# Synthesis and Structure of $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ and $(\eta^5\text{-}C_5Me_5)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$. Planar and Nonplanar Metal Geometries in 62-Electron Metal Clusters

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The cluster $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1) was prepared by the addition of $Re(CO)_4(PPh_3)(H)$ to $Os_3(CO)_{10}(\text{cyclooctene})_2$; the cluster $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2), by the addition of $(Cp^*)Os(CO)_2(H)$ to the same triosmium precursor compound. The structure of 1 was determined by X-ray crystallography. Compound 1 crystallizes in the space group $P\bar{1}$ with $a$ = 9.496(2) Å, $b$ = 9.751(2) Å, $c$ = 20.079(3) Å, $\alpha$ = 77.83(2)°, $\beta$ = 82.12(2)°, $\gamma$ = 86.62(2)°, and $Z$ = 2; $R$ = 0.028 for 3346 reflections. The molecule has a planar, diamond-like arrangement of metal atoms with the Re atom bound to the $Os_3$ triangle via two Re–Os interactions of significantly different lengths: 2.962(1), 3.108(1) Å. Bond angle data, calculations with the HYDEX program, and $^1$H NMR evidence all support the view that the hydride ligand bridges the short Re–Os vector, which is also adjacent to the $PPh_3$ ligand. The structure of 2 has also been determined by X-ray crystallography. Compound 2 crystallizes in the space group *Pbca* with $a$ = 11.802(2) Å, $b$ = 15.037(2) Å, $c$ = 31.061(4) Å, and $Z$ = 8; $R$ = 0.037 for 2129 observed reflections. In contrast to 1, cluster 2 has a nonplanar, butterfly configuration of metal atoms (the dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(2)Os(4) planes is 115.4°). Consistent with earlier observations on 62-electron tetranuclear clusters, there are only three carbonyl ligands attached to each of the hinge metal atoms in 2. The available evidence indicates the hydride bridges the hinge Os–Os bond that is also the shortest (2.793(1) Å) Os–Os bond in 2. In order to account for the difference in the structures of 1 and 2, it is proposed that in the latter structure there is both a dative and a nondative metal–metal bond that binds the 17-electron $(Cp^*)Os(CO)_2$ unit to the remainder of the cluster and that this mode of bonding is favored when there is a strong donor ligand, namely the $C_5Me_5$ ligand, attached to the wingtip metal atom.

## Introduction

Tetranuclear metal carbonyl clusters usually adopt a tetrahedral or butterfly arrangement of metal atoms.[1–3] In the absence of bridging ligands other than hydride ligands, a planar configuration of metal atoms is rarely found. We have, however, described the preparation and structure of $Os_4(CO)_{14}(L)$ (L = CO,[4] $PMe_3$[5]) and $(\eta^5\text{-}C_5Me_5)IrOs_3(CO)_{12}$,[4] which have planar metal skeletons with adjacent short and long peripheral metal–metal bonds. In unpublished work, we have found that $Os_4(CO)_{14}(CNBu^t)$ and $Os_4(CO)_{13}(PMe_3)[P(OMe)_3]$ have similar "kite-like" skeletons.[6] We have also described the molecular geometry of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$.[7] This 62-electron cluster has a planar $Os_4$ arrangement, but with only one long Os–Os bond, with the other Os–Os lengths within the range expected for Os–Os single bonds. Bond angle data, calculations with the HYDEX program,[8] and the NMR spectroscopic evidence were consistent with the view that the long Os–Os bond was not bridged by the hydride ligand.[7] This is contrary to what would be expected from the behavior of trinuclear metal carbonyl clusters where a bridging hydride ligand usually causes a lengthening of the metal–metal vector it is associated with.[9,10]

Churchill and Hollander[11] had previously described the structure of $Os_3Re(H)(CO)_{15}$ (3). It was also found to possess a planar rhomboidal arrangement of metal atoms. The structure was, however, badly disordered and in order to model that disorder some assumptions were made concerning the geometry of the molecule. Although the assumptions were entirely reasonable at the time they were made, our results suggested they may not have been correct.

In this study we report the synthesis and structure of $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ (1) and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2) in order to further probe the unusual bonding in this family of clusters. The structure of 1, which unlike 3 was not disordered, reveals a planar configuration of metal atoms with a long Re–Os bond that is believed to be unbridged. Unexpectedly, the structure of 2 has a nonplanar butterfly $Os_4$ nucleus. A reason for the different metal arrangements in 1 and 2 is presented.

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## Experimental Section

Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was treated similarly, except $P_2O_5$ was used as the drying agent. The preparations of $Re(CO)_4(PPh_3)(H)$,[12] $(Cp^*)Os(CO)_2(H)$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[13] and $Os_3(CO)_{10}(COE)_2$ (COE = cyclooctene)[14] were carried out by literature procedures. The $^{13}CO$-enriched compounds were synthesized from $^{13}CO$-enriched $Os_3(CO)_{12}$ ($\sim$35% $^{13}C$). 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. NMR spectra were recorded on a Bruker WM400 spectrometer. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

**Preparation of $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1).** A Schlenk tube with $Os_3(CO)_{10}(COE)_2$ (43 mg, 0.040 mmol) in $CH_2Cl_2$ (2 mL) and hexane (10 mL) was cooled to 0 °C, and $Re(CO)_4(PPh_3)(H)$ (22 mg, 0.039 mmol) was added; the resulting solution was stirred at 0 °C for 0.5 h, over which time the color changed from amber to red. The solution was evaporated to dryness and the remaining solid chromatographed on a silica gel column. Elution with $CH_2Cl_2$/hexane (1/4) gave the desired product, 1 (22 mg, 39%). The analytical sample was obtained as air-stable, red crystals by recrystallization from toluene/hexane: IR ($CH_2Cl_2$) $\nu$(CO) 2118 (m), 2070 (s), 2050 (m), 2036 (vs), 2013 (w), 1969 (w), 1933 (w) cm$^{-1}$; $^1H$ NMR (acetone-$d_6$, room temperature) $\delta$ −12.14 (d, $J_{PH}$ = 13.0 Hz); $^{31}P\{^1H\}$ NMR (acetone-$d_6$, room temperature, 85% $H_3PO_4$ external reference) $\delta$ 22.89 (s); $^{13}C/^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, room temperature) $\delta$ 202.3 (2C, $J_{PC}$ = 7 Hz), 195.3 (1C, $J_{PC}$ = 8 Hz), 192.1 (2C, $J_{HC}$ = 2 Hz), 188.4 (2C), 179.0 (1C), 174.3 (3C), 174.1 (1C), 171.7 (1C), 165.8 (1C). Anal. Calcd for $C_{32}H_{16}O_{14}ReOs_3$: C, 27.22; H, 1.14. Found: C, 27.39; H, 1.21.

