

Atom Transfer Reactions of (TTP)Ti(η^2 -3-hexyne): Synthesis and Molecular Structure of *trans*-(TTP)Ti[OP(Oct)₃]₂

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Atom and group transfer reactions were found to occur between heterocumulenes and (TTP)Ti(η^2 -3-hexyne), **1** (TTP = *meso*-5,10,15,20-tetra-*p*-tolylporphyrinato dianion). The imido derivatives (TTP)Ti=NR (R = ^{*i*}Pr, **2**; ^{*t*}Bu, **3**) were produced upon treatment of complex **1** with ^{*i*}PrN=C=N^{*i*}Pr, ^{*i*}PrNCO, or ^{*t*}BuNCO. Reactions between complex **1** and CS₂, ^{*t*}BuNCS, or ^{*t*}BuNCSe afforded the chalcogenido complexes, (TTP)Ti=Ch (Ch = Se, **4**; S, **5**). Treatment of complex **1** with 2 equiv of PEt₃ yielded the bis(phosphine) complex, (TTP)Ti(PEt₃)₂, **6**. Although (TTP)Ti(η^2 -3-hexyne) readily abstracts oxygen from epoxides and sulfoxides, the reaction between **1** and O=P(Oct)₃ did not result in oxygen atom transfer. Instead, the paramagnetic titanium(II) derivative (TTP)-Ti[O=P(Oct)₃]₂, **7**, was formed. The molecular structure of complex **7** was determined by single-crystal X-ray diffraction: Ti–O distance 2.080(2) Å and Ti–O–P angle of 138.43(10)°. Estimates of Ti=O, Ti=S, Ti=Se, and Ti=NR bond strengths are discussed.

Introduction

New insight concerning atom transfer reactions have emerged in the past few years. However, relatively few systematic studies involving transfer of multivalent atoms or groups to transition metal compounds have been conducted due to the lack of suitable, well-behaved low-valent metal acceptor complexes. An exemplary case was reported by Mayer involving oxidative addition and group transfer reactions with WCl₂(PMePh₂)₄.¹ From this study the W=O bond strength was estimated to be ≥ 138 kcal/mol. Similarly, rhenium–oxygen bond strengths have also been addressed.² In related group 4 transition metal complexes the large free energy barrier to oxygen atom abstraction from titanium(IV) oxo complexes is well-known.³ Consequently, Ti²⁺ is an effective reducing agent and should be a potent atom transfer acceptor. This was recently demonstrated in a previous study of Ti(II), where (TTP)Ti(η^2 -3-hexyne), **1**, was able to abstract oxygen and sulfur from a number of substrates.⁴ This reactivity is unique and has not been documented for other divalent titanium compounds under ambient conditions.⁵ In this report, further chemistry of Ti(II) is described. With new atom transfer reactions, estimates for the Ti=X multiple bond strengths are derived.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen using a Vacuum Atmospheres glovebox equipped with a Model MO-40M Dri-Train gas purifier. Benzene-*d*₆,

toluene, and hexane were freshly distilled from purple solutions of sodium benzophenone and brought into the glovebox without exposure to air. (TTP)Ti(η^2 -3-hexyne)^{4c} and ^{*t*}BuNCSe⁶ were prepared according to published procedures. Compounds ^{*t*}BuNCO and ^{*t*}BuNCS were purchased from Aldrich, vacuum-distilled, and dried by passage through a column of activated, neutral alumina. CS₂ was purchased from Fisher Scientific, vacuum-distilled, and dried over molecular sieves. The magnetization of **2** was measured at a field of 3 T over the range 6–296 K on a Quantum Design MPMS SQUID magnetometer. Corrections for the diamagnetic molar susceptibility were implemented for the porphyrin (-731×10^{-6} cgs/mol)⁷ and O=P(Oct)₃ (-302.7×10^{-6} cgs/mol).⁸ ¹H NMR data were recorded on either a Varian VXR (300

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MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometer. Chemical shifts were referenced to proton solvent impurities (δ 7.15 ppm, C_6D_5H). UV-vis data were recorded on a HP8452A diode array spectrophotometer and reported as λ_{max} in nm (log ϵ). Elemental analyses were performed by Iowa State University Instrument Services. Although hotter, longer combustion conditions were used, carbon analysis was often low. For metalloporphyrin complexes, this is likely due to the formation of metal carbides during combustion.⁹

(TTP)Ti=NⁱPr, 2. Method A: Isopropylisocyanate (44 μ L, 0.448 mmol) was added to a stirred solution of **1** (304 mg, 0.380 mmol) in toluene (\approx 10 mL). After 1 h at ambient temperature the dark blue solution was filtered and the filtrate reduced to dryness in vacuo. Recrystallization at -25 °C for 1 day from a toluene solution (8 mL) layered with heptane (4 mL) afforded analytically pure product (128 mg, 44% yield). UV/vis (toluene): 549 (4.53), 424 (5.57), 399 (shoulder, 4.70). ¹H NMR (C_6D_6 , 400 MHz): 9.24 (s, 12H, β -pyrrole), 8.27 (d, 4H, *meso*- $C_6H_4CH_3$), 8.05 (d, 4H, *meso*- $C_6H_4CH_3$), 7.31 (t, 8H, *meso*- $C_6H_4CH_3$), 2.42 (s, 12H, *meso*- $C_6H_4CH_3$), -0.45 (m, 1H, $-NCHMe_2$), -1.66 (d, 6H, $-NCHMe_2$). Anal. Calcd. for $C_{51}H_{43}N_5Ti$: C, 79.16; H, 5.60; N, 9.05. Found: C, 78.72; H, 5.67; N, 8.73. **Method B:** An NMR tube equipped with a Teflon stopcock was charged with complex **1** (14.3 mg, 17.8 μ mol), Ph_3CH (89.5 μ L of 0.1455 M in C_6D_6 , 13.0 μ mol), ⁱPrN=C=NⁱPr (3.2 μ L, 20.4 μ mol), and C_6D_6 (\approx 0.6 mL). The solution immediately darkened and the imido complex (TTP)-Ti=NⁱPr (14.2 μ mol, 79% yield) had formed over 12 h at ambient temperature. ¹H NMR (C_6D_6 , 300 MHz): ⁱPrNC, 2.84 (spt, 1H), 0.65 (d, 6H). The ¹H NMR spectrum of (TTP)Ti=NⁱPr was experimentally identical to that reported in Method A.

Reaction of Complex 1 with ⁱPrNCO. An NMR tube equipped with a Teflon stopcock was charged with complex **1** (13.1 mg, 16.4 μ mol), Ph_3CH (92.0 μ L, 0.146 M, 13.4 μ mol), ⁱPrNCO (2.60 μ L, 26.5 μ mol), and C_6D_6 (\approx 0.6 mL). Within 5 min (TTP)Ti=NⁱPr (16.6 μ mol, 100% yield) was produced. The ¹H NMR spectrum of (TTP)Ti=NⁱPr was experimentally identical to that reported in Method A.

