Synthesis and Reactivity of a Vanadium(III)−Methyl Complex Stabilized by Hexamethylsilazanate Ligands

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*Summary: The vanadium(III)−Me complex [$(Me_3Si)_2N]_2$-VMe(THF) (**1**) was prepared by reaction of the corresponding V−Cl derivative with Me_2Mg, and its X-ray crystal structure has been determined. The methyl complex reacts with 3 equiv of RNC (R = Bu^t, Xylyl) to give isocyanide-coupled products, is oxidized by styrene oxide affording a V(IV) μ-O dimer, and on heating eliminates CH_4 via metalation of a $-N(SiMe_3)_2$ ligand.*

Organometallic chemistry of paramagnetic compounds is relatively undeveloped compared to that of more commonly studied diamagnetic species.[1,2] Here we describe the synthesis and structure of a reactive 4-coordinate V(III)−methyl complex $[(Me_3Si)_2N]_2VMe$(THF) as well as its thermolysis, multiple insertion of isocyanides, and oxidation with styrene oxide. The compounds we report are highly crystalline and are therefore amenable to study by X-ray crystallography, an important factor because the d^2 electronic configuration of V(III) is high spin in most cases and typically inaccessible by EPR spectroscopy. Early studies of low-valent vanadium hydrocarbyls concentrated on complexes of the type Cp'_2VR (Cp′ = η^5-C_5H_5, η^5-C_5H_4Me, η^5-C_5Me_5), where R = alkyl, aryl, acetylide, and allyl, were well characterized.[3] More recently, the groups of Teuben and Floriani have reported a plethora of hydrocarbyl chemistry of V(III) derived from $CpVCl_2(PMe_3)_2$[4,5] and $V(Mes)_3$(THF) (Mes = 2,4,6-$Me_3C_6H_2$),[6,7] respectively,[8,9] and the syntheses of $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$[10] and $[(R_2N)_3V]_2(\mu\text{-}N_2)$ (R = *i*-Pr, Cy)[11] marked the unprecedented coordination of dinitrogen to V(III).

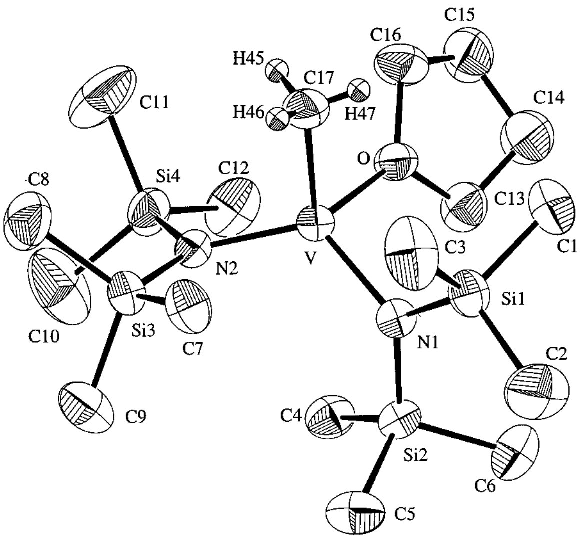

Figure 1. ORTEP drawing of $[(Me_3Si)_2N]_2VMe$(THF) (**1**) with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: V−N(1) = 1.973(2), V−N(2) = 1.943(2), V−C(17) = 2.095(4), V−O = 2.051(2), N−Si$_{av}$ = 1.733(4); O−V−C(17) = 93.3(1), O−V−N(1) = 100.06(8), N(2)−V−C(17) = 104.3(1), N(1)−V−C(17) = 116.8(1), O−V−N(2) = 117.83(9), N(1)−V−N(2) = 121.52(9).

Treatment of $[(Me_3Si)_2N]_2VCl$(THF)[12] with 1/2 equiv of Me_2Mg in THF (Scheme 1) resulted in a deep blue solution from which **1** was isolated in yields of ca. 60%. The magnetic moment of **1** is consistent with a high-spin d^2 electronic configuration (μ_{eff} = 2.72 μ_B). Formulation of $[(Me_3Si)_2N]_2VMe$(THF) as a 4-coordinate monomer was confirmed by an X-ray crystal structure (Figure 1).[13] Bond angles about V are such that the O−V−C(17) angle is the smallest (93.3(1)°) and the N(1)−V−N(2) angle is the largest (121.52(9)°). The sums of the angles about N(1) and N(2) are both near 360°, indicating that the amide ligands are probably acting as 3-electron donors[14] toward the V giving the metal a formal electron count of 14. The V−N bond lengths (V−N(1) = 1.973(2) Å; V−N(2) = 1.943(2) Å) as well as the N−Si bond lengths (N−Si$_{av}$ = 1.733(4) Å) are comparable to those in other V(III) compounds

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

[3] Connelly, N. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1981; Vol. 3, p 647.

