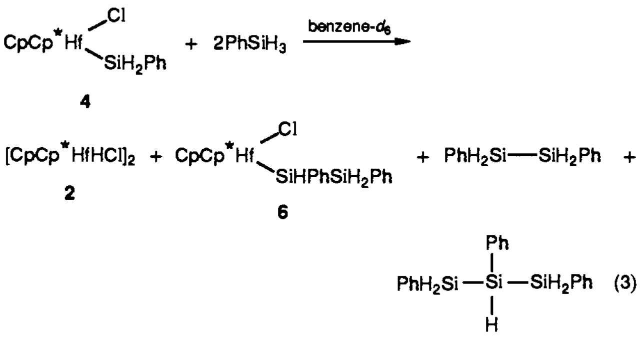
celerated by $PhSiH_3$. Under pseudo-first-order conditions with excess $PhSiH_3$, disappearance of **4** is first-order in both **4** and $PhSiH_3$ over three half-lives ($k(70\ °C) = 3.7\ (3) \times 10^{-4}\ M^{-1}\ s^{-1}$). The isotope effect, determined at 70 °C with use of excess $PhSiD_3$, is 2.7 (2). We propose that the latter conversion proceeds through concerted Si–Si bond-forming steps, as represented by eq (d). Presumably the acceleration effect of $PhSiH_3$ results from the better fit of $H–SiH_2Ph$ vs H–SiHPh(CpCp*HfCl) in the four-center transition state.

The σ-bond metathesis chemistry summarized above suggests a mechanism for the dehydrogenative polymerization of silanes by zirconocene and hafnocene derivatives (Scheme II). A coordinatively unsaturated hydride complex is implicated as an important intermediate, since Si–Si bond formation results in production of metal hydride species, and since hydride complexes themselves are active catalysts.[3] Such hydride species are readily formed in solution from catalyst precursors via σ-bond metathesis reactions (see Scheme I). Each catalytic cycle involves formation of a metal silyl derivative and free polysilane. Observed steric constraints on these σ-bond metathesis reactions suggest that the metal hydride interacts predominantly with the sterically less crowded $–SiH_2R$ end group of a polymer chain, giving linear chain growth. We also believe that steric constraints are such that one of the reacting silanes in a cycle must be primary (n or $m = 1$), resulting in chain growths of only one Si per cycle. Note that the mechanism proposed here involves reactions at only one M–X σ-bond, whereas a metal silylene-based mechanism[2] requires that two σ-bonds are used. Our results are consistent with involvement of only one σ-bond, since compounds **3**, **4**, and **5** are catalyst precursors for the polymerization of $PhSiH_3$, which quantitatively converts these chloro complexes to the corresponding hydrides $[CpCp^*MHCl]_2$.[3]

Using model reactions, we have detected the expected intermediates for the proposed mechanism. Thus $CpCp^*Hf(SiHPhSiH_2Ph)Cl$ (**6**), prepared independently from **1** and PhH_2SiSiH_2Ph and isolated as a 1:1 mixture of two diastereomers,[7] was identified (by ^1H NMR spectroscopy) in the slow oligomerization of $PhSiH_3$ by **4**. Addition of 2 equiv of $PhSiH_3$ to **4** resulted in formation of **2**, **6**, disilane, and trisilane after 24 h (33% conversion) (eq 3).[8] The latter three silicon-containing products were formed in a ratio of ca. 3:2:3. Free, oligomeric silanes are also observed during coupling reactions with $Cp^*_2HfH_2$ as catalyst. Presumably because of steric hindrance at the metal center, this hafnium hydride couples Si–H bonds very slowly. This allows observation (by ^1H NMR spectroscopy) of conversion of $PhSiH_3$ to disilane, which is followed more slowly by appearance of trisilane and finally, tetrasilane.[8] When heated to 120 °C for a day, the silane compounds are converted to higher molecular weight oligomers. These observations provide evidence for the stepwise nature of chain growth. Early in reaction of $Cp^*_2HfH_2$ with PhH_2SiSiH_2Ph, significant quantities of $PhSiH_3$ are detected, establishing reversibility of Si–Si bond formation.