**Preparation of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2).** The procedure used to prepare 2 was similar to that used to make 1 except $(Cp^*)Os(CO)_2(H)$ replaced $Re(CO)_4(PPh_3)(H)$ and a reaction time of 2 h was employed; the yield was 66%. The analytical sample of 2 was obtained as air-stable, dark red crystals by recrystallization from $CH_2Cl_2$/hexane: IR ($CH_2Cl_2$) $\nu$(CO) 2117 (w), 2095 (s), 2047 (vs), 2013 (vs), 1977 (m), 1959 (m), 1918 (w); $^1H$ NMR (toluene-$d_8$, room temperature) $\delta$ 1.60 (s), −15.67 (s); $^{13}C/^{13}C\{^1H\}$ NMR (toluene-$d_8$, −30 °C) $\delta$ 188.3 (1C), 188.0 (1C; the CC coupling was ambiguous), 186.0 (2C), 185.7 (2C), 178.1 (2C), 175.1 (2C, $J_{CH}$ = 9.0 Hz), 174.3 (2C). Anal. Calcd for $C_{22}H_{16}O_{12}Os_4$: C, 21.43; H, 1.31. Found: C, 21.65; H, 1.40.

**X-ray Structure Determinations of 1 and 2.** The following procedure was employed for both structure determinations. A crystal of suitable size (Table I) was mounted on an Enraf-Nonius diffractometer, and intensity data were collected with the use of graphite-monochromated Mo K$\alpha$ radiation. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Two intensity standards, measured every 1 h during data collection, varied randomly (to ±2%) for 1 and decreased 9% for 2. An analytical absorption correction[15] (checked against $\psi$-scan measurements) was applied to each set of the measured intensity data. Data reduction also included the small corrections for intensity scale variation and Lorentz and polarization effects.

Table I. Summary of Crystal Data and Details of Intensity Collection for $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1) and $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (2)

| | 1 | 2 |
|---|---|---|
| fw | 1412.2 | 1233.2 |
| cryst syst | triclinic | orthorhombic |
| space group | $P\bar{1}$ | *Pbca* |
| *a*, Å | 9.496(2) | 11.802(2) |
| *b*, Å | 9.751(2) | 15.037(2) |
| *c*, Å | 20.079(3) | 31.061(4) |
| $\alpha$, deg | 77.83(2) | |
| $\beta$, deg | 82.12(2) | |
| $\gamma$, deg | 86.62(2) | |
| *V*, Å$^3$ | 1799 | 5513 |
| 2$\theta$ range of unit cell, deg | 30–45 | 29–38 |
| *Z* | 2 | 8 |
| $\rho_{calc}$, g cm$^{-3}$ | 2.61 | 2.97 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 140.78 | 184.59 |
| cryst size, mm | 0.08 × 0.13 × 0.30 | 0.22 × 0.21 × 0.20 |
| transm coeff range[a] | 0.3058–0.4647 | 0.049 71–0.089 38 |
| scan method | $\omega$–2$\theta$ | $\omega$–2$\theta$ |
| scan range (2$\theta$), deg | 4–45 | 4–45 |
| scan width ($\omega$), deg | 0.9 + 0.35 tan $\theta$ | 0.9 + 0.35 tan $\theta$ |
| scan rate ($\omega$), deg min$^{-1}$ | 0.82–5.5 | 0.69–5.5 |
| no. of unique rflns | 4677 | 3570 |
| no. of obsd rflns[b] | 3346 | 2129 |
| no. of variables | 301 | 234 |
| *R*[c] | 0.028 | 0.037 |
| $R_w$[d] | 0.035 | 0.042 |
| *k*[d] | 0.0005 | 0.000 12 |
| GOF[e] | 1.2 | 1.6 |
| extinction (*g*)[f] | 0.23(2) | 0.197(17) |

[a] Absorption corrections. [b] $I_o > 2.5\sigma(I_o)$. [c] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [d] $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + k(F_o)^2]^{-1}$. [e] $GOF = (\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom}))^{1/2}$. [f] $F_c' = K|F_c|(1 + g|F_c|^{1/2}Lp_1/p_2)^{1/2}$.

The positions of the Os (and Re) atoms were determined by direct methods for 1 and from the Patterson map for 2. Subsequent electron density difference synthesis revealed the remaining non-hydrogen atoms. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and initially given isotropic thermal parameters 10% larger than the thermal parameter of the carbon to which they were attached. The coordinates and thermal parameters of carbon atoms with attached hydrogen atoms were linked so that the derived coordinates and thermal parameters included contributions from derivatives from the appropriate atom sites. Unit weights were employed initially, but at the final stage of each refinement a weighing scheme, based on counting statistics, was adopted for which $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Complex scattering factors[16] for neutral atoms were used in the calculation of structure factors. The programs used for data reduction, structural solution, and initial refinement were from the NRCVAX[17] crystal structure system; the final refinement employed the program suite CRYSTALS.[18] All computations were carried out on a Micro VAX-II computer. Crystallographic data are summarized in Table I.

**$(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$.** Background measurements were made by extending the scan width by 25% on each side of the scan. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Re, Os, P, and O atoms, and isotropic thermal parameters for C atoms. Final fractional coordinates for the non-hydrogen atoms of 1 are given in Table II, and selected bond length and angle data, in Table III.

**$(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$.** Static background measurements were made at positions 0.025° beyond each edge of the scan width. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Os and O atoms, and isotropic thermal parameters

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**Table II. Fractional Atomic Coordinates (×10⁴) and Isotropic or Equivalent Isotropic Temperature Factors (Å² × 10⁴) for $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1)**

