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Synthesis and Structural Characterization of the
First Titanium(II) Porphyrin Complex,
(η^2 -Diphenylacetylene)Oitanium
Octaethylporphyrin

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Low-Valent Titanium Porphyrin Complexes. Synthesis and Structural Characterization of the First Titanium(II) Porphyrin Complex, (1,2-Diphenylacetylene)Oitanium Octaethylporphyrin

Abstract

The anaerobic reduction of the dichlorotitanium(IV) porphyrins (OEP)TiCl₂ and (TTP)TiCl₂ (OEP = octaethylporphyrinato, TTP = meso-tetra-p-tolylporphyrinato) with LiAlH₄ in the presence of diphenylacetylene in toluene produces the 11^π-alkyne Ti(II) adducts (OEP)Ti(172-PhC≡cPh) (1) and (TTP)Ti(172-PhC≡cPh) (2). The structure of 1 has been determined by single-crystal X-ray diffraction analysis. Complex 1 crystallizes in the centrosymmetric space group C2/c with a = 49.369 (7) Å, b = 13.734 (9) Å, c = 36.042 (5) Å, β = 136.62 (1)°, V = 16784 (9) Å³, Z = 16, R = 0.061, and R_w = 0.063. The asymmetric unit of 1 contains two molecules. Alkyne C-C distances and Ti-alkyne distances are 1.30 (1) Å (C27-C28), 2.016 (5) Å (Ti1-C27), 2.015 (5) Å (Ti1-C~8), 1.30 (1) Å (C81-C62), 2.007 (7) Å (Ti2-C61), and 2.028 (7) Å (Ti2-C62).

Disciplines

Chemistry

Comments

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No reaction could be observed between the analogous diorganyl diselenides and sulfur, selenium, or tellurium. Also, no reactions occurred in all investigated systems when mechanical stirring was applied instead of ultrasound.

The solution behavior of **2a**, **3a** and **2b**, **3b** is entirely different. **2a**, **3a** establish equilibria as given in eq 4, whereas **2b**, **3b** are kinetically stable, most likely for steric

reasons. By addition of **1a** to the mixture both equilibria



are shifted almost entirely to the left. The ^{125}Te NMR data for the species involved are given in Table I.

Low-Valent Titanium Porphyrin Complexes: Synthesis and Structural Characterization of the First Titanium(II) Porphyrin Complex, (η^2 -Diphenylacetylene)titanium Octaethylporphyrin

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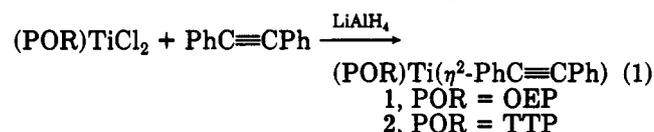
Received March 26, 1991

Summary: The anaerobic reduction of the dichlorotitanium(IV) porphyrins (OEP)TiCl₂ and (TTP)TiCl₂ (OEP = octaethylporphyrinato, TTP = *meso*-tetra-*p*-tolylporphyrinato) with LiAlH₄ in the presence of diphenylacetylene in toluene produces the π -alkyne Ti(II) adducts (OEP)Ti(η^2 -PhC≡CPh) (**1**) and (TTP)Ti(η^2 -PhC≡CPh) (**2**). The structure of **1** has been determined by single-crystal X-ray diffraction analysis. Complex **1** crystallizes in the centrosymmetric space group *C2/c* with *a* = 49.369 (7) Å, *b* = 13.734 (9) Å, *c* = 36.042 (5) Å, β = 136.62 (1)°, *V* = 16 784 (9) Å³, *Z* = 16, *R* = 0.061, and *R*_w = 0.063. The asymmetric unit of **1** contains two molecules. Alkyne C–C distances and Ti–alkyne distances are 1.30 (1) (C₂₇–C₂₈), 2.016 (5) (Ti₁–C₂₇), 2.015 (5) (Ti₁–C₂₈), 1.30 (1) (C₆₁–C₆₂), 2.007 (7) (Ti₂–C₆₁), and 2.028 (7) Å (Ti₂–C₆₂).

Despite the great interest in metalloporphyrins, the chemistry of early-transition-metal porphyrin complexes remains in an undeveloped state. A primary reason for this stems from the fact that syntheses of these complexes thermodynamically lead to the formation of high-valent oxo complexes.² The M=O groups in these metalloporphyrins are typically d⁰–d² and are often extremely difficult to cleave.³ We have recently examined the metal-centered redox chemistry of titanium oxo and titanium halide porphyrin complexes.⁴ As an extension of our work on titanium porphyrins, we have begun to investigate the chemistry of low-valent Ti porphyrin complexes. To date, Ti(III) is the lowest valent state known to exist in a titanium porphyrin complex.⁵ We report here the synthesis and structural characterization of the first Ti(II) porphyrin complexes.