This catalytic cycle appears to represent a new polymerization mechanism and is unusual as a coordination polymerization in that it involves step growth of polymer rather than chain growth. The mechanism accounts for the stringent steric requirements observed for catalysts and silane monomers, since the four-center transition states are inherently quite crowded. It is hoped that further investigation will produce a more complete understanding of factors controlling reactivity and that the proposed mechanism will lead to development of better catalytic systems that allow control of stereoregularity and molecular weights of the polysilanes.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-88-0273. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990). We thank Prof. R. H. Grubbs for valuable discussions, Prof. J. F. Harrod for the synthesis of PhH_2SiSiH_2Ph, and G. A. Vaughan for a gift of $Cp^*_2HfH_2$.

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(7) For **6** (diastereomers A and B): Anal. C, H; IR (neat, CsI, cm^{-1}) $\nu(SiH) = 2040, 2100$; ^1H NMR (benzene-d_6, 22 °C, 300 MHz) δ 1.79 (s, 30 H, Cp*, A, B), 4.65–4.92 (m, 6 H, SiH, SiH_2, A, B), 5.73 (s, 5 H, Cp, A), 5.76 (s, 5 H, Cp, B), 7.10 (m, 4 H, p-C_6H_5, A, B), 7.19 (m, 8 H, m-C_6H_5, A, B), 7.71 (m, 8 H, o-C_6H_5, A, B); ^{29}Si NMR (benzene-d_6, 22 °C, 59.6 MHz) δ –9.05, –9.86 (d, $J_{SiH} = 152$ Hz, $HfSi\mathit{H}PhSiH_2Ph$, A, B), –43.91, –50.43 (t, $J_{SiH} = 183$ Hz, $HfSiHPhSi\mathit{H}_2Ph$, A, B).

(8) Silanes were identified by mass spectroscopy and ^1H and ^{29}Si NMR spectroscopy: ^{29}Si NMR data (benzene-d_6, 22 °C, 59.6 MHz) PhH_2SiSiH_2Ph, δ –61.3 (t), $PhH_2SiSiHPhSiH_2Ph$, δ –68.0 (d), –58.6 (t), $PhH_2Si(SiHPh)_2SiH_2Ph$, δ –71.2 (d), –57.4 (t).

First Examples of Three-Coordinate Manganese(III) and Cobalt(III): Synthesis and Characterization of the Complexes $M[N(SiMe_3)_2]_3$ (M = Mn or Co)

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Received May 30, 1989

In transition-metal complexes the coordination number three is often regarded as a rarity. Nonetheless, the number of three-coordinate compounds now known is considerable.[1] Among the better known examples are the series of M^{3+} compounds $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, V, Cr, and Fe) which have been studied extensively.[2] For manganese and cobalt several three-coordinate species have also been reported.[1-7] Without exception, these involve the 2+ oxidation state, and three coordination remains unknown for the somewhat less stable 3+ oxidation state of these elements. For example, the great majority of Co^{3+} (d^6) complexes have a geometry based upon the octahedron. Moreover, they are almost always diamagnetic which gives maximized CFSE and kinetic stability. However, a small, but important, number of four- and five-coordinate Co^{3+} complexes have been reported.[8,9] Similarly, manganese(III) (and higher oxidation state) complexes are not as numerous as those of Mn^{2+}, but they have attracted considerable attention owing to their significance for biological systems.[10] Its d^4-electron configuration may, under certain

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(1) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1. The number of three-coordinate transition-metal complexes has greatly increased since this review was published.

