Structure of [(OC)₃(Me₃P)₂Re(μ-H)]₂Os₃(CO)₁₀: Change in the Site of Hydride Coordination in a Metal Cluster on Carbonyl Substitution by Trimethylphosphine

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In metal carbonyl clusters that also contain phosphine and bridging hydride ligands, it is usually found that, as far as possible, the hydrides bridge metal–metal bonds that are cis to the phosphine ligands.[1,2]

In this note we describe the synthesis and structure of [(OC)₃(Me₃P)₂Re(μ-H)]₂Os₃(CO)₁₀. The spectroscopic and structural data clearly indicate that the hydride ligands bridge the Re–Os bonds (i.e., cis to the trimethylphosphine groups). This is in marked contrast to [(OC)₅Re]₂Os₃(μ-H)₂(CO)₁₀, where the hydride atoms span two of the OsOs bonds.[3,4] We offer an explanation for this change in coordination site that may be of more general relevance to the understanding of the site preference of bridging hydride ligands in cluster compounds.

Experimental Section

Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hexane and dichloromethane were distilled under nitrogen from potassium and P₂O₅, respectively. The compounds Re(CO)₅(H),[5] Os₃(μ-H)₂(CO)₁₀,[6] and Os₃(CO)₁₀(COE)₂[7] (COE = cyclooctene) were prepared by previously published procedures.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. The electron-impact (70 eV) mass spectrum was obtained with a Hewlett-Packard 5985 GC-MS instrument. NMR spectra were recorded on either a Brucker WM400 or Brucker SY-100 spectrometer. The microanalyses were obtained by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of Re(CO)₃(PMe₃)₂(H). This compound was prepared in good yield from the reaction of excess PMe₃ with Re(CO)₅(H) in benzene at room temperature.[8] The reaction was complete after 3.5 h. The residue after removal of the solvent and excess reagents on the vacuum line was recrystallized from toluene/hexane at –78 °C to yield the desired product as a white, air-stable solid. IR (hexane): ν(CO) 2010 (s), 1929 (s), 1914 (vs) cm⁻¹. ¹H NMR (C₆D₆) (δ): major isomer, 1.18, 1.17, 1.16 (intensity ratio 5.0:2.7:4.8), –4.74 (t, J_{PH} = 28.7 Hz); minor isomer, 1.41,

1.40, 1.39 (ratio 1.3:1.1:1.4), –5.80 (t, J_{PH} = 20.9 Hz).[9] MS (EI): *m/z* 424 (M⁺). Anal. Calcd for C₉H₁₉O₃P₂Re: C, 25.53; H, 4.52. Found: C, 25.54; H, 4.48.

Preparation of [(OC)₃(Me₃P)₂Re(μ-H)]₂Os₃(CO)₁₀ (1). A solution of Os₃(CO)₁₀(COE)₂ was prepared from Os₃(μ-H)₂(CO)₁₀ (30 mg, 0.035 mmol) and cyclooctene in the presence of ethylene. The solvent (and excess cyclooctene) was removed under vacuum. To the solid Os₃(CO)₁₀(COE)₂ was added CH₂Cl₂ (1 mL) and hexane (12 mL) and the resulting solution cooled to 0 °C. To the solution was added Re(CO)₃(PMe₃)₂(H) (31 mg, 0.073 mmol) and the mixture allowed to warm with stirring to room temperature; the stirring was continued for 1.5 h. The solvent was removed on the vacuum line and the residue washed with hexane to remove any remaining Re(CO)₃(PMe₃)₂(H). The solid was recrystallized twice from CH₂Cl₂/hexane (~1:5) to yield 1 (52 mg, 88%) as bright orange, air-stable crystals. IR (CH₂Cl₂): ν(CO) 2079 (m), 2029 (vs), 1987 (s), 1953 (m), 1907 (m) cm⁻¹. ¹H NMR (C₆D₅CD₃) (δ): 1.23–1.16 (m); major isomer, –16.96 (t, J_{PH} = 13.8 Hz), –17.30 (t, J_{PH} = 14.8 Hz); minor isomer, –17.17 (t, J_{PH} = 14.3 Hz). Anal. Calcd for C₂₈H₃₈O₁₆Os₃P₂Re₂: C, 19.81; H, 2.26. Found: C, 19.97; H, 2.09.