As illustrated in eq 1, lithium aluminum hydride reduction of toluene solutions of dichlorotitanium(IV) porphyrins in the presence of diphenylacetylene produces

η^2 -alkyne complexes of Ti(II). In a typical reaction, 131



mg of (OEP)TiCl₂⁶ (0.201 mmol), 141 mg of LiAlH₄ (3.67 mmol), and 41 mg of PhC≡CPh (0.23 mmol) were stirred in toluene (40 mL) under N₂ at 22 °C. Over 12 h, the brown solution turned into the ruby red color of the alkyne adduct **1**. Filtering the reaction mixture, concentrating the filtrate to ca. 2 mL, and cooling to –20 °C for 3 days produced 78 mg of purple microcrystals (51% yield) after washing with cold pentane.⁷ The TTP⁶ analogue **2** can be prepared in a similar manner.⁷

The alkyne adducts **1** and **2** are diamagnetic complexes that exhibit sharp ¹H NMR signals. For example, in C₆D₆ the diphenylacetylene protons of **1** appear as two multiplets at 6.29 (6 H, *m*, *p* protons) and 4.37 ppm (4 H, *o* protons). The significant upfield shifts of these resonances are consistent with a structure in which the C≡C triple bond of the alkyne binds to titanium, holding the phenyl substituents above the porphyrin ring current. The porphyrin meso protons resonate as a singlet at 10.33 (4 H) ppm. This indicates that rotation of the alkyne ligand about the axis along the Ti–triple-bond centroid is rapid on the NMR time scale.

Crystals of the OEP complex **1** suitable for single-crystal X-ray diffraction were grown by cooling a toluene solution to –20 °C. Complex **1** crystallizes in the centrosymmetric space group *C2/c* with two molecules in the asymmetric unit and 16 molecules per unit cell.⁸ The large number of non-hydrogen atoms (110) in the asymmetric unit significantly increased the difficulty and complexity of the

(6) Abbreviations: OEP is the octaethylporphyrinato dianion and TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion.

(7) Analytical data for (TTP)Ti(PhC≡CPh): ¹H NMR (C₆D₆, 300 MHz) 9.06 (s, 8 H, β -H), 7.97 (d, 7.52 Hz, 8 H, –C₆H₄Me), 7.28 (m, 8 H, –C₆H₄Me), 6.45 (m, 6 H, *m*, *p* H), 4.65 (m, 4 H, *o* H), 2.40 ppm (s, 12 H, C₆H₄CH₃); UV-vis (toluene) 426 (Soret), 548, 582 nm; IR (mull) 1666 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$). Anal. Calcd (found) for C₆₂H₄₆N₄Ti: C, 83.21 (82.55); H, 5.18 (5.23); N, 6.26 (6.04). Analytical data for (OEP)Ti(PhC≡CPh): ¹H NMR (C₆D₆, 300 MHz) 10.33 (s, 4 H, meso H), 6.29 (m, 6 H, *m*, *p* H), 4.37 (m, 4 H, *o* H), 3.92 (q, 7.8 Hz, 16 H, CH₂CH₃), 1.84 ppm (t, 7.5 Hz, 24 H, CH₂CH₃); UV-vis (toluene) 408 (Soret), 532, 570 nm; IR (mull) 1701 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$). Anal. Calcd (found) for C₅₀H₅₄N₄Ti: C, 79.14 (78.59); H, 7.17 (6.77); N, 7.38 (7.09).

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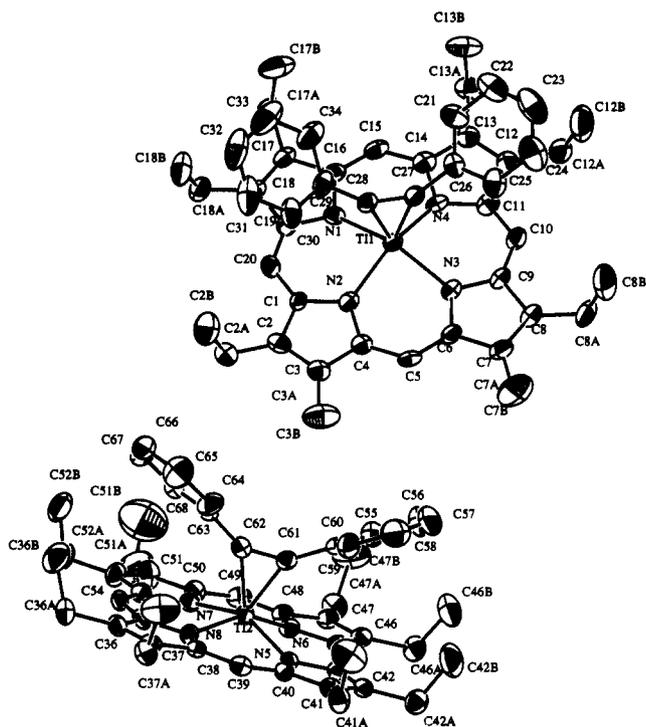


