl in THF forms the bridging cyaphide dimer Cl(Et$_3$P)$_2$Pt(\(\mu\)-\(\eta^1\), \(\eta^2\)-C=\textit{P})Pt(PEt$_3$)$_2$ (II) in good yield. This preparation is much simpler than the original (eq 3) which involved the reaction of \textit{trans}-Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] (1) with Pd(PEt$_3$)$_4$ to first generate a mixture of (Et$_3$P)$_2$ClPt(C=C) (4) and (Et$_3$P)$_2$(Cl)Pd(Mes*); complex 4 was then purified by crystallizing out (Et$_3$P)$_2$(Cl)Pd(Mes*) and finally reacted further with Pt(PEt$_3$)$_4$ to generate the product II.$^9$

In this new preparation, the intermediate isolation of complex 4 is avoided, and highly reactive Pd(0) and Pt(0) reagents are not necessary. Further, this reaction can be done on a several gram scale and gives excellent yields of complex II in pure, crystalline form.

In order to gain an understanding of how this interesting reaction proceeds, several different stoichiometries of different reagents were investigated, as was the order of addition. The use of 3 equivalents of the Na/benzophenone ketyl reducing agent was found to be ideal as more equivalents cause decomposition while fewer causes an incomplete reaction, which suggests that the two chlorides from Pt(PEt$_3$)$_2$Cl$_2$ and one chloride from Ib are removed as NaCl. The N(SiMe$_3$)$_2$ R-group is possibly removed as (SiMe$_3$)$_2$N-N(SiMe$_3$)$_2$, although this
was not investigated. Interestingly, the reaction of trans-Cl(Et,P)_2Pt[C(Cl)=PMe*] (1) with Pt(PEt_3)_2Cl_2 and 3 equivalents of sodium benzophenone ketyl also results in the formation of II, but it also gives impurities that could not be separated. In order to investigate the role of the reducing agent, a reaction was attempted between Ib and Na/benzophenone ketyl without any Pt(PEt_3)_2Cl_2 present; no reaction was apparent after six hours. Also, if Pt(PEt_3)_2Cl_2 is reduced with Na/benzophenone ketyl followed by addition of Ib, a 3^1P NMR spectrum shows that Ib is unreacted in solution. Evidently, both Ib and Pt(PEt_3)_2Cl_2 must be present during the addition of the reducing agent for this reaction to occur. The reduction reaction of Pt(PEt_3)_2Cl_2 in the presence of ethylene is known to produce Pt(PEt_3)_2C_2H_4, and it has been reported that if a suitable ligand is not present in solution the Pt(PEt_3)_2 fragment that is generated oligomerizes to Pt(0) clusters. It is possible that the Pt(PEt_3)_2 fragment that is generated in eq 5 coordinates to the C=P double bond of Ib and activates the carbon-bound Cl toward reduction by a third equivalent of Na/benzophenone ketyl, while in the absence of Ib the Pt(PEt_3)_2 oligomerizes and does not react with Ib. Similar reactions to that in eq 5 were attempted between Ib and Pt(PPh_3)_2Cl_2, Pt(Pi-Pr_3)_2Cl_2, Pt(PCy_3)_2Cl_2, and Pt(depe)Cl_2; in all cases, compound Ib remained unreacted in solution indicating that this reaction is not general for other phosphines.

**Preparation of Trinuclear Metal-Cyaphide Complexes.** The cyaphide ligand that is coordinated to two platinum centers in complex II contains a lone pair of electrons on the C=P phosphorus atom that is a potential site for further coordination. Accordingly, the reactions (eq 6) of either one-half equivalent of [Pt(Cl)_2(PEt_3)_2] or one equivalent of
W(CO)$_5$(THF) with II in THF at room temperature afford the first examples of trinuclear metal-cyaphide complexes Cl(Et$_3$P)$_2$Pt[$\mu$-n$^+$, n$^+$, n$^+$-C≡P{Pt(PEt$_3$)(Cl)$_2$}]Pt(PEt$_3$)$_2$ (III) and Cl(Et$_3$P)$_2$Pt[$\mu$-n$^+$, n$^+$, n$^+$-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (IV), respectively. Complex III forms immediately after the addition of [Pt(Cl)$_2$(PEt$_3$)]$_2$ to II and a $^{31}$P NMR spectrum of the reaction mixture showed practically quantitative conversion to III with a small amount of Pt(PEt$_3$)$_2$Cl$_2$ formed as a by-product; complex III could not be isolated in pure form as it decomposes under vacuum to unidentified materials, presumably through loss of PEt$_3$. In the reaction of W(CO)$_5$(THF) with II, the formation of complex IV is complete after 1 h and a small amount of W(CO)$_5$(PEt$_3$) forms as a by-product that was easily separated. These reactions are similar to those of the n$^+$-coordinated phosphaalkyne complexes (R$_3$P)$_2$Pt(n$^+$-R-C≡P); in these, n$^+$-coordination of the phosphaalkyne to the platinum fragment enhances the coordinating ability of the lone pair of electrons on phosphorus.$^3$,$^16$

Compounds III and IV were characterized by $^{31}$P and $^{31}$P{H} NMR spectroscopy and the structure of complex IV was determined by X-ray diffraction studies. The $^{31}$P NMR data for these compounds are compared in Table 4 along with the starting cyaphide complex (II) and the methyl isocyaphide complex (Va) which is a cationic complex of similar structure (see below). In all of these complexes, the peaks corresponding to P(x) are conveniently assigned by proton-coupled $^{31}$P NMR spectroscopy, in which the P(x) signals remain sharp, while the PEt$_3$ signals are broadened by coupling to the ethyl protons. Complex III exhibits 5 distinct signals in its $^{31}$P NMR spectrum: peaks corresponding to P(x) at $\delta$ 111.2, P(a) at $\delta$ 5.0, P(b) at
δ 15.9 and P(c) at δ 17.2 ppm were assigned based on similar signals in the $^{31}$P NMR spectrum of II, while the peak corresponding to P(d) at δ 5.2 ppm was assigned to the PEt$_3$ group in the Pt(PET$_3$)(Cl)$_2$ fragment that is coordinated to the C=P phosphorus atom. The peak for P(x) in II is split into a doublet of doublet of triplets, while the same peak in III is now split into a doublet of doublet of doublet of triplets; the extra splitting is from the PEt$_3$ ligand on the Pt(PET$_3$)(Cl)$_2$ fragment ($^2J_{P(x)P(b)} = 472.3$ Hz). This is a very large two-bond P-P coupling constant that is indicative of a trans-orientation between P(d) and P(x), similar to the trans-$^2J_{pp} = 557$ found in the bridging phosphaalkyne complex Mo$_2$(CO)$_4$(Cp)$_2$[t-BuCP[Pt(PET$_3$)(Cl)$_2$]]$^{17}$ and to the values of trans-$^2J_{pp} = 462-483$ Hz measured in a series of trans-[PtCl$_2$(PR$_3$)(PR$_3'$)]$^{18}$ complexes. The coordination of the Pt(PET$_3$)(Cl)$_2$ fragment to compound II also imparts a large change on the two-bond coupling constant between P(x) and the trans-like PEt$_3$ ligand P(b); the value of $^2J_{P(x)P(b)} = 13.7$ Hz in II increases to $^2J_{P(x)P(b)} = 148.0$ Hz in III. This effect has also been seen in η$^2$-phosphaalkyne complexes; in the complex [Pt(dppe)(η$^2$-t-BuC=Pt)], the coupling constant between the C=Pt phosphorus and the trans-P atom is 28.1 Hz, but when a Cr(CO)$_5$ fragment is coordinated to the C=Pt phosphorus atom, this value increases to 177.5 Hz.$^{16}$ In fact, all of the couplings between P(x) and the other phosphorus signals are increased upon coordination of the Pt(PET$_3$)(Cl)$_2$ group (see Table 4). Evidently, the cyaphide phosphorus atom undergoes a change in hybridization upon coordination to the metal fragment, acquiring more phosphorus s-electron character in the C=Pt bond.