| atom | *x* | *y* | *z* | *U*(iso) |
|---|---|---|---|---|
| Os(1) | 2327.4(4) | 3228.3(4) | 1444.5(2) | 333 |
| Os(2) | 1526.6(4) | 411.9(4) | 1378.0(2) | 326 |
| Os(3) | 2490.8(4) | 2530.2(5) | 139.7(2) | 348 |
| Re(1) | 1626.9(5) | 1263.3(5) | 2777.3(2) | 366 |
| P(1) | 1952(3) | 2550(3) | 3630(2) | 404 |
| O(11) | 5401(9) | 2211(10) | 1593(5) | 611 |
| O(1) | –673(9) | 4585(10) | 1489(5) | 632 |
| O(13) | 3329(11) | 6225(10) | 1163(5) | 741 |
| O(21) | 4583(9) | –801(9) | 1488(5) | 579 |
| O(22) | –1567(9) | 1602(10) | 1404(5) | 615 |
| O(23) | 404(12) | –2172(11) | 2397(5) | 752 |
| O(24) | 1238(9) | –1033(9) | 210(5) | 551 |
| O(31) | 5575(9) | 1324(10) | 180(5) | 613 |
| O(32) | –602(8) | 3639(8) | 107(5) | 519 |
| O(33) | 2209(11) | 1479(12) | –1158(5) | 714 |
| O(34) | 3650(10) | 5426(10) | –482(6) | 743 |
| O(1) | 4636(10) | –98(9) | 2933(5) | 606 |
| O(2) | –1621(10) | 2004(11) | 2882(5) | 710 |
| O(3) | 655(14) | –1454(11) | 3753(5) | 759 |
| C(11) | 4265(13) | 2547(12) | 1504(6) | 453(29) |
| C(12) | 410(13) | 4044(12) | 1458(6) | 436(29) |
| C(13) | 2942(13) | 5062(14) | 1276(7) | 554(33) |
| C(21) | 3507(13) | –302(12) | 1432(6) | 440(29) |
| C(22) | –414(13) | 1240(12) | 1389(6) | 458(29) |
| C(23) | 824(13) | –1175(13) | 2059(7) | 497(31) |
| C(24) | 1370(12) | –458(12) | 616(6) | 429(28) |
| C(31) | 4445(13) | 1757(12) | 182(6) | 468(30) |
| C(32) | 530(12) | 3216(12) | 157(6) | 425(28) |
| C(33) | 2369(14) | 1829(14) | –671(7) | 572(34) |
| C(34) | 3230(14) | 4329(14) | –269(7) | 585(34) |
| C(1) | 3581(13) | 445(13) | 2835(6) | 481(30) |
| C(2) | –428(14) | 1783(13) | 2814(6) | 476(30) |
| C(3) | 1014(14) | –409(15) | 3408(7) | 600(35) |
| C(111) | 3210(12) | 3932(12) | 3310(6) | 424(28) |
| C(112) | 2871(15) | 5327(14) | 3325(7) | 645(37) |
| C(113) | 3874(17) | 6340(18) | 3061(9) | 864(48) |
| C(114) | 5177(17) | 6044(17) | 2719(9) | 858(47) |
| C(115) | 5520(16) | 4674(15) | 2711(8) | 711(40) |
| C(116) | 4574(14) | 3637(15) | 3018(7) | 617(36) |
| C(121) | 2608(12) | 1631(12) | 4428(6) | 462(30) |
| C(122) | 3598(14) | 2236(14) | 4720(7) | 650(38) |
| C(123) | 3974(16) | 1539(15) | 5366(8) | 710(40) |
| C(124) | 3447(15) | 333(15) | 5691(8) | 688(39) |
| C(125) | 2535(15) | –290(15) | 5409(7) | 680(39) |
| C(126) | 2119(14) | 323(14) | 4764(7) | 608(35) |
| C(131) | 338(12) | 3470(12) | 3947(6) | 477(30) |
| C(132) | –346(14) | 4425(14) | 3468(8) | 686(39) |
| C(133) | –1604(16) | 5132(16) | 3672(8) | 793(44) |
| C(134) | –2156(19) | 4837(17) | 4357(9) | 920(51) |
| C(135) | –1495(18) | 3924(17) | 4832(10) | 919(50) |
| C(136) | –212(14) | 3226(14) | 4612(7) | 628(37) |
| H(0) | 2021 | 3094 | 2356 | 500 |

for C atoms. Final fractional coordinates for the non-hydrogen atoms of **2** are given in Table IV, and selected bond length and angle data, in Table V.

**Placement of the Hydride Ligand in 1 and 2.** There was no strong evidence for the hydride ligand in the final difference map of 1. Results of calculations of the "site energy" of the hydride ligand in various positions in 1 with the HYDEX program[8] are shown in Table VI. As can be seen, these calculations clearly favored the hydride ligand in a position bridging the Os(1)–Re bond. The hydride ligand was therefore placed in the calculated position (i.e., bridging Os(1)–Re) and included as a fixed contribution in the final refinement.

Immediately before the final refinement of **2**, a difference map based on low-angle reflections ($(\sin\theta)/\lambda < 0.35$ Å⁻¹) revealed the largest peak ($x = 0.605, y = 0.404, z = 0.131$) with electron density 0.57 (13) e Å⁻³ was 1.6 Å from Os(1) and 1.7 Å from Os(2) and a second peak with electron density 0.52 (13) e Å⁻³ was 1.4 Å from Os(1) and 1.2 Å from C(11). The "site energy" of a hydride ligand in each of these two approximate positions was calculated with the HYDEX program.[8] The calculations showed that a hydride ligand ($x = 0.628, y = 0.411, z = 0.130$) at 1.8 Å from both Os(1) and Os(2) had the minimum site energy, in agreement with the difference maps.

**Table III. Selected Bond Lengths (Å) and Angles (deg) for $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1)**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Os(1)–Os(2) | 2.927(1) | Os(3)–C(31) | 1.97(1) |
| Os(1)–Os(3) | 2.825(1) | Os(3)–C(32) | 1.94(1) |
| Os(1)–Re(1) | 2.962(1) | Os(3)–C(33) | 1.91(1) |
| Os(2)–Os(3) | 2.953(1) | Os(3)–C(34) | 1.90(1) |
| Os(2)–Re(1) | 3.108(1) | Re(1)–P(1) | 2.386(3) |
| Os(1)–C(11) | 1.93(1) | Re(1)–C(1) | 1.98(1) |
| Os(1)–C(12) | 1.94(1) | Re(1)–C(2) | 1.98(1) |
| Os(1)–C(13) | 1.86(1) | Re(1)–C(3) | 1.91(1) |
| Os(2)–C(21) | 1.98(1) | P(1)–C(111) | 1.81(1) |
| Os(2)–C(22) | 1.97(1) | P(1)–C(121) | 1.83(1) |
| Os(2)–C(23) | 1.92(1) | P(1)–C(131) | 1.84(1) |
| Os(2)–C(24) | 1.93(1) | $(C\text{–}O)_{range}$ = 1.11(1)–1.18(1) | |
| | Bond Angles | | |
| Os(3)–Os(1)–Os(2) | 61.75(2) | C(13)–Os(1)–Os(3) | 105.5(4) |
| Re(1)–Os(1)–Os(2) | 63.70(2) | C(13)–Os(1)–Re(1) | 128.9(4) |
| Os(3)–Os(2)–Os(1) | 57.42(2) | C(23)–Os(2)–Re(1) | 75.1(4) |
| Re(1)–Os(2)–Os(1) | 58.71(2) | C(24)–Os(2)–Os(3) | 74.8(3) |
| Os(2)–Re(1)–Os(1) | 57.59(2) | C(33)–Os(3)–Os(2) | 110.3(4) |
| Os(2)–Os(3)–Os(1) | 60.82(2) | C(34)–Os(3)–Os(1) | 89.3(4) |
| P(1)–Re(1)–Os(1) | 105.27(8) | C(3)–Re(1)–Os(2) | 101.3(4) |
| P(1)–Re(1)–Os(2) | 162.84(8) | C(3)–Re(1)–P(1) | 95.9(4) |