Reaction of Complex 1 with ⁱBuNCO. An NMR tube equipped with a Teflon stopcock was charged with complex **1** (5.93 mg, 7.43 μ mol), Ph_3CH (84.0 μ L, 0.181 M, 15.2 μ mol), ⁱBuNCO (1.2 μ L, 10.5 μ mol), and C_6D_6 (\approx 0.6 mL). Within 5 min (TTP)Ti=NⁱBu was produced in 48% yield. Allowing the solution to stand at 25 °C for 16 h produced (TTP)Ti=NⁱBu (7.39 μ mol, 99% yield) as the only observable diamagnetic porphyrin species. The ¹H NMR is identical to the literature spectrum for (TTP)Ti=NⁱBu:¹⁰ 9.24 (s, 12H, β -pyrrole), 8.32 (d, 4H, *meso*- $C_6H_4CH_3$), 8.04 (d, 4H, *meso*- $C_6H_4CH_3$), 7.34 (d, 4H, *meso*- $C_6H_4CH_3$), 7.30 (d, 4H, *meso*- $C_6H_4CH_3$), 2.42 (s, 12H, *meso*- $C_6H_4CH_3$), -1.58 (s, 9H, $-N^iBu$). CO was detected in a separate experiment with a Kratos MS50TC mass spectrometer. Calcd.: 27.99491 *m/z*. Found: 27.99491 \pm 0.0028 *m/z*.

Reaction of 1 with ⁱBuNCS. An NMR tube equipped with a Teflon stopcock was charged with **1** (10.65 mg, 13.33 μ mol), Ph_3CH (92.5 μ L, 0.1455 M, 13.46 μ mol), ⁱBuNCS (2.8 μ L, 22.07 μ mol), and C_6D_6 (\approx 0.6 mL). When the solution was allowed to stand at 25 °C for 13 h, (TTP)Ti=S (12.94 μ mol, 97% yield) was produced. ¹H NMR (C_6D_6 , 300 MHz): CNⁱBu, 0.86 (s, 9H); (TTP)Ti=S,^{4a} 9.29 (s, 12H, β -pyrrole), 8.14 (d, 4H, *meso*- $C_6H_4CH_3$), 7.95 (d, 4H, *meso*- $C_6H_4CH_3$), 7.30 (m, 8H, *meso*- $C_6H_4CH_3$), 2.41 (s, 12H, *meso*- $C_6H_4CH_3$).

Reaction of Complex 1 with CS₂. An NMR tube equipped with a Teflon stopcock was charged with complex **1** (12.2 mg, 15.3 μ mol), Ph_3CH (85.0 μ L, 0.181 M, 15.4 μ mol), CS₂ (1.2 μ L, 20.0 μ mol), and C_6D_6 (\approx 0.6 mL). Heating the solution at 80 °C for 112 h produced (TTP)Ti=S (12.5 μ mol, 82% yield). ¹H NMR (C_6D_6 , 300 MHz) (TTP)-Ti=S:^{4a} 9.29 (s, 8H, β -H), 8.14 (d, 4H, *meso*- $C_6H_4CH_3$), 7.95 (d, 4H, *meso*- $C_6H_4CH_3$), 7.30 (m, 8H, *meso*- $C_6H_4CH_3$), 2.41 (s, 12H, *meso*- $C_6H_4CH_3$).

Reaction of Complex 1 with (MeO)₂SO. An NMR tube equipped with a Teflon stopcock was charged with complex **1** (6.3 mg, 7.7 μ mol), Ph_3CH (90.5 μ L, 0.145 M, 13.1 μ mol), (MeO)₂SO (1.7 μ L, 20.0 μ mol),

and C_6D_6 (\approx 0.6 mL). Within 5 min all the 3-hexyne had been displaced and a small amount of (TTP)Ti=O was present. Allowing the solution to stand at 25 °C for 96 h produced (TTP)Ti=O in 43% yield. ¹H NMR (C_6D_6 , 300 MHz): (TTP)Ti=O,¹¹ 9.24 (s, 12H, β -pyrrole), 8.00 (d, 8H, *meso*- $C_6H_4CH_3$), 7.28 (d, 8H, *meso*- $C_6H_4CH_3$), 2.42 (s, 12H, *meso*- $C_6H_4CH_3$).

Reaction of 1 with ⁱBuNCSe. An NMR tube equipped with a Teflon stopcock was charged with **1** (12.27 mg, 15.36 μ mol), Ph_3CH (95.0 μ L, 0.146 M, 13.82 μ mol), ⁱBuNCSe (5.4 mg, 33.3 μ mol), and C_6D_6 (\approx 0.6 mL). The solution was allowed to stand at 25 °C for 4 h at which time ⁱBuNC (14.73 μ mol) and (TTP)Ti=Se (15.20 μ mol, 99% yield) were observed. Further monitoring of the sample revealed that after all the (TTP)Ti=Se was formed, (TTP)Ti(η^2 -Se₂) was being produced by the reaction between (TTP)Ti=Se and excess ⁱBuNCSe. ¹H NMR (C_6D_6 , 300 MHz): (TTP)Ti=Se,^{4a} 9.31 (s, 8H, β -H), 8.18 (d, 4H, *meso*- $C_6H_4CH_3$), 7.95 (d, 4H, *meso*- $C_6H_4CH_3$), 7.28 (m, 8H, *meso*- $C_6H_4CH_3$), 2.41 (s, 12H, *meso*- $C_6H_4CH_3$); ⁱBuNC, 0.86 (s, 9H); (TTP)Ti(η^2 -Se₂), 9.08 (s, 8H, β -H), 8.15 (d, 4H, *meso*- $C_6H_4CH_3$), 7.89 (d, 4H, *meso*- $C_6H_4CH_3$), 7.26 (m, 8H, *meso*- $C_6H_4CH_3$), 2.39 (s, 12H, *meso*- $C_6H_4CH_3$). At early times an intermediate was observed. ¹H NMR (C_6D_6 , 300 MHz) [(TTP)Ti(η^2 -ⁱBuNCSe)]: 9.01 (s, 8H, β -H), 8.43 (d, 4H, *meso*- $C_6H_4CH_3$), 7.96 (d, 4H, *meso*- $C_6H_4CH_3$), 7.29 (dd, 8H, *meso*- $C_6H_4CH_3$), 2.39 (s, 12H, *meso*- $C_6H_4CH_3$), -0.52 (s, 9H, η^2 -ⁱBuNCSe).

Reaction of 1 with Cy₃P=S. An NMR tube equipped with a Teflon stopcock was charged with **1** (8.9 mg, 11.12 μ mol), Ph_3CH (92.5 μ L, 0.146 M, 13.46 μ mol), Cy₃P=S (4.0 mg, 12.8 μ mol), and C_6D_6 (\approx 0.6 mL). After \approx 5 min (TTP)Ti=S (1.47 μ mol, 13% yield) and **1** (6.96 μ mol) were present. ¹H NMR (C_6D_6 , 300 MHz): (TTP)Ti=S,^{4a} 9.29 (s, 12H, β -pyrrole), 8.14 (d, 4H, *meso*- $C_6H_4CH_3$), 7.95 (d, 4H, *meso*- $C_6H_4CH_3$), 7.30 (m, 8H, *meso*- $C_6H_4CH_3$), 2.41 (s, 12H, *meso*- $C_6H_4CH_3$).

