to the g factor of $[Mn(Cp^*)_2]^+$.[4]

As **1**–**3** are cooled below 20 K in a field of 500 G, χ_M *and* $\chi_M T$ increase rapidly, which together with the positive Θ values observed for **1**–**3** indicate that ferromagnetic interactions dominate. However, as shown in Figure 2, χ_M for **2** reaches a maximum in the range 2–3 K and then decreases sharply, signaling an antiferromagnetic phase transition. Similar behavior is observed for **1** and **3** and the Nêel temperatures are T_N = 2.4, 2.8, and 2.3 K for **1**–**3**, respectively. The presence of significant ferromagnetic interactions in these materials, as evidenced in the susceptibilities above T_N, along with the previous observations that $[Mn(Cp^*)_2]^+$ CT salts typically exhibit large magnetic anisotropies,[3,14] suggested that **1**–**3** might exhibit metamagnetic behavior,[6] where the application of a relatively weak magnetic field causes a transition from an antiferromagnetic to a ferromagnetic ground state. We therefore investigated the field dependence of the magnetization in the range 1.85–10 K.

Field-cooled magnetization curves for **2** (Figure 2) demonstrate that **2** undergoes such a field-induced transition. As H_A is increased from 500 G, the maximum in χ_M broadens, shifts to lower temperatures, and finally disappears for $H_A > 2500$–3000 G, demonstrating the transition from antiferromagnetic to ferromagnetic behavior; similar data are obtained for **1** and **3**. Figure 3 presents magnetization isotherms for **2** recorded at 1.85, 2.20, and 2.80 K. As the temperature is reduced, the isotherms become increasingly sigmoidal. At the lowest temperature, T = 1.85 K, M first increases slowly with H_A, as for an antiferromagnet and then increases rapidly in a field-induced phase transition to the ferromagnetic state, as expected for a metamagnet with $T < T_N$.[6] The critical field at this temperature, defined as the extrapolation of the transition region to $M = 0$, is H_c = 800 G.

In the T = 1.85 K isotherm the magnetization attains the value M = 12 500 emu G/mol at the highest field employed (40 000 G; data not shown). As is typical of metamagnets where T is not far below T_N,[5a,6b] even at this field M has not fully reached the saturation magnetization value, $M_{sat} = N\beta[g_D S(D^+) + g_A S(A^-)] \approx 16\,800$ emu G/mol, expected for the ferromagnetic state when $S(D^+) = 1$ and $S(A^-) = {}^1/_2$ ($g = 2$ for both spins). However, it is far larger than $M_{sat} = N\beta[g_D S(D^+) - g_A S(A^-)] \approx 5600$ emu G/mol expected if the field-induced transition instead were to a high-field state that is ferrimagnetic. In addition, M_{sat} is expected to be lower than the theoretical value owing to the polycrystalline nature of the sample and the expected anisotropy for a metamagnet material.

Why are **1**–**3** metamagnets, whereas the Fe analogue, **4**, is not? We take the high-temperature behavior of χ_M, along with the appearance of a metamagnetic transition, to indicate that the D^+–A^- intrachain coupling in **1**–**3** is strong and ferromagnetic, as in $[Mn(Cp^*)_2][TCNQ]$,[4] but that weak interchain antiferromagnetic coupling leads to the metamagnetic behavior and field-dependent ground state demonstrated in Figure 2. In this case one might expect[15] $T_N \propto |E_{intra}E_{inter}|^{1/2}$, where E_{intra} is the intrachain near-neighbor D^+–A^- interaction, $E_{intra} \propto S_D S_A J_{DA}$, and E_{inter} is the much weaker, effective interchain interaction energy. We propose that an increase in E_{intra} in **1**–**3** caused by the increase in spin for D^+ from $S = {}^1/_2$ in **4** to $S = 1$, along with possible increases in J_{DA}, contributes to the observation of a magnetically ordered state for **1**–**3**. It is hoped that detailed magnetic–structural correlations will clarify the mechanism of spin coupling within these salts and rationalize the variation in T_N.

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Supplementary Material Available: A table of positional parameters and B_{eq} values (Å^2) for the atoms of **1** (1 page). Ordering information is given on any current masthead page.

