in reactions between nucleophilic metals and coordinated (ω-chloroalkyl)phosphines and -arsines.

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Synthesis, Structure, and Fluxional Properties of $Os_3H_3(CO)_9(SiPh_3)$, a Compound with the Formally Unsaturated $Os(\mu\text{-}H)_2Os$ Unit

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Summary: The crystal structure of $Os_3H_3(CO)_9(SiPh_3)$, prepared from $Os_3H_2(CO)_{10}$ and Ph_3SiH, reveals it to contain the formally unsaturated unit $Os(\mu\text{-}H)_2Os$ ($Os{-}Os = 2.7079$ (4) Å). The ^{1}H and ^{13}C NMR spectra of the compound indicate the bridging hydrogens and those CO ligands which are bonded to the osmium atoms in the OsH_2Os unit are fluxional.

Our interest[2] in silyl derivatives of osmium clusters has prompted us to investigate the reaction of silanes with the formally unsaturated osmium cluster $Os_3H_2(CO)_{10}$. From the reaction with Ph_3SiH in hexane at 70 °C (in an evacuated sealed flask) the compound $Os_3H_3(CO)_9(SiPh_3)$ (**1**) has been isolated.[3] The crystal structure of this derivative has been solved by conventional X-ray diffraction techniques.[4] The bridging hydrogen ligands were all located although not with great accuracy. As can be seen in Figure 1, the molecule contains doubly hydrogen-bridged, singly hydrogen-bridged, and unbridged osmium–osmium bonds. The osmium–osmium vectors $Os(\mu\text{-}H)_2Os = 2.7079$ (4) Å, $Os(\mu\text{-}H)Os = 3.0103$ (4) Å, and $Os{-}Os = 2.8550$ (4) Å are entirely consistent with these structural features.[5] The compound is thus similar to the parent compound $Os_3H_2(CO)_{10}$[6] in that it contains the formally unsaturated $Os(\mu\text{-}H)_2Os$ unit. Such groupings are still comparitively rare among transition-metal cluster compounds.[6,7]

The ^{1}H NMR spectrum of **1** in toluene-d_8 solution (Figure 2A) showed three equally intense, high-field resonances, at δ −8.58, −12.29, and −12.42, as expected from the solid-state structure. The ^{1}H NMR resonances for bridging hydride ligands usually occur in the range −15 to −23 ppm.[8] The small upfield shifts (from Me_4Si) observed for **1** can be attributed to the unsaturated nature of the cluster.[8] It is interesting that H(C) which is not directly involved in the OsH_2Os bridge also shows this abnormal shift. The signals at −8.58 and −12.42 ppm exhibited $^{187}Os{-}^{1}H$ couplings[9] of 44.1 and 44.9 Hz, respectively, and on the basis of this evidence are assigned to the hydrogen atoms H(A) and H(B) in the double bridge. (We observe a value of 46.9 Hz for this coupling in $Os_3H_2(CO)_{10}$.) For the signal at −12.29 ppm two $^{187}Os{-}^{1}H$ couplings were observed: 31.3 and 35.4 Hz.[10] This is interpreted as arising from the coupling of H(C) with the two chemically distinct osmium atoms Os(1) and Os(2) although the evidence is not inconsistent with an asymmetric hydrogen bridge.[11] Another interesting facet of the ^{1}H NMR spectrum of **1** is that the resonances attributable to H(A) and H(B) are sharp singlets (even at −40 °C) and show no evidence of $^{1}H{-}^{1}H$ coupling. This suggests there is no mixing of the three center–two electron OsHOs molecular orbitals in the OsH_2Os grouping of **1**.