(TTP)Ti(PEt₃)₂, 6. A stirred solution of complex **1** (230 mg, 0.287 mmol) in toluene (\approx 10 mL) was treated with PEt₃ (120 μ L, 0.812 mmol). After being stirred for 1.5 h at ambient temperature, the solution was filtered and the filtrate reduced to dryness in vacuo. The residue was recrystallized from a toluene/hexanes (2:1) solution that was allowed to stand at -25 °C for 1 day, which produced analytically pure black crystals of complex **6** in two crops (145 mg, 53% yield). UV/vis (toluene): 553(4.45), 426 (5.53), 406 (shoulder, 2.61). ¹H NMR (C_6D_6 , 400 MHz): 11.50 (bd, 12H, $J = 7$ Hz, P(CH₂CH₃), 7.22 (bs, 18H, P(CH₂CH₃)), 6.14 (d, 8H, $J = 8$ Hz, *meso*- $C_6H_4CH_3$), 4.82 (d, 8H, $J = 8$ Hz, *meso*- $C_6H_4CH_3$), 1.47 (s, 12H, *meso*- $C_6H_4CH_3$), -5.92 (bs, 8H, β -pyrrole). Anal. Calcd. for $C_{60}H_{66}N_4P_2Ti$: C, 75.62; H, 6.98; N, 5.88. Found: C, 75.75; H, 7.35; N, 5.80.

(TTP)Ti[(OP(Oct)₃)₂], 7. A round-bottom flask was charged with complex **1** (364 mg, 0.455 mmol) and O=P(Oct)₃ (362 mg, 0.935 mmol). Upon addition of toluene (\approx 15 mL), the stirred solution became dark blue. The solution was concentrated in vacuo after 2.5 h to a black oil (\approx 1 mL). This oil was redissolved in hexanes (\approx 24 mL) and then reduced in vacuo to 4 mL and cooled to -25 °C for 1 day, which produced analytically pure black crystals of complex **7** (355 mg, 52% yield). UV/vis (hexane): 550 (2.14), 422 (5.69), 403 (shoulder, 2.98). ¹H NMR (C_6D_6 , 300 MHz): 12.11 (bs, 12H, 2-CH₂), 10.27 (bs, 12H, 3-CH₂), 8.72 (d, 8H, *meso*- $C_6H_4CH_3$), 4.65 (bs, 12H, 4-CH₂), 4.55 (s, 12H, *meso*- $C_6H_4CH_3$), 3.03 (bs, 12H, 5-CH₂), 2.02 (bs, 12H, 6-CH₂), 1.33 (bs, 12H, 7-CH₂), 1.18 (bs, 18H, 8-CH₃), -0.43 (d, 8H, *meso*- $C_6H_4CH_3$), -33.0 (bs, 8H, β -pyrrole). ³¹P NMR (C_6D_6 , 81 MHz): 83.5 ppm, referenced to internal H₃PO₄ (0.00 ppm). (Free O=P(Oct)₃, -31.8 ppm) Anal. Calcd. for $C_{96}H_{138}N_4O_6P_2Ti$: C, 77.39; H, 9.34; N, 3.76. Found: C, 76.89; H, 9.06; N, 3.08.

Structure Determination of (TTP)Ti(PEt₃)₂, 6 and (TTP)Ti[OP(Oct)₃]₂, 7. Crystallographic data for complexes **6** and **7** are found in Table 1. A crystal of complex **7** was attached to a glass fiber and mounted on a Siemens SMART system for data collection at 173(2) K. Final cell constants were calculated from a set of 8192 strong reflections from the actual data collection. The space group $P2_1/n$ was determined from systematic absences and intensity statistics.¹² A

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Table 1. Crystal Data and Structure Refinement for Compounds (TTP)Ti(PEt₃)₂, **6**, and (TTP)Ti[OP(Oct)₃]₂, **7**

compound	(TTP)Ti(PEt ₃) ₂	(TTP)Ti[OP(Oct) ₃] ₂
empirical formula	C ₆₀ H ₆₆ N ₄ P ₂ Ti	C ₉₆ H ₁₃₈ N ₄ O ₂ P ₂ Ti
fw	953.01	1489.94
temp	173(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.9163(6)	10.2196(1)
<i>b</i> , Å	11.5404(6)	28.6024(5)
<i>c</i> , Å	20.7951(11)	15.4589(2)
α , deg	83.747(1)	90
β , deg	78.928(1)	96.169(1)
γ , deg	85.252(1)	90
vol, Å ³	2550.5(2)	4492.55(11)
<i>Z</i>	2	2
density (calcd)	1.241 Mg/m ³	1.101 Mg/m ³
absorption coeff	0.274 mm ⁻¹	0.179 mm ⁻¹
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.1262, w <i>R</i> 2 = 0.3514	<i>R</i> 1 = 0.0548, w <i>R</i> 2 = 0.1138

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|. wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}.$$

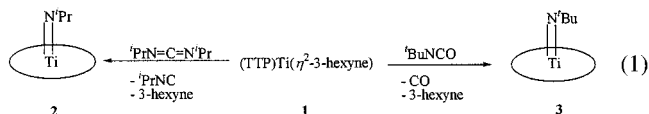
successful direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed, which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Complex **6** was treated in an analogous manner. A crystal of complex **6** was attached to a glass fiber and mounted on a Bruker CCD-1000 diffractometer for data collection at 173(2) K. A total of 28 087 data was harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time of 90 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.¹³ Final cell constants were calculated from a set of 6649 strong reflections from the actual data collection. The space group *P* $\bar{1}$ was determined from systematic absences and intensity statistics.¹⁴ 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. Because of poor quality of the diffraction data, all atoms were refined with isotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There are two symmetry-independent half molecules of complex **6** in the asymmetric unit. These half molecules occupy crystallographic inversion centers. The X-ray analysis of complex **6** confirmed atom connectivity, but did not provide reliable metrical parameters. Thus, bond distances and angles for compound **6** are not reported.

Computational Details. Density functional calculations were performed using the Amsterdam Density Functional program.¹⁵ Double- ζ Slater-type basis sets were used for C(2s, 2p), N(2s, 2p), O(2s, 2p), P(3s, 3p), and H(1s) augmented by a single 3d polarization function. A triple- ζ basis set was used for Ti(3s, 3p, 3d, 4s). The inner electron configurations were assigned to the core and were treated using the frozen core approximation. All calculations were carried out using the local density approximation due to Vosko, Wilk, and Nusair¹⁶ with nonlocal corrections for exchange due to Becke¹⁷ with nonlocal corrections for correlation due to Lee, Yang, and Parr.¹⁸ A full geometry

optimization was carried out for the [Ti(porphine)(OP(CH₃)₃)₂] complex in the spin singlet state. A spin unrestricted open-shell calculation was carried out for this molecule in a triplet state using the singlet-state optimized geometry.

