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Solution Dynamics and Crystal Structure of $\text{CpMoOs}_3(\text{CO})_{10}(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$

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The tetranuclear heterometallic complex $\text{CpMoOs}_3(\text{CO})_{10}(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ (**1**, Cp = $\eta^5\text{-C}_5\text{H}_5$, Tol = *p*-C₆H₄Me) has been examined by variable-temperature ¹³C-NMR spectroscopy and by a full three-dimensional X-ray structural analysis. Complex **1** crystallizes in the orthorhombic space group Pna2₁ with *a* = 12.960(1) Å, *b* = 11.255(1) Å, *c* = 38.569(10) Å, *V* = 5626(2) Å³ and ρ(calcd) = 2.71 g cm⁻³ for *Z* = 8 and molecular weight 1146.9. Diffraction data were collected on a CAD4 diffractometer, and the structure was refined to *R_F* = 9.7% and *R_w* = 9.9% for 2530 data (MoKα radiation). There are two essentially equivalent molecules in the crystallographic asymmetric unit. The tetranuclear molecule contains a triangulated rhomboidal arrangement of metal atoms with Os(2) and Mo at the two bridgehead positions. The metal framework is planar; the dihedral angle between Os(1)-Os(2)-Mo and Os(3)-Os(2)-Mo planes is 180°. A triply bridging (μ₃, η²) acyl ligand lies above the Os(1)-Os(2)-Mo plane; the oxygen atom spans the two bridgehead positions, while the carbon atom spans one bridgehead position and an acute apical position. The molecular architecture is completed by an η⁵-cyclopentadienyl ligand and a semi-triply bridging carbonyl ligand on the molybdenum atom, and nine terminal carbonyl ligands—four on Os(3), three on Os(1), and two on Os(2). The two hydride ligands are inferred to occupy the Os(1)-Os(2) and Mo-Os(3) edges from structural and NMR data.

Introduction

In previous work,¹ we have described that the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with $\text{Cp}(\text{CO})_2\text{Mo}(\text{CTol})$ (Cp = $\eta^5\text{-C}_5\text{H}_5$, Tol = *p*-C₆H₄Me) has yielded three MoOs₃ mixed-metal clusters including the μ₃-η²-acyl compound $\text{CpMoOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ as the major product. Initial decarbonylation of this complex with Me₃NO/MeCN followed by reaction with dihydrogen has produced the dihydride complex $\text{CpMoOs}_3(\text{CO})_{10}(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ (**1**) in a quantitative yield. Synthesis and spectroscopic characterization of compound **1** has been published.^{1a,c} We herein report full details of solution dynamics and X-ray structural analysis of the dihydrido acyl complex **1**, which has been previously shown to undergo scission of the acyl C-O bond^{1a,c} induced by the hydride ligands.

Experimental Section

General Comments. Carbon-13(¹³C) CO-enriched H₂Os₃(¹³CO)₁₀² and Cp(CO)₂Mo(CTol)³ were prepared as described in the literature. ¹³C-NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Cr(acac)₃ (ca 0.02 M) was added to ¹³C samples as a shiftless relaxation reagent.

Preparation of ¹³CO-enriched **1*** Carbon-13 CO-enriched $\text{CpMoOs}_3(^{13}\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)-CH}_2\text{Tol}]$ was prepared from the reaction of ¹³CO-enriched H₂Os₃(¹³CO)₁₀ (ca 50% enrichment) with Cp(CO)₂Mo(CTol) and then this complex was utilized to prepare $\text{CpMoOs}_3(^{13}\text{CO})_{10}(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ (**1***) by the reported procedures.^{1c}

X-ray Data Collection and Structure Solution of **1.** Crystals were grown by slow recrystallization from a mixture of dichloromethane-petroleum ether at room temper-

Table 1. Crystal Data for CpMoOs₃(CO)₁₀(μ-H)₂[μ₃-η²-C(O)CH₂Tol] (1)

formula	C ₂₄ H ₁₆ O ₁₁ MoOs ₃
fw	1146.9
cryst syst	orthorhombic
space group	Pna2 ₁
a, Å	12.960 (1)
b, Å	11.255 (1)
c, Å	38.569 (10)
V, Å ³	5626 (2)
Z	8
ρ (calcd), gcm ⁻³	2.71
temp, °C	20 ± 1
λ (MoKα), Å	0.71069
μ, cm ⁻¹	140.0

ature. Crystal quality was poor as judged by optical examination and later by weak diffracting power. The general procedures of crystal indexing and data collection have been published elsewhere.⁴ Details of the crystal data are given in Table 1. A total of 5020 reflections were measured within an octant of 2θ ≤ 50°. A semi-empirical absorption correction was applied based on ψ-scan results of two reflections (2-1 15, 2-1 11) at χ = 90°. The minimum relative transmission was 42.9%. Even the best crystal we tried contained 1518 weak reflections for which I ≤ σ(I). There were no sign of crystal decay during the data collection. Positions of the metal atoms were obtained *via* direct method. All other non-hydrogen atoms were located in the subsequent difference electron density maps. No hydrogen atoms were included in the calculation. The Cp and benzene rings were refined as rigid bodies of regular pentagon and hexagon, respectively. The carbonyls bonded to osmium atoms were restrai-

Table 2. Final Positional Parameters with Esd's for CpMoOs₃(CO)₁₀(μ-H)₂[μ₃-η²-C(O)CH₂Tol] (1)