**Table IV. Fractional Atomic Coordinates (×10⁴) and Isotropic or Equivalent Isotropic Temperature Factors (Å² × 10⁴) for $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (2)**

| atom | *x* | *y* | *z* | *U*(iso) |
|---|---|---|---|---|
| Os(1) | 5787.5(9) | 3418.6(6) | 1712.3(3) | 386 |
| Os(2) | 5793.9(9) | 3618.9(5) | 818.3(3) | 384 |
| Os(3) | 6437.1(9) | 1930.8(6) | 1186.3(3) | 422 |
| Os(4) | 3548.5(7) | 3757.8(5) | 1268.9(3) | 341 |
| O(11) | 5209(18) | 2118(11) | 2419(6) | 735 |
| O(12) | 8198(18) | 3374(14) | 2046(6) | 835 |
| O(13) | 5465(16) | 5116(12) | 2221(6) | 603 |
| O(21) | 5114(21) | 2688(13) | –23(6) | 665 |
| O(22) | 8170(17) | 3748(15) | 463(7) | 810 |
| O(23) | 5631(16) | 5485(11) | 466(6) | 612 |
| O(31) | 4029(17) | 1280(13) | 1217(10) | 928 |
| O(32) | 8917(14) | 2589(13) | 1193(8) | 789 |
| O(33) | 6775(23) | 917(15) | 338(6) | 876 |
| O(34) | 6982(22) | 513(16) | 1834(7) | 1153 |
| O(41) | 3058(20) | 2499(14) | 529(7) | 854 |
| O(42) | 3103(17) | 2388(13) | 1938(7) | 707 |
| C(11) | 5330(23) | 2621(17) | 2149(8) | 503(69) |
| C(12) | 7272(24) | 3372(16) | 1926(7) | 455(64) |
| C(13) | 5489(21) | 4493(16) | 2031(7) | 456(63) |
| C(21) | 5384(23) | 3022(17) | 288(8) | 530(69) |
| C(22) | 7289(28) | 3650(18) | 595(9) | 678(83) |
| C(23) | 5588(19) | 4800(15) | 607(7) | 377(56) |
| C(31) | 4870(23) | 1568(17) | 1189(8) | 545(68) |
| C(32) | 8024(23) | 2376(17) | 1186(9) | 570(72) |
| C(33) | 6655(24) | 1319(18) | 645(9) | 644(76) |
| C(34) | 6792(24) | 1057(19) | 1577(9) | 662(82) |
| C(41) | 3358(23) | 2965(17) | 793(8) | 604(72) |
| C(42) | 3381(27) | 2887(20) | 1661(9) | 771(86) |
| C(1) | 1922(21) | 4363(16) | 1493(7) | 507(67) |
| C(2) | 2790(20) | 4922(14) | 1651(7) | 397(57) |
| C(3) | 3358(17) | 5309(13) | 1290(7) | 388(55) |
| C(4) | 2841(19) | 4975(13) | 914(6) | 321(52) |
| C(5) | 1947(21) | 4404(16) | 1040(7) | 494(66) |
| C(6) | 936(24) | 3922(19) | 1757(8) | 784(88) |
| C(7) | 2932(22) | 5199(16) | 2120(7) | 571(72) |
| C(8) | 4202(19) | 6072(14) | 1311(7) | 470(61) |
| C(9) | 2933(22) | 5348(16) | 454(7) | 575(72) |
| C(10) | 1053(21) | 4033(17) | 744(8) | 627(79) |
| H(0) | 6050 | 4040 | 1310 | 500 |

This conclusion was further supported by a comparison of the appropriate bond angles in the geometries of $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (4),[19] $Os_3Pt(\mu\text{-}H)(CO)_{11}[P(c\text{-}C_6H_{11})_3]$ (5),[20] and $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)$ (6)[21] as shown in Table VII. In both 4 and 5 a hydride ligand is believed to bridge the hinge metal atoms,

**Table V. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (2)**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Os(1)–Os(2) | 2.793(1) | Os(3)–C(31) | 1.93(3) |
| Os(1)–Os(3) | 2.875(1) | Os(3)–C(32) | 1.99(3) |
| Os(1)–Os(4) | 3.023(1) | Os(3)–C(33) | 1.93(3) |
| Os(2)–Os(3) | 2.886(1) | Os(3)–C(34) | 1.84(3) |
| Os(2)–Os(4) | 3.004(1) | Os(4)–C(41) | 1.91(3) |
| Os(1)–C(11) | 1.89(3) | Os(4)–C(42) | 1.80(3) |
| Os(1)–C(12) | 1.88(3) | | |
| Os(1)–C(13) | 1.93(2) | $(C\text{–}O)_{range}$ = 1.09(3)–1.19(3) | |
| Os(2)–C(21) | 1.94(3) | $(C\text{–}C)_{ring}$ = 1.41(3)–1.43(3) | |
| Os(2)–C(22) | 1.90(3) | $(C\text{–}C_{Me})$ = 1.51(3)–1.57(3) | |
| Os(2)–C(23) | 1.91(2) | | |
| | Bond Angles | | |
| Os(2)–Os(3)–Os(1) | 58.01(3) | C(11)–Os(1)–Os(2) | 141.5(7) |
| Os(2)–Os(4)–Os(1) | 55.21(3) | C(12)–Os(1)–Os(2) | 110.7(7) |
| Os(3)–Os(1)–Os(2) | 61.19(3) | C(13)–Os(1)–Os(2) | 114.9(7) |
| Os(3)–Os(2)–Os(1) | 60.80(3) | C(21)–Os(2)–Os(1) | 142.7(7) |
| Os(4)–Os(1)–Os(2) | 62.05(4) | C(22)–Os(2)–Os(1) | 111.6(8) |
| Os(4)–Os(2)–Os(1) | 62.74(4) | C(23)–Os(2)–Os(1) | 116.2(6) |

**Table VI. Site Energies[a] for a Hydride Ligand in Various Positions in 1 and 2**

| 1 | | 2 | |
|---|---|---|---|
| position | site energy | position | site energy |
| Os(1)(μ-H)Re | 2.29 | Os(4)(μ-H)Os(1) | 9.66 |
| Os(2)(μ-H)Re | 10.9 | Os(4)(μ-H)Os(2) | 11.3 |
| Os(1)(μ-H)Os(2) | 9.44 | Os(3)(μ-H)Os(1) | 11.1 |
| Os(1)(μ-H)Os(3) | 24.3 | Os(3)(μ-H)Os(2) | 12.0 |
| Os(2)(μ-H)Os(3) | 13.7 | Os(1)(μ-H)Os(2) | 1.68 |
| Os(1)–H | 9.45 | Os(4)–H[b] | –0.69 |
| Os(2)–H | 19.3 | Os(3)–H | 13.8 |
| Os(3)–H | 17.6 | Os(1)–H[c] | 7.19 |
| Re–H | 19.3 | Os(2)–H[d] | 7.58 |
| | | Os(4)Os(1)Os(2)($\mu_3$-H) | 0.59 |
| | | Os(3)Os(1)Os(2)($\mu_3$-H) | 1.38 |

[a] Calculated with the HYDEX program.[8] [b] H···C(3) = 0.84 Å. [c] H···Os(4) = 2.79 Å. [d] H···Os(3) = 2.54 Å.