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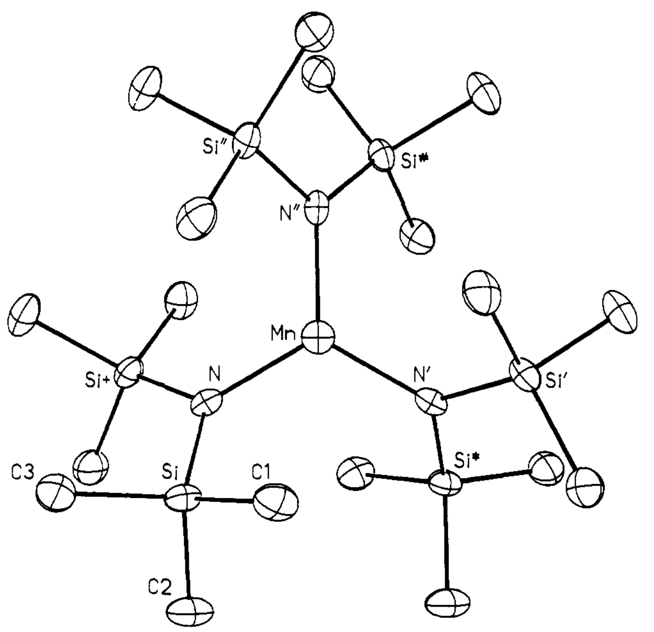

Figure 1. Computer-generated thermal ellipsoid plot of **1**, H atoms are omitted for clarity. Important bond distances (Å) and angles (deg) with values for **2** in brackets are as follows: M = Mn{Co}, M–N = 1.890 (3) {1.870 (3)}, Si–N = 1.755 (2) {1.754 (2)}, Si–N–Si = 120.4 (1) {120.6 (1)}.

conditions, favor a four-coordinate, square-planar geometry, and this is the lowest coordination number that has been authenticated for this ion. In this paper the first synthesis, spectroscopic and structural characterization of the novel three-coordinate Mn^{3+} and Co^{3+} species, $M[N(SiMe_3)_2]_3$ (M = Mn, **1**, Co, **2**), are described.

The title compounds were synthesized, in moderate yield, by treating the divalent species $M^{II}[N(SiMe_3)_2]_2$[11,12] with 1 equiv of $BrN(SiMe_3)_2$[13] in toluene solution at ca. 0 °C. Violet rod-like crystals (mp = 108–110 °C) of the manganese species **1** and similarly formed dark olive green crystals (mp = 86–88 °C) of the cobalt compound **2** were obtained upon volume reduction and cooling in a –20 °C freezer. The X-ray structures[14] of the isomorphous crystals of **1** and **2** reveal a three-coordinate planar MN_3[15] structure in both molecules. There is a crystallographically imposed 3-fold rotation axis perpendicular to the MN_3 plane in each case. The Mn-N distance is 1.890 (3) Å, and the Co–N bond length is 1.870 (3) Å. The NSi_2 plane forms a dihedral angle to the MN_3 plane of 50° for **1** and 49° for **2**. The structure of the manganese compound is illustrated in Figure 1, and the important bond distances and angles for both **1** and **2** are provided in the figure caption.

The magnetic moments of **1** and **2** in C_6D_6/C_6H_6 solution are 5.38 and 4.73 μ_B, respectively, at 297.3 K indicating high spin d^4 and d^6 configurations. The ^1H NMR spectrum of **1** at 297.3 K displays a broad singlet ($\nu_{1/2}$ = 680 Hz) at +27.3 ppm, and for **2** a somewhat narrower singlet ($\nu_{1/2}$ = 160 Hz) was observed at +1.72 ppm. The UV-vis data in cm^{-1} for pentane solutions of **1** and **2**, with ϵ values in parentheses, are as follows: **1**, 33 800 (7120), 26 740 (4220), 21 280 (4160), and 17 600 (3890); **2**, 37 300 (4500), 31 450 (3900), 22 030 (2900), and 16 670 (3600).

