ORGANOMETALLICS

Metal-metal multiple bonds. 15. Syntheses and structures of the 17-electron radical TpMo(CO)3 and the triply bonded dimer Tp2Mo2(CO)4(Mo.tplbond.Mo) (Tp = hydridotris(pyrazolyl)borate)

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Organometallics **1983**, *2*, 936-938

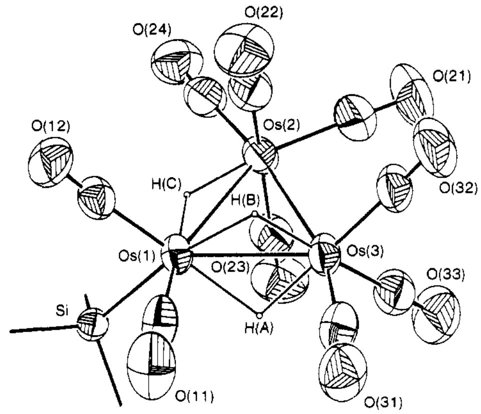

Figure 1. An ORTEP diagram of $Os_3H_3(CO)_9(SiPh_3)$; the phenyl groups have been omitted. Important bond lengths (Å) are as follows: Os(1)-Os(2) = 3.0103 (4); Os(1)-Os(3) = 2.7079 (4); Os(2)-Os(3) = 2.8550 (4); Os(1)-Si = 2.429 (2); Os(1)-H(A) = 1.99 (5); Os(3)-H(A) = 1.76 (5); Os(1)-H(B) = 1.92 (7);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

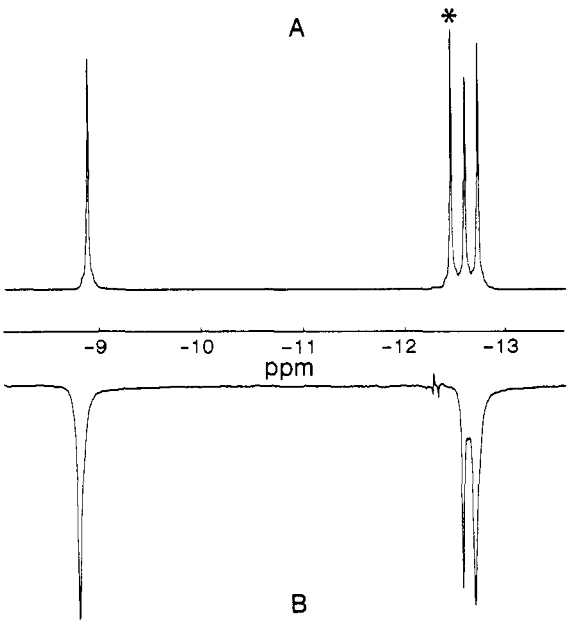

Figure 2. A: high-field region of the 400-MHz, ^1H NMR spectrum of $Os_3H_3(CO)_9(SiPh_3)$ in toluene-d_8 at ambient temperature; $Os_3H_2(CO)_{10}$ (*) was added as a reference (−12.15 ppm). The signal at −12.29 ppm is assigned as due to H(C). B: spin-saturation-transfer spectrum of the same sample, 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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gives high yields of the stable radical $TpMo(CO)_3$ (2). Upon heating in acetonitrile or toluene, the radical dimerizes with loss of CO to form the dimer $Tp_2Mo_2(CO)_4(Mo{\equiv}Mo)$ (1). The structures of 1 and 2 are presented.

Since Trofimenko's original report,[2] an extensive coordination chemistry of the hydridotris(pyrazolyl)borate ion, $HB(C_3H_3N_2)_3^-$ (= "Tp"), has been developed.[3-10] Early work emphasized the similarity of the Tp and cyclopentadienyl (Cp) ligands, although in its steric requirements, Tp may be more closely compared with the pentamethylcyclopentadienyl (Cp*) ligand.[11,12] However, the electronic nature of the Tp ligand is considerably different from Cp in that Tp hybridizes the metal orbitals into an octahedral disposition much more effectively than does Cp. Therefore, it is instructive to compare the chemistry of Tp and Cp compounds, especially where the coordination member of the Cp complexes is greater than 6.

One obvious difference between Cp and Tp chemistry is that the former is found in an extensive array of metal–metal bonded dimers and clusters, whereas none are known with η^3-Tp ligands on more than one metal.[13,14] It is ironic, therefore, that the first such dimer to be discovered, $Tp_2Mo_2(CO)_4$ (1), contains a $Mo{\equiv}Mo$ triple bond. We here report the synthesis of 1 via the unusual 17-electron radical $TpMo(CO)_3$ (2).

