3-2000

Synthesis and Reactivity of Hydrazido(2-) and Imido Derivatives of Titanium(IV) Tetratolylporphyrin

Joseph Lyndon Thorman
Iowa State University

L. Keith Woo
Iowa State University, kwoo@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/762. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Synthesis and Reactivity of Hydrazido(2-) and Imido Derivatives of Titanium(IV)
Tetratolylporphyrin

Joseph L. Thorman and L. Keith Woo*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received August 17, 1999

Titanium porphyrin hydrazido complexes (TTP)Ti=NNR₂ (TTP = meso-tetra-p-tolylporphyrinato dianion; R = Me (1), Ph (2)) were synthesized by treatment of (TTP)TiCl₃ with 1,1-disubstituted hydrazines H₂NNR₂ (R = Me, Ph) in the presence of piperidine. The nucleophilic character of the hydrazido moiety was demonstrated in the reactions of complexes 1 and 2 with p-chlorobenzaldehyde, which yielded the titanium oxo complex (TTP)-Ti=O and the respective hydrazones. Protonation of complexes 1 and 2 with phenol or water produced the 1,1-disubstituted hydrazine along with (TTP)Ti(oph)₂ or (TTP)Ti=O, respectively. Similar reactivity of p-chlorobenzaldehyde and phenol with (TTP)Ti=NNPr₂, 3, was observed. The reaction of complex 3 with nitrosobenzene cleanly formed the azo compound =Ph and the terminal oxo product (TTP)Ti=O.

Introduction

Research dedicated to early transition metal complexes possessing ligand—metal multiple bonds continues to develop. A substantial body of investigation concerning group 4 metals possessing ligand multiple bonds, 1-5 Examples of group 4 hydrazido(2-) complexes are limited to a dimeric species [Cp₂Ti(=NNR₂)₂]₅ and two monomeric complexes Cp₂Ti=NN- (TMS)₂ and (TMTAA)Ti=NNH₂. 6,7 Titanium metalloporphyrin hydrazido(2-) complexes, (TTP)Ti=NNMe₂, may offer an additional assessment of the reactivity of the Ti=Ne moiety, aided by the decreased steric bulk at the N₆. As part of a continuing study of group 4 metalloporphyrin complexes containing strong π-donor ligands, we report the synthesis and reactivity of new examples of titanium hydrazido(2-) complexes.

Experimental Section

General. All manipulations were performed under an atmosphere of nitrogen using a Vacuum Atmospheres glovebox equipped with a model MO40-1 Dri-Train gas purifier. All solvents were rigorously degassed and dried prior to use. Benzene-d₆, benzene, toluene, and hexane were freshly distilled from purple solutions of sodium benzenophenone ketyl and brought into the drybox without exposure to air. Methylene chloride and piperedine were dried by passage through a column of activated neutral alumina. Literature procedures were used to prepare (TTP)Ti=NNPr₂, 3, and (TTP)TiCl₃. The latter compound was recrystallized from CH₂Cl₂/hexane prior to use. 1,1-Dimethylhydrazine was purchased from Aldrich and dried by passage over a column of activated neutral alumina. Literature procedures were used to prepare (TTP)Ti=NNMe₂, 1. 1,1-Dimethylhydrazine was purchased from Aldrich and purified by literature procedures. 10 ¹H NMR data were recorded on either a Varian VXR (300 MHz, 20 °C) or a Bruker DRX (400 MHz, 25 °C) spectrometer. Chemical shifts were referenced to proton solvent impurities (δ 7.15, CDCl₃). UV–vis data were recorded on a HP8452A diode array spectrophotometer and reported as λ_max in nm (log ε).