Figure 1. ORTEP drawings with 50% probability thermal ellipsoids and atom-labeling schemes for the molecules of the asymmetric unit of $\text{Ti}(\text{OEP})(\text{PhC}\equiv\text{CPh})$. Main distances (Å): $\text{Ti}_1\text{-N}_1$, 2.094 (7); $\text{Ti}_1\text{-N}_2$, 2.098 (8); $\text{Ti}_1\text{-N}_3$, 2.099 (7); $\text{Ti}_1\text{-N}_4$, 2.083 (8); $\text{Ti}_1\text{-C}_{27}$, 2.016 (5); $\text{Ti}_1\text{-C}_{28}$, 2.015 (5); $\text{C}_{27}\text{-C}_{28}$, 1.30 (1); $\text{C}_{27}\text{-C}_{26}$, 1.46 (1); $\text{C}_{28}\text{-C}_{29}$, 1.474 (9); $\text{Ti}_2\text{-N}_5$, 2.086 (8); $\text{Ti}_2\text{-N}_6$, 2.093 (5); $\text{Ti}_2\text{-N}_7$, 2.104 (6); $\text{Ti}_2\text{-N}_8$, 2.095 (7); $\text{Ti}_2\text{-C}_{61}$, 2.007 (7); $\text{Ti}_2\text{-C}_{62}$, 2.028 (7); $\text{C}_{60}\text{-C}_{61}$, 1.47 (1); $\text{C}_{61}\text{-C}_{62}$, 1.30 (1); $\text{C}_{62}\text{-C}_{63}$, 1.448 (9). Main angles (deg): $\text{N}_1\text{-Ti}_1\text{-N}_4$, 85.3 (3); $\text{N}_1\text{-Ti}_1\text{-N}_2$, 87.7 (3); $\text{N}_2\text{-Ti}_1\text{-N}_4$, 150.8 (2); $\text{N}_2\text{-Ti}_1\text{-N}_3$, 84.4 (3); $\text{N}_3\text{-Ti}_1\text{-N}_4$, 87.9 (3); $\text{C}_{27}\text{-C}_{28}\text{-C}_{29}$, 142.9 (6); $\text{C}_{28}\text{-C}_{27}\text{-C}_{26}$, 142.7 (5); $\text{N}_5\text{-Ti}_2\text{-N}_6$, 88.4 (2); $\text{N}_6\text{-Ti}_2\text{-N}_7$, 150.7 (2); $\text{N}_6\text{-Ti}_2\text{-N}_8$, 85.3 (3); $\text{N}_7\text{-Ti}_2\text{-N}_8$, 84.1 (2); $\text{N}_7\text{-Ti}_2\text{-N}_5$, 88.0 (2); $\text{C}_{61}\text{-C}_{62}\text{-C}_{63}$, 143.4 (6); $\text{C}_{60}\text{-C}_{61}\text{-C}_{62}$, 140.7 (6).

structure determination. Direct methods were attempted but were unsuccessful. A new method was therefore tried and proved capable of readily determining the structure. A sharpened Patterson map was calculated, and a Patterson superposition procedure was carried out using a vector identified as a probable Ti-Ti vector.⁹ From the resulting map, the positions of all the titanium atoms in the cell plus likely positions for the coordinated nitrogens could be readily determined. Due to the size of this structure, those positions alone were ineffective at phasing the observed data. Therefore, with the titanium and nitrogen positions as departure points, the main porphyrin rings were modeled by using the PCMODEL molecular mechanics program and the resulting positions were input into the crystallographic least-squares refinement procedure. Refinement proceeded smoothly, and the remaining carbon