**Table VII. Comparison of Selected Angles (deg) for Compounds 2, 4, 5, and 6**

| | 2 | 4 | 5 | 6 |
|---|---|---|---|---|
| Os(2)–Os(1)–C(11) | 141.5 | 142.1 | 142.0 | 167.9 |
| Os(2)–Os(1)–C(12) | 110.7 | 104.4 | 106.1 | 95.0 |
| Os(2)–Os(1)–C(13) | 114.9 | 119.2 | 115.0 | 85.5 |
| Os(1)–Os(2)–C(21) | 142.7 | 137.2 | 141.7 | 158.5 |
| Os(1)–Os(2)–C(22) | 111.6 | 111.7 | 103.1 | 91.2 |
| Os(1)–Os(2)–C(23) | 116.2 | 117.7 | 116.5 | 102.2 |

whereas in **6** these atoms are thought to be unbridged. The bond angles about the hinge metal atoms clearly show the similarity among **2**, **4**, and **5** and the difference between these clusters and **6**.

All the evidence was therefore consistent with the hydride ligand as placed in the position derived from the difference map based on the low-angle reflections; it was included as a fixed contribution in the final refinement.

## Results and Discussion

The clusters $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1) and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2) were prepared by the addition of either $Re(CO)_4(PPh_3)(H)$ (for 1) or $(Cp^*)Os(CO)_2(H)$ (for 2) to $Os_3(CO)_{10}(COE)_2$ in $CH_2Cl_2$/hexane at 0 °C (eqs 1 and 2). Both **1** and **2** are air-stable, crystalline solids.

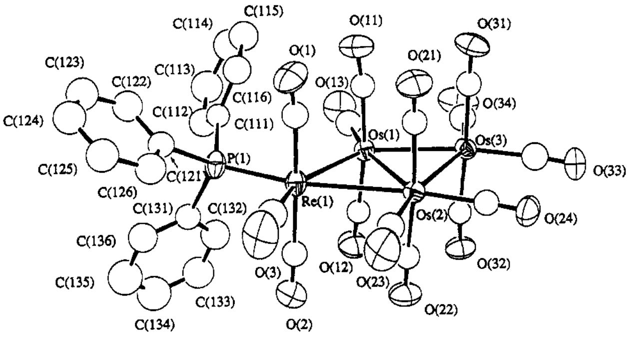

**Figure 1.** Molecular structure of $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1).

$$Os_3(CO)_{10}(COE)_2 + Re(CO)_4(PPh_3)(H) \xrightarrow{0\ °C} \underset{\mathbf{1}}{(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}} \quad (1)$$

COE = cyclooctene

$$Os_3(CO)_{10}(COE)_2 + (Cp^*)Os(CO)_2(H) \xrightarrow{0\ °C} \underset{\mathbf{2}}{(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}} \quad (2)$$

$$Cp^* = \eta^5\text{-}C_5Me_5$$

**$(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (1).** The structure of **1** as determined by X-ray crystallography (Figure 1) shows an almost planar arrangement of metal atoms; the dihedral angle between the Re–Os(1)–Os(2) and Os(1)–Os(2)–Os(3) planes is 175.2°. There are three carbonyl ligands attached to one of the hinge osmium atoms (Os(1)) but four to the other hinge metal atom (Os(2)). The bulky $PPh_3$ ligand occupies one of the least hindered sites in the molecule, namely, the equatorial site at the rhenium atom that is also cis to the lone equatorial carbonyl ligand on Os(1).

Although the Os–Os lengths in the $Os_3$ triangle of **1** vary significantly (Os(1)–Os(2) = 2.927(1) Å, Os(1)–Os(3) = 2.825(1) Å, Os(2)–Os(3) = 2.953(1) Å), they are, nevertheless, in the range expected for unbridged Os–Os single bonds. The lengths may be compared with the average Os–Os distance of 2.877 Å in $Os_3(CO)_{12}$.[22]

The Re–Os vectors are also of markedly different lengths: Re–Os(1) = 2.962(1) Å, Re–Os(2) = 3.108(1) Å. It is usually found that in trinuclear metal carbonyl clusters a singly bridging hydride ligand causes a lengthening of the metal–metal vector it is associated with.[9] For example, the Os–Os lengths of Os(μ-H)Os linkages are usually in the neighborhood of 3.0 Å.[9,10,22,23]

Unbridged Re–Os bonds would be expected to have a length close to 2.959 Å, the mean of the Re–Re bond length in $Re_2(CO)_{10}$ (3.041(1) Å)[24] and the average Os–Os length in $Os_3(CO)_{12}$ (2.877 Å).[22] The Re–Os lengths in **1**, therefore, suggest that Re–Os(2) and not Re–Os(1) is bridged by the hydride ligand. But **1** is a member of the class of planar, 62-electron clusters that, as mentioned in the Introduction, have some metal–metal bonds that are exceptionally long and are also unbridged.[4–7] Indeed, other evidence strongly favors the location of the hydride ligand as bridging the

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(20) Farrugia, L. J.; Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 177.

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(24) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

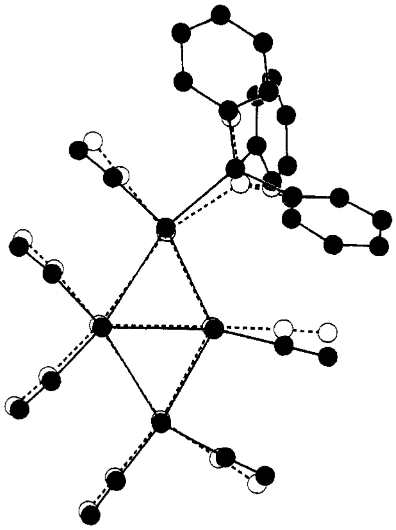

**Figure 2.** Superimposition of the structure of 1 (filled circles) on that of $Os_4(CO)_{14}(PMe_3)$ (open circles). Axial carbonyl ligands have been omitted.

shorter Re–Os bond. The HYDEX program[8] gives a site energy of 2.29 for the hydride ligand symmetrically bridging Re–Os(1) whereas all other positions investigated gave site energies of greater than 9 (Table VI). In his original study, Orpen estimated the site energies for 41 bridging hydrides with the HYDEX program and found them to occur in the range 0.2–10.6 with an average value of 2.76.[8] The site energy for the hydride bridging Re–Os(1) is almost identical to that found for $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ a cluster also believed to have a long, unbridged metal–metal bond.[7]