When a toluene-d_8 solution of **1** is warmed, the ^{1}H NMR signals assigned to H(A) and H(B) broadened indicative of exchange between the two sites. Although the broadening was significant 105 °C (400-MHz operating frequency), the peaks were still far from coalescence. Furthermore, attempts to synthesize **1** specifically labeled with deuterium, by the reaction of $Os_3H_2(CO)_{10}$ with Ph_3SiD, were unsuccessful.[12] (Even in the initial stages the ^{1}H NMR spectrum of the reaction solution showed three equally intense hydride signals due to the product.) This suggested that at the temperature of synthesis (70 °C) there was also exchange between H(C) and the hydrogens in the OsH_2Os unit which was too slow to be detected by NMR line broadening. This was confirmed by spin-saturation-transfer experiments. At room temperature, irradiation of the signal at −8.58 ppm caused marked transfer to the resonance at −12.42 ppm (as expected) but not to that due to H(C) at −12.29 ppm (which, in fact, showed a positive NOE effect) However, at 75 °C there was significant transfer to the signal at −12.29 ppm as illustrated in Figure 2B.

The ^{13}C NMR spectrum (natural abundance) of **1** in CD_2Cl_2 at room temperature showed nine resonances (180.1, 178.3, 177.3, 175.9, 173.8, 172.2, 172.1, 166.8, 166.6 ppm) which is, again, what one would expect from the solid-state structure. However, in toluene-d_8 at 100 °C (^{13}C-enriched sample) the four signals at 174.0, 172.1, 166.6, and 166.4 ppm remained sharp but the others had almost completely collapsed into the base line. These results are

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[2] (a) van Buuren, G. N.; Willis, A. C.; Einstein, F. W. B.; Peterson, L. K.; Pomeroy, R. K.; Sutton, D. *Inorg. Chem.* **1981**, *20*, 4361. (b) Willis, A. C.; van Buuren, G. N.; Pomeroy, R. K.; Einstein, F. W. B. *Ibid.* **1983**, *22*, 1162.

[3] The reaction period was 7 h, and the compound was separated (58% yield) from $Os_3H_2(CO)_{10}$ and **2** by chromatography on silica gel with hexane–benzene as the eluant. Data for **1**: yellow-orange crystals; mp 150–152 °C; IR (hexane) ν(CO) 2129 (m), 2079 (s), 2054 (s), 2048 (s), 2038 (s), 2025 (m), 2007 (ms), 1974 (m) cm^{-1}; MS *m/e* 1086 $(P)^+$. Anal. Calcd for $C_{27}H_{18}O_9SiOs_3$: C, 29.89; H, 1.67. Found: C, 29.75; H, 1.55.

[4] Crystal data (at 20.8 °C): space group $P2_1/c$; $a = 19.837$ (2) Å, $b = 9.983$ (1) Å, $c = 15.385$ (1) Å, $\beta = 98.62$ (1)°, $V = 3012.3$ Å^3, $Z = 4$, $\rho_{calcd} = 2.392$ g cm^{-3}. Intensity data were collected by line profile analysis on a Picker FACS-I automated diffractometer, graphite-monochromated Mo Kα radiation, to give 3951 reflections $I > 2.3\sigma(I)$. The structure was solved by heavy-atom methods. Non-hydrogen atoms were refined with anisotropic temperature factors. The bridging hydride atoms were refined in the least squares (fixed U), but the phenyl hydrogen atoms were held at calculated positions. Final $R_F = 0.021$ and $R_{wF} = 0.025$. Bond lengths quoted in Figure 1 are without thermal motion corrections.

[5] Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. See also papers in the series: "Structural Studies on Polynuclear Osmium Carbonyl Hydrides", e.g.: Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958.

[6] Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314.

[7] Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1982**, *21*, 3458.

[8] Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

[9] Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 754.

[10] We have measured the $^{187}Os{-}^{1}H$ couplings of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$[2] as 32.3 and 36.8 Hz (CD_2Cl_2 solution). Note also that Lewis and coworkers found $^{187}Os{-}^{1}H$ couplings in the range 14.4–38.1 Hz for bridging hydride ligands in saturated osmium clusters.[9]

[11] The OsHOs bridges as determined by the diffraction study are all asymmetric. Because of the large errors associated with the hydrogen coordinates, it cannot be certain that these asymmetries are genuine, although it would not be unreasonable in view of the different chemical characters of the three osmium atoms.

[12] Contact with chromatographic material, which is known to cause hydrogen–deuterium exchange in $Os_3H_2(CO)_{10}$[13] was avoided in these experiments.