Atom	x	y	z	U (Å ²)	Atom	x	y	z	U (Å ²)
molecule A					molecule B				
Os(1)	0.9591(2)	0.0687(3)	0.0786		Os(1)	0.7242(2)	0.0653(3)	0.2388(1)	
Os(2)	0.9944(2)	0.0975(3)	0.0058(1)		Os(2)	0.7640(2)	0.0950(3)	0.3117(1)	
Os(3)	0.8774(3)	0.0418(4)	-0.0530(1)		Os(3)	0.6478(3)	0.0411(4)	0.3705(1)	
Mo	0.8100(5)	-0.0050(8)	0.0257(2)		Mo	0.5798(5)	-0.0067(7)	0.2926(2)	
O(1)	0.8517(44)	0.1814(59)	0.0194(17)	0.0589(164)	O(1)	0.6251(28)	0.1817(36)	0.2963(1)	0.0185(94)
O(4)	0.9780(43)	-0.1918(59)	0.0283(16)	0.0578(159)	O(4)	0.7559(40)	-0.1960(54)	0.2892(15)	0.0472(139)
O(11)	1.0504(35)	0.2733(46)	0.1169(14)	0.0447(134)	O(11)	0.8079(38)	0.2834(41)	0.2004(13)	0.0510(146)
O(12)	0.8367(51)	-0.0270(70)	0.1376(20)	0.0764(211)	O(12)	0.8881(48)	-0.1217(46)	0.2223(19)	0.0729(201)
O(13)	1.1346(30)	-0.1110(42)	0.0930(14)	0.0439(136)	O(13)	0.5917(35)	0.0085(46)	0.1763(9)	0.0382(125)
O(21)	1.1923(52)	-0.0274(89)	-0.0189(25)	0.1171(318)	O(21)	0.9536(34)	0.0434(54)	0.3330(16)	0.0556(158)
O(22)	1.1067(39)	0.3093(44)	-0.0278(15)	0.0556(159)	O(22)	0.8630(43)	0.3237(34)	0.3389(17)	0.0596(172)
O(31)	1.0558(58)	0.1435(85)	-0.0944(26)	0.1271(348)	O(31)	0.8532(52)	0.1215(79)	0.4137(17)	0.0909(240)
O(32)	0.9508(74)	-0.2184(34)	-0.0472(29)	0.1294(335)	O(32)	0.5803(46)	0.2936(49)	0.3690(18)	0.0714(193)
O(33)	0.8034(42)	0.3000(35)	-0.0447(17)	0.0622(167)	O(33)	0.7368(54)	-0.2079(54)	0.3665(25)	0.1205(315)
O(34)	0.7311(52)	0.0126(74)	-0.1152(13)	0.0810(219)	O(34)	0.4864(53)	-0.0218(107)	0.4225(25)	0.1158(339)
C(2)	0.8388(32)	0.1639(44)	0.0543(12)	0.0001(92)	C(2)	0.6050(67)	0.1721(85)	0.2597(26)	0.0576(245)
C(3)	0.7537(44)	0.2388(61)	0.0681(17)	0.0267(147)	C(3)	0.5129(76)	0.2239(111)	0.2443(31)	0.0790(311)
C(4)	0.9314(77)	-0.0886(107)	0.0250(30)	0.0751(308)	C(4)	0.7008(52)	-0.1231(70)	0.2878(20)	0.0300(165)
C(7)	0.9493(44)	0.6375(60)	0.1251(17)	0.0214(137)	C(7)	0.7081(68)	0.6814(95)	0.2044(27)	0.0645(262)
C(11)	1.0004(73)	0.1916(71)	0.1118(19)	0.0850(359)	C(11)	0.7902(39)	0.2041(38)	0.2184(15)	0.0199(135)
C(12)	0.8948(103)	-0.0262(97)	0.1153(29)	0.1259(525)	C(12)	0.8415(49)	-0.0352(68)	0.2253(24)	0.0562(244)
C(13)	1.0673(32)	-0.0510(41)	0.0854(15)	0.0154(123)	C(13)	0.6347(32)	0.0167(49)	0.2023(10)	0.0098(119)
C(21)	1.1205(40)	0.0104(66)	-0.0057(22)	0.0405(196)	C(21)	0.8770(43)	-0.0126(58)	0.3208(21)	0.0438(203)
C(22)	1.0534(58)	0.2379(54)	-0.0167(22)	0.0476(227)	C(22)	0.8373(48)	0.2313(45)	0.3293(19)	0.0354(182)
C(31)	0.9881(56)	0.0875(89)	-0.0849(22)	0.0660(275)	C(31)	0.7717(61)	0.0937(123)	0.3937(31)	0.0984(408)
C(32)	0.9360(56)	-0.1187(39)	-0.0504(24)	0.0487(214)	C(32)	0.6121(67)	0.2036(35)	0.3597(21)	0.0577(244)
C(33)	0.8363(53)	0.2061(35)	-0.0435(21)	0.0427(191)	C(33)	0.6843(43)	-0.1254(26)	0.3862(17)	0.0219(139)
C(34)	0.7762(45)	0.0141(71)	-0.0898(15)	0.0394(184)	C(34)	0.5612(53)	-0.0249(75)	0.4064(17)	0.0483(226)
C(51)	0.6851(50)	-0.0513(61)	0.0715(13)	0.0460(213)	C(51)	0.4992(49)	-0.1587(61)	0.2668(19)	0.0512(213)
C(52)	0.6310(50)	0.0080(61)	0.0446(13)	0.0288(165)	C(52)	0.4463(49)	-0.0583(61)	0.2533(19)	0.0825(329)
C(53)	0.6416(50)	-0.0603(61)	0.0138(13)	0.0867(357)	C(53)	0.3956(49)	-0.0007(61)	0.2813(19)	0.0933(367)
C(54)	0.7022(50)	-0.1618(61)	0.0218(13)	0.0831(328)	C(54)	0.4172(49)	-0.0656(61)	0.3120(19)	0.0819(346)
C(55)	0.7291(50)	-0.1563(61)	0.0574(13)	0.0975(397)	C(55)	0.4812(49)	-0.1632(61)	0.3031(19)	0.1213(511)
C(61)	0.8041(49)	0.3805(50)	0.0816(16)	0.0613(260)	C(61)	0.5647(30)	0.3526(32)	0.2346(11)	0.0127(117)
C(62)	0.8523(49)	0.4673(50)	0.0615(16)	0.0975(402)	C(62)	0.5680(30)	0.3800(32)	0.1993(11)	0.0460(209)