Results

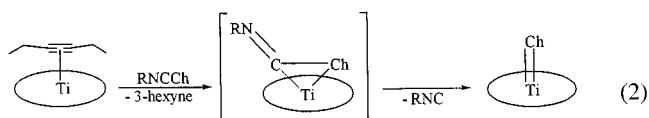
Reactivity of (TTP)Ti(η^2 -3-hexyne) with ⁱPrNCO, ^tBuNCO, and ⁱPrN=C=NⁱPr. Quantitative nitrene group transfer, as monitored by ¹H NMR spectroscopy, resulted from treatment of (TTP)Ti(η^2 -3-hexyne), **1**, with ⁱPrNCO or ^tBuNCO. Within 5 min complete displacement of 3-hexyne and a 50% production of the imido complex (TTP)Ti=NR (R = ⁱPr, **2**, ^tBu, **3**) was observed. After 16 h, quantitative formation of the imido complex occurred (eq 1).



The formation of CO was confirmed by high-resolution mass spectrometry (found: 27.99491 ± 0.0028 *m/z*; calcd.: 27.99491). Over the course of these reactions, intermediate substitution products were not observed. Because of mechanical losses, complex **2** was isolated in 44% yield. The isopropyl imido complex **2** could also be prepared by treatment of **1** with 1,3-diisopropylcarbodiimide, although mass balance was not realized during spectroscopic monitoring. In this case the yield of the imido complex (TTP)Ti=NⁱPr, **2**, was only 79% as measured by ¹H NMR. The isocyanide side product, ⁱPrNC, can also displace the alkyne from (TTP)Ti(η^2 -3-hexyne) to form a paramagnetic, ¹H NMR silent bis(isocyanide) complex, (TTP)-Ti(ⁱPrNC)₂. However, treatment of the sample with excess pyridine in an attempt to convert any NMR silent porphyrin species to the NMR active complex (TTP)Ti(py)₂ did not reveal additional Ti complexes.

Despite the reduced steric bulk of the isopropyl group, the imido complex is quite air- and water-stable in comparison to previous titanium metalloporphyrin derivatives. For example, (TTP)Ti=N^tBu, **3**, was hydrolyzed within minutes upon exposure to moisture to form free amine and (TTP)Ti=O. In contrast, the isopropyl complex, **2**, required hours to undergo complete hydrolysis.

Reactivity of (TTP)Ti(η^2 -3-hexyne) with ^tBuNCSe, ^tBuNCS, and CS₂. Quantitative displacement of the 3-hexyne was observed by ¹H NMR within minutes upon addition of ^tBuNCSe to (TTP)Ti(η^2 -3-hexyne). In addition to the appearance of the terminal selenido complex, (TTP)Ti=Se, **4**, an additional set of sharp porphyrin signals was detected at early times (eq 2).



The ratio of complex **4** to the new intermediate was 1:9 after ≈5 min. Associated with this new transient complex was a 9-proton singlet at -0.52 ppm. This signal is downfield from the ^tBu resonance of the imido species, (TTP)Ti=N^tBu, by over 1 ppm. An η^2 -C,Se bound isoselenocyanate, (TTP)Ti(η^2 -^tBuNCSe), is a reasonable formulation for this intermediate. At 20 °C the intermediate is slowly converted over 4 h to complex **4** (99% NMR yield) and ^tBuNC. Treatment of the hexyne complex

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(14) All software and sources of the scattering factors are contained in the SHELXTL V5.1 program library, G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI.

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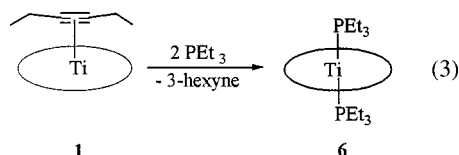
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1 with $t\text{BuNCS}$ proceeded somewhat faster to form the terminal chalcogenido $(\text{TTP})\text{Ti}=\text{S}$ (95% NMR yield after ≈ 15 min). An additional set of broad, transient NMR signals ($\Delta\nu_{1/2} = 16$ Hz) was detected, which had experimentally similar chemical shifts to those for $(\text{TTP})\text{Ti}(\eta^2\text{-}t\text{BuNCSe})$. This species is therefore assigned as an $\eta^2\text{-C,S}$ adduct, $(\text{TTP})\text{Ti}(\eta^2\text{-}t\text{BuNCS})$.

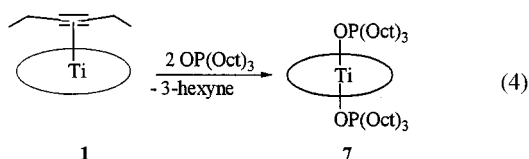
Heating a benzene- d_6 solution of **1** in the presence of ≈ 1.25 equiv of CS_2 at 80°C for 112 h produced $(\text{TTP})\text{Ti}=\text{S}$, **5**, in 87% yield by NMR. This reaction proceeded with the formation of at least five intermediate titanium porphyrin species, indicated by the number of β -pyrrole signals in the ^1H NMR spectrum.

Synthesis of $(\text{TTP})\text{Ti}(\text{PEt}_3)_2$, **6.** Although no reaction was observed between $(\text{TTP})\text{Ti}(\eta^2\text{-}3\text{-hexyne})$ and NEt_3 , $\text{N}(\text{Oct})_3$, or $\text{P}(\text{Oct})_3$, treatment with PEt_3 rapidly afforded the bis(phosphine) adduct $(\text{TTP})\text{Ti}(\text{PEt}_3)_2$, **6**, in 53% isolated yield (eq 3). This



reaction is quantitative by NMR. Although **6** is paramagnetic, its ^1H NMR signals are relatively sharp and integrations are sufficient for determining the metal:ligand stoichiometry. This situation is common for $S = 1$ Ti(II) complexes.^{4c} For example, the β -pyrrole resonance at -5.92 ppm integrated as eight protons relative to the 18-H methyl signals for the two PEt_3 ligands at 7.22 ppm. The coordination environment of titanium was found to contain *trans*- PEt_3 groups by X-ray diffraction, despite poorly diffracting crystals.¹⁹ Phosphorus signals for the PEt_3 groups were not observed in the ^{31}P NMR spectrum.

Synthesis and Structure of $(\text{TTP})\text{Ti}[\text{OP}(\text{Oct})_3]_2$, **7.** Tri-octylphosphine oxide readily displaced 3-hexyne from complex **1** within 5 min to produce the bis(phosphine oxide) adduct, $(\text{TTP})\text{Ti}[\text{OP}(\text{Oct})_3]_2$, **7** (eq 4). The significant solubility of this



compound in hexane prevented isolated yields higher than 52%. However, this reaction proceeded nearly quantitatively (93%) in an NMR tube experiment with an internal standard. Assignment of this complex as a bis(phosphine oxide) adduct was facilitated by ^1H NMR spectroscopy. The β -carbon methylene resonance (12.11 ppm) integrated as 12 protons for two $\text{OP}(\text{Oct})_3$ groups relative to the 12 proton methyl resonance (4.55 ppm) of the porphyrin tolyl groups. The ^{31}P chemical shift for complex **7** was significantly deshielded relative to that of free OPOct_3 . Similar behavior has been observed in other phosphine oxide adducts, although to a lesser extent.²⁰

Complex **7** crystallized in the highly symmetric space group $P2_1/n$. Selected bond distances and angles are given in Table

(19) A representation of complex **6** is contained in the Supporting Information, $R = 0.127$.

