

Synthesis and Structure of the Butterfly Cluster  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)^1$ 

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The cluster  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$  (**1**) has been isolated as one product from the treatment of  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$  and  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  in  $\text{CH}_2\text{Cl}_2$  with  $\text{Me}_3\text{NO}$ . The structure of **1** has been solved by X-ray crystallography: space group  $P2_1/n$  with  $a = 15.641$  (6) Å,  $b = 11.013$  (3) Å,  $c = 16.280$  (4) Å,  $\beta = 114.10$  (3)°,  $V = 2560$  Å<sup>3</sup>,  $Z = 4$ ;  $R_1 = 0.0325$ ,  $R_2 = 0.0380$  for 2503 reflections with  $I > 3\sigma(I)$  having  $2\theta < 45^\circ$ . The molecule adopts a butterfly arrangement of metal atoms with  $\text{Os}(1)\text{-Os}(2) = 2.868$  (1) Å,  $\text{Os}(1)\text{-Os}(3) = 2.886$  (1) Å,  $\text{Os}(1)\text{-Os}(4) = 2.939$  (1) Å,  $\text{Os}(2)\text{-Os}(3) = 3.115$  (1) Å, and  $\text{Os}(3)\text{-Os}(4) = 2.850$  (1) Å. The  $\text{PMe}_3$  ligand is coordinated to a wing-tip metal atom ( $\text{Os}(2)\text{-P} = 2.342$  (4) Å); the hydride ligands are believed to bridge  $\text{Os}(2)\text{-Os}(3)$  (cis to  $\text{PMe}_3$ ) and the hinge metal-metal bond ( $\text{Os}(1)\text{-Os}(3)$ ). The last assignment is based on the spectroscopic properties of **1**, which also reveal **1** to be static in solution at 0 °C. The compound is a rare example of a 62-electron butterfly cluster that has only hydride bridges. These clusters are compared with planar 62-electron clusters that have no bridging ligands.

## Introduction

We have recently described the synthesis and crystal structure of the remarkable cluster  $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$ .<sup>2</sup> This cluster has an unusual planar  $\text{Os}_4$  skeleton with two long and two short Os-Os bonds, which were rationalized in terms of three-center-two-electron metal-metal bonds. The cluster also exhibits extraordinarily nonrigidity in solution even at -89 °C.

Here we report the synthesis and crystal structure of  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$ . This compound may be regarded as derived from  $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$  by the replacement of one carbonyl ligand with two bridging hydride groups. However, in contrast to  $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$ , it has a butterfly arrangement of the metal core and is rigid in solution.

## Experimental Section

The reaction and isolation of the product 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 dried in a similar manner except that  $\text{P}_2\text{O}_5$  was used as the drying agent. The starting materials,  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ <sup>3</sup> and  $\text{Os}(\text{CO})_4(\text{PMe}_3)$ ,<sup>4</sup> were prepared by literature methods or a minor modification thereof. The <sup>13</sup>C-enriched compound was obtained from <sup>13</sup>C-enriched  $\text{Os}_3(\text{CO})_{12}$  (~35% <sup>13</sup>C). This in turn was prepared by heating  $\text{Os}_3(\text{CO})_{12}$  in toluene at 125 °C under ~1.5 atm of <sup>13</sup>C (99% <sup>13</sup>C) for 3 days.  $\text{Me}_3\text{NO}$ , as obtained commercially, was sublimed before use.

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 on a Kratos MS-50 instrument (University of British Columbia, regional facility). NMR spectra were recorded on a Bruker WM400 spectrometer. The microanalysis was performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

**Preparation of  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$  (**1**).** To a stirred solution of  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$  (100 mg, 0.12 mmol) and  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  (25 mg, 0.13 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL),  $\text{Me}_3\text{NO}$  in MeOH was added dropwise until the purple color was just discharged. The absorptions in the infrared spectrum of the original solution at 2094, 2074, and 2060  $\text{cm}^{-1}$  had disappeared after this treatment. The resulting red solution was filtered through a silica gel column (10 × 2.5 cm) and evaporated to dryness. The remaining solid was extracted with cold hexane (4 × 5 mL); the extracts were combined and chromatographed on a silica gel column (30 × 2.5 cm) with hexane/ $\text{CH}_2\text{Cl}_2$  (2/1) as the eluant. The first, pale yellow band was not identified; the second, orange band was the desired product; the third, broad brown band was identified as  $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$ ;<sup>2</sup> still further bands were not characterized. The orange band

