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

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Titanium porphyrin hydrazido complexes (TTP)Ti=NNR$_2$ (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion; R = Me (**1**), Ph (**2**)) were synthesized by treatment of (TTP)TiCl$_2$ with 1,1-disubstituted hydrazines H$_2$NNR$_2$ (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=N^{i}Pr, **3**, was observed. The reaction of complex **3** with nitrosobenzene cleanly formed the azo compound ^{i}PrN=NPh 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 in this area has focused on the relatively electron-rich metallocene derivatives.[1,2] From these studies, imido complexes have shown potential as aziridination, hydroamination, and heterocyclization catalysts. In comparison, the reactivity exhibited by the titanium imido functional group in porphyrin analogues is less extensive.[3] This lower reactivity is presumably due, in part, to steric factors involving the porphyrin ligand and the imido substituent.

Although the chemistry of imido complexes is now well established, investigation of the isolobal hydrazido moiety has been confined mainly to groups 5−7.[4] Examples of group 4 hydrazido(2-) complexes are limited to a dimeric species [CpClTi=NNR$_2$]$_2$[5] and two monomeric complexes Cp$_2$Ti=NN-(TMS)$_2$[6] and (TMTAA)Ti=NNPh$_2$.[7] Titanium metalloporphyrin hydrazido(2-) complexes, (TTP)Ti=NNR$_2$, may offer an additional assessment of the reactivity of the Ti=N moiety, aided by the decreased steric bulk at the N$_\alpha$. 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-d_6, benzene, toluene, and hexane were freshly distilled from purple solutions of sodium benzophenone ketyl and brought into the drybox without exposure to air. Methylene chloride and piperidine were dried by passage through a column of activated neutral alumina. Literature procedures were used to prepare (TTP)Ti=NiPr,[8] **3**, and (TTP)TiCl$_2$.[9] The latter compound was recrystallized from CH$_2$Cl$_2$/hexane prior to use. 1,1-Dimethylhydrazine was purchased from Aldrich and dried by passage over a column of activated neutral alumina. 1,1-Diphenylhydrazonium hydrochloride was used as received from Aldrich. Nitrosobenzene and *p*-chlorobenzaldehyde were purchased from Aldrich and purified by literature procedures.[10] ^{1}H 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, C$_6$D$_5$H). UV−vis data were recorded on a HP8452A diode array spectrophotometer and reported as λ_{max} in nm (log ϵ). Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. MS-CI studies were performed on a Finnigan TSQ 700 at 70 eV in the negative ion mode using ammonia as the ionization gas. GC−MS studies were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS).

(TTP)Ti=NNMe$_2$, 1. To a hexanes (ca. 20 mL) slurry of (TTP)-TiCl$_2$ (257 mg, 0.326 mmol) was added piperidine (132 μL, 1.33 mmol) and H$_2$N$_2$Me$_2$ (30 μL, 0.39 mmol). The blue solution was filtered after being stirred for 12 h at ambient temperature, and the solid was washed with hexanes (ca. 4 mL). This purple solid was divided into three approximately equal portions and each placed on a clean fritted filter

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and washed with 2 mL of benzene. The combined filtrates were taken to dryness to yield dark-blue (TTP)Ti=NNMe$_2$ (118.3 mg, 47% yield) and a trace of (TTP)Ti=O. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 9.16 (s, 8H, β-H), 8.20 (d, 4H, $^3J_{H-H}$ = 8 Hz, meso-C$_6$H$_4$CH$_3$), 8.04 (d, 4H, $^3J_{H-H}$ = 8 Hz, meso-C$_6$H$_4$CH$_3$), 7.31 (t, 8H, $^3J_{H-H}$ = 8 Hz, meso-C$_6$H$_4$CH$_3$), 2.42 (s, 12H, meso-C$_6$H$_4$CH$_3$), −0.28 (s, 6H, NN(CH$_3$)$_2$). UV/vis (toluene): 426 (5.65), 548 (4.64) nm. The hydrolytic sensitivity of complex **1** and resulting contamination with (TTP)Ti=O precluded satisfactory elemental analysis.