[13] Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

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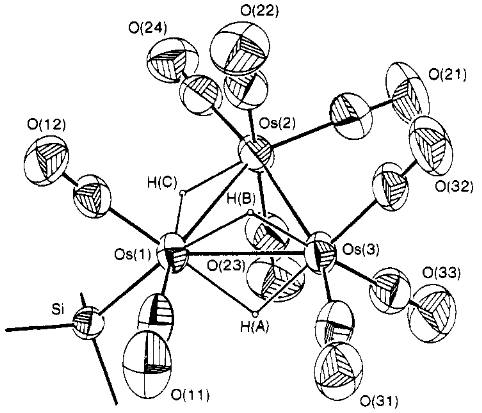

Figure 1. An ORTEP diagram of $Os_3H_3(CO)_9(SiPh_3)$; the phenyl groups have been omitted. Important bond lengths (Å) are as follows: Os(1)-Os(2) = 3.0103 (4); Os(1)-Os(3) = 2.7079 (4); Os(2)-Os(3) = 2.8550 (4); Os(1)-Si = 2.429 (2); Os(1)-H(A) = 1.99 (5); Os(3)-H(A) = 1.76 (5); Os(1)-H(B) = 1.92 (7); Os(3)-H(B) = 1.82 (7); Os(1)-H(C) = 1.89 (7); Os(2)-H(C) = 1.56 (8).

interpreted that the carbonyl ligands bonded to the osmium atoms in the OsH_2Os unit undergo exchange but those coordinated to Os(2) are rigid. This is similar to the behavior found previously for the parent compound $Os_3H_2(CO)_{10}$.[14] The two resonances at 166.6 and 166.4 ppm which (unlike most of the other resonances) showed no coupling in the ^1H-coupled ^{13}C NMR spectrum of 1 were assigned to the axial carbonyls on Os(2) i.e., C(22) and C(23).[15] That these signals remained sharp in the spectrum at 100 °C indicated that the Ph_3Si ligand was rigid with respect to the Os_3 plane[17] at this temperature (rotation of the Ph_3Si group from below to above the plane of osmium atoms could account for the exchange of H(A) and H(B)).

It is interesting to speculate that the process by which H(A) and H(B) exchange may involve an intermediate in which the hydride ligands lie in the plane of the osmium atoms in positions either side of the Os(1)–Os(3) bond: i.e., one of the hydrogen atoms lies *inside* the triangle formed by the osmium nuclei. Such a mechanism, which is equivalent to a rotation of H(A) and H(B) about the Os(1)–Os(3) bond, has several attractive features: it accounts for the equivalence of H(A) and H(B) with respect to the Ph_3Si ligand[18] and it provides a pathway by which H(A) or H(B) could slowly exchange with H(C). Such an intermediate could also allow carbonyl exchange to occur either by a terminal-bridge mechanism or by rotation of the carbonyl ligands at the individual osmium atoms.

Prolonged reaction of $Os_3H_2(CO)_{10}$ with excess Ph_3SiH in a closed vessel yields $Os_3H_2(CO)_{10}(SiPh_3)_2$ (2).[19] The presence of ten carbonyl groups in the product was clearly shown in the mass spectrum. Furthermore, the two hydride resonances exhibited in the ^1H NMR spectrum of 2 are in the region expected for bridging hydrides in a saturated cluster.[8]