Table I. Crystal Data and Details of Intensity Collection for  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$ 

formula	$\text{C}_{16}\text{H}_{11}\text{O}_{13}\text{Os}_4\text{P}$
fw	1204
color	red
space group	$P2_1/n^a$
cryst syst	monoclinic
a, Å	15.641 (6)
b, Å	11.013 (3)
c, Å	16.280 (4)
$\beta$ , deg	114.10 (3)
V, Å <sup>3</sup>	2560
Z	4
$\rho_{\text{calcd}}$ , g $\text{cm}^{-3}$	3.123
$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	199
cryst size, mm	0.11 × 0.18 × 0.27
scan method	$\omega$ -2 $\theta$
scan range (2 $\theta$ ), deg	3.0-45.0
scan width (2 $\theta$ ), deg	1.3
scan rate (2 $\theta$ ), deg/min	1.4-6.6
collcn range	$\pm h, +k, +l$
transmission coeff range	0.0141-0.164
no. of unique reflns	3544
no. of obsd reflns, $I > 3\sigma(I)$	2504
no. of variables	308
$R_1^b$	0.0325
$R_2^c$	0.0380
K factor in wtg scheme	0.0004
GOF	1.42
largest shift <sup>d</sup>	0.00
map $\sigma$ , e/Å <sup>3</sup> e	0.23
largest peak, e/Å <sup>3</sup> f	1.79
extinction parameter ( $\times 10^{-8}$ ) <sup>g</sup>	6.7 (1.3)

<sup>a</sup> Nonstandard setting for  $P2_1/c$ . Equivalent positions:  $x, y, z; 1/2 - x, 1/2 + y, 1/2 - z; -x, -y, -z; 1/2 + x, 1/2 - y, 1/2 + z$ . <sup>b</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>c</sup>  $R_2 = |\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2|^{1/2}$ . <sup>d</sup> Largest shift/error in the final cycle of refinement. <sup>e</sup> Standard deviation of the final Fourier difference map. <sup>f</sup> Largest peak in the final Fourier difference map. <sup>g</sup> Parameter is g in the formula  $F_c' = k|F_c|(1 + g|F_c|^2 Lp_2/p_1)^{-1/2}$ , where  $F_c'$  is the corrected, calculated structure factor,  $k$  is a scale factor,  $Lp$  is the Lorentz-polarization factor, and  $p_n = 1 + \cos^{2n} 2\theta$ .

was collected and the solvent removed on the vacuum line to give red, air-stable  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$  (31 mg, 26%); the analytical sample was obtained by recrystallization from hexane/ $\text{CH}_2\text{Cl}_2$  (4/3): mp 204 °C; IR (hexane)  $\nu(\text{CO})$  2101 (w), 2069 (s), 2052 (s), 2030 (s), 2016 (s), 2003 (s), 1997 (sh), 1985 (m), 1976 (w), 1971 (w), 1968 (sh)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{C}_7\text{D}_8$ , 21 °C)  $\delta$  1.03 (d,  $J_{\text{P-H}} = 10.2$  Hz), -18.33 (s, coupling not resolved), -20.40 (dd,  $J_{\text{P-H}} = 10.2$  Hz,  $J_{\text{H-H}} = 1.2$  Hz); <sup>13</sup>C (hydrogen coupled) NMR ( $\text{CD}_2\text{Cl}_2$ , CO region)  $\delta$  191.3, 190.3, 188.0, 186.7, 182.4, 181.7, 177.5, 176.8, 176.4, 175.5 (d,  $J_{\text{H-C}} = 7.2$  Hz), 175.2, 174.4 (d,  $J_{\text{H-C}} = 8.6$  Hz), 171.4 (d,  $J_{\text{H-C}} = 6.8$  Hz); MS (EI)  $m/z$  1176 ( $\text{M}^+ - \text{CO}$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{11}\text{O}_{13}\text{Os}_4\text{P}$ : C, 15.98; H, 0.92. Found: C, 16.12; H, 0.82.

