Volume 34
Number 3
February 1, 1995

Inorganic Chemistry

Communications

Synthesis and Characterization of (Imido)titanium(IV) Porphyrin Complexes. X-ray Structure of (Phenylimido)(tetratolylporphyrinato)titanium(IV)

Lisa M. Berreau, Victor G. Young, Jr., and L. Keith Woo*,[1]

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

Received August 18, 1994

Group 4 metal complexes containing terminal imido ligands have received considerable attention over the past few years.[2−7] However, metalloporphyrin species containing imido ligands are quite rare and only a small number have been characterized.[8−11] Smieja *et al.* recently reported the first X-ray crystallographic study of an organoimido metalloporphyrin complex, (TTP)Os(=NC_6H_4-*p*-NO_2)$_2$.[12,13] We now wish to report a general method for the preparation of the first (organoimido)titanium porphyrin complexes from the reaction of (TTP)$TiCl_2$ with lithium amides.

As illustrated in eq 1, treatment of (TTP)$TiCl_2$ with LiNHR results in the formation of Ti(IV) organoimido complexes. In a typical reaction, 88 mg of (TTP)$TiCl_2$[14] (0.11 mmol) and 35 mg of $LiNHC_6H_5$[15] (0.36 mmol) were stirred in toluene (15 mL) under N_2 at 22 °C. Within minutes after the addition of solvent to the solid starting materials, the green solution turned into the orange-red color of the phenylimido complex, **1**. After the reaction mixture was allowed to stir for 4 h, the solution was filtered, and the filtrate was concentrated to ca. 2 mL. Hexane (4 mL) was added, and the solution was cooled to −20 °C for 1 h. Filtration yielded an orange-red solid (58 mg, 64%) after washing with hexane and drying in vacuo.[16] The tolyl and cyclohexyl analogs, **2** and **3**, can be prepared in a similar manner.[17]

$$\begin{array}{l} \mathrm{(TTP)TiCl_2 + 2LiNHR \rightarrow (TTP)Ti{=}NR + 2LiCl + NH_2R} \\ \qquad\qquad\qquad\qquad \mathbf{1}, \mathrm{R = -C_6H_5} \\ \qquad\qquad\qquad\qquad \mathbf{2}, \mathrm{R = -C_6H_4\text{-}}p\mathrm{\text{-}CH_3} \\ \qquad\qquad\qquad\qquad \mathbf{3}, \mathrm{R = -C_6H_{11}} \end{array} \tag{1}$$

---

(1) Presidential Young Investigator, 1990−1995; Camille and Henry Dreyfus Teacher-Scholar, 1993−1998.

(2) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(3) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

(4) Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669.

(5) (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

(6) Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.

(7) Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, *7*, 2007.

(8) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

(9) (a) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K. *Inorg. Chim. Acta* **1991**, *190*, 161. (b) Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1992**, 161.

(10) Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191.

(11) Buchler, J. W.; Pfeifer, S. Z. *Naturforsch, B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1362.

(12) Abbreviations: TTP = dianion of 5,10,15,20-*meso*-tetra-*p*-tolylporphyrin. POR = general porphyrinato dianion.

(13) Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614.

(14) (a) Berreau, L. M.; Hays, J. A.; Young, V. G.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105. (b) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

(15) The lithium amide salts $LiNHC_6H_5$, $LiNHC_6H_4$-*p*-CH_3, and $LiNHC_6H_{11}$ were prepared by adding equimolar *n*-butyllithium to a diethyl ether solution of the appropriate amine at −78 °C. The reaction mixture was then allowed to warm to room temperature and stir for 2−4 h. The solvent was then removed in vacuo. The lithium salt was triturated with hexane and collected by filtration. A near-quantitative yield was obtained after washing the lithium amide with hexane and drying the product in vacuo.

(16) Analytical Data for (TTP)Ti=NC_6H_5 are as follows. ^{1}H NMR (C_6D_6, 300 MHz, ppm relative to TMS): 9.21 (s, 8H, β-H), 8.14 (d, 4H, $-C_6H_4CH_3$), 8.03 (d, 4H, $-C_6H_4CH_3$), 7.30 (d, 8H, $-C_6H_4CH_3$), 5.72 (m, 3H, *m*-, *p*-*H*), 3.85 (d, 2H, *o*-*H*), 2.41 (s, 12H, $-C_6H_4CH_3$). UV−vis (toluene, nm): 426 (Soret), 548. MS{EI} calcd (found) (*m*/*e*): 806 (807), $[M]^+$. IR (KBr, cm^{-1}): Bands associated with porphyrin ligand: 1473, 1327, 1201, 1181, 1109, 1071, 1007, 889, 846, 802, 727, 516; bands associated with =NC_6H_5, 753, 687.