The complexes **1** and **2**, in addition to being the first three-coordinate Mn(III) and Co(III) compounds, are also the first well-characterized nonchelating amide derivatives of Mn(III) and Co(III).[16] Previous attempts to synthesize them by using $LiN(SiMe_3)_2$ and various Mn(III) or Co(III) precursor salts or electrolytic oxidation were apprently unsuccessful.[17] The relatively simple route involving the addition of $BrN(SiMe_3)_2$ to the divalent precursor avoids the use of the incipient $[-N(SiMe_3)_2]^-$ ion which probably causes reduction of the oxidizing Mn(III) or Co(III) centers. This problem does not arise in the synthesis of the corresponding Ti^{3+}, V^{3+}, Cr^{3+}, or Fe^{3+} species where none of the precursor trihalides are strongly oxidizing. The crystals of **1** and **2** are isomorphous with the series $M[N(SiMe_3)_2]_3$ (M = Al, Ga, Ti, V, Cr, Fe).[1,2] The Mn–N bond length is very close to the length of the Cr–N bond, 1.903 (6) Å, in $Cr(N(SiMe_3)_2]_3$,[1] whereas the Co–N bond is considerably shorter than the Fe–N bond, 1.917 (4) Å, in $Fe[N(SiMe_3)_2]_3$.[1] Both the Mn–N and Co–N bonds are significantly shorter than the terminal M–N bonds seen in $[LiMn\{N(SiMe_3)_2\}_3]$[5] (Mn–N = 2.023 (3) Å or in the dimers $[Mn\{N(SiMe_3)_2\}_2]_2$[4,5] (Mn–N = 1.998 (3) Å), $[Co\{N(SiMe_3)_2\}_2]_2$[5] (Co–N = 1.916 (5) Å) or in the monomer $Co[N(SiMe_3)_2]_2(PPh_3)$ (Co–N = 1.928 (14) Å)[3] which involve three coordination at the metal(II) center. This is, of course, consistent with the higher oxidation state of the metals in **1** and **2**.

Since **1** and **2** possess the high spin d^4 and d^6 electron configurations they both have a ground-state ^5D term which is presumably split into an A_1', E' and E'' pattern so that at least two absorptions are expected in the visible region. For the cobalt compound **2**, the bands at 16 670 and 22 030 cm^{-1} are probably due to the $^5A_1' \rightarrow {}^5E''$ and $^5A_1' \rightarrow {}^5E'$ transitions. Higher energy bands were also observed at 31 450 and 37 300 cm^{-1} which probably arise from charge-transfer processes. In the manganese species **1** the lowest energy absorptions were observed at 17 600 and 21 280 cm^{-1} which may be due to $^5E' \rightarrow {}^5E''$ and $^5E' \rightarrow {}^5A_1'$ transitions. There are also higher energy bands at 26 740 and 33 800 cm^{-1}, and in addition there is evidence for luminescence at 23 500 cm^{-1}.

In conclusion, the compounds **1** and **2**, the first three-coordinate Mn(III) and Co(III) complexes, can be readily synthesized. Moreover, the method of synthesis is one that has not been previously described and may be applicable to other transition-metal systems.[18] They are freely soluble in relatively inert hydrocarbons such as pentane or toluene and may serve as precursors to a wider range low-coordinate Mn(III) and Co(III) species. Further studies on the chemistry of **1** and **2** including their redox properties and mechanism of formation are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Tables of crystallographic data and summary of data collection and refinement, positional parameters for non-hydrogen atoms, bond distances and angles,

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(14) Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, $C_{18}H_{54}N_3Si_6Mn$, a = 16.082 (5) Å, c = 8.436 (2) Å, Z = 2, trigonal, space group $P\bar{3}\,1c$, V = 1889.5 (8) $Å^3$, 983 unique observed data, R = 0.0695; **2**, $C_{18}H_{54}N_3Si_6Co$, a = 16.068 (9) Å, c = 8.443 (3) Å, Z = 2, trigonal, space group $P\bar{3}\,1c$, V = 1888 (1) $Å^3$, 951 unique observed data, R = 0.071.