(TTP)Ti=NNPh$_2$, 2. A mixture of H$_2$N$_2$Ph$_2$·HCl (234 mg, 1.06 mmol), piperidine (173 μL, 1.75 mmol), and 4 Å molecular sieves were stirred in hexanes (ca. 15 mL) overnight. This mixture was filtered over a pad of activated neutral alumina and the filtrate added to (TTP)-TiCl$_2$ (154 mg, 0.196 mmol) and piperidine (ca. 2 mmol). This solution slowly turned from red-brown to dark-red over 13 h, at which time it was filtered and the solid washed with hexanes (3 × 6 mL). The dark-blue solid was placed on a clean fritted filter and washed with 2 mL of benzene. The benzene was removed in vacuo to afford analytically pure (TTP)Ti=NNPh$_2$ (39.7 mg, 23% yield). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 9.13 (s, 8H, β-H), 8.05 (d, 8H, $^3J_{H-H}$ = 8 Hz, meso-C$_6$H$_4$CH$_3$), 7.28 (d, 8H, $^3J_{H-H}$ = 8 Hz, meso-C$_6$H$_4$CH$_3$), 6.31 (m, 6H, m-, p-NN(C$_6$H$_5$)$_2$), 4.34 (d, 4H, $^3J_{H-H}$ = 8 Hz, o-NN(C$_6$H$_5$)$_2$), 2.41(s, 12H, meso-C$_6$H$_4$CH$_3$). MS Calcd (found) [M$^+$]: 898.95 (898.3) m/z. Anal. Calcd (found) for C$_{60}$H$_{46}$N$_6$Ti: C, 80.17 (79.97); H, 5.16 (5.24); N, 9.35 (8.49). UV/vis (toluene): 426 (5.61), 547 (4.69) nm.

Reaction of (TTP)Ti=NNMe$_2$ with p-Chlorobenzaldehyde. An NMR tube was charged with complex **1** (12.8 mg, 9.90 μmol), p-chlorobenzaldehyde stock solution (7.0 μL, 1.726 M, 12.1 μmol), Ph$_3$CH (89 μL, 0.1814 M) as an internal standard, and C$_6$D$_6$ (ca. 0.5 mL). After the mixture was allowed to stand overnight at ambient temperature, (TTP)Ti=O (9.43 μmol, 95%) and the hydrazone[11] (7.74 μmol, 82%) were detected. GC−MS of p-chlorobenzaldehyde N,N-dimethylhydrazone, Calcd (found) [M$^+$]: 182.65 (182) m/z. ^{1}H NMR of (TTP)Ti=O (C$_6$D$_6$, 300 MHz): δ 9.24 (s 8H, β-H), 8.00 (m, 8H, o-C$_6$H$_4$Me), 7.28 (m, 8H, m-C$_6$H$_4$Me), 2.42 (s, 12H, CH$_3$). ^{1}H NMR of p-chlorobenzaldehyde N,N-dimethylhydrazone in C$_6$D$_6$ (300 MHz): δ 7.39 (d, 2H, −C$_6$H$_4$Cl), 7.14 (d, 2H, −C$_6$H$_4$Cl), 6.80 (s, 1H, N=CH), 2.52 (s, 6H, CH$_3$).

Reaction of (TTP)Ti=NNPh$_2$ with p-Chlorobenzaldehyde. An NMR tube was charged with complex **2** (4.95 mg, 5.51 μmol), p-chlorobenzaldehyde stock solution (4.2 μL, 1.726 M, 7.25 μmol), Ph$_3$CH (92.6 μL, 0.1814 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). The mixture was allowed to stand at ambient temperature for 180 h at which time (TTP)Ti=O (5.23 μmol, 95%) was observed. The hydrazone[12] could not be quantified because of the interfering internal standard and porphyrin signals. GC−MS of p-chlorobenzaldehyde N,N-diphenylhydrazone, Calcd (found) [M$^+$]: 306.79 (307) m/z.