In Figure 2 the ORTEP diagram of the molecular framework in the metal plane of 1 is superimposed on the corresponding framework of $Os_4(CO)_{14}(PMe_3)$. The latter cluster contains no hydride ligands and has adjacent short (2.779(2), 2.784(2) Å) and long bonds (2.982(2), 3.013(2) Å) around the $Os_4$ periphery.[5] As can be seen from the figure, the displacement of the in-plane ligands of 1 relative to those in $Os_4(CO)_{14}(PMe_3)$ is entirely consistent with the hydride bridging the short Re–Os(1) bond. As a reviewer has pointed out, the Os–Os bond in $Os_4(CO)_{14}(PMe_3)$ that corresponds to the bridged Re–Os bond in 1 has an unusually short length of 2.779(2) Å. The Re–Os distance of $Re(\mu\text{-}H)Os$ in 1 of 2.962(1) Å therefore represents a significant lengthening over this distance, even when the different covalent radii of rhenium and osmium are taken into account.

The P–H coupling constant of 13.0 Hz exhibited by the hydride resonance in the $^1H$ NMR spectrum of 1 is also consistent with this placement of the hydride ligand;[25] that is, the triphenylphosphine and hydride groups have a cis arrangement in the cluster. It is usually found in metal carbonyl clusters that have phosphorus-donor and hydride ligands that the hydride ligands will, as far as possible, bridge metal–metal bonds that are cis to the phosphorus ligand.[26]

The $^{13}C/^{13}C\{^1H\}$ NMR spectra for 1, discussed below, are less definitive as to the location of the proton in the cluster. We believe, however, that the available evidence more strongly supports the hydride ligand as located along the short, Re–Os(1), rather than the long, Re–Os(2), bond.

Churchill and Hollander[11] have reported the structure of $ReOs_3(H)(CO)_{15}$ (3) prepared by Knight and Mays by the acidification of an anion presumed to be $[ReOs_3(CO)_{15}]^-$ (i.e., a route different from that used to prepare 1).[27] The structure of 3 was disordered, and in their model Churchill and Hollander made some assumptions about the structure that were entirely reasonable at the time. In that model the wingtip positions were occupied by $Os(CO)_4$ groups and the hinge positions by $Re(CO)_4$ and $Os(H)(CO)_3$ (i.e., a terminal hydride ligand) groups statistically distributed over the two sites. The model was supported by the thermal motion parameters of the heavy atoms.[11]

A model for the structure of 3 based on that of 1 in which the $PPh_3$ ligand has been replaced by a carbonyl group appears to also satisfy the results of Churchill and Hollander. There are only two crystallographically distinct metal–metal distances for 3, namely, the average peripheral metal–metal length and the hinge metal–metal length.[11] It is noteworthy that the former length (2.962 Å) is close to the average value for these lengths in 1 (2.957 Å). Furthermore, the hinge metal–metal length in 3 (2.944(1) Å) is close to that in 1 (Os(1)–Os(2) = 2.927(1) Å). If one of the hinge positions in 3 were occupied by a Re atom, then by analogy to 1 it would be expected that this length would be somewhat longer than 2.959 Å, which, as discussed above, is the length expected for a Re–Os single bond. In $Re_2Os_3(\mu\text{-}H)_2(CO)_{20}$, which has two unbridged Re–Os bonds, the average Re–Os distance was 2.962 Å (there were two independent molecules in the unit cell).[28] For these reasons, we believe that 3 probably has a structure similar to 1, with the Re atom in a wingtip position and the hydride ligand bridging one of the Re–Os vectors.

The $^1H$ NMR spectrum of 1 in acetone-$d_6$ exhibits a doublet centered at $\delta$ −12.14. As mentioned previously, the P–H coupling constant (of 13.0 Hz) is consistent with a cis arrangement of the H and $PPh_3$ ligands.[25] The $^1H$ NMR resonances of $Os(\mu\text{-}H)Os$ linkages usually occur to high field of $\delta$ −15 whereas those of terminal Os–H linkages usually appear to low field of $\delta$ −15.[23] The hydride resonance for 1 therefore has a chemical shift in the region expected if the hydride ligand were in a terminal position on Os(1), a position analogous to that originally proposed for the hydride ligand in 3 (see above). If the hydride ligand did occupy such a position, however, the $^1H$ NMR resonance would not be expected to show P–H coupling.

The $^{13}C\{^1H\}$ NMR spectrum of $^{13}CO$-enriched 1, in $CD_2Cl_2$ at ambient temperature (Figure 3) is consistent with a rigid structure in solution that is identical to that in the solid state, if it is assumed that one of the resonances due to one set of axial carbonyls on an Os atom is degenerate with the signal due to an equatorial CO on an Os atom. A partial assignment of the resonances in the spectrum is possible. The two signals to lowest field at $\delta$

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[25] (a) *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 119. (b) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* 1966, 1407.

[26] For example: (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1977, *16*, 2397. (b) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* 1982, *21*, 3304. (c) Farrugia, L. J.; Howard, J. A. K.; Mitroprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1981, 1274. (d) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Hursthouse, M. B.; Abdul Malik, K. M.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* 1987, 1869. (e) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P. *Organometallics* 1991, *10*, 394. (f) Farrugia, L. J.; Rae, S. E. *Organometallics* 1991, *10*, 3919. (g) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* 1991, *30*, 4611. (h) Wang, W.; Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* 1992, *31*, 5150.