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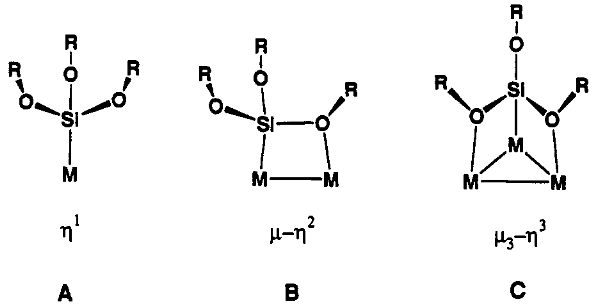
Unusual Coordination Properties of Trialkoxysilyl Groups in Metal Cluster Complexes. Synthesis, Structure, and Reactivity of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3](\mu\text{-}H)$

Alkoxysilanes are widely used in metal-catalyzed hydrosilation reactions because of their high reactivity.[1] In most cases, trialkoxysilyl groups coordinate to metal atoms in the conventional η^1 mode (A) that is commonly found for trialkyl- and triarylsilyl groups. Recent reports by Braunstein et al. of the first examples of μ-η^2-siloxyl groups (B) in binuclear metal complexes have provided the first evidence that the alkoxy groups are not always innocent spectators in metal complexes.[2] We now wish to report the first example of a μ_3-η^3-siloxyl ligand (C) in a trinuclear metal complex as further evidence of the unusual coordination properties of these ligands.



The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $HSi(OEt)_3$ at 25 °C for 1 h has yielded the complex $Os_3(CO)_{10}(NCMe)[Si(OEt)_3](\mu\text{-}H)$ (**1**; 84%). Compound **1** was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses.[3] The crystal contains two independent but structurally similar molecules in the asymmetric crystal unit.[4,5] An ORTEP drawing of the molecular structure of one of these is shown in Figure 1. The molecule consists of a triangular triosmium cluster with an η^1-$Si(OEt)_3$ ligand, type A, coordinated to only one metal atom,

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(3) A solution of $Os_3(CO)_{10}(NCMe)_2$, 103.9 mg (0.111 mmol), in 60 mL of CH_2Cl_2 was allowed to react with 61.7 μL (0.334 mmol) of triethoxysilane at 25 °C for 1 h. The product was separated by TLC using a 3/2 CH_2Cl_2/hexane solvent mixture to yield 98.8 mg (84% yield) of **1**. IR, ν(CO) (cm^{-1}), in hexane: 2103 (m), 2065 (vs), 2041 (vs), 2021 (vs), 2008 (s), 2000 (vs), 1988 (vs), 1976 (m). ^{1}H NMR, δ, in $CDCl_3$: 3.89 (q, CH_2, 6 H), 2.57 (s, $NCCH_3$, 3 H), 1.27 (t, CH_3, 9 H), −16.40 (s, OsH, 1 H). Satisfactory elemental analyses (C, H, N) have been obtained. Yellow crystals of **1** were grown from a CH_2Cl_2/petroleum ether solution by slow evaporation of solvent at 25 °C.

(4) Crystal data for **1**: space group = $P\bar{1}$, a = 16.630 (5) Å, b = 20.062 (7) Å, c = 9.501 (2) Å, α = 101.04 (3)°, β = 103.22 (2)°, γ = 106.26°, Z = 4, 3603 reflections, R = 0.051.

(5) Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. All data were processed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied.

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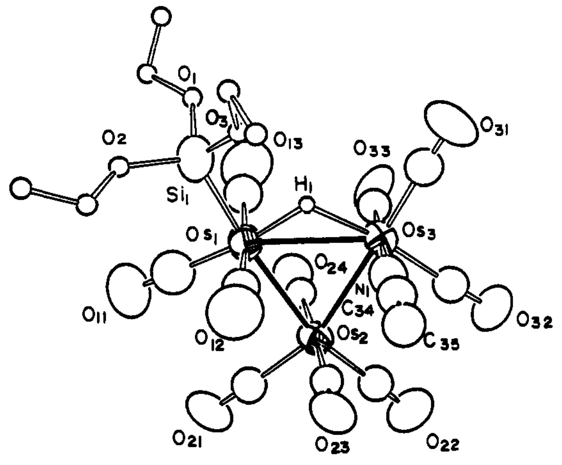

Figure 1. ORTEP diagram of $Os_3(CO)_{10}(NCMe)[Si(OEt)_3](\mu\text{-}H)$ (1) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.894 (3), Os(1)–Os(3) = 3.008 (2), Os(2)–Os(3) = 2.888 (2), Os(4)–Os(5) = 3.010 (2), Os(4)–Os(6) = 2.900 (2), Os(5)–Os(6) = 2.902 (2), Os(1)–Si(1) = 2.39 (1), Os(4)–Si(2) = 2.39 (1).