X-ray Analysis of 1. A single crystal (0.078 × 0.16 × 0.24 mm) of 1 as prepared above was mounted on an Enraf Nonius CAD-4F diffractometer, and intensity data were collected at ambient temperature with the use of graphite-monochromated Mo Kα radiation. The unit cell was determined from 25 well-centered reflections (30° ≤ 2θ ≤ 40°). The data were collected in the range +h, ±k, and ±l. Two intensity standards, measured every 1 h of acquisition time, varied randomly within ±3% during the data collection. An analytical absorption correction[10] (checked against ψ-scan measurements) was applied to the measured intensity data. Data reduction included the small corrections for intensity scale variation and corrections for Lorentz and polarization effects.

The positions of the Re and Os atoms were determined by direct methods. Subsequent electron density difference synthesis revealed the remaining non-hydrogen atoms. Because of the large thermal parameters for P(3) and P(4), and two carbon atoms attached to each of these phosphorus atom, these six atoms were divided into two half-atom pairs and each pair given a single isotropic thermal parameter. An extinction parameter was included in the refinement. The final least-squares refinement of 353 parameters for 3983 observed (of 5779 unique) reflections ($I \geq 2.5 \sigma(I)$) and 22 restraints (for distances between Re(2) and the four half-occupancy phosphorus atom sites and for lengths of all P–C bonds) included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Re, Os, P(1), P(2), and O atoms, and one isotropic temperature factor for each full C atom. Hydrogen atoms were placed in calculated positions and their contributions included in the derivation of the shifts (and esd's) for atoms to which they were bonded. They were given fixed isotropic thermal parameters. A weighting scheme, based on counting statistics, was applied for which ⟨w(|Fₒ| – |Fᴄ|)²⟩ was near constant as a function of both |Fₒ| and (sin θ)/λ. The highest peak in the final electron density difference map was 1.2 (2) e Å⁻³ and occurred 1.28 Å from Os(2). Complex scattering factors for neutral atoms were used in the calculation of structure factors.[11]

The programs used for data reduction, structural solution, and initial refinement were from the NRCVAX crystal structure system.[12] The program suite CRYSTALS was employed in the final refinement.[13] All computations were carried out on a MicroVAX-II computer. Crystallographic data are summarized in Table I; the final positional and isotropic or equivalent isotropic thermal parameters are given in Table II; selected distances and angles are given in Table III. Additional experimental details, the coordinates and temperture factors for the hydrogen atoms, anisotropic temperature factors, and additional bond length and angle data are deposited as supplementary material.

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Table I. Crystal Data for 1

a, Å	9.421 (3)	formula	$C_{28}H_{38}O_{16}Os_3P_4Re_2$
b, Å	14.920 (2)	cryst syst	triclinic
c, Å	17.214 (2)	space group	$P\bar{1}$
α, deg	71.19 (1)	λ, Å	0.709 30
β, deg	78.25 (2)	V, Å^3	2223.1
γ, deg	79.22 (2)	Z	2
2θ range, deg	4–45	obsd data^a	3983
R^b	0.028	params	353
$R_w{}^c$	0.034	GOF^d	2.1

^{a} $I_0 \geq 2.5\sigma(I_0)$. ^{b} $R = \sum\|F_o\| - |F_c\|/\sum|F_o|$. ^{c} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + 0.0002F_o{}^2]^{-1}$. ^{d} GOF $= (\sum w(|F_o| - |F_c|)^2/$ (degrees of freedom))$^{1/2}$.