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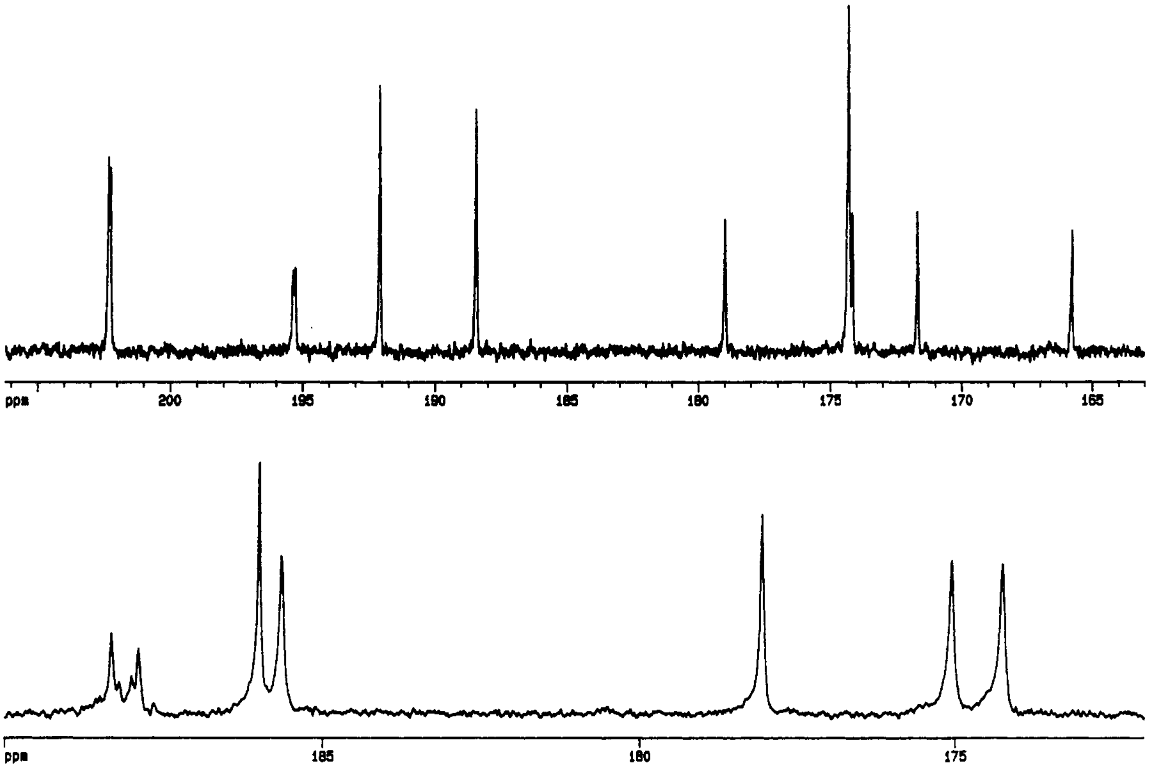

**Figure 3.** $^{13}C\{^1H\}$ NMR spectra in the carbonyl region for 1 (top) and 2 (bottom). Conditions are reported in the Experimental Section.

202.3 and 195.3 are confidently assigned to the axial and equatorial carbon atoms on the Re atom, respectively, on the basis of their chemical shift, their intensity, and their exhibition of P–C coupling. The resonance at δ 192.1 is attributed to the axial carbonyls on Os(1) since it is in the region associated with axial carbonyls of $Os(CO)_4$ groupings,[29,30] has an intensity of 2, and shows a small coupling in the $^1H$-coupled $^{13}C$ NMR spectrum. The peak at δ 188.4 is assigned to the axial carbonyls attached to Os(3) since the peak also appears in the chemical shift region for axial carbonyls of $Os(CO)_4$ units that are attached to the rest of the metal cluster via two metal–metal interactions. The remaining signal of intensity 2, believed isochronous with one of intensity 1, at δ 174.3 is, therefore, assigned to the axial carbonyls of Os(2). This is an unusual chemical shift for such resonances; as noted previously for related clusters,[5] this may be attributable to the unusual bonding in these tetranuclear clusters (this is discussed below).

The signal of intensity 1 at δ 179.0 is assigned to the equatorial carbon on Os(1) (i.e., C(13), Figure 1) because it shows a small coupling to hydrogen in the $^1H$-coupled $^{13}C$ NMR spectrum and because, similarly to the resonance of the axial carbonyls on Os(1), the resonance is shifted downfield from the region normally associated with equatorial carbonyls in osmium carbonyl clusters.[29] The resonance at highest field (of intensity 1) is assigned to the carbon trans to the long Re–Os(2) bond (i.e., C(24)).

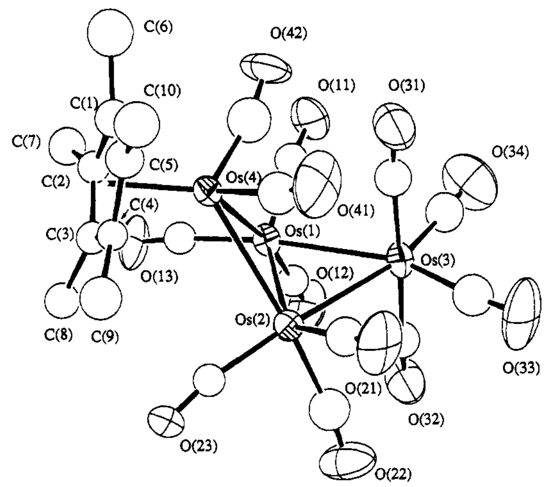

**Figure 4.** Molecular structure of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2).

As discussed below, we believe this is a dative metal–metal bond and we have previously observed that carbonyl ligands trans to such bonds occur at particularly high fields.[30] The assignment of the remaining signals of intensity 1 to C(23), C(33), and C(34) is uncertain at present.

**$(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (2).** Like 1, 2 is a 62-electron cluster, but the X-ray crystal structure (Figure 4) reveals that it has a nonplanar butterfly rather than a planar skeleton of metal atoms. The dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(2)Os(4) planes in 2 is 115.4°. The Os–Os bond lengths within the cluster are given in Table V, along with other selected bond length and angle data. As for 1, the location of the hydride ligand in 2 was studied in detail (Experimental Section). The final difference map based on low-angle reflections, results from the HYDEX program,[8] and a comparison of bond angle data with related clusters were consistent with the

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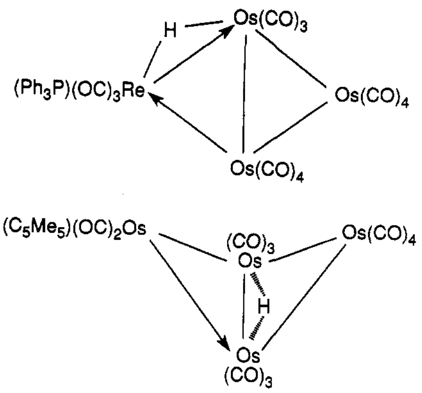
hydride ligand as located across the hinge Os(3)–Os(4) bond. Remarkably, this bond at 2.793(2) Å is the shortest Os–Os bond in **2**. We have observed similar behavior in the Os–Os bond lengths in $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$.[19] The differences in the Os–Os lengths in these clusters can, in part, be attributed to the different coordination numbers of the metal atoms in the clusters: the shorter Os–Os bond lengths involve osmium atoms with only three terminal ligands.