C(63)	0.8979(49)	0.5655(50)	0.0775(16)	0.0583(231)	C(63)	0.6133(30)	0.4858(32)	0.1882(11)	0.0513(219)
C(64)	0.8952(49)	0.5768(50)	0.1135(16)	0.0963(400)	C(64)	0.6553(30)	0.5642(32)	0.2124(11)	0.0453(206)
C(65)	0.8469(49)	0.4900(50)	0.1336(16)	0.0863(349)	C(65)	0.6520(30)	0.5368(32)	0.2477(11)	0.0323(165)
C(66)	0.8014(49)	0.3918(50)	0.1176(16)	0.0411(187)	C(66)	0.6067(30)	0.4310(32)	0.2587(11)	0.0423(191)

Numbers in parentheses are estimated standard deviations in the least significant digits. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3} [U_{11}\sin^2\alpha + U_{22}\sin^2\beta + U_{33}\sin^2\gamma + 2U_{12}\sin\alpha\sin\beta\cos\gamma + 2U_{13}\sin\alpha\sin\gamma\cos\beta + 2U_{23}\sin\beta\sin\gamma\cos\alpha] / [1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]$

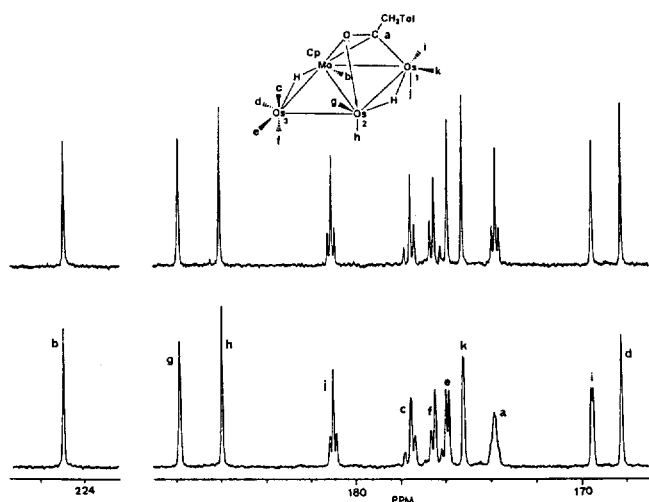


Figure 1. ^{13}C -NMR spectra (75 MHz, CD_2Cl_2 , -10°C) of compound **1***: (upper) ^1H -decoupled and (lower) ^1H -coupled.

ned as well: for each molecule, Os-CO and C-O distances were tied to common values which were optimized within 1.93-1.97 Å and 1.14-1.16 Å, respectively. The least-squares refinement employing anisotropic thermal parameters for the metal atoms and isotropic ones for the other atoms were converged to $R_F=9.7\%$ and $R_wF=9.9\%$ for 2530 reflections with $F \geq 6\sigma(F)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + (0.26F)^2]$. Final positional and thermal parameters for non-hydrogen atoms are given in Table 2. All calculations were performed on a VAX computer using the SDF⁵ and SHELX⁶ program packages.

Results and Discussion

Solution Dynamics of 1. The solution dynamics of compound **1**, $\text{CpMoOs}_3(\text{CO})_6(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C}(\text{O})\text{CH}_2\text{Tol}](\mathbf{1}^*)$ have been examined by variable-temperature ^{13}C -NMR spectroscopy. The limiting low temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1*** in CD_2Cl_2 was obtained at -10°C (see Figure 1) and is consistent with the molecular structure observed in the solid state (vide infra). The spectrum shows eleven carbonyl resonances at δ 224.9, 187.8, 185.9, 181.0 ($^2J_{\text{CC}}=23.4$ Hz), 177.5 ($^2J_{\text{CC}}=34.6$ Hz), 176.5 ($^2J_{\text{CC}}=34.6$ Hz), 175.9, 175.3, 173.6 ($^2J_{\text{CC}}=23.4$ Hz), 169.5, and 168.2 (each of intensity 1). The most downfield signal at δ 224.9 is assigned to the carbonyl group *b* on the molybdenum atom. This resonance lies in the reported region for terminal carbonyls on a molybdenum atom containing a cyclopentadienyl ligand.¹ The remaining resonances can be assigned on the basis of their temperature behavior and by consideration of carbon-carbon and