Complex IV exhibits 4 distinct signals in its $^{31}$P NMR spectrum; the peaks corresponding to P(a) at δ 3.1, P(b) at δ 16.6 and P(c) at δ 13.9 ppm were assigned based on similar signals in the $^{31}$P NMR spectrum of II and III, while the peak at δ 41.4 ppm was assigned to P(x) based on a sharp proton-coupled $^{31}$P NMR signal and the doublet of doublet of triplets splitting pattern. The chemical shift of 41.4 ppm is 66 ppm upfield from that of P(x) in compound II and is similar to the upfield shift of 42 ppm that was measured upon
coordination of a W(CO)$_3$ fragment to the CsP phosphorus atom in the $\eta^2$-phosphaalkyne complex [Pt(dppe)($\eta^2$-t-BuC=P)].$^{16}$ The coordination of the W(CO)$_3$ group to complex II results in increased $^{31}$P-$^{31}$P coupling constants (see Table 4) similar to those for III. The two-bond coupling constant between P(x) and the trans-like PEt$_3$ ligand P(b) is again very large $^{2}J_{P(x)P(b)} = 152.9$ Hz, and similar to that ($^{3}J_{P(x)P(b)} = 148.0$ Hz) in III. Only one set of platinum satellites ($^{3}J_{P(x)Pt(1)} = 507$ Hz) could be distinguished for P(x) in compound IV because of the complexity of this signal; this coupling constant is larger than that (255 Hz) in II, but still a bit smaller than that (676 Hz) in Ib. Although no tungsten satellites could be found for P(x), the signal for P(b) exhibited an unusually large three bond coupling to tungsten ($^{3}J_{WP(b)} = 150.77$ Hz), most likely because of the enhanced coupling between P(x) and P(b).

**X-Ray Crystal Structure of Cl(Et$_3$P)$_2$Pt[$\mu$-$\eta^1$, $\eta^1$, $\eta^2$.**  
Cl=P[W(CO)$_3$]Pt(PEt$_3$)$_2$ (IV). A thermal ellipsoid drawing of IV (Figure 2) shows that the complex contains a W(CO)$_3$ fragment attached to the CsP phosphorus atom and has many structural features in common with the X-ray-determined structure of complex II.$^9$ Both of the platinum atoms in IV are in planar environments; the sum of angles around Pt(1) as defined by C(1), P(2), P(3) and Cl(1) is 360.1°, while the sum of angles around Pt(2) as defined by C(1), P(1), P(4) and P(5) is 360.4°. The C(1)-P(1) distance (1.663(9) Å) in IV is the same within error as that (1.666(6) Å) in II indicating that coordination of the W(CO)$_3$ unit has not dramatically changed the character of the cyaphide C-P bond. This distance is similar to a C-P double-bond distance (e.g., 1.67 Å in Ph(H)C=PMes*)$^{19}$ and to the C-P distance (1.67(2) Å) in the $\eta^2$-phosphaalkyne complex [Pt(PPh$_3$)$_2$($\eta^2$-t-BuC=P)].$^{20}$ and is consistent with backbonding from Pt(2) into the $\pi^*$ orbital of the CsP bond affording some metallacyclophosphapropene character in this 3-atom unit in IV. The Pt(1)-C(1)-P(1) angle (145.2(6)°) is bent from linearity similar to that in II (144.0(3)°) and the W(1)-P(1)-C(1) angle (136.1(3)°) is bent even further, also consistent with metallacyclophosphapropene character in this complex. The W(1)-P(1) distance (2.531(3) Å) is very similar to the W-P bond length
(2.539(3) Å) in the bridging phosphaalkyne complex Mo$_2$(CO)$_4$(Cp)$_2$($t$-BuCP[W(CO)$_3$])$^{21}$ and is slightly longer than typical W-P distances in structurally characterized W(CO)$_4$(PR$_3$)$_2$ complexes (e.g., 2.502 Å in cis-W(CO)$_4$(PMe$_3$)$_2$).$^{22}$ The Pt(2)-C(1) distance (2.104(9) Å) in IV is slightly longer than the corresponding distance (2.083(5) Å) in II, while the Pt(1)-C(1) distances (1.952(9) Å in IV and 1.950(6) Å in II) are the same within error. However, the Pt(2)-P(1) distance (2.292(3) Å) in IV is shorter than the corresponding distance (2.337(2) Å) in II. This is consistent with more s-electron character on phosphorus in the C=P bond.

**Alkylation Reactions of Cl(Et$_3$P)$_2$Pt($\mu$-η$^1$, η$^2$-C=P)Pt(P(Et$_3$)$_2$ (II).** The reaction (eq 7) of three equivalents of MeI with Cl(Et$_3$P)$_2$Pt($\mu$-η$^1$, η$^2$-C=P)Pt(P(Et$_3$)$_2$ (II) in THF for 12 h at 25°C results in the formation of the methyl isocyaphide complex