[4] Nieman, J.; Scholtens, H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *186*, C12.

[5] Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.

[6] Seidel, W.; Kreisel, G. *Z. Chem.* **1974**, *14*, 25.

[7] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 886.

[8] For studies of hydrocarbyl derivatives of the CpV(III) fragment, see the following and references therein: Buijink, J.-K.; Kloetstra, K. R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1996**, *15*, 2523.

[9] For studies of the reaction chemistry of $V(Mes)_3$(THF) see the following and references therein: (a) Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1794. (b) Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1802. (c) Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1811.

[10] Buijink, J.-K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004.

[11] Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.

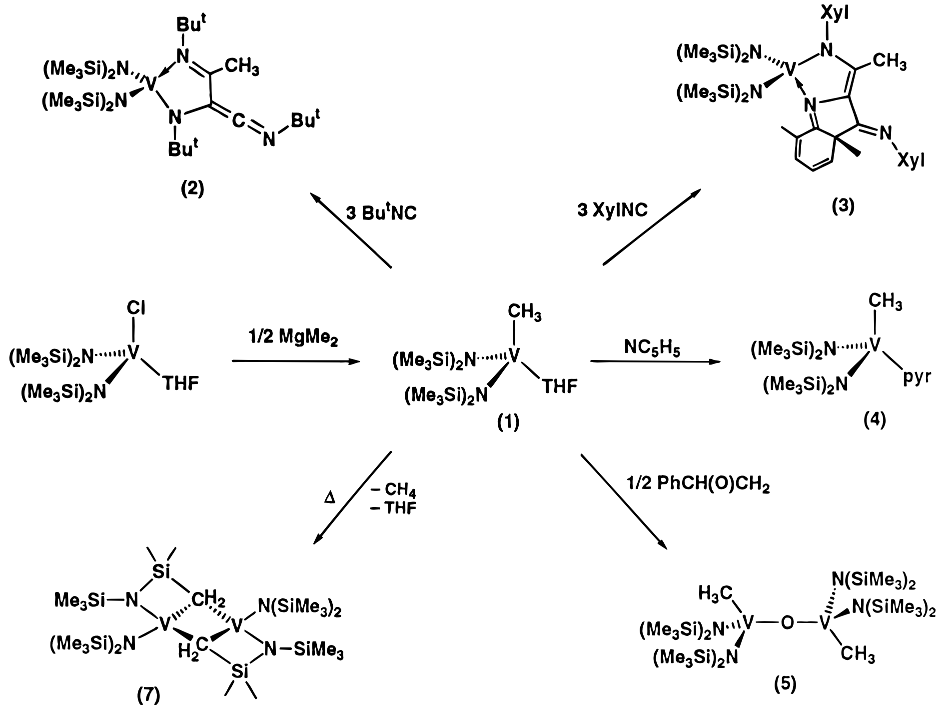
[12] Berno, P.; Minhas, R.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.

[13] Crystallographic data for **1**: $C_{17}H_{47}N_2OSi_4V$, monoclinic, $P2_1/c$, a = 8.4393(2) Å, b = 17.3149(3) Å, c = 19.1506(4) Å, β = 99.134(1)°, V = 2762.92(13) Å^3, Z = 2, ρ_{calcd} = 1.10 g/cm^3, μ = 5.41 cm^{-1}, T = 159 K. Data were collected using a Siemens SMART diffractometer/CCD area detector and the structure refined on F using standard least-squares and Fourier techniques. The final residuals for 414 variables refined against 3018 data for which $I > 3\sigma(I)$ were R = 0.0346 and R_w = 0.0441.

[14] The covalent convention is followed in counting electrons. See: Crabtree, R. H. *The Organometallic Chemistry of the Elements*, 2nd ed.; Wiley: New York, 1994.