(20) Winter, C. H.; Sheridan, P. H.; Lewkebandara, T. S.; Heeg, M. J.; Proscia, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 1095. (b) McKarns, P. J.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1996**, *35*, 5968. (c) Mimoun, H.; Postel, M.; Casabianca, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1982**, *21*, 1303. (d) Postel, M.; Casabianca, F.; Gauffreteau, Y.; Fischer, J. *Inorg. Chim. Acta* **1986**, *113*, 173. (e) Winter, C. H.; Lewkebandara, T. S.; Proscia, J. W.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 1227.

Table 2. Selected Intramolecular Bond (\AA) Distances and Angles (deg) of Complex **7**

Ti—O	2.080(2)	Ti—O—P	138.43(10)
O—P	1.513(2)	O—Ti—N2	95.95(7)
Ti—N1	2.064(2)	O—Ti—N1	89.39(7)
Ti—N2	2.071(2)		
Ti—N1	2.064(2)		
Ti—N2	2.071(2)		

2. The titanium resides in an octahedral coordination environment with the pyrrole nitrogens in the equatorial plane and the $\text{OP}(\text{Oct})_3$ ligands occupying the axial positions (Figure 1). A

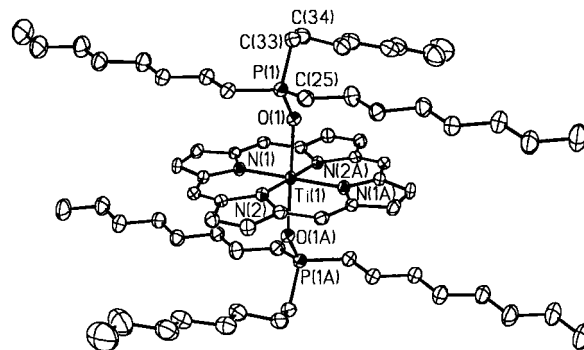


Figure 1. Thermal ellipsoid representation of $(\text{TTP})\text{Ti}[\text{OP}(\text{Oct})_3]_2$. Thermal ellipsoids drawn at the 50% probability level. Toly groups have been omitted.

number of Ti(IV) complexes containing O-bound phosphine oxide ligands have been crystallographically characterized,²⁰ but there appears to be only one Ti(II) compound containing Ti—O bonds. The Ti—O bond distances in complex **7** (2.080(2) \AA) are significantly longer than the Ti—O single-bond distances observed for $\text{Ti}(\text{OPh})_2(1,2\text{-bis}(\text{dimethylphosphino})\text{ethane})_2$ (1.891(6), 1.930(6) \AA).²¹ The tetravalent imido complex, $\text{TiCl}_2(=\text{N}^t\text{Bu})(\text{OPPh}_3)_2$, possesses Ti—O bonds of 2.008(6) and 2.047(6) \AA and Ti—O—P angles of $159.2(4)^\circ$ and $154.6(4)^\circ$.^{20a} The Ti—O—P angle of $138.43(10)^\circ$ in complex **7** is surprisingly acute in light of the potential steric interaction between the octyl groups and the porphyrin macrocycle. This appears to be the most acute M—O—P bond angle observed for a monodentate phosphine oxide—transition metal complex.^{22,23} Although crystallographically characterized transition metal phosphine oxide analogues are known in a variety of oxidation states and coordination environments, no clear trend exists with M—O—P bond angles.²³ The Ti—O vector in complex **7** is canted with respect to the normal of the N_4 plane by 6° , resulting in a Ti—P distance of 3.365 \AA . This is well outside of an η^2 -bonding interaction.^{24,25} The O—P bond distance in **7** (1.513(2) \AA) is comparable to those of free phosphine oxides (1.490–1.498 \AA).²⁶ The $\text{OP}(\text{Oct})_3$ moiety in **7** is perhaps best described by

(21) Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 4167.

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(24) The sum of the covalent radii of Ti and O (1.98–2.05 \AA) and Ti and P (2.38 \AA): (a) Porterfield, W. W. *Inorganic Chemistry*, 2nd ed.; Academic Press: San Diego, CA, 1998; p 214. (b) Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1984; p 52.

(25) For a theoretical treatment of diatomic ligand coordination modes to transition metals: (a) Hoffmann, R.; Chen, M. M. L.; Thorn, D. L. *Inorg. Chem.* **1977**, *16*, 503. (b) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

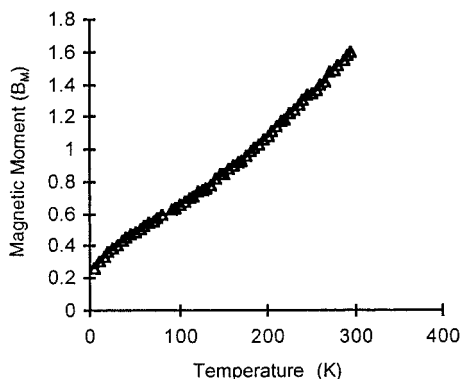


Figure 2. Magnetic moment vs temperature plot for complex 7.

the limiting phosphonium representation, $R_3P^+-O^-$.²⁷ A wavy distortion²⁸ is observed in the deviations from the mean plane containing the 24-atom porphyrin core and titanium [Ti (0), N1 (3), N2 (-16), C1 (-5), C2 (-5), C3 (3), C4 (6), C5 (8), C6 (-5), C7 (1), C8 (1), C9 (-5), C10 (7 pm)]. Although there are no short intermolecular contacts, the wavy distortion and relatively small Ti–O–P angle may result from the bulky OP(Oct)₃ groups. Two of the octyl groups extend linearly and lie in a coplanar manner to the porphyrin. The third octyl group achieves similar spacing relative to the porphyrin by rotation around the C33–C34 bond. The pyrrole nitrogen, N2 is eclipsed by the Ti–O–P unit. Since the Ti–O1 vector cants toward N2A, N2 is displaced out of the porphyrin plane toward O1.

The variable temperature magnetic behavior found for complex 7 is displayed in Figure 2. At 296 K the magnetic moment is 1.60 μ_B and falls smoothly to 0.25 μ_B at 41 K. This behavior is analogous to that of (TTP)Ti(4-picoline)₂.^{4a} These values are much lower than the spin-only value of 2.83 μ_B for two unpaired electrons.

Discussion

Group and Atom Transfer Reactions. The porphyrin macrocycle serves as a robust framework for studying group and atom transfer reactions of transition metal complexes.²⁹ This is particularly true in cases where multielectron redox processes are involved. The porphyrin ligand prevents severe structural reorganizations that typically accompany large changes in formal metal oxidation states. Our development of low-valent Ti porphyrin complexes, (TTP)Ti(η^2 -alkyne), has been very useful in this regard. The Ti(II) complex is an extremely potent reductant and a versatile atom acceptor reagent. In an extension of our previous atom transfer work, we have examined the chemistry of (TTP)Ti(η^2 -3-hexyne) with heterocumulenes. New reactions described in this work provide alternate synthetic methods for preparing Ti(IV) complexes in addition to providing a means of estimating Ti=X multiple bond strengths. It should be noted that the atom/group transfer reactions here were not inhibited by the presence of added 3-hexyne.