Reaction of (TTP)Ti=N^{i}Pr with p-Chlorobenzaldehyde. An NMR tube was charged with complex **3**, (TTP)Ti=N^{i}Pr, (6.8 mg, 8.76 μmol), p-chlorobenzaldehyde (3.8 mg, 27 μmol), Ph$_3$CH (93.5 μL, 0.1743 M) as an internal standard, and CDCl$_3$ (ca. 0.6 mL). Allowing the tube to stand at ambient temperature for 20 h produced (TTP)Ti=O (8.76 μmol, 100%) and ^{i}PrN=CH(C$_6$H$_4$-p-Cl) (8.76 μmol, 100%). GC−MS of p-chlorobenzylidene isopropylamine, Calcd (found) [M$^+$]: 181.66 (182) m/z. ^{1}H NMR (CDCl$_3$): δ 8.25 (s, 1H, N=CH), 7.65 (d, 2H, ClC$_6$H$_4$), 7.36 (d, 2H, ClC$_6$H$_4$), 3.54 (m, 1H, NCH(Me)$_2$), 1.26 (d, 6H, NCH-(Me)$_2$).

Reaction of (TTP)Ti=NNMe$_2$ with Phenol. An NMR tube was charged with complex **1** (7.3 mg, 9.43 μmol), phenol (16 μL, 1.23 M, 19.68 μmol), Ph$_3$CH (96 μL, 0.1743 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). Complex **1** was consumed within approximately 5 min to produce (TTP)Ti(OPh)$_2$ (9.43 μmol, 100%) and 1,1-dimethyl-hydrazine (9.83 μmol, 100%). ^{1}H NMR of (TTP)Ti(OPh)$_2$ in C$_6$D$_6$ (300

MHz): δ 9.02 (s, 8H, β-H), 8.01 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C$_6$H$_4$Me), 7.26 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C$_6$H$_4$Me), 5.83 (overlapping d and t, 6H, m-, p-C$_6$H$_5$), 2.67 (m, 4H, o-C$_6$H$_5$), 2.38 (s, 12H, CH$_3$). ^{1}H NMR of H$_2$NNMe$_2$ (C$_6$D$_6$, 300 MHz): δ 2.45 (br, 2H, NH), 2.15 (s, 6H, CH$_3$).

Reaction of (TTP)Ti=NNPh$_2$ with Phenol. An NMR tube was charged with complex **2** (6.63 mg, 7.37 μmol), PhOH (16.2 μL, 1.23 M, 19.9 μmol), Ph$_3$CH (92 μL, 0.1743 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). Complex **2** was consumed within approximately 5 min to produce (TTP)Ti(OPh)$_2$ (7.11 μmol, 96%) and 1,1-diphenyl-hydrazine (7.37 μmol, 100%). ^{1}H NMR of H$_2$NNPh$_2$ (C$_6$D$_6$, 300 MHz): δ 7.11 (m, 8H), 6.84 (m, 2H), 3.30 (s, 2H, NH).

Reaction of (TTP)Ti=N^{i}Pr with Phenol. An NMR tube was charged with imido complex **3** (1.4 mg, 1.81 μmol), PhOH (3.6 μL, 1.23 M, 4.43 μmol), Ph$_3$CH (89 μL, 0.1448 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). Allowing the solution to stand at ambient temperature for 21 h produced (TTP)Ti(OPh)$_2$ (1.68 μmol, 93%). The methyl signal of the amine product, NH^{i}Pr, was obscured by residual hexane.

Reaction of (TTP)Ti=NNMe$_2$ with Water. An NMR tube was charged with complex **1** (2.61 mg, 3.37 μmol), H$_2$O (0.4 μL, 22 μmol), Ph$_3$CH (54 μL, 0.1743 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). Complex **1** was consumed within approximately 5 min to produce (TTP)Ti=O (3.37 μmol, 100%) and 1,1-dimethylhydrazine (3.34 μmol, 99%).