S0276-7333(96)00706-6 CCC: $12.00

Scheme 1



containing the bis(trimethylsilyl)amide ligand.[12,15–17] The THF ligand is datively coordinated with a V–O bond length (2.051(2) Å) close to those observed in (mesityl)$_3$V(THF) (2.069(4) Å)[7] and (Ph$_2$N)$_3$V(THF) (2.059(2) Å).[11] Relative to other structurally characterized species containing the V–Me unit, the V–C(17) distance is on the shorter end at 2.095(4) Å. For comparison, V–C distances of 2.310(5), 2.31(1), and 2.219(4) Å are observed in the complexes *trans*-(DMPE)$_2$VMe$_2$,[18] (DMPE)$_2$V(CO)$_2$Me,[19] and CpVMe(DMPE)[20,21] (DMPE = 1,2-bis(dimethylphosphino)ethane), respectively, consistent with the greater coordination numbers and lower metal oxidation states for these cases. More similar V–C bond lengths are seen in the V(IV) dimer [CpVMe(μ-N-*p*-tolyl)]$_2$ (2.090(4) Å)[22] and the V(V) bimetallic Li(μ-NSiBu$^t_3$)$_2$VMe$_2$ (2.057(8), 2.043(5) Å).[23]

Hoping that the bis[bis(trimethylsilyl)amide] ligand system would provide a stable vanadium fragment to explore the chemistry of the V(III)–C σ-bond, we first investigated the reactivity of **1** with isocyanides. The reaction between 3 equiv of Bu^{t}NC and **1** led to the loss of THF and the coupling of the three Bu^{t}NC units as shown in Scheme 1. The N,N-chelate ring of **2** binds formally with one dative and one coordinate covalent V–N interaction forming a five-membered diazametallacyle with an exocyclic keteneimine functionality.[24] A strong absorption in the IR spectrum at 1987 cm^{-1} may be attributed to the keteneimine,[25] and a medium band at 1518 cm^{-1} is consistent with a C=N double bond. The magnetic moment of **2** was measured as 2.79 μ_B, and its ^{1}H NMR spectrum was featureless. Related connectivity resulting from the insertion of Bu^{t}NC into the Ta–H bond of (ArO)$_2$Cl$_2$TaH(PMe$_2$Ph)$_2$ (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) has been reported.[26,27] As in that system, we assume the coordination of a third equivalent of isocyanide to an intermediate keteneimine affords the isolated product, an assumption substantiated by the analogous additions of phosphines and isocyanides to the isolable metalloxy ketene derivative Cp*$_2$ThCl[OC(CO)SiR$_3$] (Cp* = η^5-C$_5$Me$_5$; SiR$_3$ = Si(SiMe$_3$)$_3$, SiBu^{t}Ph$_2$).[28]

Reaction of **1** with 3 equiv of XylNC (Xyl = 2,6-Me$_2$C$_6$H$_3$) gave violet solutions from which compound **3** was isolated in good yield. The IR spectrum shows a strong $\nu_{C=N}$ at 1636 cm^{-1} and lower energy $\nu_{C=C}$ bands. While the coordination sphere about the vanadium is similar to that in **2**, further rearrangement involving a

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[15] Berno, P.; Gambarotta, S. *J. Chem. Soc., Chem Commun.* **1994**, 2419.

[16] Berno, P.; Gambarotta, S. *Organometallics* **1994**, *13*, 2569.

[17] Berno, P.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822.

[18] Morris, R. J.; Wilson, S. R.; Girolami, G. S. *J. Organomet. Chem.* **1994**, *480*, 1.

[19] Protasiewicz, J. D.; Bianconi, P. A.; Williams, I. D.; Liu, S.; Rao, C. P.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 4134.

[20] Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946.

[21] Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Huffman, J. C.; Jagner, S.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354.

[22] Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1995**, *497*, 161.

[23] de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1990**, *9*, 2207.