(Cl)(Et$_3$P)Pt($\mu$-C=PMe)Pt(P(Et$_3$)$_2$ (Vc) with concomitant formation of the phosphonium salt (MeP(Et$_3$)$_2$)$^+$ I. This reaction entails the conversion of a cyaphide (C=P) ligand to an isocyaphide (C=PMe) ligand and substitution of a coordinated P(Et$_3$) ligand (lost as (MeP(Et$_3$))$^+$ I) with an iodide ligand; thus, the MeI acts both as a methylating agent and as a phosphine scavenger in this reaction. Although complex Vc is stable in THF solution at room temperature for several weeks, suitable crystals could not be obtained for an X-ray diffraction study as the compound only forms an oil. However, the complex is likely isostructural with the previously obtained semi-bridging isocyaphide complex (Cl)(Et$_3$P)Pt($\mu$-C=PMe*)Pt(P(Et$_3$)$_2$ (Cl) (2)$^9$ based upon its $^{31}$P NMR spectrum (Table 5) and the $^{13}$C-$^{31}$P coupling constants obtained from the use of $^{13}$C-labeled MeI in this reaction. Thus, the $\eta^1$, $\eta^2$-cyaphide ligand in II is converted to a semi-
bridging isocyaphide ligand in Vc with the formation of a Pt-Pt bond. This reaction has some precedent in related isocyanide chemistry as the conversion of coordinated cyanide (C=N) ligands to isocyanide (C=NR) ligands with various alkylating agents is a well known synthetic route to isocyanide complexes, although these reactions have only been carried out on terminal cyanide complexes. This new synthetic route to an isocyaphide complex is much different than the reaction (eq 1) of the phosphavinyl complex trans-Cl(Et3P)2Pt[C(Cl)=PMe2*] (1) with Pt(PEt3)4 to generate the semi-bridging isocyaphide complex (Cl)(Et3P)Pt(μ-C=PMes*)Pt(PMe2)2(Cl) (2) or the reactions (eq 2) of [Cp2(CO)2Fe2(μ-CO)(μ-CSMe)] with RP(H)(SiMe3) and DBU to generate the bridging isocyaphide complexes [Cp2(CO)2Fe2(μ-CO)(μ-C=PR)] (3); both of these syntheses were limited by the use of bulky aryl R-groups on the CPR phosphorus atom. In contrast, the reaction of II with MeI allows for the formation of an isocyaphide with a sterically small methyl group and could conceivably be a more general route to diplatinum isocyaphide complexes. In order to test this, the reaction in eq 7 was attempted with several different alkyl and aryl halides (e.g., benzyl bromide, i-propyl iodide, allyl bromide, o-iodo toluene and 2,4,6-tri-tert-butylbenzyl bromide) under the same reaction conditions and stoichiometry as in the MeI reaction. The reactions of both benzyl bromide (BnBr) and i-propyl iodide (i-PrI) with II afforded similar isocyaphide products (Cl)(Et3P)Pt(μ-C=PBn)Pt(PMe2)2(Br) (VI) and (Cl)(Et3P)Pt(μ-C=Pi-Pr)Pt(PMe2)2(I) (VII), respectively, as evidenced by 31P NMR spectroscopy (see Table 5). However, the benzyl derivative could not be separated from impurities that were present, and the i-Pr derivative was unstable and decomposed before the reaction was complete. The reaction of allyl bromide with II formed completely different products that could not be isolated, while the aryl halides did not react with compound II, even after stirring for several days at room temperature. However, the results with BnBr and i-PrI are encouraging and suggest that other alkyl halides may be successful in this reaction.
Complex Vc was characterized by $^{31}$P, $^{31}$P{'H} and $^{13}$C{'H} NMR spectroscopy. The
$^{31}$P NMR spectrum of complex Vc shows very similar chemical shifts and coupling constants
(Table 5) to those measured in the semi-bridging isocyaphide complex (Cl)(Et$_3$P)Pt(μ-
C=PMes*)Pt(PEt$_3$)$_2$(Cl) (2)$^9$ and is thus proposed to exhibit the same structure. The $^{31}$P
NMR spectrum of Vc exhibits three different signals. The peak at δ 155.4 ppm, assigned to
P(x), is split into a doublet of triplets with two different $^{195}$Pt satellites, indicative of the
unsymmetrical, semibridging bonding mode of the C=PMe ligand. The doublet ($^{2}J_{^{31}P(x)^{195}Pt} = 15.3$ Hz) arises from coupling to the single PEt$_3$ ligand (P(b)) on Pt(2), while the triplet
($^{3}J_{^{31}P(x)^{195}Pt} = 12.1$ Hz) results from coupling to the two equivalent PEt$_3$ ligands (P(a)) on Pt(1).
The larger coupling constant to platinum ($^{2}J_{^{31}P(x)^{195}Pt} = 564.7$ Hz) is assigned to coupling with the
4-coordinate platinum Pt(2), while the smaller Pt-P coupling constant ($^{2}J_{^{31}P(x)^{195}Pt} = 231.9$ Hz) is
assigned to coupling with the 5-coordinate platinum atom Pt(1); these assignments are made
based upon the assignments in compound 2 and by the larger $J_{pp}$ coupling constants that are
typically found in platinum complexes with lower coordination numbers.$^{24}$ From these $J_{pp}$
coupling constants, the signal at δ 8.7 ppm is assigned to P(a), while the signal at δ 21.52 is
assigned to P(b). Because the signal for P(a) is farther upfield than the analogous peak in 2,
while the peaks for P(b) have quite similar chemical shifts, it is assumed that the iodide ligand
is on the platinum that contains the two P(a) PEt$_3$ groups (Pt(1)). One of the unique aspects of
the $^{31}$P NMR spectra of Vc, which gives precedent to it being isostructural with 2, is the large
differences in the one-bond $J_{pp}$ coupling constants in the signals corresponding to P(a) and
P(b); for P(a) in Vc, the value of $^{1}J_{^{31}P(a)^{195}Pt} = 2338.9$ Hz is similar to those found in trans-
Pt(PEt$_3$)$_2$X$_2$ complexes,$^{24}$ while for P(b), the value of $^{1}J_{^{31}P(b)^{195}Pt} = 5173.7$ Hz is very large and
more similar to those found in three-coordinate Pt(0) complexes.$^{24}$ This difference in the $J_{pp}$
coupling constants is greater in Vc than in compound 2 and has been discussed previously in
the analogous semibridging carbonyl complex (Cl)(Ph$_3$P)Pt(μ-CO)Pt(PPh$_3$)$_2$(Cl) (4) which is
very similar in structure to Vc and 2, but with PPh$_3$ instead of PEt$_3$ ligands and a semibridging
CO ligand in place of the CPR ligands. Complex 4 exhibits a value of $^1J_{pp} = 2680$ Hz for the two equivalent 5-coordinate platinum PPh$_1$ groups (P(a)) and a value of $^1J_{pp} = 5440$ Hz in the 4-coordinate platinum PPh$_3$ group (P(b)) (see Table 5 for further comparisons). This difference was rationalized by suggesting some degree of mixed valence character between the two platinum atoms. To further verify that the methyl group is attached to the phosphorus atom in complex Vc, the reaction was carried out using $^{13}$C-labeled MeI. The $^{31}$P NMR spectrum of labeled Vc exhibited an extra doublet in the signal for P(x) from coupling to the labeled methyl group with $^1J_{pxc} = 48.9$ Hz. This value is similar to the value of $^1J_{pc} = 51.1$ Hz found in the phosphonium salt (MePEt$_3$)$^+I_-$ product of this reaction. Interestingly, the signal for P(b) also exhibited a small coupling ($^1J_{pxc} = 10.6$ Hz) to the methyl group. The $^{13}$C NMR signal for the methyl group occurred at δ 10.5 and was split into a doublet of doublets by P(x) and P(b). This peak also exhibited a small Pt-C coupling constant of $^3J_{pc} = 51.2$ Hz, which is most likely a coupling with Pt(2) which is bonded more strongly to the CPR group.

The $^{31}$P NMR spectra of complexes VI and VII (Table 5) are quite similar to those of Vc, and these compounds are proposed to be of similar structure. These spectroscopic results, along with comparisons with those of compounds 2 and 4, strongly suggest that complexes Vc, VI and VII contain semibridging isocyaphide ligands.