(17) Analytical Data for (TTP)Ti=NC_6H_4-*p*-CH_3 are as follows. ^{1}H NMR (C_6D_6, 300 MHz, ppm relative to TMS): 9.21 (s, 8H, β-H), 8.15 (d, 4H, $-C_6H_4CH_3$), 8.04 (d, 4H, $-C_6H_4CH_3$), 7.30 (d, 8H, $-C_6H_4CH_3$), 5.53 (d, 2H, *m*-*H*), 3.81 (d, 2H, *o*-*H*), 2.41 (s, 12H, $-C_6H_4CH_3$), 1.29 (s, 3H, $-CH_3$). UV−vis (toluene, nm): 426 (Soret), 548. IR (KBr, cm^{-1}): Bands associated with porphyrin ligand, 1491, 1333, 1324, 1202, 1181, 1109, 1070, 1006, 847, 798. 724, 525. MS{EI} calcd (found) (*m*/*e*): 821 (821), $[M]^+$. Anal. Calcd (found) for $C_{55}H_{43}N_5Ti$: C, 80.36 (80.29); H, 5.28 (5.47); N, 8.52 (8.20). Analytical data for (TTP)Ti=NC_6H_{11} are as follows. ^{1}H NMR (C_6D_6, 300 MHz, ppm relative to TMS): 9.24 (s, 8H, β-H), 8.31 (d, 4H, $-C_6H_4CH_3$), 8.05 (d, 4H, $-C_6H_4CH_3$), 7.34 (d, 8H, $-C_6H_4CH_3$), 2.42 (s, 12H, $-C_6H_4CH_3$), 0.31 (br, 1H, −Cy), 0.19 (br, 1H, −Cy), −0.25 (br, 2H, −Cy), −0.42 (br, 1H, −Cy), −0.65 (br, 2H, −Cy), −0.97 (br, 2H, −Cy), −1.59 (br, 2H, −Cy). UV−vis (toluene, nm): 424 (Soret), 548. IR (KBr, cm^{-1}): Major bands associated with porphyrin ligand, 1445, 1335, 1202, 1181, 1107, 1070, 1006, 886, 846, 798, 723, 524; MS{EI} calcd (found) (*m*/*e*): 813 (813), $[M]^+$.

0020-1669/95/1334-0527$09.00/0

The new porphyrin complexes were characterized by ^{1}H NMR, UV−vis, and IR spectroscopy. The ^{1}H NMR spectra confirm the expected diamagnetism of these d^0 Ti(IV) complexes. For the phenyl- and tolylimido complexes, the β-pyrrole resonance appears as a sharp singlet at 9.21 ppm. This signal is shifted downfield slightly for the cyclohexyl derivative, appearing as a singlet at 9.24 ppm. These chemical shifts are very similar to that observed for (TTP)Ti=O (9.24 ppm), suggesting that the oxo and imido ligands exhibit similar π-donating ability to the titanium atom. The porphyrin tolyl protons appear as two doublets, each integrating to four protons, and a multiplet, integrating to eight protons. The magnetic equivalence of the four tolyl groups is consistent with a time-averaged C_{4v} symmetry of the metalloporphyrin complexes. The protons associated with the axial imido ligand are shifted upfield relative to those of the corresponding free amine. This phenomenon is consistent with the position of the imido substituent above the porphyrin ring current.

The electronic absorption spectra of **1**−**3** are characteristic of porphyrin complexes with an intense Soret peak at 426 nm (R = $-C_6H_5$, $-C_6H_5$-*p*-CH_3) or 424 nm (R = $-C_6H_{11}$) and an additional Q-band at 548 nm. These absorption spectra are similar to those of other titanium porphyrins.[18] Addition of THF to a toluene solution of (TTP)Ti=NC_6H_5 produces no change in position or intensity of the absorption maxima, indicating that THF does not appear to bind to the position trans to the imido group.

Infrared spectra of complexes **1**−**3** exhibit intense porphyrinato stretching modes in the region of 1500 to 500 cm^{-1}.[16,17] These bands are similar to those observed in the spectrum of (TTP)Ti=O. Although the Ti=O stretch in (TTP)Ti=O is readily observed as an intense band at 983 cm^{-1},[18-20] unambiguous assignment of a metal nitrogen double bond stretch has not been possible. However, two additional bands are present in the spectrum of (TTP)Ti=NC_6H_5 (753 and 687 cm^{-1}) and may be assigned as the out-of-plane bending and puckering modes associated with the phenyl ring of the imido ligand.