**X-ray Structure Determination for **1**.** Crystals of **1** of acceptable quality were grown from hexane/ $\text{CH}_2\text{Cl}_2$ ; a crystal of suitable size (Table I) was mounted on an Enraf-Nonius CAF4F diffractometer. Diffraction

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**Table II.** Fractional Coordinates for Os<sub>4</sub>(μ-H)<sub>2</sub>(CO)<sub>13</sub>(PMe<sub>3</sub>)

atom	x	y	z
Os(1)	0.33486 (4)	0.10071 (5)	0.05491 (4)
Os(2)	0.30382 (4)	-0.14812 (5)	0.08784 (4)
Os(3)	0.26492 (4)	-0.05045 (5)	-0.10381 (4)
Os(4)	0.14666 (4)	0.13670 (5)	-0.08784 (4)
P(1)	0.2452 (4)	-0.3469 (4)	0.0686 (4)
C(1)	0.320 (2)	-0.452 (2)	0.154 (2)
C(2)	0.136 (2)	-0.363 (2)	0.080 (2)
C(3)	0.227 (2)	-0.419 (2)	-0.036 (2)
C(11)	0.291 (1)	0.161 (2)	0.137 (1)
O(11)	0.269 (1)	0.206 (1)	0.191 (1)
C(12)	0.454 (1)	0.065 (1)	0.144 (1)
O(12)	0.526 (1)	0.046 (1)	0.201 (1)
C(13)	0.374 (1)	0.256 (2)	0.031 (1)
O(13)	0.403 (1)	0.346 (1)	0.022 (1)
C(21)	0.204 (1)	-0.081 (2)	0.115 (1)
O(21)	0.150 (1)	-0.047 (1)	0.141 (1)
C(22)	0.376 (1)	-0.157 (2)	0.216 (2)
O(22)	0.418 (1)	-0.160 (2)	0.292 (1)
C(23)	0.416 (2)	-0.189 (2)	0.075 (1)
O(23)	0.488 (1)	-0.217 (1)	0.076 (1)
C(31)	0.344 (1)	-0.176 (1)	-0.117 (1)
O(31)	0.386 (1)	-0.249 (1)	-0.132 (1)
C(32)	0.153 (1)	-0.119 (2)	-0.190 (1)
O(32)	0.085 (1)	-0.160 (1)	-0.243 (1)
C(33)	0.279 (1)	0.046 (2)	-0.194 (1)
O(33)	0.289 (1)	0.101 (1)	-0.248 (1)
C(41)	0.086 (1)	-0.001 (2)	-0.063 (1)
O(41)	0.042 (1)	-0.082 (1)	-0.055 (1)
C(42)	0.116 (1)	0.252 (2)	-0.018 (1)
O(42)	0.097 (1)	0.320 (1)	0.025 (1)
C(43)	0.042 (1)	0.151 (1)	-0.201 (1)
O(43)	-0.024 (1)	0.161 (1)	-0.264 (1)
C(44)	0.211 (1)	0.254 (2)	-0.131 (1)
O(44)	0.246 (1)	0.324 (1)	-0.161 (1)

data were collected at 20 ± 1 °C with the use of graphite-monochromated Mo Kα<sub>1</sub> radiation (λ = 0.7930 Å). Background measurements were made by extending the scan range by 25% on each side of the scan. Two standard reflections were monitored at least every 2 h during data collection, and intensity data were scaled appropriately. Accurate cell dimensions were assigned on the basis of 19 carefully centered high-angle (2θ > 21°) reflections widely scattered in reciprocal space. Lorentz, polarization, and analytical absorption<sup>5</sup> corrections were applied. ψ scans were obtained for six reflections throughout the 2θ range of data collection having χ near 90°. Crystal faces were measured with an independently mounted optical telescope fitted with a filar eyepiece.

