

Radical Synthesis of a Heterobinuclear μ -Oxo Complex: Reaction of $V(O)(O-i-Pr)_3$ with $Ti(NRAr)_3$ ($R = C(CD_3)_2CH_3$, $Ar = 3,5-C_6H_3Me_2$)

Paulus W. Wanandi, William M. Davis, and Christopher C. Cummins*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Michael A. Russell and Dean E. Wilcox*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received October 7, 1994

Titanium reagents that mediate the reduction of carbonyl compounds enjoy widespread utility in a variety of guises. Pinacol couplings¹ and the McMurry reaction² are two noteworthy examples. The formation of stable titanium ketyl complexes has recently been demonstrated by addition of ketones to monomeric $Ti(OSi-t-Bu)_3$.³ Such reactions involve electron transfer to the carbonyl carbon with formation of an M–O linkage and erasure of the carbonyl π nexus.³ We wondered whether a high-valent metal oxo complex might function similarly upon treatment with a suitable Ti(III) reagent, to furnish a stable heterobinuclear μ -oxo complex. To investigate this possibility, we prepared and characterized $Ti(NRAr)_3$ ($R = C(CD_3)_2CH_3$, $Ar = 3,5-C_6H_3Me_2$) and examined its reaction with $V(O)(O-i-Pr)_3$ as detailed herein.

Green $Ti(NRAr)_3$ was prepared by treating orange $Ti(Cl)(NRAr)_2$ with sodium amalgam in benzene.⁵ An ORTEP drawing of $Ti(NRAr)_3$ is given in Figure 1.⁶ The molecule exhibits several interesting structural features, of which the most striking is the trigonal planar TiN_3 unit (the three N–Ti–N angles sum to 360°).⁷ An unanticipated aspect of the structure is that two bonding modes are exhibited for the NRAr ligand. The “normal” bonding mode, in which the Ar residue is oriented perpendicular to the contiguous nitrogen trigonal plane, is found for one of the NRAr moieties (that which includes N(3)). The other two NRAr ligands adopt a distorted bonding mode that

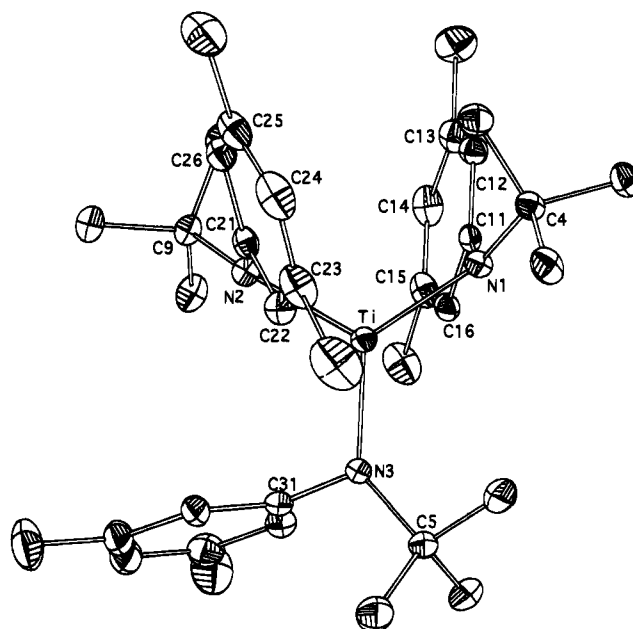
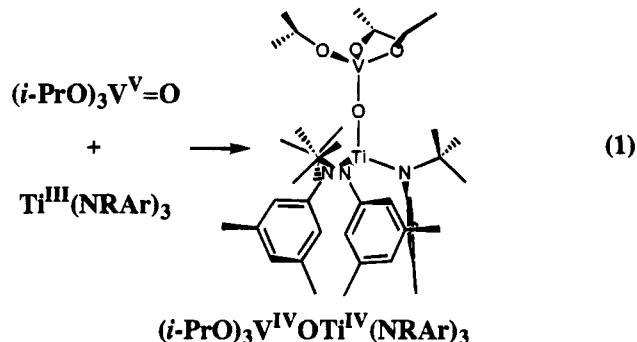