(15) (a) The MN_3 moiety, although planar in $M[N(SiMe_3)_2]_3$ (M = Al, Ga, Ti, V, Cr, or Fe), has been found to be pyramidal in the case of europium(III),[15b] scandium(III),[15b] ytterbium(III),[1] and neodymium(III)[15c] $N(SiMe_3)_2$ derivatives. (b) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669. (c) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317.

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anisotropic thermal parameters, and hydrogen coordinates, a computer-generated thermal ellipsoid plot of $Co[N(SiMe_3)_2]_3$, **2**, and synthetic details (10 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of a Novel Oxo-Bridged Dinuclear Iron(III) Complex Containing Only Oxygen Donating Ligands

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Received May 30, 1989

The iron-containing enzymes, methane monooxygenase (MMO),[1] ribonucleotide reductase (RR),[2,3] and purple acid phosphatase (PAP),[2,4,5] are believed to contain oxo- or hydroxo- and carboxylato-bridged dinuclear iron centers similar to that in hemerythrin.[6] Despite this similarity, the functions of these proteins are intriguingly diverse, comprising monooxygenase, reductase, and oxygen transport activities.[7] This diversity may be caused by different coordination environments in the proteins afforded, inter alia, by different terminal ligands that anchor the bridged dinuclear iron cores to the polypeptide chains. For example, EXAFS data for MMO and RR indicate more oxygen coordination to iron in these enzymes than in hemerythrin.[1c,2] Many μ-oxobis(μ-carboxylato)diiron(III) complexes have been prepared by using either exclusively nitrogen or mixed oxygen/nitrogen donor terminal ligands to model physical properties of these proteins.[8] We report here the synthesis and characterization of the first such complex with exclusive oxygen coordination, $[Fe_2O(O_2CCH_3)_2\{[OP(OEt)_2]_3Co(C_5H_5)\}_2]$ (**1**). The unique magnetic and spectroscopic properties exhibited by this complex afford important new benchmarks for evaluating structural proposals concerning the diiron centers in MMO, RR, and PAP.

An acetonitrile solution of $Na\{[OP(OEt)_2]_3Co(C_5H_5)\}$[9] (1.10 g, 1.97 mmol, 20 mL) was slowly added to a mixture of $(Et_4N)_2[Fe_2OCl_6]$[10] (0.600 g, 1.0 mmol) and excess $NaO_2CCH_3\cdot 3H_2O$ (0.40 g, 2.9 mmol) in 20 mL of acetonitrile. After stirring for an hour, the red reaction mixture was filtered and concentrated. Slow cooling to −10 °C afforded red prisms (0.800 g, 57%) which proved to be suitable for X-ray diffraction study.[11]