and washed with 2 mL of benzene. The combined filtrates were taken
dryness to yield dark-blue (TTP)Ti=NNMe₂ (118.3 mg, 47% yield) and
a trace of (TTP)Ti=O. ¹H NMR (CD₂₃, 300 MHz): δ 11.96 (s, 8H, J=H-
H, 8 Hz, meso-C₆H₄CH₃), 8.04 (d, 4H, J=H-H, 8 Hz, meso-C₆H₄CH₃),
2.42 (s, 12H, meso-C₆H₄CH₃). ¹³C NMR (CD₂₃): δ 166.68 (s, 12N, C₆H₄CH₃),
126.53 (d, 6N, CH₃). ¹³C NMR of (TTP)Ti=NNMe₂ (CD₂₃, 300 MHz): δ 10.95 (s, 8H,
J=H-H, 8 Hz, meso-C₆H₄CH₃), 7.75 (s, 8H, J=H-H, 8 Hz, meso-C₆H₄CH₃),
4.24 (s, 12H, meso-C₆H₄CH₃). ¹H NMR of (TTP)Ti=O in CD₂₃

(11) ¹H NMR of an authentic sample of p-chlorobenzaldehyde N,N-
dimethylhydrazine (CDCl₃, 300 MHz): δ 7.70 (d, 2H, J=H-H, 8 Hz, p-
C₆H₄CH₃), 7.55 (d, 2H, J=H-H, 8 Hz, p-C₆H₄CH₃), 7.10 (d, 2H, J=H-
H, 8 Hz, p-C₆H₄CH₃), 5.83 (s, 1H, J=H-H, 8 Hz, p-C₆H₄CH₃), 3.88 (s, 6H,
N(CH₃)₂). ¹³C NMR of p-chlorobenzaldehyde N,N-dimethylhydrazine in CD₂₃
(12) Kamitori, Y.; Hojo, M.; Masuda, R.; Fujitani, T.; Ohsawa, S.; Yokoyama,

Thornan and Woo

Synthesis and Properties of Hydrazido(2-) Complexes.
Treatment of the dichloro complex (TTP)TiCl₂ with a 1,1-
disubstituted hydrazine in hexanes in the presence of a base
(eq 1) afforded the hydrazido complexes (TTP)Ti=NNR₂ (R-
Me (1), Ph (2)). In the absence of a base, a 1:1 mixture of
the hydrazido complex 1 and the 1,1-dimethylhydrazonium salt
was observed by ¹H NMR. It was not possible to clearly
separate the two products in large-scale reactions. When bases
such as triethylamine, picoline, pyridine, 1,2,3,4-tetrahydro-
quinoine, and 2,2,6,6-tetramethylpiperidine were used, the
solubilities of the hydrazido complexes and the ammonium salts
were similar and impeded purification. Piperidine was found to
be an adequate but not ideal base because separating the
piperidinium salt from the product still proved to be difficult
and resulted in modest isolated yields (20–50%) of the
hydrazido complexes. Alternative routes, such as the use of
LiNH₂ or H₂NNR₂ in the presence of Li₂B₄ as well as other


1320 Inorganic Chemistry, Vol. 39, No. 6, 2000

Kamitori, Y.; Hojo, M.; Masuda, R.; Fujitani, T.; Ohsawa, S.; Yokoyama,
reaction solvents, led only to intractable paramagnetic products. Attempted synthesis of a diazenoid species from 1,2-diphenylhydrazine in the presence of piperidine also led to intractable paramagnetic products. Although complex 2 was robust in solution at elevated temperatures (ca. 350 K), complex 1 was not and decomposed to paramagnetic species, as indicated by $^1$H NMR spectroscopy.

Because of the large ring current of the porphyrin macrocycle, the $^1$H NMR resonances associated with the substituents on the bound hydrazido ligand were significantly shifted upfield relative to the hydrazine. For example, the methyl resonance was shifted upfield approximately 2.5 ppm from that of the free hydrazine. The phenyl signals for complex 2 were similarly shifted upfield. For example, the o-NNPh$_2$ proton doublet (4.34 ppm) found for 2 was shifted upfield from the free hydrazine (7.11 ppm). The $^1$H NMR spectra showed that the substituents on the hydrazido(2-) moiety were equivalent on the NMR time scale (223–300 K). This observation supported the formulation of the hydrazido(2-) unit as an $\eta^1$-bound ligand.