The radical, 2, may be prepared by a variety of one-electron oxidations of the anion[2] $TpMo(CO)_3^-$ as shown in eq 1. Although $AgBF_4$, Ph_3CPF_6, and Cp_2FePF_6 all

$$TpMo(CO)_3^- + Ox \xrightarrow[25\ °C]{CH_2Cl_2} \underset{2}{TpMo(CO)_3\cdot} + Red \quad (1)$$

$$Tp = HBPz_3^-$$

convert the anion to yellow-brown 2, best results are obtained with the ferricinium cation oxidation, from which 2 can be isolated in 71% yield.[15] Compound 2 is stable at room temperature in the absence of oxygen. In toluene solution at 25 °C, 2 exhibits an unresolved ESR signal (width at half-height $\approx$ 30 G) at $g = 1.98$, and in CH_2Cl_2 solution, ν_{CO} absorptions are observed at 2000 and 1965 cm^{-1}.

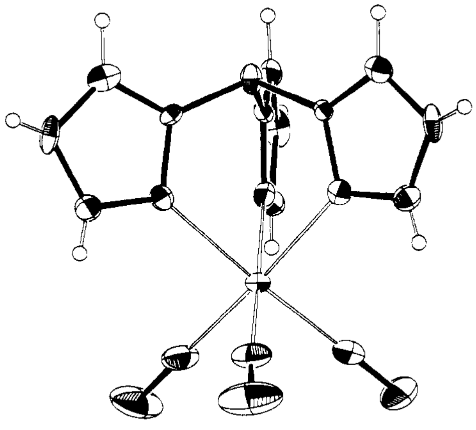

Figure 1. ORTEP plot of the radical $TpMo(CO)_3$ (2) (Tp = $HB(N_2H_3)_3^-$). Distances: Mo–N = 2.207 (7) Å and Mo–C = 2.013 (11) Å. Angles: C–Mo–N = 94.8 (3)°, C–Mo-C = 87.8 (4)° and N–Mo–N = 82.5 (3)°.

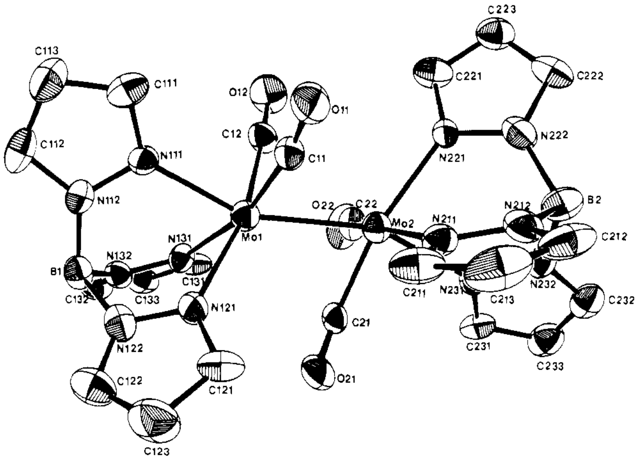

Figure 2. ORTEP plot of the triple bonded dimer $Tp(CO)_2Mo{\equiv}Mo(CO)_2Tp$ (Tp = $HB(N_2C_3H_3)_3^-$).

The structure of the radical, 2, has been confirmed by X-ray diffraction.[16] The molecule lies on a crystallographic C_3 axis but has nearly strict C_{3v} symmetry (Figure 1).

Unlike the $CpMo(CO)_3\cdot$ radical which is unstable with respect to its dimer, radical, 2, prefers to maintain its pseudooctahedral geometry, as a result of the electronic and steric requirements of the Tp ligand. However, in refluxing acetonitrile or toluene, 2 rapidly loses a mole of CO and forms the deep green, triply bonded dimer, 1, in essentially quantitative yield (eq 2).[17] Note that the formation of the triply bonded dimer with loss of CO maintains the coordination number of 6 about Mo.

$$\underset{2}{2TpMo(CO)_3\cdot} \xrightarrow[\Delta]{} \underset{1}{Tp(CO)_2Mo{\equiv}Mo(CO)_2Tp} + 2CO \quad (2)$$

This compound exhibits ν_{CO}(KBr) at 1950, 1866, 1830, and 1815 cm^{-1}. Both ^1H and ^{13}C NMR at room temperature show local C_s symmetry at the Tp ligand (the pyrazolyl resonances occur as two sets in a 2:1 ratio) which indicates that the Tp ligands are not undergoing rotation about the Mo–B axis. The CO resonances occur at δ 232 and 229, which are within the range typical for terminal

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[2] (a) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

[3] Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

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[8] Strainer, M. V. R.; Takats, J. *Inorg. Chem.* **1982**, *21*, 4050.