The osmium atoms were located by conventional methods; the other non-hydrogen atoms were located from Fourier difference maps. Extinction was indicated and added as a refined variable;<sup>6</sup> the -2,2,2 reflection was omitted from the refinement since it suffered from extinction (ωΔ<sup>2</sup> = 441). Unit weights were used during the initial stages of refinement. After anisotropic refinement, the weight, w, for each reflection was set to be w = [σ<sup>2</sup>(F) + K|F|<sup>2</sup>]<sup>-1</sup> and the value of K adjusted to remove trends in the average ωΔ<sup>2</sup>/λ in the error analysis. Methyl hydrogen atom positions were generated from initial positions located on a Fourier difference map that employed inner data only. Attempts to locate the positions of the bridging hydride ligands from this Fourier map were unsuccessful. Final convergence was achieved by full-matrix least-squares refinement. The largest peaks in the final Fourier difference map were in the vicinity of the osmium atoms. Crystallographic data and details of the data collection are given in Table I, atomic coordinates in Table II, and bond length and angle data in Table III. Neutral-atom scattering factors with anomalous dispersion corrections were employed.<sup>7</sup> The computer programs used were from "The VAX 750/780 Crystal Structure System"<sup>8</sup> except that for the atomic thermal ellipsoid diagram, which was made with the SNOOP program.<sup>9</sup>

**Table III.** Selected Molecular Dimensions for Os<sub>4</sub>(μ-H)<sub>2</sub>(CO)<sub>13</sub>(PMe<sub>3</sub>)

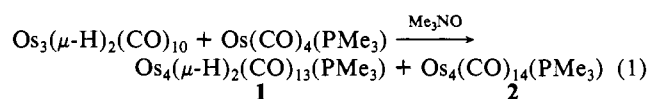
Bond Lengths (Å)			
Os(1)-Os(2)	2.868 (1)	Os(4)-C(43)	1.90 (2)
Os(1)-Os(3)	2.886 (1)	Os(4)-C(44)	1.94 (2)
Os(1)-Os(4)	2.939 (1)	P(1)-C(1)	1.82 (2)
Os(2)-Os(3)	3.115 (1)	P(1)-C(2)	1.79 (3)
Os(3)-Os(4)	2.850 (1)	P(1)-C(3)	1.80 (3)
Os(2)-P(1)	2.342 (4)	C(11)-O(11)	1.17 (3)
Os(1)-C(11)	1.86 (2)	C(12)-O(12)	1.15 (2)
Os(1)-C(12)	1.87 (2)	C(13)-O(13)	1.12 (2)
Os(1)-C(13)	1.91 (2)	C(21)-O(21)	1.14 (2)
Os(2)-C(21)	1.94 (2)	C(22)-O(22)	1.13 (3)
Os(2)-C(22)	1.93 (2)	C(23)-O(23)	1.16 (2)
Os(2)-C(23)	1.91 (2)	C(31)-O(31)	1.15 (2)
Os(3)-C(31)	1.89 (2)	C(32)-O(32)	1.13 (2)
Os(3)-C(32)	1.93 (2)	C(33)-O(33)	1.13 (3)
Os(3)-C(33)	1.89 (2)	C(41)-O(41)	1.15 (2)
Os(4)-C(41)	1.92 (2)	C(42)-O(42)	1.15 (2)
Os(4)-C(42)	1.89 (2)	C(43)-O(43)	1.13 (2)
		C(44)-O(44)	1.16 (2)