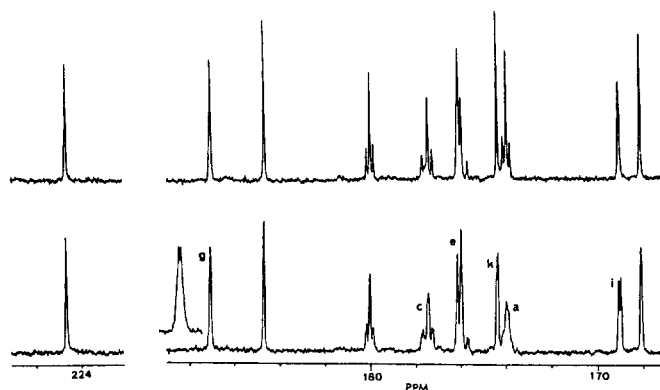


Figure 2. Variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (75 MHz, CDCl_3) of compound **1***.

carbon-hydrogen coupling patterns. The resonances at δ 177.5 and 176.5 exhibit an AB pattern of ^{13}C satellites ($^2J_{\text{CC}}=34.6$ Hz), characteristic of inequivalent trans diaxial carbonyls,⁷ *c* and *f*. The signal at δ 181.0 shows ^{13}C satellites ($^2J_{\text{CC}}=23.4$ Hz) and is assigned to the carbonyl ligand *j* trans to the acyl carbon *a*. The latter resonance is at δ 173.6 with ^{13}C satellites. The ^1H -coupled ^{13}C -NMR spectrum of **1*** in CD_2Cl_2 revealed that three resonances at δ 175.9 ($^2J_{\text{CH}}=11.1$ Hz), 175.3 ($^2J_{\text{CH}}=4.2$ Hz), and 169.5 ($^2J_{\text{CH}}=7.1$ Hz) are doublets due to a coupling to trans hydride ligands (see Figure 1). The acyl carbon signal *a* also becomes broad presumably due to a weak coupling to the hydride ligand, H(1).

Variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1*** in CDCl_3 are shown in Figure 2. The spectrum at -10°C shows eleven carbonyl resonances at δ 224.7, 187.2, 185.1, 180.2 ($^2J_{\text{CC}}=23.1$ Hz), 177.4 ($^2J_{\text{CC}}=34.5$ Hz), 176.1 ($^2J_{\text{CC}}=34.5$ Hz), 175.9, 174.5, 173.4 ($^2J_{\text{CC}}=23.1$ Hz), 168.9, and 168.0. The general pattern of spectrum at -10°C in CDCl_3 is essentially identical to that in CD_2Cl_2 except that one of the resonance due to trans diaxial carbonyls, *c* and *f*, shifted upfield and overlapped with the carbonyl signal at δ 175.9. Couplings to hydride ligands for the three resonances at δ 175.9 ($^2J_{\text{CH}}=11.8$ Hz), 174.5 ($^2J_{\text{CH}}=5.1$ Hz), 168.9 ($^2J_{\text{CH}}=7.3$ Hz) were also verified by obtaining ^1H -coupled ^{13}C -NMR spectrum at -10°C . However, when ^1H -coupled ^{13}C -NMR spectrum was taken at 23°C in CDCl_3 , six resonances at δ 187.2 ($^2J_{\text{CH}}=2.3$ Hz), 177.4 ($^2J_{\text{CH}}=4.6$ Hz), 175.9 ($^2J_{\text{CH}}=11.8$ Hz), 174.5 ($^2J_{\text{CH}}=5.1$ Hz), 173.4 (broad), and 168.9 ($^2J_{\text{CH}}=7.8$ Hz) show respective C-H couplings to trans hydride ligands (see Figure 3). These C-H couplings lead to clear location of the two hydride ligands and definitive assignment of carbonyl groups. The H(2) ligand bridges the Mo-Os(3) edge and the Mo-H(2)-Os(3) plane is coplanar with the Mo-Os(2)-Os(3) plane. Therefore, the resonance at δ 177.4 which shows both trans diaxial C-C and

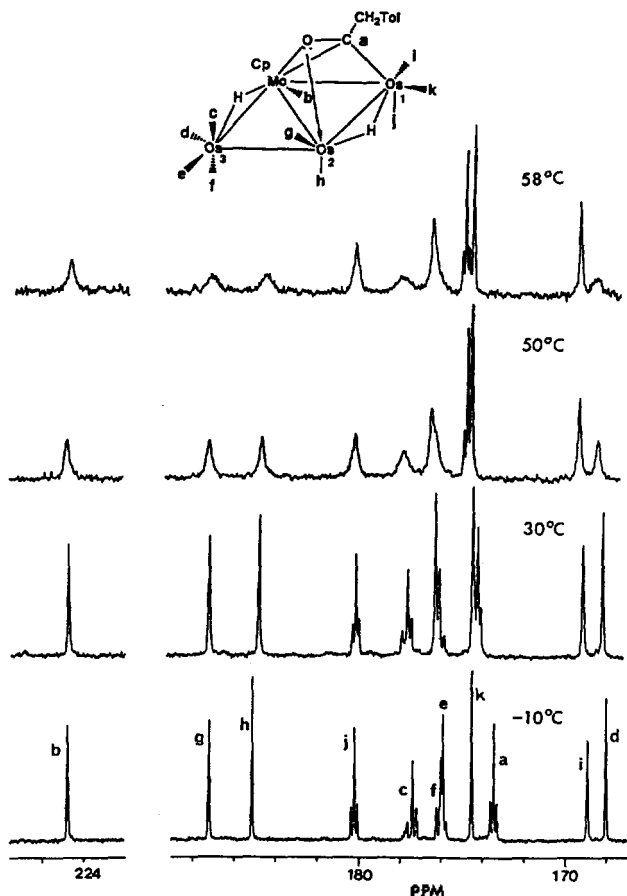


Figure 3. ^{13}C -NMR spectra (75 MHz, CDCl_3 , 23°C) of compound **1***: (upper) ^1H -decoupled and (lower) ^1H -coupled.