**Mechanistic Studies of the Formation of (Cl)(Et$_3$P)Pt($\mu$-C=PM)Pt(PEt$_3$)$_2(I)$ (Vc).** A likely pathway (Scheme 1) for the formation of complex Vc from complex II is the initial methylation of the C=O phosphorus atom to generate a cationic $\eta^1$, $\eta^3$-isocyaphide intermediate (Va). The iodide anion can then attack at Pt(2) to generate the
bridging isocyaphide intermediate \( \text{Vb} \), which loses a PEt\(_3\) group and forms a metal-metal bond to generate the product \( \text{Vc} \). An intermediate similar to \( \text{Vb} \) was postulated in the reaction (eq 1) of the phosphavinyl complex \( \text{trans-Cl}(\text{Et}_3\text{P})_2\text{Pt}([\text{C(Cl)}=\text{PMe}_3^*]) \) (1) with Pt(PEt\(_3\))\(_4\) to generate the semi-bridging isocyaphide complex \( \text{(Cl)(Et}_3\text{P})\text{Pt}(\mu-\text{C}=\text{PMe}_3^*)\text{Pt}(\text{PEt}_3)_2(\text{Cl}) \) (2). In an attempt to verify this pathway by isolation of the cationic \( \eta^1, \eta^2 \)-isocyaphide intermediate (\( \text{Va} \)), complex II was reacted with one equivalent of MeI in the presence of two equivalents of NaBPh\(_4\) in THF at room temperature. The color of the solution turned to a very deep ruby red color after 1h, and a \( ^{31}\text{P} \) NMR spectrum (see below) showed a new complex that matches the structure drawn for \( \text{Va} \) where the iodide anion has been replaced with \( (\text{BPh}_4^-)' \). This complex was then isolated in reasonably pure form by filtering the solution and adding hexanes to form an oil of mainly \( \text{Va} \). When a ten-fold excess of NaI was then added to a solution of \( \text{Va} \) in THF, the color changed from deep red to light orange in 10 min, and a \( ^{31}\text{P} \) NMR spectrum showed that this complex was completely converted to the semibridging isocyaphide complex \( \text{Vc} \), which strongly suggests that \( \text{Va} \) is an intermediate that forms before \( \text{Vc} \) in the reaction of MeI with complex II. In a separate experiment, complex II was reacted with MeOTf in THF; the color turned to deep red in a matter of minutes and a \( ^{31}\text{P} \) NMR spectrum of the solution again showed complex \( \text{Va} \) where a triflate anion is substituted for the iodide anion. Reaction of this solution with a ten-fold excess of NaI afforded complex \( \text{Vc} \), providing further evidence
for the pathway outlined in Scheme 1. Although there was no evidence in the $^{31}$P NMR spectra for other intermediates, $\text{Vb}$ is a likely intermediate that explains the rearrangement of the $\eta^1, \eta^2$-isocyaphide ligand in $\text{Va}$ to the semibridging isocyaphide ligand in $\text{Vc}$. In contrast to $\text{Vc}$, which contains a Pt-Pt bond, the $^{31}$P NMR spectrum (see below) of $\text{Va}$ suggests that there is no Pt-Pt bond in this cationic isocyaphide complex. Clearly, compound $\text{Va}$ does not contain a semibridging isocyaphide similar to $\text{Vc}$, and it is not clear why substitution of a PEt$_3$ group in $\text{Va}$ by an iodide anion causes this rearrangement to take place. Complex $\text{Va}$ contains the first example of an $\eta^1, \eta^2$-bridging isocyaphide ligand.

Although complex $\text{Va}$ could not be isolated in pure form, the $^{31}$P NMR spectrum is characteristic of an $\eta^1, \eta^2$-bridging isocyaphide structure and shows features (Table 4) very similar to those in the spectra of the $\eta^1, \eta^1, \eta^2$-bridging trimetallic cyaphide complexes with a Pt(Cl)$_2$(PEt$_3$) fragment (III) and a W(CO)$_5$ fragment (IV) on the cyaphide phosphorus atom. The signal at $\delta$ 34.7 ppm in $\text{Va}$, assigned to P(x), is shifted 120 ppm upfield from the corresponding P(x) peak in $\text{Vc}$; this shift is most consistent with an $\eta^1, \eta^2$-bridged species. Interestingly, the chemical shift is quite similar to that ($\delta$ 41.4 ppm) in the tungsten-coordinated cyaphide complex IV, which differs only in that it is neutral and contains a W(CO)$_5$ group in place of the Me group on $\text{Va}$. Also supporting the proposed structure is the fact that the splitting patterns and coupling constants in $\text{Va}$, III and IV are all quite similar (Table 4). The coupling constants between P(x) and the PEt$_3$ groups again are larger than those in the $\eta^1, \eta^2$-cyaphide complex (II), with the most dramatic effect again being a large coupling ($^1J_{\text{P(x)P(b)}} = 148.9$ Hz) between P(x) and P(b). This is very similar to the $^1J_{\text{P(x)P(b)}}$ values found in III ($^1J_{\text{P(x)P(b)}} = 148.0$ Hz) and IV ($^1J_{\text{P(x)P(b)}} = 152.9$ Hz). The $^{195}$Pt-$^{31}$P coupling constants found in $\text{Va}$ are also similar to those found in III and IV (Table 4) and provide further evidence for the proposed structure. Since there is no $^{195}$Pt-$^{31}$P coupling of P(a) with Pt(2) or between P(b) and P(c) with Pt(1), the existence of a Pt-Pt bond in $\text{Va}$ is doubtful; in $\text{Vc}$ and 2 which contain Pt-Pt bonds, these couplings to the platinum atom of the adjacent metal fragment were somewhat
large (43-512 Hz). To further verify that the methyl group is attached to the cyaphide phosphorus atom, complex Va was prepared by reacting complex II with labeled MeI in the presence of NaBPh₄. The ³¹P NMR spectrum of this labeled complex exhibited additional doublets [P(x) (¹J_P(x)C = 71.5 Hz), P(b) (¹J_P(b)C = 8.4 Hz) and P(c) (¹J_P(c)C = 12.6 Hz)] as a result of coupling to the labeled methyl group. The ¹³C NMR spectrum also displayed a peak for the methyl group at δ 8.7 ppm that was split into a doublet of doublets of doublets by these three phosphorus atoms. These results are entirely consistent with the proposed structure of Va and indicate that the attachment of a W(CO)₅, Pt(Cl)₂(PEt₃) or Me⁺ group to the cyaphide phosphorus atom in complex II gives products with very similar ³¹P NMR spectra and structures.

Summary

Comparison of the reactivity of the new phosphavinyl complex trans-Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ib) with the previously obtained complex trans-Cl(Et₃P)₂Pt[C(Cl)=PMes⁺] (I)¹² has shown that the substitution of the Mes⁺ group with a N(SiMe₃)₂ group does not result in large changes in the NMR properties or structural features of these two complexes; the structure of (Ib) was determined by X-ray diffraction studies to be quite similar to that of I with no evidence for conjugation from the nitrogen lone pair of electrons into the C=P double bond. However, compound Ib showed much different reactivity than that of I and reacted with Pt(PEt₃)₂Cl₂ and Na/benzophenone ketyl to afford a new synthetic route to the previously obtained η¹, η²-bridged cyphide dimer Cl(Et₃P)₂Pt(μ-η¹, η²-C≡P)Pt(PEt₃)₂ (II). This reaction provided a much simpler and more efficient preparation of complex II and allowed us to further study the reactivity of this useful complex. Thus, complex II was reacted with one-half equivalent of [Pt(Cl)₂(PEt₃)]₂ or with one equivalent of W(CO)₅(THF) to generate the first examples of trinuclear metal cyaphide complexes Cl(Et₃P)₂Pt[μ-η¹, η¹,C≡P{Pt(PEt₃)(Cl)₂}Pt(PEt₃)]₂ (III) and Cl(Et₃P)₂Pt[μ-η¹, η¹,C≡P{Pt(PEt₃)(Cl)₂}Pt(PEt₃)]₂ (IV).
CH₃P[W(CO)₅]Pt(PEt₃)₂ (IV), respectively, in which the lone pair of electrons on the
cyaphide (CsP) phosphorus atom has been utilized to coordinate to a third metal fragment. The
structure of the tungsten adduct (IV) was determined by X-ray diffraction studies and showed
that the cyaphide ligand has some metallacyclophosphapropene character as both the
Pt(PEt₃)₂Cl and the W(CO)₅ fragments are bent back from the axis of the CsP bond. Complex
II also reacted with alkylation agents to generate semibridging isocyaphide complexes of the
type (Cl)(Et₃P)Pt(μ-C=PR)Pt(PEt₃)₂(X); when R = Me (Vc), it was found that a cationic η¹,
η²-bridging isocyaphide complex [(Cl)(Et₃P)₂Pt(μ-η¹, η²-Cs=PMe)Pt(PEt₃)₂] (I) (Va) formed
first in this reaction and was isolated as the triflate salt by reacting complex II with MeOTf.
This complex was converted into the semibridging isocyaphide complex (Vc), by reacting it
with excess NaI. These alkylation reactions represent the first examples of conversion of a
cyaphide (CsP) ligand into an isocyaphide (Cs=PR) ligand and demonstrate that isocyaphide
complexes with non-bulky alkyl groups can be stabilized on transition metals. The ³¹P NMR
spectrum of the triflate salt of complex Vc strongly suggests that this is the first example of a
complex containing an η¹, η²-bridged isocyaphide ligand and demonstrates a further
coordination mode of these new ligands.