Angles (deg)			
Os(2)-Os(1)-Os(3)	65.56 (2)	Os(3)-Os(4)-C(43)	107.8 (5)
Os(2)-Os(1)-Os(4)	94.86 (3)	Os(1)-Os(4)-C(42)	91.9 (5)
Os(3)-Os(1)-Os(4)	58.59 (3)	Os(2)-P(1)-C(1)	113.3 (9)
Os(1)-Os(2)-Os(3)	57.48 (2)	Os(2)-P(1)-C(2)	114.6 (7)
Os(2)-Os(3)-Os(1)	56.96 (2)	Os(2)-P(1)-C(3)	116.2 (8)
Os(2)-Os(3)-Os(4)	91.50 (3)	Os(1)-C(11)-O(11)	175 (2)
Os(1)-Os(3)-Os(4)	61.64 (3)	Os(1)-C(12)-O(12)	177 (2)
Os(3)-Os(4)-Os(1)	59.77 (2)	Os(1)-C(13)-O(13)	175 (2)
C(21)-Os(2)-C(23)	169.1 (7)	Os(2)-C(21)-O(21)	172 (2)
C(41)-Os(4)-C(44)	168.4 (7)	Os(2)-C(22)-O(22)	179 (2)
Os(2)-Os(1)-C(11)	93.7 (6)	Os(2)-C(23)-O(23)	173 (2)
Os(2)-Os(1)-C(12)	81.0 (5)	Os(3)-C(31)-O(31)	174 (2)
Os(2)-Os(1)-C(13)	170.1 (5)	Os(3)-C(32)-O(32)	179 (2)
Os(1)-Os(2)-C(22)	100.6 (5)	Os(3)-C(33)-O(33)	178 (2)
Os(3)-Os(2)-P(1)	106.4 (1)	Os(4)-C(41)-O(41)	174 (2)
Os(2)-Os(3)-C(31)	110.1 (6)	Os(4)-C(42)-O(42)	179 (2)
Os(2)-Os(3)-C(32)	89.4 (5)	Os(4)-C(43)-O(43)	174 (2)
Os(2)-Os(3)-C(33)	158.8 (6)	Os(4)-C(44)-O(44)	177 (2)

## Results and Discussion

The cluster, Os<sub>4</sub>(μ-H)<sub>2</sub>(CO)<sub>13</sub>(PMe<sub>3</sub>) (**1**), was prepared by the addition of Me<sub>3</sub>NO in methanol to a solution of Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>10</sub> and Os(CO)<sub>4</sub>(PMe<sub>3</sub>) in CH<sub>2</sub>Cl<sub>2</sub>. It was isolated after chromatography as bright red, air-stable crystals in 26% yield. The other major product from the reaction was Os<sub>4</sub>(CO)<sub>14</sub>(PMe<sub>3</sub>) (**2**)<sup>2</sup> (eq 1); other minor products were not identified. In the absence of

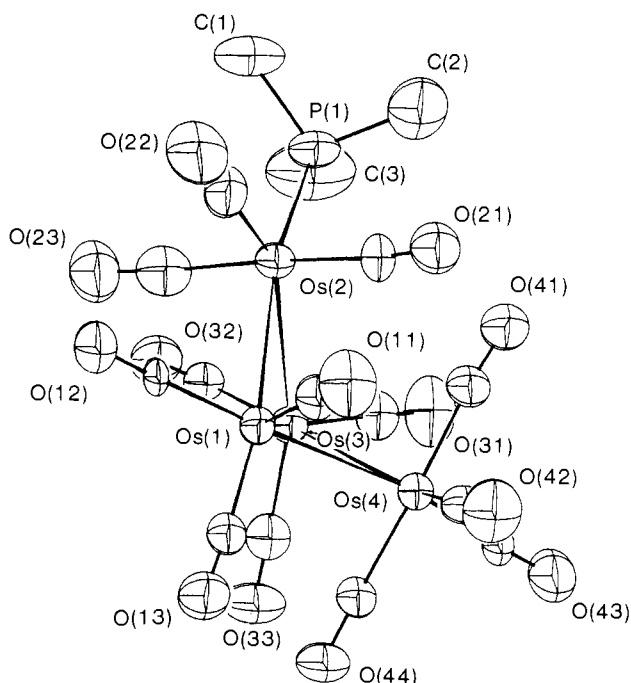


Me<sub>3</sub>NO, Os(CO)<sub>4</sub>(PMe<sub>3</sub>) reacts more slowly with Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>10</sub> to give Os<sub>3</sub>(CO)<sub>11</sub>[Os(CO)<sub>4</sub>(PMe<sub>3</sub>)] (**3**) as the major product.<sup>2</sup> This suggests that the formation of **1** occurs by the initial removal of CO from Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>10</sub> by Me<sub>3</sub>NO, followed by the addition of Os(CO)<sub>4</sub>(PMe<sub>3</sub>) to the resulting species, rather than via the intermediate HOs<sub>3</sub>(μ-H)(CO)<sub>10</sub>[Os(CO)<sub>4</sub>(PMe<sub>3</sub>)]. (It is known that Os(CO)<sub>4</sub>(PMe<sub>3</sub>) can act as donor ligand, e.g., as in **3**.)<sup>2</sup>