[24] Connectivity in compounds **2** and **3** have been confirmed by X-ray crystal structures, the full details of which will be presented in a full paper. The valence bond formalisms drawn in Scheme 1 are consistent with the solid-state data. Crystallographic data for **2**: C$_{28}$H$_{66}$N$_5$Si$_4$V, monoclinic, $P2_1/n$, a = 17.2448(3) Å, b = 11.2213(2) Å, c = 20.8749(2) Å, β = 107.325(1)°, V = 3856.23(13) Å^3, Z = 4, ρ_{calcd} = 1.10 g/cm^3, μ = 4.04 cm^{-1}, T = 155 K. Data were collected and the structure refined as for **1**. The final residuals for 343 variables refined against 4137 data for which $I > 3\sigma(I)$ were R = 0.0393 and R_w = 0.0528. Crystallographic data for **3**: C$_{40}$H$_{66}$N$_5$Si$_4$V, monoclinic, $P2_1/n$, a = 10.4622(5) Å, b = 20.3892(10) Å, c = 20.7733(10) Å, β = 96.250(1)°, V = 4404.93(62) Å^3, Z = 4, ρ_{calcd} = 1.18 g/cm^3, μ = 3.67 cm^{-1}, T = 168 K. Data were collected and the structure refined as for **1**. The final residuals for 414 variables refined against 3018 data for which $I > 3\sigma(I)$ were R = 0.0432 and R_w = 0.0518.

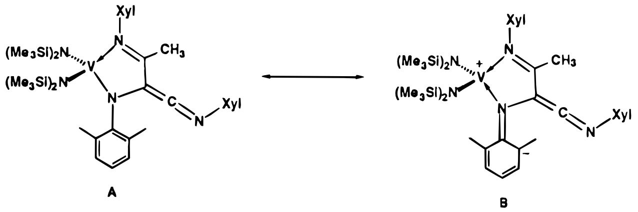
[25] Barker, M. W.; McHenry, W. E. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1980; p 701.

[26] Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1233.

[27] Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 3232.

[28] Radu, N. S.; Engeler, M. P.; Gerlach, C. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 3621.

Xyl group is apparent. There is literature precedent[29] that **3** is derived from the Xyl analog of **2** and that the transformation is driven by the accessibility of resonance structure **B** and the greater π-delocalization in the product ligand system. Significantly, reactions between **1** and XylNC in ratios of 1:1 or 1:2 also led to isolation of **3** in corresponding diminished yields, suggesting that the rate-determining step comes early in the oligomerization. Attempts to trap intermediates by conducting similar reactions with the pyridine adduct **4** or with **1** in the presence of PEt_3 or PMe_2Ph (4 equiv) did not divert the course of the reaction.



Oxidation of **1** with $^1/_2$ equiv of styrene oxide yielded a green, (μ-oxo)vanadium(IV) dimer (**5**). This is notable since, due to the strength of the V═O double bond, species containing the [V−O−V] unit without other oxo ligands are relatively rare.[30−34] The reaction probably proceeds by the coordination of an initially formed vanadium(V) oxo (i.e. $[(Me_3Si)_2N]_2V(O)(Me)$, **6**) to **1,** as seen in the syntheses of $[(Mes)_3V]_2(\mu\text{-}O)$,[35] $\{V[OC(Mes){=}NPh]_3\}_2(\mu\text{-}O)$,[35] or $(Pr^iO)_3VOTi(NRAr)_3$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$).[36] In fact, C_6D_6 solutions of **1** or **5** treated with 1 equiv of styrene oxide turned clear yellow over several hours and exhibit spectroscopic profiles consistent with clean conversion to **6**,[37] although to-date we have been unable to isolate **6** as a pure, crystalline solid. Complex **5** is paramagnetic ($\mu_{eff} = 1.74\ \mu_B$/V), gives a broad singlet in the ^1H NMR for the $SiMe_3$ groups and has a strong band in the IR spectrum at 709 cm^{-1} attributable to the V−O−V stretch.

The dimer **5** crystallizes[38] with a C_2 axis passing through the bridging O atom (Figure 2). The V−O bond length (1.7943(4) Å) and the V−O−V* angle (178.2(2)°) are similar to those in other structurally characterized $[V{-}O{-}V]^{n+}$ compounds described above. The shorter V−Me distance (2.054(3) Å) relative to that in **1** simply reflects the +1 increase in the V oxidation state on going to **5**.