Table 3. Atom and Group Transfer Reactions Utilizing (TTP)Ti(η^2 -3-hexyne)

reagent	bond cleavage by 1 ^a	bond strength (kcal/mol)
(CH ₃) ₂ S=O	yes ^b	87 ^c
Ph ₂ S=O	yes ^b	89 ^c
(MeO) ₂ S=O	yes ^d	116 ^c
(tolyl) ₂ OS=O	no ^b	113 ^c
Ph ₃ P=O	no ^d	128 ^e
^t BuNC=O	no (C=O) ^d	133 ^f
^t BuN=CO	yes (N=C) ^d	
Ph ₃ As=O	no ^d	103 ^g
^t BuNC=S	yes ^d	71 ^h
Ph ₃ P=S	yes ⁱ	88 ^j
Cy ₃ P=S	yes ^d	98 ^j
SC=S	yes ^d	103 ^c
^t BuNC=Se	yes ^d	
Ph ₃ P=Se	yes ⁱ	67 ^j
(TMS)N=N ₂	yes ^k	40 ^l
ⁱ PrNC=N ⁱ Pr	yes ^d	

^a Reactions were performed at 20 °C in C₆D₆ and monitored by ¹H NMR unless otherwise indicated. ^b Reference 4b. ^c Reference 31e. ^d This work. ^e Reference 31c. ^f Value for MeNC=O, ref 31e. ^g Reference 31d. ^h Value for MeNC=S, ref 31e. ⁱ Reference 4a. ^j Reference 31a. ^k Reference 10. ^l Value for ^tBuN=N₂, ref 31b.

Attempts at establishing absolute values for the Ti–alkyne bond strengths by monitoring thermal ligand dissociation in solution ¹H NMR spectroscopy were unsuccessful. The ¹H NMR signals of (TTP)Ti(η^2 -3-hexyne) broadened irreversibly into the baseline upon heating to 373 K, precluding quantification of the species in solution. For (TTP)Ti(η^2 -PhC≡CPh), no dissociation was observed up to 373 K. Thus, a lower estimate of the Ti–alkyne bond energy is ≥ 12 kcal/mol as no dissociation was observed.³⁰ With this Ti–alkyne bond strength and tabulated bond strengths for small molecules (Table 3),³¹ estimates of the Ti=X bond strengths were determined for (TTP)Ti=X (X = O, S, Se, NR). Cleavage of the sulfur–oxygen double bond in dimethyl sulfite requires 116 kcal/mol. With the estimated bond energy of the Ti–alkyne fragment, a Ti=O bond strength of ≥ 128 kcal/mol is obtained. In comparison, theoretically and thermochemically derived Ti=O bond strengths are 143 kcal/mol³² and 146 kcal/mol [TiO₂(g)].³³ Furthermore, Ti–O single bond energies have been found to range from 89 to 115 kcal/mol.³⁴ On the basis of the sulfur atom abstraction between **1** and Cy₃P=S, a Ti=S bond strength of ≥ 110 kcal/mol is calculated. Selenium atom transfer between Ph₃P=Se and **1** provides a lower limit to the Ti=Se bond of 79 kcal/mol. Similarly, nitrene group transfer from RNCO to **1** involves cleavage of the nitrogen–carbon double bond, which requires ≈ 88 kcal/mol. Thus, the titanium–nitrogen bond energy in (TTP)Ti=NR is ≥ 100 kcal/mol.

Although similar atom and group transfer reactions were found with compounds **6** and **7**, these reactions required heating.

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Table 4. Metrical Parameters for Selected Atom Transfer Partners

	Ti–N (average)/Å	Ti–Ct ^a
(OEP)Ti(η^2 -Et–C≡C–Et)	2.094 ^b	0.54 ^b
(OEP)Ti=O	2.114 ^c	0.603(6) ^c
	S–C/Å	C–S–C/deg
Me ₂ S=O	1.80 ^d	97.3 ^d
Me ₂ S	1.82 ^e	105.0 ^e
Ph ₂ S=O	1.76 ^d	97.3 ^d
(<i>p</i> -MeC ₆ H ₅) ₂ S	1.75 ^e	109.0 ^e
	P–C/Å	C–P–C/deg
Ph ₃ P=S	1.817 ^f	105.7 ^f
Ph ₃ P	1.83 ^g	102.0 ^g
Cy ₃ P=S	1.839 ^f	108.0 ^f
Cy ₃ P	1.868 ^g	103.8 ^g

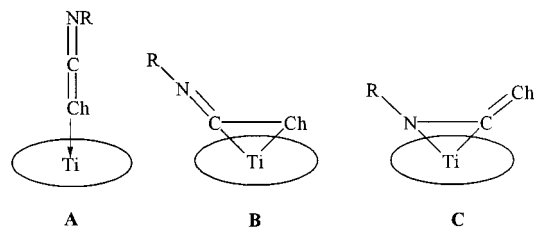
^a Ti displacement out-of-mean porphyrin plane. ^b Reference 45. ^c Reference 46. ^d Reference 47. ^e Reference 48. ^f Reference 49. ^g Reference 26a.

For example, formation of (TTP)Ti=N(SiMe₃) from treatment of complex **7** with N₃(SiMe₃) required heating the reaction mixture to 60 °C. In contrast, the facile reaction between the alkyne adduct, **1**, and N₃(SiMe₃) occurred at ambient temperature. Heating a solution of the bis(phosphine) species, **6**, in the presence of dimethyl sulfite produced (TTP)Ti(OMe)₂,⁹ (TTP)Ti=O, and Et₃P=S.

Attempts at oxygen atom abstraction from CO₂, (PhO)₃PO, (Et₂N)₃PO, and Ph₃PO were unsuccessful despite the ability of low-valent Ti(II) complexes to break such strong bonds.³⁵ The reverse reaction, oxygen atom transfer from (TTP)Ti=O to ^tBuNC, POct₃, PPh₃, or P(OPh)₃, was also not observed. Use of diphenylacetylene or pyridine to trap the reactive (TTP)Ti(II) intermediate also failed to promote atom transfer. Clearly, a kinetic barrier must exist in the spontaneous direction for these oxygen atom transfer couples.

In the above atom transfer analysis for Ti=X bond strengths, the issue of reorganization energies should be addressed. Table 4 lists metrical parameters of selected atom transfer partners for comparison. Because X-ray structures for (TTP)Ti=O and (TTP)Ti(η^2 -RC≡CR) are unknown, structural parameters for octaethylporphyrin analogues are presented. Metrical parameters for (TTP)Ti=S and (TTP)Ti=Se are also unknown. From the data in Table 4, it is clear that the reduced and oxidized Ti porphyrin complexes have very similar Ti–N distances and Ti out-of-plane displacements. Also, oxygen abstraction from sulfoxides results in small changes in S–C bond distances (Δ = 0.02 Å) and C–S–C angles (Δ = 8°–12°). Similarly, phosphine sulfides and the corresponding phosphines have very similar P–C bond lengths and C–P–C angles. Consequently reorganization energies for atom transfer reactions involving these species are likely to be small. Nonetheless, the bond strengths determined above must still be considered as rough estimates.