Experimental Section

General Procedure. All manipulations were carried out under a dry, oxygen-free
argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent
grade and dried by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran
(THF) and diethyl ether (Et₂O) were distilled over sodium benzophenone ketyl, while hexanes
and dichloromethane (CH₂Cl₂) were distilled over CaH₂.

The ³¹P{¹H} and ³¹P NMR spectra were recorded on a Bruker AC 200-MHz
spectrometer using 85% H₃PO₄ (8 0.00 ppm) as the external standard. The ¹³C{¹H} and ¹³C
NMR spectra were recorded on a Bruker DRX 400-MHz spectrometer using CDCl₃ as the
internal standard. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The compounds Pt(PEt₃)₄, Pt(Cl)₂(PEt₃), [Pt(Cl)₂(PEt₃)]₂, Pt(PR₃)₂Cl₂ and Na/benzophenone ketyl were prepared by literature methods. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh₃, which was recrystallized from MeOH. Methyl iodide (MeI) and methyl triflate (MeOTf) were purchased from Aldrich and used without further purification. W(CO)₅(THF) was prepared by photolysis of W(CO)₆ in THF for 6 h at 20°C.

**Preparation of trans-Cl(Et₃P)Pt[C(Cl)=PN(SiMe₃)₂] (Ib) through Intermediate cis-Cl(Et₃P)Pt[C(Cl)=PN(SiMe₃)₂] (Ia).** To a cooled (-50°C) solution of Pt(PEt₃)₄ (1.50 g, 2.25 mmol) in hexanes (20 mL) was added Cl₂C=PN(SiMe₃)₂ (0.616 g, 2.25 mmol). A ³¹P{¹H} NMR spectrum taken 10 min after the addition (-50°C) showed complete conversion to Ia. After the solution had warmed to 0°C over the course of 30 min, a ³¹P{¹H} NMR spectrum showed that compound Ia had completely isomerized to Ib. The almost colorless solution was warmed to room temperature over the course of 10 min and the solvent was removed under vacuum. The residue was treated with 20 mL of hexanes, filtered, and the filtrate was concentrated to 10 mL. A white precipitate formed, which was found to be Pt(PEt₃)₂Cl₂ by comparison of its ³¹P NMR spectrum with that of an authentic sample. The precipitate was filtered off and the filtrate was concentrated to 5 mL under vacuum. The light orange/brown solution was cooled slowly to -78°C for 3 d after which time large, light yellow crystals had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give Ib (1.24 g, 78%). ³¹P{¹H} NMR (hexanes) (see eq 4 for atom labels) for Ia, -50°C: δ(P(x)) 225.1 (dd, ³¹J_{P(x)P(b)} = 33.0 Hz, ³¹J_{P(x)P(a)} = 8.3 Hz, δ(P(b)) 10.1 (dd, ³¹J_{P(b)P(a)} = 33.0 Hz, δ(P(a)) 5.6 (dd, ³¹J_{P(a)P(b)} = 16.2 Hz, ³¹J_{P(a)P(x)} = 1908 Hz). For Ib, 25°C: δ(P(x)) 222.3 (t, ³¹J_{P(x)P(b)} = 20.0 Hz, ³¹J_{P(x)P(a)} = 676.0 Hz).
\[ \delta(P(a)) \ 14.1 \ (d, J_{P(a)P(b)} = 20.0 \text{ Hz}, J_{P(a)Pt} = 2680 \text{ Hz}). \]  
Analyzed (for \( C_{i5}H_{88}Cl_{i2}N_{i}P_{i}Pt_{i}Si_{i2} \)): C, 32.34; H, 6.86; N, 1.98. Found: C, 31.25; H, 6.62; N, 1.87.

**Preparation of \( \text{Cl}(\text{Et}_3\text{P})_2\text{Pt}(\mu-\eta^1, \eta^1-\text{C}=\text{P})\text{Pt}(\text{PEt}_3)_2 \) (II).** To a dry mixture of \( \text{trans-Cl}(\text{Et}_3\text{P})_2\text{Pt}[\text{C(Cl)=PN(SiMe}_3)_2\text{]} \) (Ib) (1.00 g, 1.42 mmol) and \( \text{Pt}(\text{PEt}_3)_2\text{Cl}_2 \) (0.747 g, 1.49 mmol) at room temperature was added dropwise with stirring 20.8 mL of a solution of 0.204 M Na/benzophenone ketyl in THF (4.25 mmol) (the molarity of the Na/benzophenone solution was determined by quenching a measured amount with water, and titrating with standardized HCl solution). The addition was done at a rate that was determined by the color change; as the color turned blue, addition was halted until the color changed back to orange. The total time of the addition was ca 45 min, after which time the color of the solution was dark red with a large amount of NaCl precipitate. The solution was filtered through Celite and the solvent was removed from the filtrate under vacuum. Extended drying under vacuum, especially with heating, was found to cause decomposition. The dark red residue was treated with hexanes (30 mL), filtered through Celite and the filtrate was reduced in volume to 10 mL.

A \(^{31}\text{P} \) NMR spectrum of this solution showed pure II, however benzophenone was present as the only impurity. The solution was cooled slowly to -78°C and kept at this temperature for 1 week, after which time dark red crystals of II had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give II (1.05 g, 79%). Compound II was characterized by comparison of its \(^{31}\text{P} \) NMR spectrum with that of an authentic sample. \(^{31}\text{P}\{^1\text{H}\} \) NMR (THF) (see eqn 5 for atom labels): \[ \delta(P(x)) 107.0 \ (dtt, J_{P(x)P(b)} = 13.7 \text{ Hz}, J_{P(x)P(c)} = 10.7 \text{ Hz}, J_{P(x)Pt} = 10.7 \text{ Hz}, J_{P(x)Pt} = 255 \text{ Hz}, J_{P(1)P(2)} = 58 \text{ Hz}), \delta(P(c)) 18.6 \ (dd, J_{P(c)P(b)} = 35.1 \text{ Hz}, J_{P(c)P(c)} = 10.7 \text{ Hz}, J_{P(c)Pt} = 3619 \text{ Hz}, J_{P(1)P(2)} = 137 \text{ Hz}), \delta(P(b)) 15.0 \ (ddt, J_{P(b)P(c)} = 35.1 \text{ Hz}, J_{P(b)P(b)} = 4.5 \text{ Hz}. J_{P(1)P(2)} = 3155 \text{ Hz}), \delta(P(a)) 4.9 \ (dd, J_{P(a)P(a)} = 10.7 \text{ Hz}, J_{P(a)P(b)} = 4.5 \text{ Hz}, J_{P(1)P(a)} = 2936 \text{ Hz}). \]
Preparation of \( \text{Cl(Et}_3\text{P)}_2\text{Pt[\mu-\eta}^1, \eta^1, \eta^2-\text{C}=\text{P}\{\text{Pt(PEt}_3\text{)}(\text{Cl})_2\}\text{Pt(PEt}_3\text{)}_2 \) (III).