Os(1)–Si(1) = 2.39 (1) Å. There is a hydride ligand (located but not refined) that bridges the longest metal–metal bond, Os(1)–Os(3) = 3.008 (2) Å, $\delta = -16.40$ ppm, ten linear carbonyl ligands, and an acetonitrile ligand coordinated to Os(3) in an axial coordination site.

When heptane solutions of **1** were heated to reflux for 20 min under a nitrogen purge, it was transformed to the new compound $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3](\mu\text{-}H)$ (**2**) in 62% yield. Compound **2** was characterized by a combination of IR, ^1H NMR, and single-crystal X-ray diffraction analyses.[6] An ORTEP drawing of the molecular structure of **2** is shown in Figure 2.[5,7] The molecule consists of a triangular triosmium cluster with an η^3-$Si(OEt)_3$ ligand bridging one face of the cluster, type C. The silicon atom is bonded to one metal atom, Os(3)–Si = 2.32 (1) Å, while the oxygen atoms of two of the ethoxy groups are coordinated to the two neighboring osmium atoms, one to each. The Os–O distances are similar, Os(1)–O(1) = 2.26 (1) Å and Os(2)–O(2) = 2.16 (2) Å. These are similar to the Os–O distances observed in the oxoanion-capped cluster complex $Os_3(CO)_9(\mu_3\text{-}O_3SO)(\mu\text{-}H)_2$.[8] The Si–O distances appear to be significantly different, Si–O(1) = 1.47 (2) Å, Si–O(2) = 1.88 (2) Å, and Si–O(3) = 1.77 (3) Å; however, the presence of significant disorder in the positions of all three ethyl groups may have adversely affected the accuracy of these values.[9] A hydride ligand (located and refined) bridges the long Os(2)–Os(3) bond, 2.965 (1) Å. In solution, compound **2** exists as a mixture of two isomers in a 3/7 ratio, as indicated by the presence of two hydride resonances, $\delta = -9.61$ and -13.38 ppm. The second isomer in solution is believed to differ from the one in the solid state only by the location of the bridging hydride ligand (i.e. hydride bridging the Os(1)–Os(2) bond).

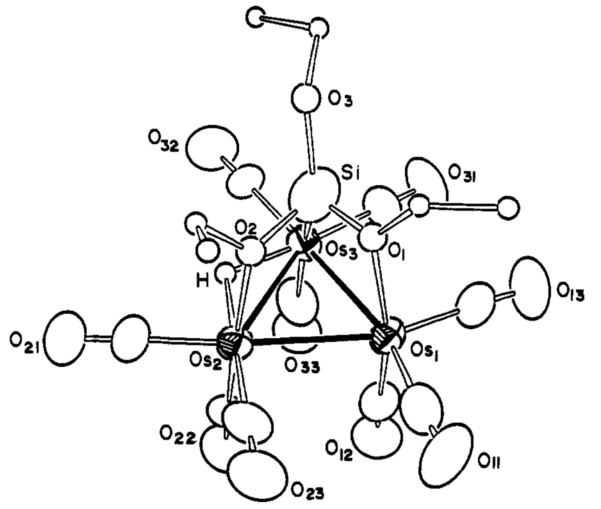

Figure 2. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3](\mu\text{-}H)$ (2) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.848 (2), Os(1)–Os(3) = 2.817 (2), Os(2)–Os(3) = 2.965, Os(3)–Si = 2.32 (1), Os(1)–O(1) = 2.26 (1), Os(2)–O(2) = 2.16 (2).