weak C-H couplings ($J_{\text{CH}} = 4.6$ Hz) is assigned to the carbonyl ligand *c*. The H(1) ligand bridges the Os(1)-Os(2) edge and occupies a position such that the Os(1)-H(1)-Os(2) plane is perpendicular to the Mo-Os(1)-Os(2) plane and is oriented to the opposite side of the acyl ligand. The H(1) ligand, therefore, couples to four trans carbonyls, *g* (187.2 ppm), *k* (174.5 ppm), *a* (173.4 ppm), and *i* (168.9 ppm): the resonance at δ 168.9 with a relatively large coupling (7.8 Hz) of these four resonances is assumed to be due to the carbonyl ligand *i* which is supposed to have the largest of hydrogen-metal-carbon angles among the four carbonyl ligands.

The resonances due to the two hydrides in the ^1H -NMR spectrum of **1** appear at δ -12.2 and -17.6 as singlets, which are in the region expected for edge-bridging hydrogens.⁸ The H(1) ligand (-17.6 ppm) is, therefore, proposed to be edge-bridging, although the possibility that the H(1) ligand triply-bridges the Mo-Os(1)-Os(2) face cannot be completely ruled out. The resonance at δ -12.2 is assigned to H(2) due to the observation that a hydrogen atom bridging a heterometal and osmium generally has a resonance at lower field than hydrogen bridging two osmium atoms.⁸

As the temperature is raised from -10°C to 58°C (see Figure 2), the five resonances at δ 180.2 (*j*), 176.1 (*f*), 174.5 (*k*), 173.4 (*a*), and 168.9 (*i*) remain sharp, while the other six resonances at δ 224.7 (*b*), 187.2 (*g*), 185.1 (*d* or *h*), 177.4 (*c*), 175.9 (*e*), and 168.9 (*d* or *h*) broaden to the same extent.

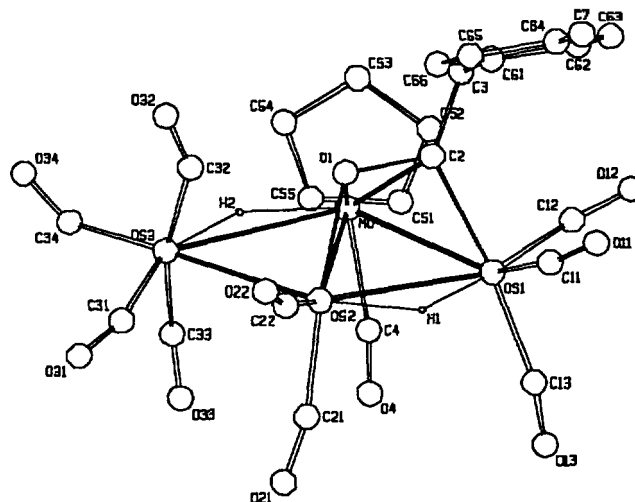


Figure 4. Molecular geometry and atomic labelling scheme for **1A**.

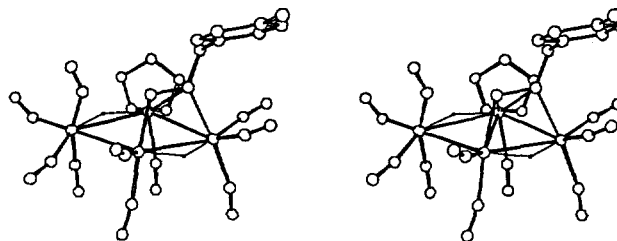


Figure 5. Stereoscopic view of **1A**.

This change may be due to localized threefold (*c*, *d*, and *e*) exchange at the $(\text{CO})_4\text{Os}(3)$ center and intermetallic carbonyl ligand (*b*, *g*, and *h*) exchange between the Mo and Os(2) centers. The localized threefold exchange at the $(\text{CO})_4\text{Os}(3)$ center has been previously observed for the analogous centers in $\text{HOs}_3(\text{CO})_{10}(\text{COCH}_3)_9$ and $\text{CpMoOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C}(\text{O})\text{CH}_2\text{Tol}]$ ($M = \text{W}^7, \text{Mo}^{1c}$). The resonances at δ 176.1 is assigned to the carbonyl group *f*, which is not involved in the localized threefold exchange and thus remains sharp. Of the two signals at δ 185.1 and 168.9 (*d* and *h*), the resonances at δ 185.1 is assigned to the axial carbonyl *h* while the signal at δ 168.9 is assigned to the equatorial carbonyl *d*. These assignments are based upon earlier observations that the resonances of axial carbonyls occur at lower field than those of equatorial carbonyls.¹⁰ It is apparent that the activation barriers for carbonyl exchange processes increase as $\text{Os}(2) = \text{Os}(3) = \text{Mo} < \text{Os}(1)$.