Results and Discussion

Addition of $Re(CO)_3(PMe_3)_2(H)$ to $Os_3(CO)_{10}(COE)_2$ (COE = cyclooctene) in hexane at room temperature gave $[(OC)_3-(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (1) in excellent yield (eq 1). The compound was isolated as bright orange, air-stable crystals.

$$Os_3(CO)_{10}(COE)_2 + 2Re(CO)_3(PMe_3)_2(H) \rightarrow$$
$$[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10} \quad (1)$$
$$\mathbf{1}$$
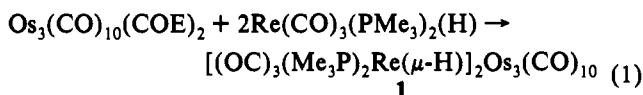
The X-ray crystal structure of **1** (Figure 1) reveals an arrangement of non-hydrogen ligands similar to that in $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$ (**2**), prepared by Shapley, Churchill, and co-workers using a method analogous to that shown in eq 1.[3] The metal–metal bond lengths (and angles) in the two clusters are, however, very different as is shown in Figure 2.

It is well established that the presence of a single bridging hydride ligand is generally associated with a lengthening of a metal–metal vector compared to that when it is unbridged.[14] In trinuclear osmium carbonyl clusters, the lengths of unbridged Os–Os bonds are usually within ±0.05 Å of 2.877 Å, the average Os–Os length in $Os_3(CO)_{12}$, whereas the Os–Os distances in Os-(μ-H)Os linkages are normally around 3.0 Å.[15–17] As can be seen from Figure 2, the Os–Os bond lengths in **2** clearly indicate that the hydride ligands bridge Os(1)–Os(2) and Os(2)–Os(3).[4] Furthermore, the Re–Os distances in the molecule are as expected for unbridged bonds: the distances are close to 2.959 Å, the mean of the bond length in $Re_2(CO)_{10}$ (3.041 (1) Å)[18] and the average Os–Os length is $Os_3(CO)_{12}$ (2.877 Å).[16]

In contrast, the Os–Os lengths in **1** (Figure 2) indicate that none is bridged by a hydride ligand; the longest Os–Os distance is 2.929 (1) Å. On the other hand, the Os–Re lengths in **1** (3.268 (1) and 3.270 (1) Å) are some 0.3 Å longer than the corresponding lengths in **2**. The metal–metal bond lengths in **1** are, therefore, consistent with the view that the hydride ligands bridge the Re–Os rather than Os–Os bonds. The bond angles in **1** support this view: for example, the Os(2)–Os(1)–Re(1) and Os(3)–Os(2)–Re(2) angles in **1** are 120.96 (3) and 118.79 (3)°, respectively, whereas in molecule A of **2** the corresponding angles are 103.93 (10) and 103.97 (9)°. (The molecular dimensions of the two independent molecules of **2** are not, in a chemical sense, significantly different.[4]) The $Re(CO)_3(PMe_3)_2(H)$ ligands are assumed to be bound to their respective osmium atoms via three-center, two-electron bonds. This type of bonding was proposed

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Thermal Parameters (Å^2 × 10^2) for the Non-Hydrogen Atoms of 1