To a dry mixture of \( \text{Cl(Et}_3\text{P)}_2\text{Pt(\mu-\eta}^1, \eta^1, \eta^2-\text{C}=\text{P})\text{Pt(PEt}_3\text{)}_2 \) (II) (0.100 g, 0.106 mmol) and \( \text{[Pt(\text{Cl})}_2\text{(PEt}_3\text{)}_2]_2 \) (0.0408 g, 0.0531 mmol) at room temperature was added 10 mL of THF with stirring. The color turned from dark orange to light orange immediately. A \(^{31}\text{P} \) NMR spectrum taken after 5 min of stirring showed quantitative formation of III, with a small amount of \( \text{Pt(PEt}_3\text{)}_2\text{Cl}_2 \) present (characterized by comparison of its \(^{31}\text{P} \) NMR spectrum with that of an authentic sample). The volume of the solvent was reduced to 2 mL, and 5 mL of hexanes was added to precipitate the \( \text{Pt(PEt}_3\text{)}_2\text{Cl}_2 \) impurity. The solution was filtered, and a \(^{31}\text{P} \) NMR spectrum of the filtrate showed very pure III. Compound III is stable in hexanes for several days at -30°C, but decomposes at room temperature in about 1 d. Compound III could not be purified for elemental analysis as it decomposed to unidentified products under vacuum and was characterized by \(^{31}\text{P} \) NMR spectroscopy. \(^{31}\text{P} \{^{1}\text{H} \} \) NMR (THF) (see eq 6 for atom labels):

\[ \delta(\text{P(x)}) \text{ 107.0} (\text{dddt}, J_{\text{P(x)}\text{P(d)}} = 472.3 \text{ Hz}, J_{\text{P(x)}\text{P(b)}} = 148.0 \text{ Hz}, J_{\text{P(x)}\text{P(c)}} = 42.5 \text{ Hz}, J_{\text{P(x)}\text{P(z)}} = 21.4 \text{ Hz}), \delta(\text{P(c)}) \text{ 17.2} (\text{ddd}, J_{\text{P(c)}\text{P(x)}} = 42.5 \text{ Hz}, J_{\text{P(c)}\text{P(b)}} = 22.0 \text{ Hz}, J_{\text{P(c)}\text{P(z)}} = 8.7 \text{ Hz}, J_{\text{P(c)}\text{P(y)}} = 2926 \text{ Hz}), \delta(\text{P(b)}) \text{ 15.9} (\text{ddd}, J_{\text{P(b)}\text{P(x)}} = 148.0 \text{ Hz}, J_{\text{P(b)}\text{P(b)}} = 56.0 \text{ Hz}, J_{\text{P(b)}\text{P(c)}} = 8.7 \text{ Hz}, J_{\text{P(b)}\text{P(y)}} = 2926 \text{ Hz}), \delta(\text{P(d)}) \text{ 5.21} (\text{ddd}, J_{\text{P(d)}\text{P(x)}} = 472.3 \text{ Hz}, J_{\text{P(d)}\text{P(b)}} = 56.0 \text{ Hz}, J_{\text{P(d)}\text{P(c)}} = 22.0 \text{ Hz}, J_{\text{P(d)}\text{P(y)}} = 3020 \text{ Hz}), \delta(\text{P(z)}) \text{ 5.0} (\text{d}, J_{\text{P(z)}\text{P(x)}} = 21.4 \text{ Hz}, J_{\text{P(z)}\text{P(y)}} = 2829 \text{ Hz}) \]

(The \(^{105}\text{Pt}-^{31}\text{P} \) coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings).

Preparation of \( \text{Cl(Et}_3\text{P)}_2\text{Pt[\mu-\eta}^1, \eta^1, \eta^2-\text{C}=\text{P}\{\text{W(\text{CO})}_3\}\text{Pt(PEt}_3\text{)}_2 \) (IV). To a solution of \( \text{Cl(Et}_3\text{P)}_2\text{Pt(\mu-\eta}^1, \eta^1, \eta^2-\text{C}=\text{P})\text{Pt(PEt}_3\text{)}_2 \) (II) (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added \( \text{W(\text{CO})}_3(\text{THF}) \) (0.531 mmol) in THF (20 mL) with stirring. The color of the solution turned from dark orange to dark red after 1 h of stirring. The solvent volume was reduced to ca 3 mL under vacuum, and 15 mL of hexanes was added. The flask was cooled to -30°C for 1 h with formation of an oily-solid impurity. The solution was filtered, the filtrate was reduced in volume to 5 mL and then cooled slowly to -78°C for 3 d
after which time light orange crystals of IV had formed. The crystals were isolated by cannulating off the mother liquor, washing them with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give IV (0.375 g, 56%). $^{31}$P{$^1$H} NMR (THF) (see eq 6 for atom labels): $\delta$(P(x)) 41.4 (ddt, $^2$J$_{P(x)P(b)}$ = 152.9 Hz, $^2$J$_{P(x)P(c)}$ = 38.7 Hz, $^3$J$_{P(x)P(a)}$ = 18.9 Hz, $^1$J$_{P(t)P(x)}$ = 507 Hz), $\delta$(P(c)) 13.9 (dd, $^2$J$_{P(c)P(x)}$ = 38.7 Hz, $^2$J$_{P(c)P(b)}$ = 9.1 Hz, $^1$J$_{P(t)P(c)}$ = 2917 Hz), $\delta$(P(b)) 16.6 (dd, $^2$J$_{P(b)P(x)}$ = 152.9 Hz, $^2$J$_{P(b)P(c)}$ = 9.1 Hz, $^1$J$_{P(t)P(b)}$ = 3568 Hz), $\delta$(P(a)) 3.1 (d, $^3$J$_{P(t)P(a)}$ = 18.9 Hz, $^1$J$_{P(t)P(a)}$ = 2818 Hz).

**Preparation of [(Cl(Et$_3$P)Pt(μ-η$^1$, η$^2$-C=PMe)Pt(PEt$_3$)$_2$(I)] (Ve).** To a stirred solution of Cl(Et$_3$P)$_2$Pt(μ-η$^1$, η$^2$-C=Pt(PEt$_3$)$_2$ (II) (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added MeI (0.226 g, 1.59 mmol) all at once. After stirring for 12 h at 25°C, the color had changed from dark orange to light orange and a precipitate of [MePEt$_3$] had formed (characterized by comparison of its $^{31}$P NMR with an authentic sample). The solution was filtered, the solvent was removed from the filtrate under vacuum, and the residue was treated with 25 mL of hexanes. After reducing the solvent under vacuum to 5 mL, the solution was filtered and cooled slowly to -78°C for 2 d to form an oil of Ve that was pure by $^{31}$P NMR spectroscopic studies (Yield 0.386 g, 75%). A similar preparation was carried out using $^{13}$C-labeled MeI in order to obtain $^{13}$C-$^{31}$P coupling constants. $^{31}$P{$^1$H} NMR (THF) (see eq 7 for atom labels): $\delta$(P(x)) 155.4 (dt, $^3$J$_{P(x)P(b)}$ = 15.3 Hz, $^3$J$_{P(x)P(a)}$ = 12.1 Hz, $^2$J$_{P(t)P(x)}$ = 564.7 Hz, $^2$J$_{P(t)P(b)}$ = 231.9 Hz), $\delta$(P(b)) 21.5 (d, $^3$J$_{P(b)P(a)}$ = 15.3 Hz, $^1$J$_{P(t)P(b)}$ = 5173.7 Hz, $^2$J$_{P(t)P(b)}$ = 463.4 Hz), $\delta$(P(a)) 8.7 (d, $^3$J$_{P(a)P(x)}$ = 12.1 Hz, $^1$J$_{P(t)P(a)}$ = 2338.9 Hz, $^2$J$_{P(t)P(a)}$ = 43.5 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_5$): $\delta$(CH$_3$P) 10.5 (dd, $^1$J$_{CP(x)}$ = 48.9 Hz, $^4$J$_{CP(b)}$ = 10.6 Hz, $^3$J$_{CP(t)}$ = 51.2 Hz).