Figure 1. Structural diagram of $Ti(NRAr)_3$ with labeling scheme. Non-hydrogen atoms are represented as thermal ellipsoids at the 30% probability level. Selected bond distances (Å): Ti–N(1), 2.005(3); Ti–N(2), 1.992(3); Ti–N(3), 1.933(3); Ti–C(11), 2.495(3); Ti–C(16), 2.523(4); Ti–C(21), 2.537(4); Ti–C(22), 2.510(4); C(11)–C(12), 1.428(4); C(12)–C(13), 1.376(5); C(13)–C(14), 1.396(5); C(14)–C(15), 1.370(5); C(15)–C(16), 1.406(5); C(11)–C(16), 1.409(4); C(21)–C(22), 1.407(4); C(22)–C(23), 1.400(5); C(23)–C(24), 1.383(5); C(24)–C(25), 1.395(5); C(25)–C(26), 1.376(5); C(21)–C(26), 1.418(5). Selected bond angles (deg): N(1)–Ti–N(2), 116.8(1); N(1)–Ti–N(3), 125.7(1); N(2)–Ti–N(3), 117.5(1); Ti–N(1)–C(11), 92.9(2); Ti–N(1)–C(4), 138.6(2); N(1)–C(11)–C(16), 115.6(3); N(1)–C(11)–C(12), 128.0(3); Ti–N(2)–C(21), 95.8(2); Ti–N(2)–C(9), 138.4(2); N(2)–C(21)–C(22), 115.1(3); N(2)–C(21)–C(26), 128.7(3); Ti–N(3)–C(31), 112.9(2); Ti–N(3)–C(5), 132.0(2).

permits their Ar residues to approach the metal center, one on either side of the TiN_3 trigonal plane. This bonding mode is reminiscent of the η^3 bonding mode sometimes observed for benzyl ligands⁸ and is signaled by similar bond alternations in the aryl rings. Only the “normal” NRAr ligand is oriented properly for overlap of its nitrogen lone pair with a vacant Ti d-orbital that lacks Ti–N σ^* character, and the Ti–N(3) distance of 1.933(3) Å reflects this: the Ti–N(1) and Ti–N(2) distances are 2.005(3) and 1.992(3) Å, respectively. The frozen-glass EPR spectrum of $Ti(NRAr)_3$ in toluene is indicative of an anisotropic species,⁹ whereas the molecule’s solution ²H NMR spectrum shows only a single resonance down to $-95^\circ C$ (a fluxional process presumably renders the three NRAr ligands equivalent in solution).

Addition of colorless $V(O)(O-i-Pr)_3$ (1.0 equiv) to an ether solution of $Ti(NRAr)_3$ brings about a color change to yellow-green (eq 1). This color change is accompanied by clean



replacement of the broad ²H NMR signal characteristic of Ti-

- (1) Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733.
 (2) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
 (3) Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66.
 (4) Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.
 (5) Preparation of $Ti(NRAr)_3$: $Ti(Cl)(NRAr)_2$ (0.60 g, 0.953 mmol) was stirred with Na/Hg (0.10 g, 4.35 mmol of Na; 15 g of Hg) in 35 mL of benzene for 60 h at $28^\circ C$. The dark green reaction mixture was filtered through a bed of Celite. Evaporation of benzene from the filtrate left crude $Ti(NRAr)_3$ as a dark green solid. Three recrystallizations from pentane at $-35^\circ C$ gave pure $Ti(NRAr)_3$ as a bright green crystalline solid (0.411 g, 0.691 mmol, 73%), mp $135-137^\circ C$. ²H NMR (C_6H_6 , external $C_6D_6 = 7.15$ ppm): 4.64 ppm (s, $\Delta\nu_{1/2} = 46$ Hz). Magnetic susceptibility (Evans method, C_6D_6): $\mu_{eff} = 2.2 \mu_B$. EIMS: M^+ calcd, 594.49; found, 594.7 (9%). Anal. Calcd for $C_{36}H_{36}D_{18}N_3Ti$: C, 72.69; H, 9.15; N, 7.06. Found: C, 72.51; H, 8.98; N, 6.80.
 (6) Crystal data for $Ti(NRAr)_3$: $a = 10.601(1) \text{ \AA}$, $b = 10.810(1) \text{ \AA}$, $c = 15.958(1) \text{ \AA}$, $\alpha = 103.74(1)^\circ$, $\beta = 93.22(1)^\circ$, $\gamma = 96.33(1)^\circ$, $V = 1759.0(6) \text{ \AA}^3$, space group $P1$, $Z = 2$, mol wt = 576.74 for $C_{36}H_{36}D_{18}N_3Ti$, and $\rho(\text{calcd}) = 1.153 \text{ g/cm}^3$; $R = 0.057$ and $R_w = 0.049$.
 (7) Examples of three-coordinate Ti(III) complexes are reported as follows. (a) $Ti(N(SiMe_3)_2)_3$: Alyea, E. C.; Bradley, D. C.; Copperthwaite, R. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1580. (b) $Ti(CH(SiMe_3)_2)_3$: Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45. Barker, G. K.; Lappert, M. F.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1978**, 734. (c) $Ti(O-2,6-t-Bu_2C_6H_3)_3$: Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995. (d) $Ti(OSi-t-Bu)_3$: see ref 3 above. None of these complexes has been characterized by X-ray crystallography, although the structure of $Ti(N(SiMe_3)_2)_3$ has been cited as unpublished results in a review article on three-coordination in metal complexes: Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