atom	x/a	y/b	z/c	U(iso)
Os(1)	6953.4 (6)	850.6 (3)	2018.8 (3)	380
Os(2)	7250.4 (6)	2497.1 (3)	2479.5 (3)	385
Os(3)	5216.2 (6)	2631.0 (3)	1355.0 (3)	464
Re(1)	9002.2 (6)	−1187.3 (3)	2658.2 (3)	373
Re(2)	7292.2 (6)	4354.8 (3)	3083.3 (3)	411
P(1)	9104 (4)	−1212 (2)	4087 (2)	518^a
P(2)	11431 (4)	−664 (2)	2060 (2)	513^a
P(3)	4682 (7)	5011 (5)	3184 (5)	496 (14)^{a,b}
P(30)	4623 (7)	4798 (5)	3438 (5)	496 (14)^{a,b}
P(4)	8001 (8)	5478 (5)	1689 (4)	486 (13)^{a,b}
P(40)	7516 (9)	5642 (5)	1770 (4)	486 (13)^{a,b}
O(11)	4616 (11)	124 (7)	3523 (6)	677
O(12)	9448 (13)	1415 (7)	601 (6)	762
O(13)	5721 (12)	−182 (8)	1090 (7)	791
O(21)	5067 (13)	1784 (7)	4051 (6)	749
O(22)	9669 (14)	3201 (9)	1033 (7)	932
O(23)	9604 (12)	1582 (7)	3547 (6)	687
O(31)	2936 (12)	2063 (8)	2918 (7)	860
O(32)	7598 (14)	3205 (8)	−118 (7)	991
O(33)	3702 (15)	4664 (7)	880 (7)	822
O(34)	3753 (16)	1885 (9)	306 (7)	983
O(41)	6040 (11)	−1973 (7)	3367 (7)	687
O(42)	8763 (12)	−1253 (8)	913 (6)	751
O(43)	10559 (12)	−3215 (7)	3028 (8)	805
O(51)	6910 (15)	2868 (8)	4803 (7)	946
O(52)	10605 (12)	3716 (9)	2882 (9)	907
O(53)	7783 (13)	5773 (8)	3913 (7)	839
C(11)	5501 (15)	423 (9)	2954 (8)	479 (33)
C(12)	8505 (16)	1233 (10)	1123 (9)	555 (36)
C(13)	6204 (15)	199 (9)	1452 (8)	531 (35)
C(21)	5822 (16)	2060 (10)	3440 (9)	588 (38)
C(22)	8704 (17)	2909 (10)	1572 (9)	633 (40)
C(23)	8691 (15)	1946 (9)	3137 (8)	463 (32)
C(31)	3828 (18)	2258 (10)	2362 (10)	646 (41)
C(32)	6735 (17)	2957 (10)	477 (10)	658 (42)
C(33)	4342 (18)	3902 (12)	1052 (9)	742 (45)
C(34)	4281 (18)	2165 (11)	714 (10)	688 (43)
C(41)	7130 (15)	−1656 (9)	3105 (8)	507 (34)
C(42)	8848 (15)	−1201 (9)	1568 (8)	528 (35)
C(43)	9942 (17)	−2428 (11)	2896 (9)	632 (40)
C(44)	9109 (19)	−2399 (8)	4815 (9)	906 (54)^a
C(45)	7587 (13)	−527 (9)	4564 (8)	694 (43)^a
C(46)	10671 (13)	−842 (10)	4311 (9)	732 (45)^a
C(47)	12933 (13)	−1497 (9)	2513 (9)	797 (48)^a
C(48)	12026 (17)	−593 (11)	972 (6)	742 (45)^a
C(49)	11776 (16)	465 (7)	2121 (8)	643 (40)^a
C(51)	6980 (16)	3408 (10)	4146 (9)	595 (38)
C(52)	9338 (19)	3934 (11)	2957 (9)	691 (42)
C(53)	7593 (17)	5239 (10)	3583 (9)	630 (40)
C(54)	3438 (36)	4119 (23)	3671 (22)	1062 (91)^{a,b}
C(540)	3633 (38)	3919 (22)	4250 (18)	1062 (91)^{a,b}
C(55)	4093 (17)	5800 (8)	3849 (8)	759 (47)^a
C(56)	3866 (40)	5784 (23)	2289 (16)	995 (84)^{a,b}
C(560)	3546 (36)	5088 (26)	2605 (17)	995 (84)^{a,b}
C(57)	7473 (37)	6730 (10)	1633 (22)	839 (72)^{a,b}
C(570)	6570 (34)	6802 (13)	1816 (22)	839 (72)^{a,b}
C(58)	7166 (17)	5461 (11)	830 (6)	753 (46)^a
C(59)	9956 (15)	5448 (25)	1355 (23)	935 (81)^{a,b}
C(590)	9377 (19)	5916 (25)	1381 (23)	935 (81)^{a,b}

^{a} Atomic parameters affected by restraints. ^{b} Occupancy = 0.5.

many years ago by Kaesz and co-workers as present in $(OC)_5Re(\mu\text{-}H)ReMn(CO)_9$.[19]