The $^{13}C\{H\}$ NMR spectrum of $^{13}CO$-enriched **2**, in toluene-$d_8$ at −30 °C, in the carbonyl region exhibits seven signals in an approximate ratio of 1:1:2:2:2:2:2 (Figure 3). This is consistent with the view that **2** has the same structure, (i.e., with a mirror plane) in solution as found in the solid state, with the hydride ligand lying in the mirror plane or rapidly oscillating about the plane. In the $^1H$-coupled $^{13}C$ NMR spectrum only one of the signals that was a singlet in the $^{13}C\{^1H\}$ NMR spectrum split into a doublet, indicative of coupling to hydrogen. Furthermore, this signal is to higher field, where we have previously observed the resonances of the carbonyls of $Os(CO)_3$ groups to occur compared to those of $Os(CO)_4$ units.[31] We believe the only reasonable interpretation of these results is that the hydride ligand is stereochemically rigid at this temperature and bridges the hinge, Os(1)–Os(2), bond. The chemical shift of the hydride resonance ($\delta$ −15.67) in the $^1H$ NMR spectrum of **2** is consistent with a bridging, rather than terminal, hydride ligand.[23]

The $^{13}C$ NMR signal at $\delta$ 175.1 that exhibits the coupling to hydrogen is assigned to the carbon atoms trans to the hydride ligand, namely, C(11) and C(21). Assignment of the remaining resonances in the $^{13}C$ NMR spectrum is as follows. The peaks at $\delta$ 188.3 and 188.0 are assigned to the axial carbons on Os(3) (i.e., C(31) and C(32)): they are the only peaks of intensity 1, and furthermore, they exhibit $^{13}C$–$^{13}C$ coupling, as expected for chemically different carbonyls in a trans arrangement (the compound contained ~35% $^{13}CO$).[32] The resonance at $\delta$ 186.0 is tentatively assigned to the carbonyl carbons on Os(4) (C(41), C(42)). This resonance is more intense than the other signals nominally of intensity 2. Because of their close proximity to the methyl hydrogens these carbon atoms are expected to have a shorter $T_1$, which would lead to a somewhat more intense $^{13}C$ NMR signal. For the same reason, the signal due to these carbonyls is expected to exhibit an NOE in the $^{13}C\{^1H\}$ spectrum, which was observed. It is also commonly observed that the resonances of carbonyls attached to a metal atom to which electron-donating ligands are coordinated are shifted downfield, rather than upfield.[33] The peak at $\delta$ 185.7 is attributed to the equatorial carbonyls on Os(3) (i.e., C(33) and C(34)): it is in the region expected for the signals of equatorial carbonyls of $Os(CO)_4$ groups, which is downfield from the region where the resonances of $Os(CO)_3$ groupings occur.[29,31] The signal at $\delta$ 178.1 is assigned to carbon atoms C(13) and C(23) since it is more intense than the other signals attributed to the $Os(CO)_3$ units, as would be expected for the carbons of these units that are closest to the methyl hydrogens, for reasons given above. It is also expected that the remaining carbons of the $Os(CO)_3$ units would have similar $^{13}C$ NMR chemical shifts since they both point away from the Cp* ligand and toward the $Os(CO)_4$ grouping. The remaining signal, at $\delta$ 174.3, is therefore assigned to C(12) and C(22).

**Chart I**



**Comparison of the Structures of 1 and 2.** As we have previously pointed out, 62-electron, osmium-containing clusters appear to adopt a planar metal arrangement when one of the hinge metal atoms has four terminal ligands whereas a butterfly configuration is found when both hinge atoms have only three terminal ligands.[19] For example, $Os_4(CO)_{14}(PMe_3)$ has a planar $Os_4$ metal framework[5] whereas $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ has a butterfly $Os_4$ skeleton.[19] In this way, the metal atoms in question have approximate octahedral coordination if the hinge metal–metal bond is ignored. The structures of **1** and **2** are in agreement with this generalization: **1** has an $Os(CO)_4$ grouping in a hinge position and has a planar arrangement of metal atoms; **2** has $Os(CO)_3$ groupings in both the hinge sites and possesses a butterfly configuration of metal atoms.

We next address the question of why **1** and **2** have these different arrangements of metal atoms, even though their chemical composition is similar. A simple view of the bonding in **1** is depicted in Chart I. In order for each metal atom to achieve an 18-electron configuration, it is proposed that the bond between the osmium atom of the hinge $Os(CO)_4$ unit and the rhenium atom is a dative bond and that the bond of the rhenium atom to the other hinge osmium atom is a three-center, two-electron Re($\mu$-H)Os linkage. That dative metal–metal bonds might be present in the metal framework of metal cluster compounds was first proposed in 1979.[34] We have also described numerous complexes that have an unbridged, donor–acceptor bond between osmium and a second transition metal atom.[30,35] We also recently reported the structures of two complexes that are believed to have two dative metal–metal bonds in tandem.[30a,36] Complexes in which three-center, two-electron Re($\mu$-H)M (M = transition metal) bonds are believed to be present have been known for some time.[37]

A proposal for the metal–metal bonding in **2** is also depicted in Chart I. In the proposed view, the 17-electron

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$(Cp^*)Os(CO)_2$ fragment is bound to the rest of the cluster via one dative and one nondative Os–Os bond (these bonds may be transposed to the arrangement shown in Chart I).

A comparison of the positions of the CO stretches of $(Cp^*)Os(CO)_2(H)$ (2001, 1941 cm$^{-1}$)[13] to those of $Re(CO)_4(PPh_3)(H)$ (2082, 1991, 1977, 1964 cm$^{-1}$)[12] indicates there is more electron density on the osmium atom in $(Cp^*)Os(CO)_2$ than on the rhenium atom in $Re(CO)_4(PPh_3)$ (or $Re(CO)_3(PPh_3)$). This increased electron density would be expected to favor the structure found for 2 rather than one similar to that found for 1. This is because the osmium atom to which the Cp* ligand is attached acts as the donor atom in the dative metal–metal bond in 2, whereas it would be the acceptor atom in a structure analogous to that of 1. We and others have observed that, not unexpectedly, apparently stronger dative metal–metal bonds are formed when stronger $\sigma$-donor ligands are attached to the donor metal atom.[30,36,38]

Relevant to this discussion is that we have observed a changeover in the structures of $Os_4(CO)_{15}(L)$ (L = CO, P-donor ligand, CNBu$^t$) clusters, a changeover from a puckered-square arrangement of metal atoms with no dative metal–metal bonds to a spiked triangular geometry with one dative and three nondative metal–metal bonds (i.e., $(L)(OC)_4Os{\rightarrow}Os_3(CO)_{11}$); and this occurs as the $\sigma$-donor properties of L increase.[3a]

An alternative view of the bonding in 2 is that it is a formally unsaturated cluster similar to $Os_3(\mu\text{-}H)_2(CO)_{10}$,[39] but with one of the bridging hydride ligands replaced with the isolobal $(Cp^*)Os(CO)_2$ unit. In other words, the $(Cp^*)Os(CO)_2$ fragment is bound to the rest of the cluster via a three-center, two-electron bond where each unit contributes one electron to the bond. Given the propensity of osmium to form dative metal–metal bonds in organometallic complexes, we favor the former interpretation for the bonding in 2.

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**Supplementary Material Available:** Tables of hydrogen atom coordinates, anisotropic thermal parameters, and additional bond length and angle data for 1 and 2 (10 pages). Ordering information is given on any current masthead page.

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