Crystal Structure of 1. The crystal consists of discrete ordered arrangement of $\text{CpMoOs}_3(\text{CO})_{10}(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-C}(\text{O})\text{CH}_2\text{Tol}]$, which are mutually separated by normal van der Waals distances. There are two equivalent molecules (**A** and **B**) in the crystallographic asymmetric unit. Figure 4 shows the scheme used for labelling atoms in both molecules and is an illustration of molecule **A**. A stereoscopic view of molecule **A** is given in Figure 5. Interatomic distances and angles with their estimated standard deviation (esd's) are listed in Tables 3 and 4. The tetranuclear molecule contains a planar triangulated rhomboidal arrangement of metal atoms, with Os(2) and Mo atoms at the bridgehead positions. The dihedral

Table 3 Interatomic Distances (Å) and Esd's for CpMoOs₃(CO)₁₀(μ-H)₂ [μ₃-η²-C(O)CH₂Tol] (1)

	Molecule A	Molecule B		Molecule A	Molecule B
(A) Metal-Metal Distances					
Os(1)-Os(2)	2.862(3)	2.868(4)	Os(2)-Os(3)	2.799(5)	2.790(5)
Os(1)-Mo	2.928(7)	2.934(8)	Os(3)-Mo	3.203(8)	3.178(8)
Os(2)-Mo	2.763(7)	2.748(7)			
(B) Metal-(μ₃-η²-Acyl) Distances					
Os(1)-C(2)	2.111(45)	2.146(92)	Mo-C(2)	2.228(50)	2.400(97)
Os(2)-O(1)	2.142(59)	2.133(38)	Mo-O(1)	2.180(68)	2.204(41)
(C) Distances within the C(O)CH₂Tol Ligand					
O(1)-C(2)	1.371(18)	1.438(107)	C(63)-C(64)	1.395(86)	1.395(55)
C(2)-C(3)	1.486(77)	1.456(140)	C(64)-C(7)	1.078(87)	1.518(109)
C(3)-C(61)	1.801(88)	1.640(126)	C(64)-C(65)	1.395(84)	1.395(59)
C(61)-C(62)	1.395(84)	1.394(59)	C(65)-C(66)	1.395(83)	1.395(52)
C(62)-C(63)	1.395(83)	1.395(52)	C(66)-C(61)	1.395(86)	1.395(55)
(D) Metal-Carbonyl Distances					
Os(1)-C(11)	1.959(79)	1.931(47)	Os(3)-C(31)	1.958(79)	1.931(96)
Os(1)-C(12)	1.960(115)	1.933(71)	Os(3)-C(32)	1.963(49)	1.932(46)
Os(1)-C(13)	1.962(44)	1.929(42)	Os(3)-C(33)	1.958(44)	1.934(32)
Os(2)-C(21)	1.957(60)	1.932(61)	Os(3)-C(34)	1.960(58)	1.931(69)
Os(2)-C(22)	1.958(69)	1.928(57)	Mo-C(4)	1.833(106)	2.051(72)
(E) Possible Metal...Carbon (Semibridging Carbonyl) Distances					
Os(1)...C(4)	2.746(118)	2.859(72)			
Os(2)...C(4)	2.367(117)	2.746(78)			
(F) Carbon-Oxygen (Carbonyl) Distances					
C(11)-O(11)	1.142(99)	1.154(69)	C(31)-O(31)	1.142(119)	1.153(124)
C(12)-O(12)	1.142(141)	1.152(92)	C(32)-O(32)	1.145(62)	1.151(78)
C(13)-O(13)	1.143(62)	1.152(56)	C(33)-O(33)	1.140(61)	1.153(76)
C(21)-O(21)	1.141(101)	1.153(78)	C(34)-O(34)	1.142(79)	1.152(103)
C(22)-O(22)	1.143(87)	1.154(69)	C(4)-O(4)	1.315(133)	1.090(93)
(G) Metal-Cp Ligand Distances					
Mo-C(51)	2.452(88)	2.239(69)	Mo-C(54)	2.256(67)	2.333(65)
Mo-C(52)	2.435(64)	2.371(68)	Mo-C(55)	2.344(63)	2.214(68)
Mo-C(53)	2.315(65)	2.427(64)			

Table 4 Selected Interatomic Angles (deg) with Esd's for CpMoOs₃(CO)₁₀(μ-H)₂ [μ₃-η²-C(O)CH₂Tol] (1)