Reaction of (TTP)Ti=NNPh$_2$ with Water. An NMR tube was charged with complex **2** (8.54 mg, 9.50 μmol), H$_2$O (0.4 μL, 22 μmol), Ph$_3$CH (50 μL, 0.1743 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). After the tube was allowed to stand at ambient temperature for 44 h, (TTP)Ti=O (9.44 μmol, 99%) was detected by ^{1}H NMR. The free hydrazine was not quantified because of decomposition.

Reaction of (TTP)Ti=N^{i}Pr with Nitrosobenzene. An NMR tube was charged with (TTP)Ti=N^{i}Pr (4.61 mg, 5.96 μmol), PhNO (0.8 mg, 7.47 mmol), Ph$_3$CH (91 μL, 0.1448 M) as an internal standard, and C$_6$D$_6$ (ca. 0.6 mL). After approximately 5 min at ambient temperature quantitative production of (TTP)Ti=O and PhN=N^{i}Pr[13] was observed. GC−MS of PhN=N^{i}Pr, Calcd (found) [M$^+$]: 148.21(149) m/z. ^{1}H NMR of PhN=N^{i}Pr (CDCl$_3$): δ 7.35 (t, 2H, m-PhNN^{i}Pr), 7.19 (t, 1H, p-PhNN^{i}Pr), 6.68 (d, 2H, o-PhNN^{i}Pr), 3.88, (spt, 1H, PhNN^{i}Pr), 1.24 (d, 6H, PhNN^{i}Pr).

Results and Discussion

Synthesis and Properties of Hydrazido(2-) Complexes. Treatment of the dichloro complex (TTP)TiCl$_2$ with a 1,1-disubstituted hydrazine in hexanes in the presence of a base (eq 1) afforded the hydrazido complexes (TTP)Ti=NNR$_2$ (R
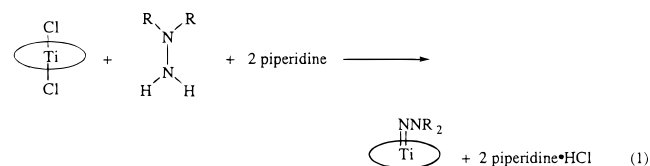
= Me (**1**), Ph (**2**)). In the absence of a base, a 1:1 mixture of the hydrazido complex **1** and the 1,1-dimethylhydrazonium salt was observed by ^{1}H NMR. It was not possible to cleanly separate the two products in large-scale reactions. When bases such as triethylamine, picoline, pyridine, 1,2,3,4-tetrahydro-quinoline, 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 LiNHNR$_2$ or H$_2$N$_2$R$_2$ in the presence of Li^{n}Bu as well as other

(11) ^{1}H NMR of an authentic sample of p-chlorobenzaldehyde N,N-dimethylhydrazone (CD$_2$Cl$_2$, 300 MHz): δ 7.48 (d, 2H, p-ClC$_6$H$_4$C(H)-NNMe$_2$), 7.28 (d, 2H, p-ClC$_6$H$_4$C(H)NNMe$_2$), 7.15 (s, 1H, p-ClC$_6$H$_4$C(H)NNMe$_2$), 2.95 (s, 6H, p-ClC$_6$H$_4$C(H)NNMe$_2$). Wiley, R. H.; Slaymaker, S. C.; Kraus, H. *J. Org. Chem.* **1957**, *22*, 204.