Changes in the site of coordination of a hydride ligand upon replacement of a carbonyl by a phosphine ligand has been observed previously. For example, in $Ru_4(\mu\text{-}H)_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ hydrogen atoms bridge all three edges of the tetrahedron connected

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Table III. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths

Os(1)–Os(2)	2.8889 (8)	2.889[a]	Os(2)–Os(3)	2.9289 (9)	2.931[a]
Os(1)–Os(3)	2.8668 (8)	2.869[a]	Os(2)–Re(2)	3.2680 (8)	3.269[a]
Os(1)–Re(1)	3.2701 (9)	3.272[a]			

Bond Angles

Os(3)–Os(1)–Os(2)	61.18 (2)	C(33)–Os(3)–C(31)	94.1 (7)
Re(1)–Os(1)–Os(2)	120.96 (2)	C(33)–Os(3)–C(32)	89.0 (7)
Re(1)–Os(1)–Os(3)	176.44 (2)	C(34)–Os(3)–Os(1)	95.4 (5)
C(11)–Os(1)–Os(2)	93.7 (4)	C(34)–Os(3)–Os(2)	155.2 (5)
C(11)–Os(1)–Os(3)	94.0 (4)	C(34)–Os(3)–C(31)	95.0 (6)
C(11)–Os(1)–Re(1)	88.7 (4)	C(34)–Os(3)–C(32)	91.4 (7)
C(12)–Os(1)–Os(2)	86.2 (4)	C(34)–Os(3)–C(33)	98.1 (7)
C(12)–Os(1)–Os(3)	89.2 (4)	P(1)–Re(1)–Os(1)	100.71 (9)[b]
C(12)–Os(1)–Re(1)	88.2 (4)	P(1)–Re(1)–P(2)	95.5 (1)[b]
C(12)–Os(1)–C(11)	176.3 (6)	P(2)–Re(1)–Os(1)	99.16 (8)[b]
C(13)–Os(1)–Os(2)	154.9 (4)	C(41)–Re(1)–Os(1)	83.0 (4)
C(13)–Os(1)–Os(3)	93.7 (4)	C(41)–Re(1)–P(1)	86.3 (4)[b]
C(13)–Os(1)–Re(1)	84.0 (4)	C(41)–Re(1)–P(2)	176.9 (4)[b]
C(13)–Os(1)–C(11)	88.6 (5)	C(42)–Re(1)–Os(1)	79.5 (4)
C(13)–Os(1)–C(12)	93.0 (6)	C(42)–Re(1)–P(1)	177.4 (4)[b]
Os(3)–Os(2)–Os(1)	59.04 (2)	C(42)–Re(1)–P(2)	87.0 (4)[b]
Re(2)–Os(2)–Os(1)	175.01 (2)	C(42)–Re(1)–C(41)	91.2 (6)
Re(2)–Os(2)–Os(3)	118.79 (2)	C(43)–Re(1)–Os(1)	167.9 (5)
C(21)–Os(2)–Os(1)	86.9 (4)	C(43)–Re(1)–P(1)	88.8 (5)[b]
C(21)–Os(2)–Os(3)	91.7 (4)	C(43)–Re(1)–P(2)	87.3 (5)[b]
C(21)–Os(2)–Re(2)	88.7 (4)	C(43)–Re(1)–C(41)	90.3 (6)
C(22)–Os(2)–Os(1)	93.9 (5)	C(43)–Re(1)–C(42)	90.7 (6)
C(22)–Os(2)–Os(3)	90.7 (4)	P(3)–Re(2)–Os(2)	100.7 (2)[b]
C(22)–Os(2)–Re(2)	90.6 (5)	P(4)–Re(2)–Os(2)	97.6 (2)[b]
C(22)–Os(2)–C(21)	177.6 (6)	P(4)–Re(2)–P(3)	94.7 (3)[b]
C(23)–Os(2)–Os(1)	98.7 (4)	C(51)–Re(2)–Os(2)	80.1 (4)
C(23)–Os(2)–Os(3)	157.7 (4)	C(51)–Re(2)–P(3)	92.1 (5)[b]
C(23)–Os(2)–Re(2)	83.5 (4)	C(51)–Re(2)–P(4)	173.1 (5)[b]
C(23)–Os(2)–C(21)	88.5 (6)	C(52)–Re(2)–Os(2)	81.8 (5)
C(23)–Os(2)–C(22)	89.1 (6)	C(52)–Re(2)–P(3)	176.0 (5)[b]
Os(2)–Os(3)–Os(1)	59.78 (2)	C(52)–Re(2)–P(4)	81.7 (5)[b]
C(31)–Os(3)–Os(1)	86.1 (4)	C(52)–Re(2)–C(51)	91.5 (6)
C(31)–Os(3)–Os(2)	84.8 (4)	C(53)–Re(2)–Os(2)	167.5 (4)
C(32)–Os(3)–Os(1)	89.3 (5)	C(53)–Re(2)–P(3)	88.6 (5)[b]
C(32)–Os(3)–Os(2)	87.7 (5)	C(53)–Re(2)–P(4)	89.9 (4)[b]
C(32)–Os(3)–C(31)	172.5 (6)	C(53)–Re(2)–C(51)	91.3 (6)
C(33)–Os(3)–Os(1)	166.4 (5)	C(53)–Re(2)–C(52)	89.5 (7)
C(33)–Os(3)–Os(2)	106.6 (5)		