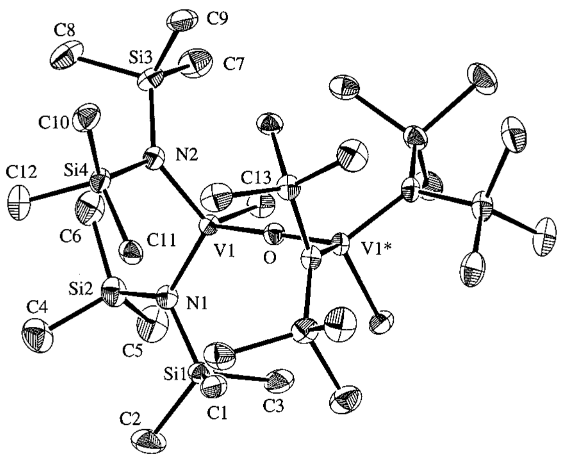


Figure 2. ORTEP drawing of $\{[(Me_3Si)_2N]_2VMe\}_2(\mu\text{-}O)$ (**5**) with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: V−N(1) = 1.881(2), V−N(2) = 1.908(2), V−C(13) = 2.054(3), V−O = 1.7943(4), Si−N$_{av}$ = 1.767(5); V−O−V* = 178.2(2), N(1)−V−C(13) = 97.0(1), O−V−C(13) = 99.0(1), O−V−N(2) = 110.6(1), N(1)−V−N(2) = 114.0(1), N(2)−V−C(13) = 114.2(1), O−V−N(1) = 120.31(8).

Thermolysis of **1** in hexanes (80 °C, 5 min) resulted in the loss of coordinated THF and the elimination of CH_4 to yield the known V(III) dimer $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ (**7**) in 73% yield. This compound was previously isolated from the reaction of $VCl_3(THF)_3$ with 3 equiv of $LiN(SiMe_3)_2$.[12] Monitoring by NMR spectroscopy in C_6D_6 showed the reaction to be very clean with only signals attributable to **7**,[39] THF, and CH_4 being detected. Metalation of the $-N(SiMe_3)_2$ ligand by a γ-hydrogen elimination across a M−X bond (X = Cl, H/D, Me, Et, CH_2SiMe_3) has been recognized in other early transition metal (d^0),[40−42] and f-block[43,44] systems. In the present case we suspect the elimination of CH_4 is preceded by the dissociation of THF to give the 3-coordinate intermediate $[(Me_3Si)_2N]_2VMe$; mechanistic studies into this aspect of the reactivity and related chemistry are in progress.

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Supporting Information Available: Text giving synthetic and characterization details for compounds **1**−**5** and **7** and experimental details for the X-ray structures of compounds **1** and **5** including tables of bond distances and angles, atomic coordinates and *B* values, and anisotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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[29] Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56.

[30] Chandrasekhar, P.; Bird, P. H. *Inorg. Chem.* **1984**, *23*, 3677.

[31] Money, J. K.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1987**, *26*, 944.

[32] Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363.

[33] Brand, S. G.; Edelstein, N.; Hawkins, C. J.; Shalimoff, G.; Snow, M. R.; Tiekink, E. R. T. *Inorg. Chem.* **1990**, *29*, 434.

[34] Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911.

[35] Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 762.

[36] Wanandi, P. W.; Davis, W. B.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 2110.

[37] Spectroscopic data for **6**: ^1H NMR (300 MHz, C_6D_6) δ 1.29 (s, V−*Me*, $\Delta\nu_{1/2}$ ca. 25 Hz), 0.39 (s, $SiMe_3$); ^{51}V NMR (78.94 MHz, C_6D_6) δ 222 ($\Delta\nu_{1/2}$ ca. 180 Hz). IR (KBr, mineral oil): $\nu_{V=O}$ = 1014 cm^{-1}.

[38] Crystallographic data for **5**: $C_{26}H_{78}N_4OSi_8V_2$, orthorhombic, *Fdd*2, a = 10.3064(2) Å, b = 26.3320(4) Å, c = 33.6771(2) Å, V = 9139.54(28) Å^3, Z = 8, ρ_{calcd} = 1.15 g/cm^3, μ = 6.42 cm^{-1}, T = 156 K. Data were collected and the structure refined as for **1**. The final residuals for 341 variables refined against 2550 data for which $I > 3\sigma(I)$ were R = 0.0208 and R_w = 0.0259.

[39] Although **7** is paramagnetic, C_6D_6 solutions show several low-intensity resonances in the ^1H NMR spectrum that are indicative of the complex. ^1H NMR (300 MHz, C_6D_6): δ 0.96, 0.64, 0.39, 0.21, −1.2.

[40] Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29.

[41] Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3627.

[42] Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

[43] Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728.

[44] Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.