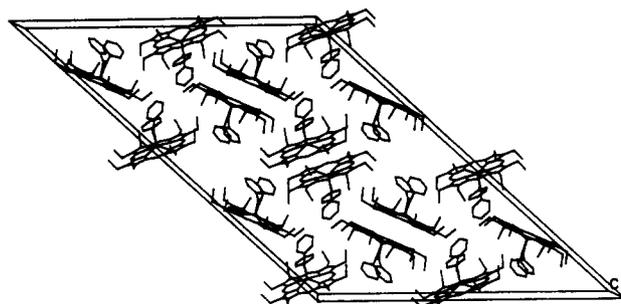


Figure 2. Crystal-packing diagram for $\text{Ti}(\text{OEP})(\eta^2\text{-PhC}\equiv\text{CPh})$.

atom positions were revealed with use of difference Fourier calculations. Further details concerning this method of structure determination will be published elsewhere.¹⁰

The two molecules in the asymmetric unit of **1** are shown in Figure 1, and both have some features similar to those of a molybdenum analogue $(\text{TTP})\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})$, characterized by Weiss.¹¹ The geometry about each Ti is square pyramidal, with the four pyrrole nitrogens forming the basal plane and the alkyne triple bond at the apical site. The titanium atom is displaced from the mean 24-atom porphyrin core toward the alkyne by 0.54 Å. The $\text{Ti}_1\text{-C}_{27}$ and $\text{Ti}_1\text{-C}_{28}$ distances are 2.016 (5) and 2.015 (5) Å, and the $\text{C}_{27}\text{-C}_{28}$ distance is 1.30 (1) Å. In the second molecule, $\text{Ti}_2\text{-C}_{61}$ and $\text{Ti}_2\text{-C}_{62}$ distances are 2.007 (7) and 2.028 (7) Å and the $\text{C}_{61}\text{-C}_{62}$ distance is 1.30 (1) Å.

Two structural aspects of **1** differ greatly from those of the Mo analogue. In the Mo complex, the porphyrin ligand is saddle-shaped. The Ti complex **1** possesses a nearly planar porphyrin core. The largest deviation from planarity is 0.064 (6) Å at C_9 . The planarity of the porphyrin core is very likely related to the formation of intermolecular $\pi\text{-}\pi$ interactions¹² between pairs of porphyrins in the lattice, as shown in Figure 2. The interplanar distance that separates the porphyrins in an associated pair is 3.36 Å. The other structural difference between these two alkyne complexes involves the orientation of the $\text{C}\equiv\text{C}$ vector in the molecule. In the Mo case, this vector eclipses two trans pyrrole nitrogens. However, in the Ti complex, the $\text{C}\equiv\text{C}$ vector bisects cis pyrrole nitrogens. For example, the torsional angle between the $\text{C}_{27}\text{-C}_{28}$ and $\text{N}_1\text{-N}_3$ vectors is 47.1°. This orientational difference presumably arises from steric factors. In both cases, the alkyne aligns in a manner that minimizes nonbonded interactions between the alkyne phenyl rings and the porphyrin substituents.

The bonding in the titanium complexes discussed here can be regarded as involving a four-electron-donor alkyne ligand, as was proposed for the Mo analogue.¹³ A comparison of $(\text{OEP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ with $\text{Cp}_2\text{Ti}(\text{CO})(\eta^2\text{-PhC}\equiv\text{CPh})$ ¹⁴ supports this classification. The 18-electron rule suggests that the acetylene ligand is formally a 2-electron donor in the cyclopentadienyl complex. The longer $\text{Ti-C}_{\text{alkyne}}$ distances (2.107 (7) and 2.230 (7) Å) are in accord with this formalism. Although the alkyne C-C distances are similar in the two structures (1.285 (10) Å in $\text{Cp}_2\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})\text{CO}$), the $\text{C}\equiv\text{C}$ stretching frequencies for the two complexes are consistent with a two-electron-donor acetylene ($\nu_{\text{C}\equiv\text{C}} = 1780 \text{ cm}^{-1}$) in

(8) $\text{Ti}(\text{OEP})(\eta^2\text{-PhC}\equiv\text{CPh})$ crystallizes in the centrosymmetric space group C2/c with $a = 49.369$ (7) Å, $b = 13.734$ (9) Å, $c = 36.042$ (5) Å, $\beta = 136.62$ (1)°, $V = 16784$ (9) Å³, $Z = 16$, $R = 0.061$ and $R_w = 0.063$. The calculated density ($\text{C}_{20}\text{H}_{14}\text{N}_4\text{Ti}$, $M_r = 758.90$) per unit cell is 1.201 g/cm³. Data were collected at -40 °C on a Rigaku AFC6R diffractometer with Mo K α radiation using an ω -scan technique over the range $4.0 < 2\theta < 50.1^\circ$. Unique reflections (6219) with $I > 3\sigma(I)$ were used after correction for absorption. All non-hydrogen atoms were refined anisotropically.