**Formation of [Cl(Et$_3$P)$_2$Pt(μ-η$^1$, η$^2$-C=PMe)Pt(PEt$_3$)$_2$]$_2$ (Va). Method A.** To a stirred solution of Cl(Et$_3$P)$_2$Pt(μ-η$^1$, η$^2$-C=Pt(PEt$_3$)$_2$ (II) (0.350 g, 0.372 mmol) in THF (15 mL) at room temperature was added MeOTf (0.0610 g, 0.372 mmol) all at once. After stirring for 5 min, the color of the solution changed from dark orange to dark, ruby red.
The volume of the solution was reduced to 2 mL and 15 mL hexanes was added to form a dark red oil that separated from solution. The remaining light red solution was removed from the oil with a cannula, and the oil was washed with 3x8 mL portions of hexanes to afford the triflate anion of Va (crude yield 0.279 g, 68%). A $^{31}$P NMR spectrum showed that this oil contained a small amount of impurities which were more prevalent after 1 d. Complete decomposition was evident after 1 week at room temperature. (The $^{31}$P NMR spectrum was the same as that for the BPh$_4^-$ salt below).

**Method B.** To a stirred solution of Cl(ET$_3$P)$_2$Pt($\mu$-η$^1$, η$^2$-C=Pt)Pt(PEt$_3$)$_2$ (II) (0.200 g, 0.212 mmol) and NaBPh$_4$ (0.145 g, 0.425 mmol) in THF (10 mL) at room temperature was added MeI (0.302 g, 0.212 mmol) all at once. The color of the solution turned from dark orange to very dark red after 3 h of stirring. The solution was treated with 10 mL of hexanes, and a large amount of oily precipitate formed. The solution was filtered, and the solvent in the filtrate was removed under vacuum. The residue was dissolved in 2 mL of THF, and 15 mL of hexanes was added to form a dark red oil that separated from the solution. The oil was isolated by cannulating off the solution, washing with 3x8 mL portions of hexanes followed by 3x5 mL portions of Et$_2$O to afford the BPh$_4^-$ salt of Va (crude yield 0.103 g, 38%). A similar preparation was carried out using $^{13}$C-labeled MeI in order to obtain $^{13}$C-31P coupling constants. $^{31}$P{^1}H NMR (THF) (see Scheme 1 for atom labels): δ(P(x)) 34.7 (ddt, $^2$J$_{P(x)P(b)}$ = 148.9 Hz, $^2$J$_{P(x)P(c)}$ = 23.8 Hz, $^3$J$_{P(x)P(a)}$ = 20.6 Hz), δ(P(c)) 20.1 (dd, $^2$J$_{P(c)P(x)}$ = 23.8 Hz, $^2$J$_{P(c)P(b)}$ = 10.2 Hz, $^1$J$_{P(c)P(b)}$ = 2441 Hz), δ(P(b)) 18.7 (ddt, $^2$J$_{P(b)P(x)}$ = 148.9 Hz, $^2$J$_{P(b)P(c)}$ = 10.2 Hz, $^2$J$_{P(b)P(a)}$ = 5.7 Hz, $^3$J$_{P(b)P(a)}$ = 3640 Hz), δ(P(a)) 8.1 (dd, $^2$J$_{P(a)P(x)}$ = 20.6 Hz, $^4$J$_{P(a)P(b)}$ = 5.7 Hz, $^1$J$_{P(a)P(b)}$ = 2661 Hz). (The $^{195}$Pt-31P coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings). $^{13}$C{^1}H NMR (THF): δ(CH$_3$P) 8.7 (ddd, $^1$J$_{CP(x)}$ = 71.5 Hz, $^3$J$_{CP(c)}$ = 12.6 Hz, $^3$J$_{CP(b)}$ = 8.4 Hz).
Conversion of \([\text{Cl}(\text{Et}_3\text{P})_2\text{Pt}(\mu$-$\eta^1, \eta^2$-$\text{C=PMMe})\text{Pt}($\text{PEt}_3)_2\text{]}^+ (\text{Va})\) to \([\text{Cl}($\text{Et}_3\text{P}$)$\text{Pt}(\mu$-$\text{C}=\text{PMe})\text{Pt}($\text{PEt}_3)_2\text{(I)}} (\text{Vc})\). To a stirred solution of Va (0.100 g, 0.0784 mmol) in THF (20 mL) at room temperature, prepared as in Method B above, was added NaI (0.118 g, 0.784 mmol) as a solid. After stirring for 10 min, the color had changed from dark red to light orange. The solvent was removed under vacuum, and the residue was taken up in 20 mL of hexanes. The solution was filtered over Celite, and the filtrate was shown to contain mainly Vc by a $^3$P NMR spectrum, but could not be isolated pure as it contained impurities that likely resulted from decomposition of Va before or during the reaction.

X-ray Crystallographic Study of trans-$\text{Cl}($\text{Et}_3\text{P})_2\text{Pt}[\text{C(Cl)=P(SiMe}_3)_2]_2 (\text{Ib})$. Diffraction-quality crystals of Ib were obtained by recrystallization from hexanes at -78°C. Data collection and reduction information are given in Table I. A light orange crystal of Ib was mounted on a glass fiber for data collection. Cell constants were determined from reflections found in a rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° 2θ. The data were corrected for Lorentz and polarization effects. A correction based on nonlinear decay in the three standard reflections was applied to the data. An absorption correction based on measured crystal faces was applied. The space group Pbca was unambiguously determined by systematic absences and intensity statistics. A successful direct methods solution was calculated which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined as riding-atoms with C-H distances of 0.96 Å. The hydrogen atoms in methylene groups were refined with individual isotropic displacement parameters while methyl hydrogen atoms were refined as groups. Selected bond distances and bond angles are given in Table 2.

X-ray Crystallographic Study of $\text{Cl}($\text{Et}_3\text{P})_2\text{Pt}[\mu$-$\eta^1, \eta^1, \eta^2$-$\text{CsP(W(CO)}_3]$\text{Pt}($\text{PEt}_3)_2 (\text{IV})$. Diffraction-quality crystals were obtained by slow
evaporation of an Et₂O solution of IV. Data collection and reduction information are given in Table 1. An orange crystal of IV was mounted on a glass fiber for data collection. An initial set of cell constants was calculated from reflections taken from three sets of 20 frames. Final cell constants were calculated from a set of 5625 strong reflections taken during the data collection. The space group P2₁/n was unambiguously determined by systematic absences and intensity statistics. A hemisphere-type data collection was employed in which a randomly oriented region of space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω, providing a high degree of redundancy. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. One triethylphosphine group (P4) was disordered in a 0.50:0.50 ratio, and required the use of 426 restraints. The P4 group is duplicated (P4') in order to make a separate group, both of which have the same parameters. These groups were refined isotropically with additional restraints and the other triethylphosphine groups in the molecule were used to group the two partially occupied groups in SHELXTXL SAME restraints. Selected bond distances and bond angles are given in Table 3.