Ligand Exchange Reactions. The reported ligand exchange reactions of titanocene and bis(pentadienyl) titanium(II) derivatives have dealt largely with CO and phosphines.^{5,36} The system in this work has made use of a wide variety of axial donor ligands. The metalloporphyrin fragment (TTP)Ti(II) has a preference for strong σ -donors, exhibited by displacement of

**Figure 3.** Bonding modes of isocyanates.

THF with picoline. The triethylphosphine ligands in complex **6** are rapidly displaced by pyridine and OP(Oct)₃. Treatment of complex **6** with excess diphenylacetylene produced an equilibrium mixture of the diamagnetic monoacetylene complex, (TTP)Ti(η^2 -PhC≡CPh), and complex **6** ($K \sim 0.2$). Further variable temperature analysis of this equilibrium was prevented by decomposition of the Ti(II) complexes to uncharacterized, NMR-silent products. In the presence of excess pyridine, the trioctylphosphine oxide ligands in complex **7** are only partially displaced to form a mixed species, (TTP)Ti[OP(Oct)₃](py).

There is a contrasting ability to displace 3-hexyne from complex **1** with OP(Ph)₃ compared to the phosphate OP(OPh)₃. The phosphine oxide completely displaces the alkyne ligand within minutes. Treatment of compound **1** with the phosphate results in no displacement, even at 80 °C. This can be attributed to the less nucleophilic character of the phosphate.³⁷ Likewise, the phosphine imine, Et₃P=NSiMe₃, undergoes no reaction with complex **1**.

Atom Transfer Intermediates. The binding of heterocumulenes to mid- and late-transition metals has been well established.³⁸ However, isolable examples of early-transition metal–heterocumulene complexes are rare. Known low-valent metal complexes include examples of η^1 -CO₂, η^2 -CO₂, η^2 -CS₂, and η^2 -RNCNR.³⁹ The reaction between **1** and ^tBuNC=Ch (Ch = S, Se) yields a diamagnetic, short-lived species observed by NMR. This transient compound possesses a nine-proton singlet at –0.52 ppm, which is assigned to a ^tBu group of a coordinated ligand. Because the chalcogenido complexes, (TTP)Ti=Ch, do not bind additional donor ligands, it does not seem likely that this intermediate is a simple isocyanide or isochalcocyanate adduct of the terminal chalcogenido compound. Moreover, (TTP)Ti=Ch, free ^tBuNC, and ^tBuNC=Ch are quantitatively accounted for in the ¹H NMR spectrum. Likewise, the 3-hexyne is accounted for as either bound (–0.12 (q), –0.87 (t)) or free (2.05 (q), 1.00 (t)). Thus, it is reasonable to assign this intermediate as a titanium complex containing only one bound ^tBuNC=Ch, structure **A**, **B**, or **C** (Figure 3). Given the

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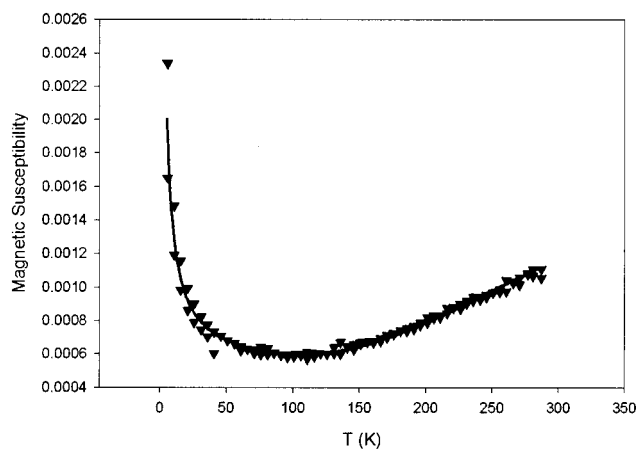


Figure 4. Fit of data to model with a ground state singlet and excited triplet state at 576 cm^{-1} , 0.3% of paramagnetic impurity ($S = 1$) and a constant amount added to the susceptibility (0.0005 cgsu).

diamagnetism of the intermediate and its subsequent conversion to terminal sulfido and selenido products, the η^2 -bound form **B** may be the most likely formulation. The reaction of **1** with RNCO produces an imido product. Thus, form **C** is the most likely intermediate for the alkyl isocyanate adduct. The formation of terminal chalcogenido complexes, $(\text{TTP})\text{Ti}=\text{Ch}$, from RNCS and RNCSe rather than imido production can be traced to weaker $\text{C}=\text{Ch}$ bonds relative to the $\text{C}=\text{N}$ bond.

Magnetic Properties of Complex 7. The temperature-dependent magnetic susceptibility of complex **7** is shown in Figure 4. The susceptibility falls with decreasing temperature to near diamagnetism and then increases sharply at liquid helium temperatures. The magnetic moment for this complex at room temperature, $\approx 1.6\ \mu_{\text{B}}$, is significantly lower than that for a triplet, $S = 1$, ground state expected for an octahedral d^2 titanium(II) complex of $2.83\ \mu_{\text{B}}$. This moment falls rapidly to $\approx 0.25\ \mu_{\text{B}}$ at liquid helium temperatures.

There appears to be two possible explanations for this behavior. Either the complex has a diamagnetic $S = 0$ ground state with a thermally accessible excited triplet state or there is a spin equilibrium involving an $S = 0$ and an $S = 1$ state. Attempts to fit the temperature variation of the magnetic moment in terms of a ground state singlet and thermally accessible triplet state with the inclusion of a small amount of a paramagnetic impurity gave qualitative agreement with the observed data. However, the main discrepancy between the calculated and observed regions of the fit was in the “diamagnetic” region between 40 and 150 K where the difference, 500×10^{-6} cgsu, is of the same order of magnitude as the diamagnetic corrections for the sample. An excellent fit to the data could be obtained by the addition of this quantity to the model. This gave a ground-state singlet with excited triplet state at 576 cm^{-1} and 0.3% of paramagnetic impurity ($S = 1$) (Figure 4). This additional temperature-independent contribution to the susceptibility may well be due in part to contributions from second-order Zeeman (temperature-independent paramagnetism) effects. These would normally be expected to be smaller ($< 100 \times 10^{-6}$ cgsu) for titanium(II) complexes; however, the close proximity of the singlet and triplet states may give rise to a larger effect.