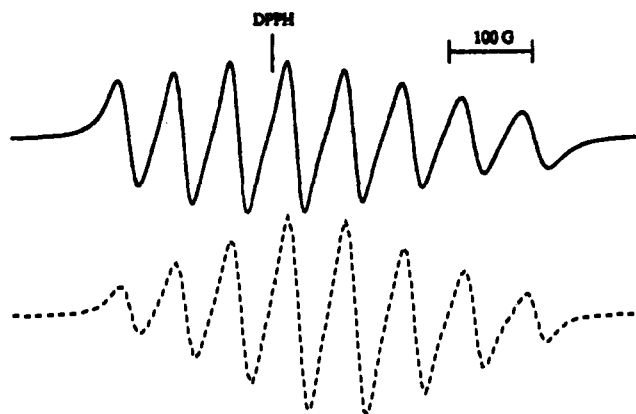


Figure 2. Solution EPR spectrum of $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$ in toluene at 240 K (—) and simulation (---) with parameters given in the text.

$(\text{NRAr})_3$ (4.64 ppm, $\Delta\nu_{1/2} = 46$ Hz), with a sharper peak corresponding to the single product (2.29 ppm, $\Delta\nu_{1/2} = 10$ Hz). All characterization data are consistent with formulation of this product as the heterobinuclear μ -oxo complex depicted in eq 1;¹⁰ the complex is a crystalline solid obtained in high yield. An X-ray diffraction study confirmed the proposed connectivity for $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$;¹¹ the V—O—Ti linkage lies on a crystallographic threefold axis, and the propellor conformation adopted by the $\text{Ti}(\text{NRAr})_3$ moiety is nearly identical to that observed for other $\text{M}(\text{X})(\text{NRAr})_3$ complexes ($\text{M} = \text{Ti}$, $\text{X} = \text{Cl}$;⁴ $\text{M} = \text{Sn}$, $\text{X} = \text{I}$, CH_3 ¹²).

The solution EPR spectrum (toluene, 240 K; Figure 2) of the binuclear complex consists of an octet ($A_{\text{iso}}(^{51}\text{V}) = 63.9 \times 10^{-4} \text{ cm}^{-1}$), centered at $g_{\text{iso}} = 1.957$. This g_{iso} value and the observed ^{51}V hyperfine splitting are strikingly similar to the literature EPR data for $\text{V}(\text{O}-t\text{-Bu})_4$ ($A_{\text{iso}}(^{51}\text{V}) = 64 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\text{iso}} = 1.964$).¹³ The frozen-glass EPR spectrum (toluene, 77 K) of $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$ is indicative of an axially-symmetric system, and a reasonable simulation can be obtained

(8) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.

(9) See supplementary material for EPR data and experimental procedure.

(10) Preparation of $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$: a -35 °C solution of $\text{Ti}(\text{NRAr})_3$ (399.6 mg, 0.672 mmol) in 10 mL of ether was added to a thawing solution of $\text{V}(\text{O})(\text{O}-i\text{-Pr})_3$ (164.0 mg, 0.672 mmol) in 5 mL of ether. After the mixture was stirred for 3 h at 30 °C, evaporation of solvent provided a yellow-green solid. Three recrystallizations (pentane, -35 °C) yielded pure $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$ (434.7 mg, 0.518 mmol, 77%), mp 154–156 °C. ^1H NMR (ppm, C_6D_6): 6.76 (s, para ArH, $\Delta\nu_{1/2} = 10$ Hz), 6.11 (s, ortho ArH, $\Delta\nu_{1/2} = 77$ Hz), 4.15 (s, $\text{OCH}(\text{CH}_3)_2$, $\Delta\nu_{1/2} = 203$ Hz), 2.23 (s, ArCH_3 , $\Delta\nu_{1/2} = 12$ Hz), 2.20 (s, $\text{C}(\text{CD}_3)_2\text{CH}_3$, very broad); no signal corresponding to $\text{OCH}(\text{CH}_3)_2$ was located. ^2H NMR (Et_2O , external $\text{C}_6\text{D}_6 = 7.15$ ppm): 2.29 ppm (s, $\Delta\nu_{1/2} = 10$ Hz). Magnetic susceptibility (Evans method, C_6D_6): $\mu_{\text{eff}} = 2.4 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{45}\text{H}_{57}\text{D}_{18}\text{N}_3\text{O}_4\text{TiV}$: C, 64.42; H, 9.01; N, 5.01. Found: C, 64.76; H, 9.22; N, 4.84.