[9] Reger, D. L.; Targuini, M. E. *Inorg. Chem.* **1982**, *21*, 840.

[10] Shaver, A. *J. Organomet. Chem. Libr.* **1977**, *5*, 157.

[11] Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504.

[12] May, S.; Reinsalu, P.; Powell, J. *Inorg. Chem.* **1980**, *19*, 1582.

[13] $Tp_2Mo_2(OAc)_2(Mo \overset{4}{-} Mo)$ contains one η^2-Tp and one Tp ligand which bonds tightly with two of the three nitrogens and weakly with the third: Collins, D. M.; Cotton, F. A.; Murrillo, C. A. *Inorg. Chem.* **1978**, *15*, 1861.

[14] For Tp dimers which do not contain metal–metal bonds, see: (a) Mealli, C.; Arcus, C. G.; Wilkinson, T. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711; (b) See ref 11.

[15] Solid $Fc^+PF_6^-$ was added to a suspension of $(Et_4N)(TpMo(CO)_3)$ in CH_2Cl_2. The reaction is over in a few minutes. Hexane is added and the CH_2Cl_2 stripped out of the mixture. Filtration gives a mixture of solid Et_4NPF_6 and the product 2. This solid is taken up in THF and filtered, and the filtrate concentrated and cooled to give pure 2.

[16] $a = b = 11.359$ (4) Å, $c = 8.161$ (2) Å (at −169 °C), $\gamma = 120°$, $V = 911.9$ Å^3, $Z = 2$, space group $P\bar{3}$ (No. 147).

[17] Compound 1 may be prepared from isolated 2 or in one step by oxidizing the anion in CH_3CN solution with $FcPF_6$, stripping off the CH_3CN solvent, subliming out the resulting ferrocene, and treating the residue with toluene. This solution is then filtered to remove the salts and concentrated to give 1 which is collected and washed with hexane.

carbonyls on molybdenum but considerably downfield from the CO resonance in $Cp_2Mo_2(CO)_4$, **3**, viz., δ 196.[1b]

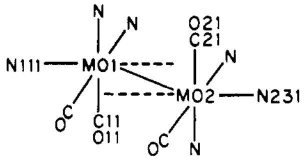
The formation of triply bonded **1** from the radical, **2**, parallels the formation of **3** from $Cp_2Mo_2(CO)_6$. The latter transformation has been shown to proceed via the radical pathway shown in eq 3.[18,19]

$$Cp_2Mo_2(CO)_6 \xrightarrow[h\nu]{\Delta \text{ or}} 2CpMo(CO)_3\cdot \overset{-CO}{\rightleftharpoons} 2CpMo(CO)_2 \rightarrow \mathbf{3} \quad (3)$$

The structure[20] of **1** is shown in Figure 2. Unlike the Cp analogue $Cp_2Mo_2(CO)_4$ (**3**) which has a linear Cp–Mo–Mo–Cp axis,[21] the Tp–Mo–Mo–Tp axis is bent (ω = 153 ± 1°) and thus resembles $Cp_2Cr_2(CO)_4$ (ω = 162°)[22] and $Cp^*{}_2Mo(CO)_4$ (**4**, $Cp^* = C_5Me_5$) (ω = 168°).[23] The $Mo\equiv Mo$ distance in **1**, 2.507 (1) Å, may be compared to the $Mo\equiv Mo$ distances of 2.448 (1) and 2.488 (3) Å in **3** and **4**, respectively.[21,23] Although the increased $Mo\equiv Mo$ distances in **1** and **4** relative to **3** may be ascribed to the increased steric bulk of the Cp* and Tp ligands, increased electron donation from these liquids (vis-à-vis Cp) would be expected to populate M–M antibonding molecular orbitals and lead to increased $Mo\equiv Mo$ distances.[22]

The overall symmetry of **1** approximates C_2, with the C_2 axis bisecting the $Mo\equiv Mo$ bond and the N211–Mo2–Mo1–N121 dihedral angle. The N donor atoms may be arranged into two sets. One set, consisting of N111 and N231, have their N–Mo bonds nearly parallel and approximately *trans* to the $Mo\equiv Mo$ bond and are called "axial" (averge $Mo–N_{ax}$ = 2.21 + 0.01, average $Mo–Mo–N_{ax}$ = 154 + 2°). The other four N donors are essentially trans to the carbonyls and are called "equatorial" (average $Mo–N_{eq}$ = 2.23 ± 0.01, average $N_{eq}–Mo–CO$ = 166.6 ± 0.7).