Crystals of (TTP)Ti=NC_6H_5, **1**, suitable for single-crystal X-ray diffraction were grown by layering a benzene solution of **1** with hexane. Complex **1** crystallized in the centrosymmetric space group $P\bar{1}$ with 2 molecules per unit cell.[21] The porphyrin framework of (TTP)Ti=NC_6H_5 is saddle-shaped. The geometry about the Ti is square-pyramidal with the four pyrrole nitrogens forming the basal plane and the imido group at the apical site. The titanium atom is displaced from the mean plane of the pyrrole nitrogens toward the imido ligand by 0.52 Å. The Ti−N(5) distance is 1.703(2) Å and compares well with that reported for $(OAr')_2Ti{=}NC_6H_4C_6H_4NC_4Et_4$ (Ti−N = 1.708(5) Å, Ti−N−C = 170.4(4)°; OAr′ = 2,6-diisopropylphenoxide)[5b] but is noticeably shorter than the distance reported for $(Ar'O)_2Ti{=}NC_6H_5(py')_2$ (Ti−N = 1.719(3) Å, Ti−N−C = 173.1(3)°; py′ = 4-pyrrolidinopyridine).[5a] The imido ligand is nearly linear with a Ti−N(5)−C(21) angle of 170.6(2). The slight deviation from 180° is possibly due to close intermolecular contacts with adjacent methyl groups. For example, C(107) of one molecule is 3.693 Å from C(24) of the imido phenyl of a neighboring molecule. Consequently, the nearly linear Ti−N−C angle is suggestive of substantial Ti−N$_{\text{imido}}$ triple bond character.

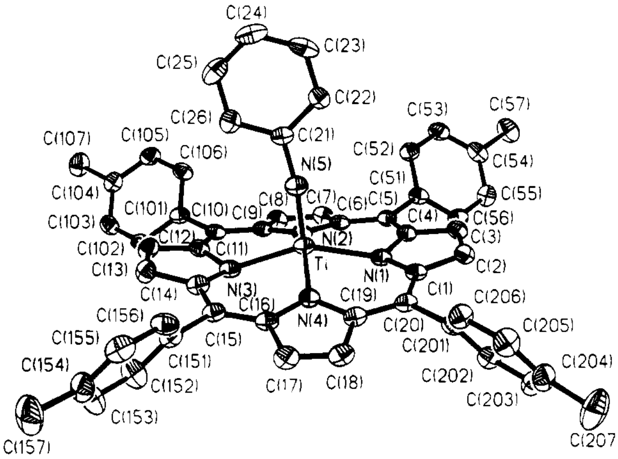

Figure 1. Molecular structure and atom-numbering scheme for (TTP)-Ti=$NC_6H_5{\cdot}C_6H_6$ (**1**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Ti−N_5, 1.703(2); Ti−N_1, 2.101(3); Ti−N_2, 2.100(2); Ti−N_3, 2.098(2); Ti−N_4, 2.104(2); N_5−C_{21}, 1.386(4). Selected bond angles (deg): Ti−N_5−C_{21}, 170.6(2); N_1−Ti−N_4, 86.29(9); N_2−Ti−N_4, 150.64(9); N_2−Ti−N_3, 86.45(9); N_3−Ti−N_1, 151.68(9); N_2−Ti−N_1, 86.35(9); N_3−Ti−N_4, 86.69(9).

As illustrated in eq 2, the imido complexes are readily hydrolyzed to the corresponding free amine and (TTP)Ti=O.[22]

$$\text{(TTP)Ti{=}NPh} + \text{H}_2\text{O} \rightarrow \text{(TTP)Ti{=}O} + \text{H}_2\text{NPh} \quad (2)$$

$$\text{(TTP)Ti{=}NPh} + \text{PPh}_3 + \text{PhC{\equiv}CPh} \rightarrow \text{no reaction} \quad (3)$$

$$\text{(TTP)Ti{=}S} + {}^1\!/_8\text{S}_8 \rightarrow \text{(TTP)TiS}_2 \quad (4)$$

$$\text{(TTP)Ti{=}NPh} + \text{S}_8 \rightarrow \text{no reaction} \quad (5)$$

Treatment of (TTP)Ti=NC_6H_5 with PPh_3 in the presence of an alkyne results in no reaction (eq 3).[23] In contrast, chromium porphyrin organoimido complexes have been reported to yield the corresponding phosphinimine and Cr^{II}(POR) when treated with PPh_3.[10] Finally, it has been shown that treatment of terminal sulfido- and selenidotitanium porphyrin complexes with the elemental chalcogenide results in the formation of a perchalcogenido species (eq 4).[24] In an attempt to prepare a mixed (Ti−N−S) three-membered metallacycle, (TTP)Ti=NPh

---

(18) Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87.