(11) Crystal data for $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$: $a = 17.315(3)$ Å, $c = 14.330(2)$ Å, $V = 3721(2)$ Å³, space group $P3$, $Z = 3$, mol wt = 839.04 for $\text{C}_{45}\text{H}_{57}\text{D}_{18}\text{N}_3\text{O}_4\text{TiV}$, and $\rho(\text{calcd}) = 1.123 \text{ g/cm}^3$; $R = 0.082$ and $R_w = 0.081$. Full details will be published elsewhere.

(12) Laplaza, C.; Davis, W. M.; Cummins, C. C. *Organometallics* **1995**, *14*, 577.

(13) Kokoszka, G. F.; Allen, H. C., Jr.; Gordon, G. *Inorg. Chem.* **1966**, *5*, 91.

with $g_{\parallel} = 1.949$ ($A_{\parallel}(^{51}\text{V}) = 153.8 \times 10^{-4} \text{ cm}^{-1}$) and $g_{\perp} = 1.961$ ($A_{\perp}(^{51}\text{V}) = 19.0 \times 10^{-4} \text{ cm}^{-1}$);⁹ these values compare very favorably with the corresponding parameters reported for $\text{V}(\text{O}-t\text{-Bu})_4$: $g_{\parallel} = 1.940$ ($A_{\parallel}(^{51}\text{V}) = 125 \times 10^{-4} \text{ cm}^{-1}$) and $g_{\perp} = 1.984$ ($A_{\perp}(^{51}\text{V}) = 36 \times 10^{-4} \text{ cm}^{-1}$).¹³ Consistent with EPR data indicating that the unpaired electron is localized on vanadium, ^1H NMR resonances for the $\text{Ti}(\text{NRAr})_3$ portion of the molecule are relatively sharp, whereas the signals ascribed to the $\text{V}(\text{O}-i\text{-Pr})_3$ moiety are severely broadened.¹⁴ No reaction is observed between $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$ and methyl iodide (3 equiv, 24 h, 29 °C), showing that formation of the binuclear complex (eq 1) is irreversible.¹⁵

Examples of μ -oxo bridge assembly by inner-sphere electron transfer have been documented; the reaction has been referred to as incomplete oxygen atom transfer.^{16,17} A profitable way of viewing eq 1 is as an analogue of the classic Taube experiment, in which $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ reduces $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ with chlorine atom transfer.¹⁸ With oxygen as the bridging atom (eq 1), the successor complex does not dissociate because only one electron is transferred. We view the $\text{OTi}(\text{NRAr})_3$ portion of the binuclear complex as a bulky and relatively inert "titanoxide" ligand, which we hope will facilitate the synthesis and study of new low-coordinate vanadium complexes.

Acknowledgment. C.C.C. thanks the MIT Department of Chemistry for financial support. P.W.W. thanks the Undergraduate Research Opportunities Program at MIT for support. M.A.R. is grateful for a R. W. Young Fellowship. We thank Aaron L. Odom for assistance with the X-ray crystallography.

Supplementary Material Available: Experimental details for the X-ray structure of $\text{Ti}(\text{NRAr})_3$, tables of positional parameters, bond lengths and angles, and experimental details for the collection of EPR data for $(i\text{-PrO})_3\text{VOTi}(\text{NRAr})_3$ and $\text{Ti}(\text{NRAr})_3$ (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9432978

(14) La Mar, G. N.; Horrocks, W. D., Jr.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(15) $\text{Ti}(\text{NRAr})_3$ reacts rapidly with CH_3I to produce diamagnetic $\text{Ti}(\text{I})(\text{NRAr})_3$. Wanandi, P. W.; Cummins, C. C. Unpublished results.

(16) For reviews that include references to this type of bridge assembly, see: (a) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125. (b) West, B. O. *Polyhedron* **1989**, *8*, 219. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. Several examples of VOV bridge assembly have been studied recently; see, for example: (d) Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 762. (e) Knopp, P.; Wiegardt, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363. (f) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911. (g) Brand, S. G.; Edelstein, N.; Hawkins, C. J.; Shalimoff, G.; Snow, M. R.; Tiekink, E. R. T. *Inorg. Chem.* **1990**, *29*, 434.

(17) For coordination of $\text{M}(\text{O})\text{Cp}_2$ ($\text{M} = \text{Mo}$, W) to rhodium and iridium centers (without electron transfer), see: (a) Pilato, R. S.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 1986. For coordination of VO^{2+} species to $\text{Sn}(\text{IV})$, see: (b) Cashin, B.; Cunningham, D.; Gallagher, J. F.; McArdle, P. *Polyhedron* **1989**, *8*, 1753.

(18) Taube, H. In *Nobel Lectures in Chemistry 1981–1990*; Frängsmyr, T., Malmström, B. G., Eds.; World Scientific: Singapore, 1992; p 113.