[a] Corrected values based on rigid body motion of the metal atoms.
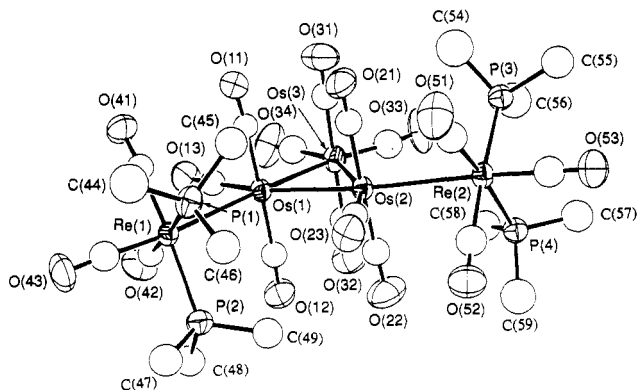[b] One or more atoms were affected by restraints.

Figure 2. ORTEP drawings of the inner atoms of **1** (A) and molecule A of [(OC)₅Re]₂Os₃(μ-H)₂(CO)₁₀ (**2**) (B) with the metal–metal bond lengths (Å). The standard deviations in the bond lengths are no more than 0.003 Å.

Chart I

Figure 1. Molecular structure of [(OC)₃(Me₃P)₂Re(μ-H)]₂Os₃(CO)₁₀ (**1**).

to the Ru atom to which both phosphorus atoms are coordinated.[20] This leaves two adjacent tetrahedral edges free of hydrogen atoms. In the parent compound, Ru₄(μ-H)₄(CO)₁₂, two opposite edges are left unbridged (D_{2d} structure).[21] In Os₃(μ-H)(μ-S₂CH)(CO)₁₀ both bridging ligands span the same Os–Os vector, whereas in Os₃(μ-H)(μ-S₂CH)(CO)₉(PMe₂Ph) the hydride bridges the Os–

Os bond that is cis to the PMe₂Ph group and the sulfur ligand bridges a second Os–Os vector.[22]

As mentioned in the Introduction, it is usually found in carbonyl cluster compounds that also contain phosphine and bridging hydride ligands that, as far as possible, the hydride ligands bridge the metal–metal bonds that are cis to the phosphorus atoms.[1,15,20,22] This, even though these metal–metal bonds are invariably the more sterically hindered bonds. The bonds are, however, expected to be the more electron rich: because of the poorer π-acceptor properties of phosphine ligands compared to the CO group there should be less delocalization of the electron density in the metal–metal bond onto the neighboring ligands as shown in Chart I (L = PMe₃). Molecular orbital calculations for Ru₃(CO)₁₂ have shown that this type of interaction (i.e., L = CO) is significant.[23]