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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 complex **1**, 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*-NN*Ph₂* 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 η^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).[14] As is generally the case for disubstituted hydrazido(2-)


$$(2)$$

$$(3)$$
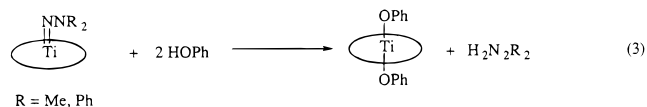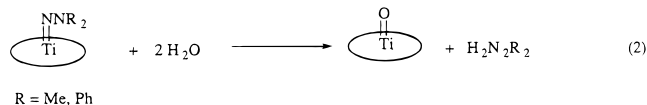
complexes, N−N bond cleavage was not observed in these protonolysis reactions.[15] The extreme hydrolytic susceptibility of complex **1** precluded a satisfactory elemental analysis, while complex **2** was found to be somewhat more inert. In the presence of approximately 1 equiv of phenol, a 1:1 mixture of the bis(phenoxide), (TTP)Ti(OPh)₂, and unreacted hydrazido, **2**, was present.

Exchange of the NNR₂ group was not observed upon treatment of (TTP)Ti═NNR₂ with free hydrazine H₂N₂R′₂ (R = Me, R′ = Ph; R = Ph, R′ = Me). The protonation of complexes **1** and **2** was not detected in the presence of excess HNPh₂ or H₂NPh. 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 hydrazine 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 H₂NNR₂.[7]

Treatment of complexes **1** or **2** with approximately 1 equiv of *p*-chlorobenzaldehyde slowly produced the hydrazone *p*-Cl−C₆H₄C(NNR₂)H (R = Me, Ph) and (TTP)Ti═O in nearly quantitative yield as monitored by ^{1}H NMR (eq 4). Reactions

$$(4)$$
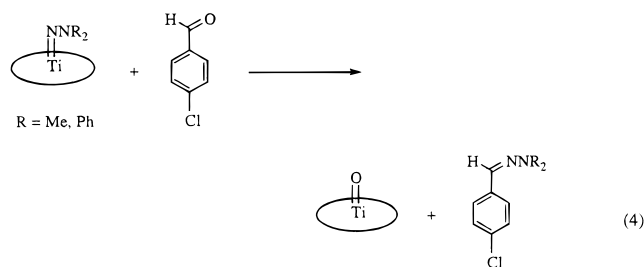
with a larger ratio of the aldehyde to hydrazido complex proceeded to completion over a shorter period of time. The reaction rate of the diphenylhydrazido complex **2** with aldehyde was qualitatively slower than that of the dimethyl analogue **1**. This was consistent with a less nucleophilic N$_\alpha$ of the hydrazido moiety in complex **2**.

Reactivity of (TTP)Ti═N^{i}Pr. Although (TTP)Ti═N^{i}Pr, **3**, did not undergo nitrene transfer in the presence of a variety of substrates such as OPR₃, OAsPh₃, RNCNR, and R₂CO, it did undergo nitrene metathesis reactions with nitroso compounds. Facile and quantitative production of the unsymmetric diazene compound PhN═N^{i}Pr resulted from reaction of complex **3** with nitrosobenzene (eq 5). Low-valent titanium complexes have been

$$(5)$$
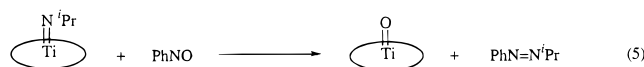
found to mediate the coupling of nitrene groups derived from nitroso compounds.[16,17] It was proposed that these reactions progressed through two different bimetallic intermediates in order to explain the presence of azo- and azoxy-coupling products. In the case presented here we conclude that the diazene 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[18] and palladium[19] nitrene intermediates to produce azoxybenzene.[16b] If an azoxybenzene were 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.[20] Zr imido complexes have previously been demonstrated to convert ketones and aldehydes to imines.[21] 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

The (TTP)Ti═NNR₂ complexes were investigated in an effort to further elucidate the reactivity of the titanium−nitrogen double bond found in metalloporphyrin complexes. The hy-

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drazido complexes exhibited behavior similar to that of the imido species (TTP)Ti═N^{i}Pr in the presence of protic reagents. Nitrene group transfer from the titanium imido complex, (TTP)Ti═N^{i}Pr, 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$_\alpha$ of the nitrene group, the metalloporphyrin Ti═N moiety exhibits moderate reactivity.