In the presence of water or phenol, both complexes 1 and 2 were converted to (TTP)Ti=O or (TTP)Ti(OPh)$_2$, respectively, and to the appropriate 1,1-disubstituted hydrazine (eqs 2 and 3). As is generally the case for disubstituted hydrazido(2-) complexes, N–N bond cleavage was not observed in these protonolysis reactions. The extreme hydrolytic susceptibility of complex 1 precluded a satisfactory elemental analysis, while that of complex 2 was found to be somewhat more inert. In the presence of approximately 1 equiv of phenol, a 1:1 mixture of the bis(phenoxy), (TTP)Ti(OPh)$_2$, and unreacted hydrazido, 2, was present.

Exchange of the NN$_3$ group was not observed upon treatment of (TTP)Ti=NN$_3$ with free hydrazine H$_2$NR$_2$(R = Me, R’ = Ph; R = Ph, R’ = Me). The protonation of complexes 1 and 2 was not detected in the presence of excess HNPh$_2$ or H$_2$NPh. This is in line with the higher acidity of hydrazines relative to amines. Consequently, the potentially direct route to complexes 1 and 2 by treatment of the imido compound 3 with the respective hydrazide was unproductive. The hydrazido and imido complexes were only minor components in an otherwise intractable mixture of products. This is in contrast to the tetramethyltetraazaannulene analogues, (TMtAA)Ti=NR, which cleanly produce hydrazido(2-) complexes on treatment with H$_3$NNR$_3$.

Treatment of complexes 1 or 2 with approximately 1 equiv of p-chlorobenzaldehyde slowly decomposed the hydrazido $p$-Cl–C$_6$H$_4$(CNNR$_2$)$_3$H (R = Me, Ph) and (TTP)Ti=O to a nearly quantitative yield as monitored by $^1$H NMR (eq 4). Reactions with a larger ratio of the aldehyde to hydrazido complex proceeded to completion over a shorter period of time. The reaction rate of the diphenylhydrazido complex 2 with aldehyde was qualitatively slower than that of the dimethyl analogue 1. This was consistent with a less nucleophilic N$_3$ of the hydrazido moiety in complex 2.

**Reactivity of (TTP)Ti=NPr.** Although (TTP)Ti=NPr, 3, did not undergo nitrene transfer in the presence of a variety of substrates such as OP$_3$, OAS$_2$, RNCR, and R$_2$CO, it did undergo nitrene metathesis reactions with nitroso compounds. Facile and quantitative production of the unsymmetric diazene compound PhN=N=Pr resulted from reaction of complex 3 with nitrosobenzene (eq 5). Low-valent titanium complexes have been found to mediate the coupling of nitrene groups derived from nitroso compounds. It was proposed that these reactions progressed through two different bimetallic intermediates in order to explain the presence of azo- and azoxy-coupling products. In the case presented here we conclude that the diazene product is produced from a monomeric intermediate in which the nitrosobenzene is bound to the titanium cis to the imido group. Nitrosobenzene has been used as a trapping agent for reactive rhodium and palladium nitrene intermediates to produce azoxybenzene. If an azoxybenzene was formed from the reaction of complex 3 with PhNO, it would likely be reduced rapidly to a diazene by the coproduct (TTP)Ti(II). The nucleophilic character of nitrene groups has often been displayed by reaction with aldehydes. Zr imido complexes have previously been demonstrated to convert ketones and aldehydes to imines. Likewise, the reaction of complex 3 with three equiv of p-chlorobenzaldehyde at 20 °C produced (TTP)Ti=O and p-chlorobenzylidene isopropylamine in 20 h. In the presence of only 1 equiv of aldehyde, complete consumption of the imido complex required approximately 4 weeks.

**Conclusion**

drazido complexes exhibited behavior similar to that of the imido species (TTP)Ti=NPr in the presence of protic reagents. Nitrene group transfer from the titanium imido complex, (TTP)Ti=NPr, resulted from treatment with p-chlorobenzaldehyde or nitrosobenzene to yield the respective imine or diazene. The hydrazido derivatives also reacted with p-chlorobenzaldehyde to form the subsequent hydrazone. These results show that by reducing the steric constraint at the N<sub>R</sub> of the nitrene group, the metalloporphyrin Ti=N moiety exhibits moderate reactivity.

Acknowledgment. We are grateful for financial support from the Camille and Henry Dreyfus Foundation.