	Molecule A	Molecule B		Molecule A	Molecule B
(A) Intermetallic Angles					
Mo-Os(1)-Os(2)	57.0(2)	56.5(2)	Mo-Os(3)-Os(2)	54.3(2)	54.4(2)
Os(1)-Os(2)-Mo	62.7(2)	62.9(2)	Os(3)-Os(2)-Mo	70.3(2)	70.0(2)
Os(2)-Mo-Os(1)	60.3(2)	60.5(2)	Os(2)-Mo-Os(3)	55.4(2)	55.6(2)
Os(1)-Os(2)-Os(3)	133.0(1)	133.0(1)	Os(1)-Mo-Os(3)	115.7(2)	116.1(2)
(B) M-M-CO Angles					
Mo-Os(1)-C(11)	146.6(26)	141.9(15)	Os(2)-Os(3)-C(31)	93.1(24)	82.0(34)
Mo-Os(1)-C(12)	111.7(15)	121.8(25)	Os(2)-Os(3)-C(32)	87.4(25)	75.4(25)
Mo-Os(1)-C(13)	93.9(36)	91.8(13)	Os(2)-Os(3)-C(33)	77.6(22)	92.4(19)
Os(2)-Os(1)-C(11)	121.1(23)	103.7(17)	Os(2)-Os(3)-C(34)	170.5(18)	168.7(23)
Os(2)-Os(1)-C(12)	147.0(33)	148.3(13)	Mo-Os(3)-C(31)	147.0(23)	136.1(33)
Os(2)-Os(1)-C(13)	95.4(17)	101.8(27)	Mo-Os(3)-C(32)	84.6(27)	83.7(24)
Os(1)-Os(2)-C(21)	107.5(24)	103.3(24)	Mo-Os(3)-C(33)	84.5(23)	82.0(20)
Os(1)-Os(2)-C(22)	126.1(24)	121.3(21)	Mo-Os(3)-C(34)	118.6(18)	116.9(21)

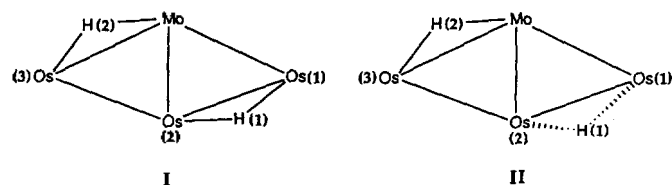
Mo-Os(2)-C(21)	125.2(21)	116.5(19)	Os(1)-Mo-C(4)	65.8(36)	67.4(22)
Mo-Os(2)-C(22)	142.9(22)	148.6(18)	Os(2)-Mo-C(4)	57.8(36)	68.0(21)
Os(3)-Os(2)-C(21)	99.0(23)	97.2(23)	Os(3)-Mo-C(4)	80.5(36)	88.9(22)
Os(3)-Os(2)-C(22)	91.8(24)	98.8(21)			
(C) Metal-Carbon-Oxygen Angles					
Os(1)-C(11)-O(11)	146.8(66)	162.9(49)	Os(3)-C(31)-O(31)	155.6(87)	165.5(91)
Os(1)-C(12)-O(12)	146.0(94)	157.3(66)	Os(3)-C(32)-O(32)	166.6(75)	148.5(71)
Os(1)-C(13)-O(13)	170.6(50)	163.7(45)	Os(3)-C(33)-O(33)	165.6(70)	158.0(52)
Os(2)-C(21)-O(21)	165.6(80)	156.3(62)	Os(3)-C(34)-O(34)	162.1(68)	149.8(82)
Os(2)-C(22)-O(22)	165.7(64)	166.7(54)	Mo-C(4)-O(4)	147.8(83)	168.0(67)
(D) M-C-M, M-O-M, M-M-O, and H-C-C Angles Involving the O(1)-C(2) system					
Mo-C(2)-Os(1)	84.8(18)	80.2(31)	Mo-O(1)-Os(2)	79.5(22)	78.6(13)
Mo-Os(1)-C(2)	49.3(13)	53.7(26)	Mo-Os(2)-O(1)	50.9(17)	51.8(11)
Os(1)-Mo-C(2)	45.9(12)	46.1(22)	Os(2)-Mo-O(1)	49.7(15)	49.5(10)
Os(2)-Os(1)-C(2)	68.0(13)	71.9(26)	Os(1)-Os(2)-O(1)	70.9(17)	68.9(11)
Mo-C(2)-O(2)	70.0(34)	64.4(99)	Mo-O(1)-C(2)	73.8(35)	79.4(42)
Os(3)-Os(2)-O(1)	80.1(17)	82.5(11)	Os(3)-Mo-O(1)	70.6(17)	72.7(11)
C(2)-Mo-O(1)	36.2(21)	36.1(26)	Os(3)-Mo-C(2)	106.4(13)	108.7(23)
(E) Other Angles at the "Acyl" Carbon Atom					
C(3)-C(2)-Mo	122.5(35)	116.1(67)	C(3)-C(2)-Os(1)	132.7(38)	132.6(76)
(F) Other Angles within the C(O)CH ₂ Tol Ligand					
O(1)-C(2)-C(3)	111.1(47)	121.3(81)	C(63)-C(64)-C(65)	120.0(54)	120.0(35)
C(2)-C(3)-C(61)	109.7(43)	96.4(70)	C(63)-C(64)-C(7)	117.2(65)	126.2(51)
C(3)-C(61)-C(62)	128.4(51)	115.5(50)	C(7)-C(64)-C(65)	120.3(66)	113.8(49)
C(3)-C(61)-C(66)	111.1(47)	124.4(52)	C(64)-C(65)-C(66)	120.0(56)	120.0(36)
C(61)-C(62)-C(63)	120.0(56)	120.0(36)	C(65)-C(66)-C(61)	120.0(55)	120.0(38)
C(62)-C(63)-C(64)	120.0(55)	120.0(38)	C(66)-C(61)-C(62)	120.0(54)	120.0(35)

angle between Mo-Os(1)-Os(2) and Mo-Os(2)-Os(3) planes is 180°. The observed geometry is entirely consistent with that expected for a tetranuclear complex with 62 valence electrons.¹¹ The Os(1) and Os(2) atoms are bonded to three and two terminal carbonyl ligands, respectively, and the Os(3) atom is coordinated to four terminal carbonyls. The molybdenum atom is coordinated to a semitriply bridging carbonyl ligand and an η^5 -cyclopentadienyl ring.