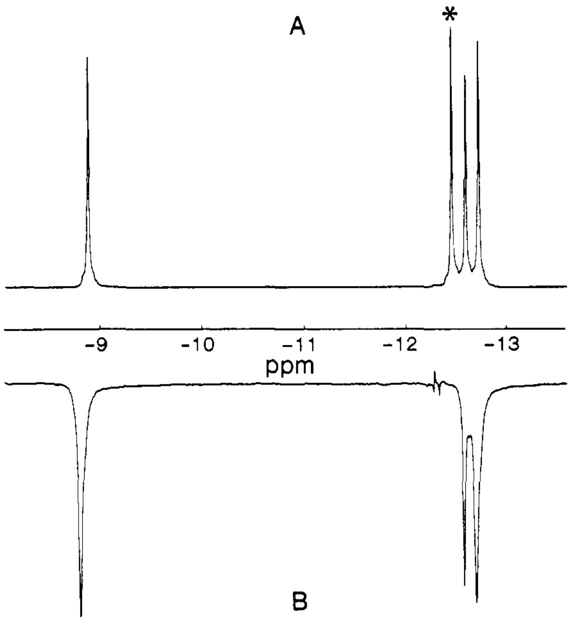

Figure 2. A: high-field region of the 400-MHz, ^1H NMR spectrum of $Os_3H_3(CO)_9(SiPh_3)$ in toluene-d_8 at ambient temperature; $Os_3H_2(CO)_{10}$ (*) was added as a reference (−12.15 ppm). The signal at −12.29 ppm is assigned as due to H(C). B: spin-saturation-transfer spectrum of the same sample, only at 75 °C. Irradiation was at the low field peak (−8.58 ppm). Note the tranfer to the signal due to H(C). The resonances at −8.58 and −12.42 ppm are broadened because of rapid exchange of H(A) and H(B).

Our investigations of the reactions of $Os_3H_2(CO)_{10}$ with group 4 hydrides are continuing, as is the study of the chemistry of 1. Of interest is that, unlike $Os_3H_2(CO)_{10}$,[20] 1 does not undergo ready reaction with CH_2N_2.

Acknowledgment. We are grateful to the Natural Science and Engineering Council of Canada for financial support. We would also like to thank Dr. A. S. Tracey and Mrs. M. Tracey, for assistance in the NMR experiments.

Supplementary Material Available: Tables of the positional and anisotropic thermal parameters, bond lengths and angles, observed and calculated structure factors for 1 (34 pages). Ordering information is given on any current masthead page.

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(14) Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* **1981**, *213*, 207.

(15) This assignment may appear unusual since the ^{13}C NMR resonances of $Os(CO)_4$ units in metal clusters are normally in the range 175–185 ppm with those due to the axial carbonyls to lower field than the corresponding signals of the radial ligands.[14] However, in $Os_3H_3(CO)_9CMe$, where the assignment of the ^{13}C NMR resonances is unambiguous, the signal due to the axial carbonyls is at 166.7 ppm which is to higher field than that due to the equatorial ligands.[16] This effect may be a consequence of the bridging hydrides in $Os_3H_3(CO)_9CMe_3$ and 1.

(16) Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1976**, *104*, 225.

(17) As found[2a] for $Os_3H_3(CO)_9(SiMeCl_2)_3$, there is probably rapid rotation, on the NMR time scale, about the Os–Si bond.

(18) The Os(1)Os(2)Os(3)–SiOs(1)Os(3) dihedral angle is 88.4°.

(19) Reaction period 24 h. Compound isolated by chromatography on silica gel (benzene eluant). Data for 2: yellow crystals; mp 174–176 °C; IR (CH_2Cl_2) ν(CO) 2127 (w), 2099 (ms), 2084 (m), 2043 (s), 2029 (sh), 1976 (m) cm^{-1}; MS *m/e* 1372 $(P)^+$; ^1H NMR (high-field region, CD_2Cl_2 solution) δ −16.48 (d, $J_{^{187}Os-^1H}$ = 33.4, 36.3 Hz), −16.70 (d, $J_{^{187}Os-^1H}$ = 32.0, 34.9 Hz, $J_{^1H-^1H}$ = 1.4 Hz). Anal. Calcd for $C_{46}H_{32}O_{10}Si_2Os_3$: C, 40.28; H, 2.35. Found: C, 40.39; H, 2.23.

(20) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

Metal–Metal Multiple Bonds. 15. Syntheses and Structures of the 17-Electron Radical $TpMo(CO)_3$ and the Triply Bonded Dimer $Tp_2Mo_2(CO)_4(Mo{\equiv}Mo)$ (Tp = Hydridotris(pyrazolyl)borate)[1]

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Summary: Oxidation of the anion $TpMo(CO)_3^-$ (Tp = hydridotris(pyrazolyl)borate) with, e.g., Ag^+ or ferricenium ion

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(1) (a) Part 14: Gerlach, R. F.; Duffy, D. N.; Curtis, M. D. *Organometallics* **1983**, *2*, 000. (b) Part 13: D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg. Chem.* **1983**, *22*, 849.

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