A Mo–CO bond lies opposite to each axial nitrogen as shown



These carbonyls have shorter Mo–C distances (average = 1.93 ± 0.01 Å) and more acute Mo–Mo–CO angles (average = 70.5 ± 1.5°) than the other two carbonyls (average Mo–CO = 1.96 ± 0.01 Å, average Mo–Mo–CO = 83.4 (4)°). Thus it appears that one carbonyl on each molybdenum interacts across the $Mo\equiv Mo$ bond with the residual "octahedral hydrid" on the remote Mo.

The reactivity of the radical, **2**, and the triply bonded dimer, **1**, are currently under investigation and will be reported in due course.

Acknowledgment. M.D.C. and K.-B.S. thank the National Science Foundation (Grant No. CHE-8206153) and the AMAX Foundation for support of this work. K.-B.S. also thanks the donors and the Department of Chemistry (UM) for a James E. Harris Fellowship. We also are grateful to the bloomington Academic Computing Service and the University of Michigan Computing Center for computing time. We also express our appreciation to Professor L. F. Dahl for a preprint of the structural characterization of complex **4**.

Registry No. **1**, 85803-20-9; **2**, 85803-21-0; $TpMo(CO)_3^-$, 47314-50-1.

Supplementary Material Available: Table I, fractional coordinates for $TpMo(CO)_3\cdot$ (**2**), Table II, fractional coordinates for $Tp_2Mo_2(CO)_4\cdot CHCl_3$ (**1**), Tables III and IV, listing of F_o vs. F_c for **2** and **1**, respectively (17 pages). Ordering information is given on any current masthead page.

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[20] a = 12.995 (2) Å, b = 16.974 (4) Å, c = 29.396 (6) Å, V = 6484 (2) Å^3, Z = 8; ρ(obsd) = 1.72 g cm^{-3} ρ(calcd) = 1.74 g cm^{-3}; space group *Pbca* (No. 61).

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Catenated Sulfur Ligands: The Synthesis of Metal Disulfanes and the Structures of *cis*-$(PPh_3)_2Pt(C_8H_4NO_2)SSCH(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3SS\text{-}p\text{-}C_6H_4CH_3$

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Summary: Treatment of $(\eta^5\text{-}C_5H_5)W(CO)_3SH$ with RSNpht, RSSNpht and RS(O)Npht gave complexes which contain novel catenated sulfur ligands, namely, $(\eta^5\text{-}C_5H_5)W(CO)_3S_xR$, where x = 2 and 3, and $(\eta^5\text{-}C_5H_5)W(CO)_3SS(O)R$, respectively, where R = $CH_2C_6H_5$ and $p\text{-}C_6H_4CH_3$ and Npht = *N*-phthalimido. The complexes $(\eta^5\text{-}C_5H_5)W(CO)_3S_xR$, where x = 2 and 3, tend to desulfurize spontaneously in solution. The complexes *cis*-$(PPh_3)_2Pt(Npht)(S_xR')$, where x = 1 and 2 and R' = $CH_2CH_2CH_3$, $CH(CH_3)_2$, $CH_2C_6H_5$, $p\text{-}C_6H_4CH_3$, and Npht, were prepared by oxidative addition of $R'S_xNpht$ to $(PPh_3)_2PtC_2H_4$. The complexes where x = 2 do not lose sulfur in solution. The X-ray structure of the complexes *cis*-$(PPh_3)_2Pt(Npht)SSCH(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3SS\text{-}p\text{-}C_6H_4CH_3$ confirm the presence of the disulfide linkage with S–S distances and M–S–S–C torsional angles of 2.037 (4) Å and 89.5° and 2.053 (4) Å and 63.1°, respectively.

There is strong interest in complexes containing catenated polysulfur ligands. Several new cyclic compounds such as Cp_2MS_5, where M = Zr and Hf,[2] $[C_5(CH_3)_5]_2MS_3$, where M = Ti and Zr,[2] $(Et_4N)_2MoS(S_4)_2$,[3] and others[4] have recently been reported. Metal complexes containing the linear arrangement MS_xR which are analogues of organic polysulfides are rare.[5] In view of sulfur's pronounced

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