The present molecule has a triply bridging acyl ligand, C(2)-O(1), associated with the triangular Mo-Os(1)-Os(2) face. The μ_3 - η^2 -acyl ligand acts as a net five-electron donor to the cluster. The C(2)-O(1) distance of 1.371(18) Å of molecule A suggests significant activation of this bond; this is far closer to the accepted C-O single-bond distance of 1.43 Å than to the unperturbed C=O double-bond distance of 1.215 ± 0.005 Å found in aldehydes and ketones.¹² We note here that the following C-O distances have been observed for the μ_3 - η^2 -acyl ligands: 1.32(2) Å in [Fe₃(CO)₉(μ_3 - η^2 -MeCO)]⁻¹³ and 1.372(20) Å in CpWOs₃(CO)₁₁[μ_3 - η^2 -C(O)CH₂Tol].⁷ The μ_3 - η^2 -acyl ligands found in the present complex I and in the other cluster compounds represent possible models for chemisorbed acyl fragments on metal surfaces.

The metal-metal bond distances in A and B show identical trends: the osmium-osmium distances in A are (in order) Os(1)-Os(2) = 2.862(3), Os(2)-Os(3) = 2.799(5) Å and the molybdenum-osmium distances are (in order) Mo-Os(3) = 3.203(8), Mo-Os(1) = 2.928(7) and Mo-Os(2) = 2.763(7) Å. The bridgehead Mo-Os(2) bond length of 2.763(7) Å is far shorter than

the Mo-Os(1) and Mo-Os(3) bond distances; this is presumably a result of this edge being bridged by O(1). A similar feature was observed in both the [Fe₃(CO)₉(μ_3 - η^2 -MeCO)]⁻¹² anion and the CpWOs₃(CO)₁₁[μ_3 - η^2 -C(O)CH₂Tol]⁷ cluster complex. The positions of the two hydride ligands were not located directly from X-ray data. The Mo-Os(3) bond distance is significantly longer than the remaining Os-Mo distances. This edge is believed to be associated with a single, unsupported μ -hydride ligand.¹⁴ The presence of the bridging hydride ligand, H(2), is further confirmed by the enlargement of M-M-CO angles coplanar with and adjacent to the M-H-M linkages,¹⁵ <Mo-Os(3)-C(34) = 118.6 (18)° in A and 116.9 (21)° in B. The other hydride ligand, H(1), is associated with the Os(1)-Os(2) edge; the Os(1) and Os(2) centers are formally "electron-deficient" (17e each, not taking into account contribution from the two hydrides). The Os(1)-H(1)-Os(2) plane can occur at various angles relative to the Mo-Os(1)-Os(2) plane. Cases of interest in the present discussion are those where the Os(1)-H(1)-Os(2) plane is either coplanar (as in I) with or perpendicular (as in II) to the Mo-Os(1)-Os(2) plane. The carbonyl ligands CO(11) and CO(22) in I



and CO(13) and CO(21) in II are coplanar with and adjacent to the Os(1)-H(1)-Os(2) plane, respectively. The angles of $\angle\text{Os}(2)\text{-Os}(1)\text{-C}(11)$ and $\angle\text{Os}(1)\text{-Os}(2)\text{-C}(22)$ are large than those of $\angle\text{Os}(2)\text{-Os}(1)\text{-C}(13)$ and $\angle\text{Os}(1)\text{-Os}(2)\text{-C}(21)$ as listed in Table 4. These data support the structure I in the solid state. However, the spectral pattern in solution supports the structure II in the solution state. The bridging hydride in I would show a coupling to only one trans carbonyl carbon C(12), whereas that in II would exhibit couplings to the three trans carbonyl carbons, C(11), C(12), and C(22). The latter coupling patterns were observed in the ^{13}C -NMR spectrum (23°C , CDCl_3) of \mathbf{I}^* (vide supra).

The carbonyl ligand on the molybdenum atom with Mo-C(4)=1.833 (106) Å in A is semi-triply bridging; there are some interactions with the Os(1) and Os(2) atoms, with Os(1)⋯C(4)=2.746(118) Å and Os(2)⋯C(4)=2.367(117) Å. The formal electron counts of I at the metal atoms are as follows: Mo, $18\frac{1}{2}e$; Os(1), $17\frac{1}{2}e$; Os(2), $17\frac{1}{2}e$; Os(3), $18\frac{1}{2}e$. "Semibridging" carbonyl ligands are often known to distribute electron density more evenly around a metal cluster framework.¹⁶ The semi-triply bridging carbonyl ligand, CO(4), with respect to the Mo-Os(1)-O(2) face is in the appropriate location to effectively donate electron density from the formally "electron-rich" Mo to the "electron-deficient" Os(1) and Os(2).

All other features of the molecular geometry are within the expected range. Individual Os-CO distances range from 1.929(42) Å through 1.963(49) Å, C-O bond lengths range from 1.141(101) Å through 1.154(69) Å and Os-C-O angles are in the range $146.0(94)$ - $170.6(50)^\circ$. Molybdenum-carbon (Cp) distances vary from 2.214(68) through 2.452(88) Å.

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