Acknowledgment

We thank the donors of The Petroleum Research Fund (grant 27360-AC3), administered by the American Chemical Society, and the National Science Foundation (grant CHE-9414242) for support of this research.
References


(31) SHELXTL-Plus V5.0, Siemens Industrial Automation Inc., Madison, WI.
Table 1. Crystal and Data Collection Parameters for trans-Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ib) and Cl(Et₃P)₂Pt[μ-η¹, η¹, η¹-C≡P{W(CO)₅}]Pt(PEt₃)₂ (IV).

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²R = Σ||F_o|−|F_c||/Σ|F_o|.  
R_w = [Σw(|F_o|−|F_c|²)/Σw|F_o|²]¹/²;  
w = 1/σ²(|F_o|).  
²Quality -of-fit =

[Σw(|F_o|−|F_c|²)/(N_{obs}−N_{parameters})]¹/².
Table 2. Selected Bond Distances (Å) and Angles (deg) for trans-
Cl(Et₃P)₂Pt[C(Cl)=PN(SiMe₃)₂] (Ib)

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Numbers in parentheses are estimated standard deviations in the least significant digits.
Table 3. Selected Bond Distances (Å) and Angles (deg) for Cl(\text{Et}_3\text{P})_2\text{Pt}[\eta^1,\eta^1,\eta^2-\text{C}≡\text{P}(\text{W(CO)}_5)]\text{Pt(PEt}_3)_2 (IV).

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*Numbers in parentheses are estimated standard deviations in the least significant digits.*
Table 4. Comparison of $^{31}$P NMR data (THF) for $\text{Cl(}\text{Et}_3\text{P)}_2\text{Pt[}\mu-\eta^1, \eta^1, \eta^2-\text{C}≡\text{P}]\text{Pt(PEt}_3\text{)}_2$ (II) with those of the complexes $\text{Cl(}\text{Et}_3\text{P)}_2\text{Pt[}\mu-\eta^1, \eta^1, \eta^2-\text{C}≡\text{P}\{\text{ML}_n\}]\text{Pt(PEt}_3\text{)}_2$, where $\text{ML}_n = \text{Pt(Cl)}_3(\text{PEt}_3)$ (III), W(CO)$_5$ (IV), Me$^+$ (Va).

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<th>$\delta$ P(a)</th>
<th>$^3J_{\text{P}(x)-\text{Pt}}$</th>
<th>$^2J_{\text{P}(c)-\text{Pt}}$</th>
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<th>$^2J_{\text{P}(a)-\text{Pt}}$</th>
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a) See eqns 5, 6 and Scheme 1 for atom labels.
Table 5. Comparison of $^3$P NMR data for (CI)(Et$_3$P)Pt($\mu$-C=PMes*)Pt(PEt$_3$)$_2$(Cl) (2), (CI)(Ph$_3$P)Pt($\mu$-CO)Pt(PPh$_3$)$_2$(Cl) (4), and complexes (CI)(Et$_3$P)Pt($\mu$-C=PR)Pt(PEt$_3$)$_2$(X) (Vc: R = Me, X = I; VI: R = Bn, X = Br; VII: R = i-Pr, X = I)

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a) See eqn 7 for atom labels.
**Figure Captions**

**Figure 1.** Thermal ellipsoid drawing of trans-Cl(\(\text{Et}_3\text{P}\))_2\text{Pt}[\text{Cl}], \text{C}[\text{Cl}]\equiv\text{PN}(\text{SiMe}_3)_2] \text{(Ib).}

**Figure 2.** Thermal ellipsoid drawing of Cl(\(\text{Et}_3\text{P}\))_2\text{Pt}[\mu-\eta^1, \eta^1, \eta^2]-\text{C}[\text{W}(\text{CO})_5] \text{Pt}(\text{PET})_2 \text{(IV).}
Figure 1.
Figure 2.
GENERAL SUMMARY

The oxidative addition reactions of zerovalent Ni, Pd and Pt phosphine complexes with dihalophosphaalkene compounds resulted in the formation of several complexes containing new carbon-phosphorus multiply bonded ligands. When \( \text{M(P} \text{Et}_3)_4 \) was reacted with \( \text{Cl}_2\text{C=PN(SiMe}_3)_2 \), phosphavinyl complexes (I) were observed with \( \text{M} = \text{Pd, Pt and Ni} \). However, when \( \text{M(P} \text{P} \text{h}_3)_4 \) was reacted with \( \text{Cl}_2\text{C=PN(SiMe}_3)_2 \), only in the case of \( \text{M} = \text{Pd} \) was a phosphavinyl complex (I) observed, which underwent \( \text{PPh}_3 \) rearrangement upon warming to form a phosphavinyl phosphonium complex (II). In the case of \( \text{M} = \text{Ni} \), a phosphavinyl intermediate (I) was postulated, but only the phosphavinyl phosphonium complex (II) was observed; this nickel complex was not isolated, but reacted with another equivalent of \( \text{Ni(P} \text{P} \text{h}_3)_4 \) to generate the first example of a phosphavinylidene phosphorane complex (III). When \( \text{Ni(P} \text{P} \text{h}_3)_4 \) was reacted with \( \text{Cl}_2\text{C=PMes}_* \), again a phosphavinyl phosphonium complex (II) formed, but having a proton in place of the chloride on the C-P
carbon; this was the first reported example of a complex containing a phosphavinyl phosphonium ligand. Evidently, the presence of PPh₃ ligands favors the formation of the phosphavinyl phosphonium complexes, while PEt₃ tends to stabilize the phosphavinyl complexes. When two equivalents of Pd(PEt₃)₄ were reacted with Cl₂C=PN(SiMe₃)₂, the first example of a phosphonio-methylene(imino)metallophosphorane (IV) formed. This complex underwent hydrolysis to form the first example of a phosphonio-methylene(oxo)phosphorane complex. Several of these compounds exhibited interesting substitution reactions and the structures that were obtained provided insights into the bonding properties of these new carbon-phosphorus unsaturated ligands.

A new high-yield synthesis of the η¹, η³-bridging cyaphide (C≡P⁻) dimer (V) was developed. This complex reacted with various alkyl halides to afford semi-bridging isocyaphide (C≡PR) complexes (VII). In the case of R = Me, an intermediate η¹, η²-bridging isocyaphide complex (VI) was isolated during this reaction; this is the first example of an isocyaphide ligand coordinated in this type of bridging mode. These reactions demonstrated that isocyaphide complexes with non-bulky alkyl groups can be stabilized on transition metals and may provide for further functionalization of these interesting ligands.

The η¹, η³-bridging cyaphide (C≡P⁻) complex (V) was found to contain a further ligation site by virtue of its lone pair of electrons on the C≡P phosphorus atom; thus, the first examples of trinuclear metal-cyaphide complexes were obtained by coordination of this phosphorus atom to a W(CO)₅ fragment and a Pt(Cl)₃(PEt₃) fragment.
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