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$\text{Cp}_2\text{Ti}(\text{CO})(\eta^2\text{-PhC}\equiv\text{CPh})$ and a four-electron-donor acetylene ($\nu_{\text{C}\equiv\text{C}} = 1701 \text{ cm}^{-1}$) in $(\text{OEP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$. Finally, the ^{13}C NMR spectrum for $(\text{OEP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ provides further support for this bonding interaction. The ^{13}C chemical shift for the $\text{C}\equiv\text{C}$ carbon occurs at 219.4 ppm. Despite a significant upfield shift due to the porphyrin ring current,¹⁵ this signal falls well within the region expected for a four-electron-donor ligand.¹⁶ In this regard, the alkyne complexes 1 and 2 represent the first metallo-

porphyrins that contain Ti(II). Reactivity studies of these novel complexes are also consistent with a Ti(II) formalism.¹⁷

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Supplementary Material Available: Text detailing the data collection and listings of atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for 1 (41 pages); a listing of calculated and observed structure factors for 1 (43 pages). Ordering information is given on any current masthead page.

(15) ^{13}C resonances for ligands held above a porphyrin are typically shifted 20 ppm upfield relative to those for the non-porphyrin analogues. See for example: (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* 1982, 104, 302. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* 1985, 4, 1887.

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Articles

Mechanism of the Photoreaction between $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ (M = Mo, W) and Allylic Halides

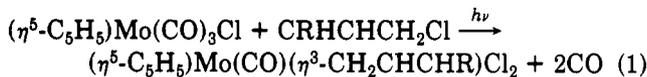
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Received November 1, 1990

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$ in the region of 100 K in allyl halide leads to CO loss and the generation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^2\text{-C}_3\text{H}_5\text{X})\text{Cl}$ (X = Cl, Br, I). This molecule reacts thermally to produce $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\eta^3\text{-C}_3\text{H}_5)\text{ClX}$. The activation barrier to this reaction is 34 kJ/mol (X = Cl). This is contrasted with the results obtained upon photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ with allyl halides (M = Mo, X = Br; M = W, X = Cl, Br, I). Although initial formation of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\eta^2\text{-C}_3\text{H}_5\text{CX})\text{X}$ is observed upon photolysis, the subsequent thermal chemistry differs. Warming results in halogen loss to produce $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{X}][\text{X}]$. For M = W, X = Cl the activation barrier for the reaction is 69 kJ/mol. When it is warmed further, $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{X}][\text{X}]$ decomposes to produce $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{X}_3$. These results are discussed in terms of an electron transfer from the metal to the coordinated allyl halide.

Herein we report a study of the mechanism of the photoreaction between $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ (M = Mo, W) and allylic halides. This reaction was recently reported by Davidson and Vasapollo¹ to generate, in the case of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$, good yields of the allylic product according to eq 1. The products obtained for the other



metals were not the allylic complexes but rather the complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Cl}_3$ and $[\text{CrCl}_2(\eta^5\text{-C}_5\text{H}_5)]$. It was postulated that the difference in reactivity arises from an initial CO loss product that undergoes oxidative addition with allyl halide to generate $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{Cl}_2(\eta^1\text{-CH}_2\text{CHCHR})$ for each of the metals. The differing reactions of these species were suggested to account for the variation in reactivity.

We have recently studied the reaction of allyl halides with a variety of transition-metal centers. Complexes of

the type $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n$ (M = Mn, $n = 3$; M = Co, Rh, $n = 2$) were found to lose CO upon photolysis to generate complexes in which the allyl was bound as an olefin, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{n-1}(\eta^2\text{-C}_3\text{H}_5\text{X})$. In each case we were able to show that, at an appropriate temperature, the η^2 -allylic olefin underwent an intramolecular electron-transfer reaction to yield the allylic products, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{n-1}(\eta^3\text{-C}_3\text{H}_5)^+$.²

Since no reason for a difference in reactivity between the complexes we studied and the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ series was obvious to us, we decided to investigate this reaction. It should be noted that several reports have established that the initial reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ (M = Mo, W) upon photolysis is CO loss.³⁻⁵ Here we describe our efforts to determine the result of photolysis in the presence of allyl halides. Related studies include the investigation of the mechanism of the photoreaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$ with other halocarbons.⁵ The main points we will address in this study are the overall mech-

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