**Structure of 1.** A view of the molecule is given in Figure 1; bond lengths and angles are given in Table III. The bridging hydride ligands were not located. As can be seen, the core of the molecule consists of a butterfly arrangement of metal atoms; the dihedral angle between the Os(1)-Os(2)-Os(3) and Os(1)-Os(3)-Os(4) planes is 112.7°. This is the common configuration observed for 62-electron clusters and is in agreement with the theories of cluster bonding.<sup>10</sup> As recently pointed out in a review

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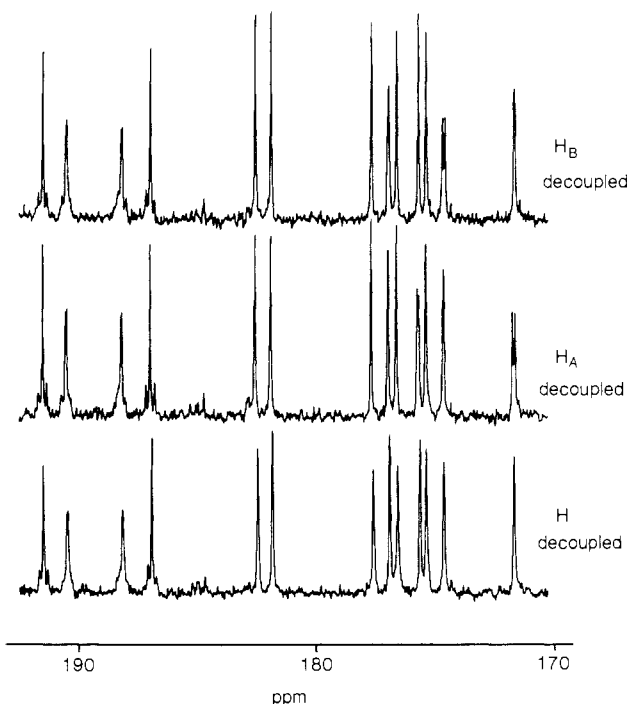


**Figure 1.** Molecular structure of  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$  (**1**).

of butterfly clusters,<sup>11</sup> there are, however, very few examples of 62-electron butterfly clusters with only hydride bridges. To our knowledge, the only other examples in the literature are  $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\text{CNMe})_2]^+^{12}$  and  $[\text{Re}_4(\mu\text{-H})_5(\text{CO})_{14}]^-$ .<sup>13</sup> The 60-electron clusters  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2$ <sup>14</sup> and  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}[\text{P}(\text{C}_6\text{H}_{11})_3]$ <sup>15</sup> and the 58-electron cluster  $\text{Os}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2$ <sup>16</sup> also have butterfly frameworks with only hydride bridges.

The Os–Os bond lengths in **1** are Os(1)–Os(2) = 2.868 (1) Å, Os(1)–Os(3) = 2.886 (1) Å, Os(1)–Os(4) = 2.939 (1) Å, Os(2)–Os(3) = 3.115 (1) Å, and Os(3)–Os(4) = 2.850 (1) Å. The Os(2)–Os(3) vector is undoubtedly bridged by a hydride ligand: metal–metal bonds are usually lengthened when bridged by a hydride ligand.<sup>17</sup> The assignment of a hydride substituent between Os(2) and Os(3) is also consistent with the spectroscopic results reported below and previous observations that, where possible, hydrides invariably bridge positions that are cis to phosphorus ligands.<sup>15</sup> As will be discussed, we do not believe the second hydride ligand bridges the next longest Os–Os bond (Os(1)–Os(4)). The reason that the Os(1)–Os(4) bond is lengthened to most Os–Os bonds found in clusters is unclear. It may be that alternation of long and short metal–metal bonds around the periphery of the cluster best relieves the interaction between the inward-leaning axial carbonyls on Os(2) and Os(4). This interaction appears severe; the C(21)···C(41) contact is 2.87 (2) Å, and the dihedral angle between the planes Os(2)–Os(4)–C(41) and Os(4)–Os(2)–C(21) is 51.1 (9)°.