Electronic Structure Calculations for Complex 7. Insight into the electronic structure of this complex was facilitated by computations using density functional theory. A full geometry optimization with no symmetry restraints was performed on the molecule $\text{Ti}(\text{porphine})[\text{OP}(\text{CH}_3)_3]_2$ as a model for complex **7**. It was assumed that the electronic ground state was a singlet

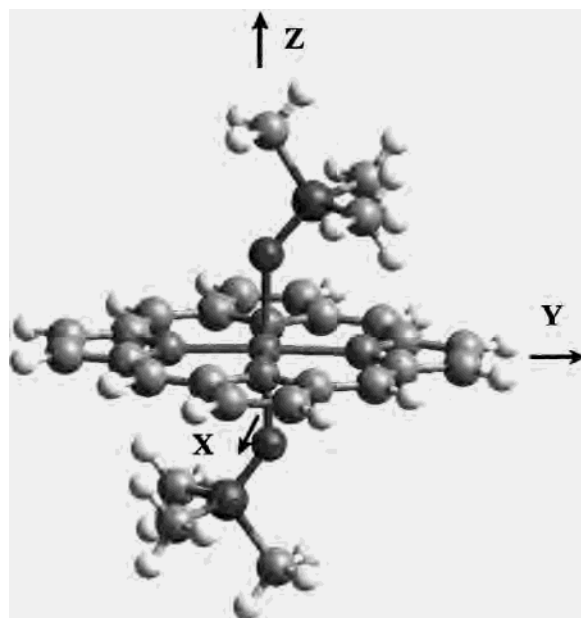


Figure 5. Calculated structure for $\text{Ti}(\text{porphine})[\text{OP}(\text{CH}_3)_3]_2$.

($S = 0$). The calculated structure was in good agreement with that determined for complex **7** (Figure 5). The Ti–O and P–O bond lengths were calculated to be 2.10 and 1.53 Å, respectively, in comparison to the measured values of 2.080 and 1.513 Å. The Ti–O–P angle was calculated to be 141.7° (average) compared to the X-ray value of 138.43° . A Mulliken population analysis gave charges of 1.78, -0.85 , and 0.87 for the Ti, O, and P atoms. This is consistent with the $\text{R}_3\text{P}^+-\text{O}^-$ representation of the coordinated phosphine oxide. The Ti d orbital population was found to be 2.03.

With the molecular geometry calculated for the singlet state, the energy of the lowest lying triplet state was calculated to be only 0.19 kcal/mol higher in energy. Thus, the singlet and triplet states in this molecular geometry are nearly degenerate. Examination of the frontier orbitals showed the HOMO to be composed of a titanium d_{xz} orbital antibonding with respect to an O p_π orbital of the phosphine oxide and one component of the porphine e_g (π) molecular orbital. The Ti d_{xz} orbital was also a component of other lower lying occupied molecular orbitals. The LUMO and LUMO+1 consist mainly of the Ti d_{xy} and d_{yz} orbitals, respectively (Figure 6). All three of these orbitals are nearly degenerate.

These calculations support the conclusion drawn from the magnetic properties of complex **7**, which show the ground state to be a spin singlet in close proximity to a triplet state. The nature of the ground state of complex **7** is counter to that expected from Hund’s rules. The three “ t_{2g} ” titanium orbitals are nearly degenerate yet the singlet state is the lowest. There are two reports relevant to this observation: (1) The diamagnetism of the titanium(II) complex $\text{Ti}(\text{dppe})_2\text{Me}_2$ reported by Girolami et al.⁴⁰ and (2) the observation of a singlet ground state with a thermally accessible triplet state in the C_{60}^{2-} dianion.⁴¹ In the first complex, the interelectron interaction has been reduced such that pairing of electrons in a lower energy titanium orbital gives a lower energy singlet state⁴² while in the second system there is formally a triply degenerate set of

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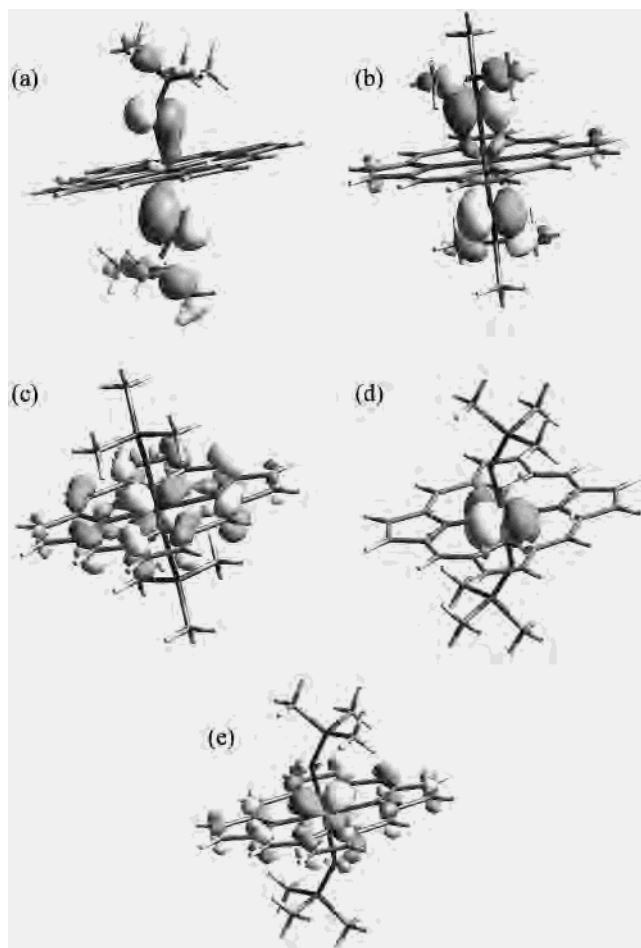


Figure 6. Bonding and frontier orbitals for Ti(porphine)[OP(CH₃)₃]₂: (a) Ti(d)–O (p_π) bonding, (b) Ti(d_{xz})–O (p_π) bonding, (c) HOMO Ti(d_{xz}), (d) LUMO Ti(d_{xz}), and (e) LUMO+1 Ti(d_{yz}).

highly delocalized molecular orbitals. The observed behavior in complex **7** appears more like the second case.

The observed chemical shifts of the porphyrin β pyrrole protons at –33.0 ppm are in keeping with the nature of the occupied orbitals in the thermally accessible triplet state, which are the titanium d_{xz} and d_{yz} orbitals that mix with the porphyrin e_g molecular orbitals, allowing delocalization of the unpaired

spin on the β carbons atoms. This observation is well-known in the NMR spectra of paramagnetic iron porphyrins.⁴³ In the intermediate spin iron(III) porphyrins, which have singly occupied d_{xz} and d_{yz} orbitals, similar upfield shifts are observed.⁴⁴

Conclusion

The Ti(II) complex, (TTP)Ti(η²-3-hexyne), **1**, is a potent reductant and a versatile inner-sphere acceptor reagent. Treatment of complex **1** with a variety of heterocumulenes such as RN=CO, ^tPrN=CN^tPr, CS₂, ^tBuNC=S, and ^tBuNC=Se results in group or atom transfer and formation of the multiply bonded species (TTP)Ti=NR, (TTP)Ti=S, or (TTP)Ti=Se. In addition, complex **1** abstracts an oxygen from (MeO)₂S=O to produce (TTP)Ti=O. These reactions were useful in determining estimates for Ti=O, Ti=S, Ti=Se, and Ti=NR bond strengths.

Notably, complex **1** does not abstract oxygen from O=P(Oct)₃. Instead, simple substitution occurs to produce the bis-ligand adduct (TTP)Ti[OP(Oct)₃]₂, **7**. Density functional calculations indicate that the magnetic properties of this complex arise from a ground state singlet state with a thermally accessible triplet state.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of (TTP)Ti[O=P(Oct)₃] and (TTP)Ti(PEt₃)₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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