(19) Data for (TTP)Ti=O are as follows. IR (KBr, cm^{-1}): Major bands associated with porphyrin ligand, 1488, 1335, 1203, 1182, 1109, 1071, 1008, 847, 800, 727, 522; Ti=O, 983.

(20) (a) Richard, P.; Poncet, J. L.; Barbe, J. M.; Guilard, R.; Goulon, J.; Rinaldi, D.; Cartier, A.; Tola, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1451. (b) Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782.

(21) (TTP)Ti=NC_6H_5 crystallizes in the centrosymmetric space group $P\bar{1}$ with a = 13.338(4) Å, b = 13.740(2) Å, c = 13.861(3) Å, α = 91.86(2)°, β = 100.20(2)°, γ = 112.09(2)°, V = 2302.9(9) Å^3, Z = 2, $R1$ = 0.0552, and $wR2$ = 0.1502. The calculated density ($C_{54}H_{41}N_5$-Ti, M = 807) per unit cell is 1.278 g/cm^3. Data were collected at −60 °C on a Siemens P4RA diffractometer with Cu Kα radiation using an $\omega-2\theta$ scan technique over the range 3.26 < 2θ < 56.74°. Unique reflections (5334) with $I > 2\sigma(I)$ were used after correction for absorption. All non-hydrogen atoms except for those in the solvent were refined anisotropically.

(22) An NMR tube containing a C_6D_6 solution of (TTP)Ti=NC_6H_5 and sealed under N_2 with a rubber septum was injected with 1 μL of degassed water. The ^{1}H NMR spectrum clearly showed the complete conversion of the imido complex to (TTP)Ti=O and the free amine. Signals for (TTP)Ti=O (C_6D_6, 300 MHz, ppm): 9.24 (s, 8H, β-H), 7.99 (d, 8H, $-C_6H_4CH_3$), 7.28 (d, 8H, $-C_6H_4CH_3$), 2.42 (s, 12H, $-C_6H_4CH_3$). Signals for $C_6H_5NH_2$: 7.05 (t, $-C_6H_5NH_2$), 6.7 (t, 1H, $-C_6H_5NH_2$), 6.3 (d, 2H, $-C_6H_5NH_2$), 5.4 (br, 2H, $C_6H_5NH_2$).

(23) An NMR tube containing a C_6D_6 solution of (TTP)Ti=NC_6H_5 (1.6 mg, 1.98 × 10^{-3} mmol), PPh_3 (3.7 mg, 1.41 × 10^{-2} mmol), and PhC≡CPh (7.0 mg, 3.93 × 10^{-2} mmol) and sealed under nitrogen was monitored at ambient temperature over a 15 day period. ^{1}H NMR spectra indicated that no reaction occurred.

(24) Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.

was treated with elemental sulfur (eq 5). After stirring of the mixture with mild heating for 12 h in toluene/THF, no reaction was detected by ^1H NMR.[25] Further studies involving the synthesis and reactivity of early transition metal porphyrinato organoimido complexes are underway.

Acknowledgment. Funding for this work was provided by a Department of Education GAANN Fellowship to L.M.B., the National Science Foundation, through PYI Award CHE-9057752, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Complete listings of data collection parameters, atomic coordinates, bond distances and angles, thermal parameters, and hydrogen coordinates for **1** (18 pages). Ordering information is given on any current masthead page.

IC940980M

---

(25) (TTP)Ti=NC_6H_5 (7.0 mg, 8.66×10^{-3} mmol) was treated with S_8 (2.4 mg, 9.38×10^{-3} mmol) in a solution of 10 mL of toluene and 5 drops of THF for 12 h with mild heating under a N_2 atmosphere. After the heat was removed and the reaction mixture had cooled to room temperature, the solvent was removed in vacuo. A ^1H NMR in C_6D_6 of the reaction mixture indicated that no reaction had taken place.