Fehlner has discussed the energetics of the formation of E–H–M versus M–H–M formation (E = main group element, M =

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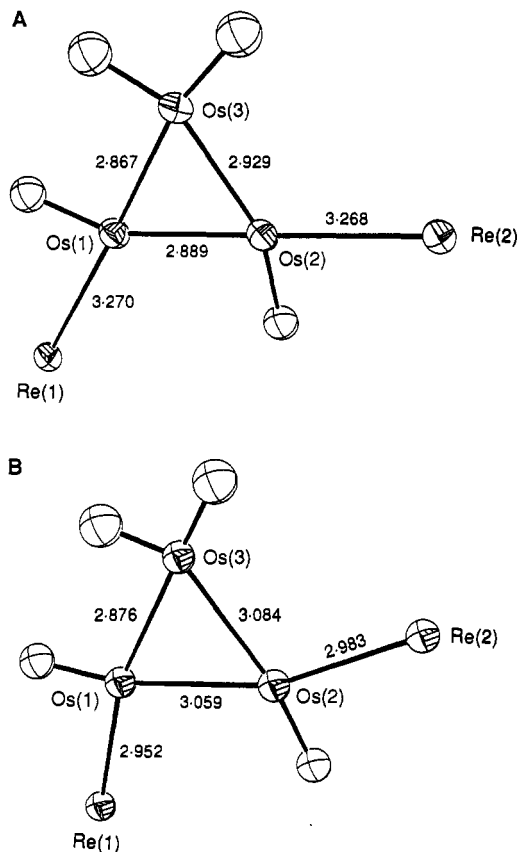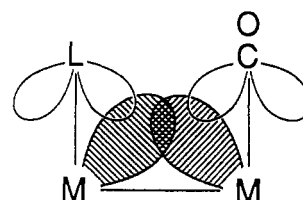
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transition metal). He concluded that, for a fixed metal atom type, as the electronegativity of the main group increases, M–H–M is favored over E–H–M and, for a constant main group atom, as the electronegativity of the metal is increased, E–H–M is favored over M–H–M.[24] Although a somewhat different approach, Fehlner's views are consistent with that presented above.

The view that a hydride ligand will bridge the most electron-rich metal–metal bond may be of general applicability. For example, we have reported a number of osmium carbonyl clusters with ER_3 (E = Si, Sn; R = organic group) and bridging hydride ligands.[25] In all cases there is a bridging hydride across the Os–Os bond that is also cis to the ER_3 ligand.

The ^1H NMR spectrum of **1** in toluene-d_8 exhibits two strong triplets in a 1:1 ratio at δ –16.96 (J_{PH} = 13.8 Hz) and –17.30 (J_{PH} = 14.8 Hz). This is consistent with the view that the major form of **1** in solution has the same structure as found in the solid state. The size of the P–H coupling constants indicates that a given hydride ligand is cis to the nearest PMe_3 groups.[26] It is impossible from the available evidence to determine if there is free rotation about the Re(μ-H)Os bonds of **1** in solution.

There is also a minor triplet in the spectrum at δ –17.17 (J_{PH} = 14.3 Hz). This signal increased in intensity relative to the other hydride signals when the spectrum was recorded in acetone-d_6. This behavior is interpreted in terms of a second isomer of **1**, with the $Re(CO)_3(PMe_3)_2(H)$ ligands trans to the same Os–Os bond, in equilibrium with the major isomer. Similar isomers have been observed for $Os_3(CO)_{10}(PR_3)_2$ and $(OC)_5$-$M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W) clusters.[27]

Supplementary Material Available: Tables of additional crystal data and data collection parameters (Table SI), fractional hydrogen atomic coordinates (Table SII), anisotropic temperature factors (Table SIII), and additional bond length and angles (Table SIV) for **1** (7 pages). Ordering information is given on any current masthead page.

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