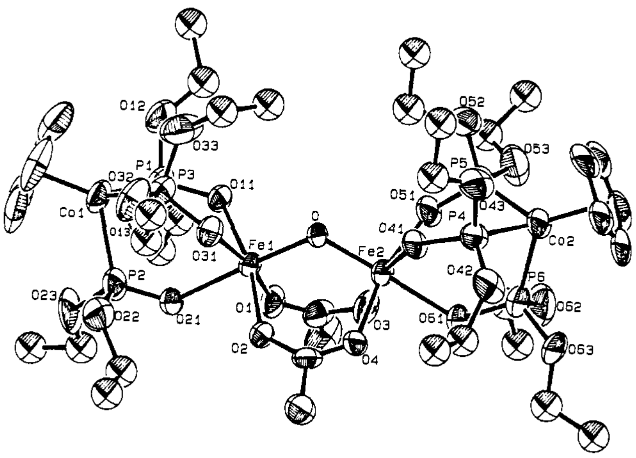

Figure 1. ORTEP drawing of **1** showing the 40% probability thermal ellipsoids and atom labels for all the metal oxygen and phosphorus atoms. Carbon atoms on ethyl groups are represented as isotropic spheres with $B = 6.0$ Å^2 for clarity; atom disorder is not shown. Selected interatomic distances (Å) and angles (deg) are as follows: Fe(1)–O, 1.799 (6); Fe(2)–O, 1.791 (6); Fe(1)–O(11), 2.066 (6); Fe(1)–O(21), 2.137 (7); Fe(1)–O(31), 2.048 (8); Fe(2)–O(41), 2.057 (7); Fe(2)–O(51), 2.079 (8); Fe(2)–O(61), 2.125 (7); Fe(1)–O(1), 2.012 (9); Fe(1)–O(2), 2.023 (7); Fe(2)–O(3), 2.039 (8); Fe(2)–O(4), 2.036 (8); Fe(1)–O–Fe(2), 124.4 (4).

Table I. Selected Structural, Magnetic, and Spectroscopic Properties of **1** and **2**

	1[a]	**2**[b]
Structural Properties		
∠Fe–O–Fe, deg	124.4 (4)	123.6 (1)
$Fe–O_{oxo}$, Å	1.799 (6), 1.791 (6)	1.788 (2), 1.780 (2)
Fe···Fe, Å	3.174 (2)	3.146 (1)
av Fe–O μ-carboxylate, Å	2.028	2.043
av Fe–L cis to μ-oxo, Å	2.06	2.15
av Fe–L trans to μ-oxo, Å	2.13	2.19
Mössbauer[c] and Magnetic Data		
δ, mm s^{-1}	0.58 (3)	0.52 (3)
ΔE_Q, mm s^{-1}	1.84 (5)	1.60 (5)
J, cm^{-1}	−108.5 (4)	−121.3 (1)
μ_{eff}/Fe, μ_B[d]	1.87	1.71
Electronic Spectral Data[e]		
	247 (2.91×10^4)	262 (3375), 339 (4635)
	357 (6.63×10^3)	358 (sh), 457 (505)
	471 (208)	492 (460)
	501 (94, sh)	528 (sh)
	569 (95)	695 (70)
		993 (3.5)
Resonance Raman Data		
ν_s Fe–O–Fe, cm^{-1}[f]	510 (496)	528 (511)
max enhancement, nm[g]	356.4 (1.87×10^3)	406.7 (1.78×10^3)[a]

[a] This work. [b] Reference 8a. [c] Mössbauer parameters are obtained at 4.2 K. [d] Values of μ_{eff} are reported for $CDCl_3$ solution at 298 K as measured by the Evans NMR method (Evans, D. F. *J. Chem. Soc.* **1958**, 2003). [e] λ reported in nm in a CH_3CN solution of **1** and a CH_2Cl_2 solution of **2**. Numbers in parentheses are molar extinction coefficients per iron atom. [f] Numbers in parentheses are the ^{18}O shifted values. [g] Values in parentheses are molar Raman scattering intensities relative to the 704 cm^{-1} methylene chloride band.

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(11) Crystal data for $\mathbf{1}\cdot 2CH_3CN$ ($C_{42}H_{82}P_6O_{23}N_2Co_2Fe_2$), $M_r = 1398.52$ at 298 K: space group $P\bar{1}$, $a = 12.062$ (2) Å, $b = 15.733$ (4) Å, $c = 18.667$ (6) Å, $\alpha = 111.64$ (2)°, $\beta = 96.62$ (2)°, $\gamma = 98.83$ (2)°, $V = 3196$ Å^3, $Z = 2$, $\rho_{calcd} = 1.453$ g cm^{-3}, $\rho_{meas} = 1.44$ (1) g cm^{-3}. For 4719 unique, observed reflections and 610 parameters, the current discrepancy indices are $R = 0.0704$, $R_w = 0.0849$. Recollection of the data at low temperature and further refinement to resolve solvent and partial disorder are planned, details of which will be reported at a later date.

0002-7863/89/1511-8046$01.50/0