Compound **2** will add 2 equiv of CO at 69 °C/1 atm to yield the new compound $Os_3(CO)_{11}[Si(OEt)_3](\mu\text{-}H)$ (**3**; 77%), which is believed to be structurally similar to **1** with a CO ligand in place of the NCMe ligand.[10] At 97 °C under a nitrogen purge, compound **2** is regenerated from **3** in 37% yield in 1.5 h. We are currently investigating the nature of the addition of other small molecules to **1** and **2**.

Recent studies have shown that the widely used hydrosilation catalysts derived from platinum halides[11] are colloidal in character.[1a,12] The exact form of the interaction of trialkoxysilyl groups with these colloids remains to be established. The present results further demonstrate that in metal cluster complexes bridging coordinations that involve interactions with oxygen atoms can be important. It is probable that these modes of coordination will extend to large clusters and even to colloids.

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Supplementary Material Available: For both structural analyses, tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (21 pages); tables of structure factors for compounds 1 and 2 (39 pages). Ordering information is given on any current masthead page.

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(6) 47.6-mg (0.045-mmol) sample of **1** in 75 mL of heptane was heated to reflux for 20 min under a nitrogen purge. The product was isolated by TLC using a 7/3 hexane/CH_2Cl_2 solvent mixture as the eluent. This yielded 25.9 mg of yellow $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3)](\mu\text{-}H)$ (**2**; 62% based on the amount of **1** consumed). IR, $\nu(CO)$ (cm^{-1}), in hexane: 2090 (s), 2062 (vs), 2052 (vs), 2032 (vs), 2021 (s), 2012 (vs), 2007 (vs), 1991 (vs), 1976 (m), 1968 (m), 1956 (m), 1944 (m). ^1H NMR, δ, in CD_2Cl_2 solution (**2** exists as a mixture of isomers in a 3/7 ratio a/b at 25 °C): 4.03 (dq, CH_2, 2 H, $^2J_{HH} = 10.6$ Hz, $^3J_{HH} = 7.0$ Hz, b), 3.93 (dq, CH_2, 1 H, $^2J_{HH} = 10.5$ Hz, $^3J_{HH} = 7.1$ Hz, a), 3.74 (dq, CH_2, 1 H, $^2J_{HH} = 10.4$ Hz, $^3J_{HH} = 7.1$ Hz, a), 3.68 (q, CH_2, 2 H, $^3J_{HH} = 6.9$ Hz, b), 3.64 (complex multiplet, CH_2, 3 H, a), 3.28 (dq, CH_2, 2 H, $^2J_{HH} = 10.7$ Hz, $^3J_{HH} = 7.0$ Hz, b), 3.25 (unresolved dq, CH_2, 1 H, a), 1.15 (t, CH_3, 3 H, $^3J_{HH} = 7.1$ Hz, b), 1.14 (t, CH_3, 3 H, $^3J_{HH} = 7.1$ Hz, a), 1.08 (t, CH_3, 3 H, $^3J_{HH} = 6.9$ Hz, a), 1.07 (t, CH_3, 3 H, $^3J_{HH} = 6.6$ Hz, a), 1.06 (t, CH_3, 6 H, $^3J_{HH} = 7.1$ Hz, b), -9.61 (s, Os*H*, 1 H, b), -13.38 (s, Os*H*, 1 H, a). Isomer a is the isomer observed in the solid state. Satisfactory elemental analyses (C, H) have been obtained.

(7) Crystals of **2** were grown from slow evaporation of a hexane solution at 25 °C. Crystal data: space group = $P2_1/n$, $a = 9.504$ (2) Å, $b = 18.856$ (8) Å, $c = 13.776$ (3) Å, $\beta = 94.37$ (2)°, $Z = 4$, 1955 reflections, $R = 0.047$.

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(9) All three ethyl groups exhibited extensive disorder. A satisfactory disorder model could not be devised. Carbon C(6) could not be refined to a credible position and was fixed in the position observed in a difference Fourier synthesis.

(10) A 48.0-mg (0.048-mmol) sample of **2** in 75 mL of hexane was heated to reflux in the presence of a slow purge of CO for 4 h. The product was separated by TLC with a 1/1 hexane/methylene chloride solvent mixture to yield 8.9 mg of unreacted **2** and 31.1 mg of $Os_3(CO)_{11}[Si(OEt)_3](\mu\text{-}H)$ (**3**; 77% yield based on amount of **2** consumed).

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