**Spectroscopic Properties of 1.** The mass spectrum of **1** showed an ion of highest mass corresponding to  $[\text{M}^+ - \text{CO}]$ . This suggests that **1** may be converted to the 60-electron cluster  $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\text{PMe}_3)$  on pyrolysis, in a manner similar to that for **2**.<sup>2</sup> This possibility has, however, not yet been investigated. The



**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  and selectively H-decoupled  $^{13}\text{C}$  NMR spectra (carbonyl region) of **1** ( $^{13}\text{CO}$ -enriched;  $\text{CD}_2\text{Cl}_2$  solution).  $\text{H}_\text{A}$  is the proton that gives rise to the  $^1\text{H}$  NMR signal at  $\delta$  -20.40;  $\text{H}_\text{B}$ , the signal at  $\delta$  -18.33.

infrared spectrum of **1** in hexane shows 11 terminal-CO-stretching absorptions, which is consistent with the solid-state structure that lacks any element of symmetry. The  $^1\text{H}$  NMR spectrum of **1** in toluene- $d_8$  at 21 °C exhibits two resonances in the bridging hydride region: a doublet of doublets at  $\delta$  -20.4 ( $\text{H}_\text{A}$ ,  $J_{\text{P-H}} = 10.2$  Hz,  $J_{\text{H-H}} = 1.2$  Hz) and an unresolved doublet at  $\delta$  -18.3 ( $\text{H}_\text{B}$ ). The  $\text{H}_\text{A}$  resonance may be assigned to the hydride that bridges Os(2)–Os(3); the P–H coupling constant is typical of a hydride ligand located in a cis position to a phosphine ligand.<sup>14,15,18</sup> The small H–H coupling shown by this resonance suggests the second hydride ligand bridges on Os–Os bond adjacent to Os(2)–Os(3). (We have observed couplings in this range in triangular  $\text{Os}_3$  clusters with two chemically different Os( $\mu\text{-H}$ )Os groupings.<sup>19</sup>)

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $^{13}\text{CO}$ -enriched **1** in  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$  at 0 °C exhibits 13 different carbonyl resonances (Figure 2). This is as expected from the solid-state structure and also indicates that the compound is rigid in solution at this temperature. In contrast, **2** is fluxional in solution even at -89 °C.<sup>2</sup> (This suggests the nonrigid properties of **2** are associated with the unusual metal–metal bonding in the compound.)

The four resonances to lowest field in the spectrum of **1** may be assigned to the axial carbonyls attached to the osmium atoms with four terminal ligands. These resonances have  $^{13}\text{C}$ – $^{13}\text{C}$  couplings expected for a trans arrangement of two chemically different carbonyls and the level of  $^{13}\text{CO}$  enrichment of **1** used in the experiment. The middle two of these four signals are unresolved doublets due to phosphorus coupling. These signals may therefore be assigned to C(21) and C(23). In trinuclear osmium clusters the resonances of axial carbonyls are usually to lowest field of the carbonyl resonances.<sup>20,21</sup> The other resonances in the spectrum of **1** cannot be assigned. None of these remaining

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signals exhibit phosphorus coupling: it has been observed previously that there is phosphorus coupling to axial but not to equatorial carbonyls of  $\text{Os}(\text{CO})_3(\text{PR}_3)$  groups in trinuclear osmium clusters<sup>20,22</sup> and in **2**.

In an attempt to assign the position of the second hydride ligand, the  $^{13}\text{C}$  NMR spectrum of  $^{13}\text{C}$ -enriched **1** was determined with the protons of the hydride ligands selectively decoupled (Figure 2). With  $\text{H}_B$  decoupled only one resonance (at  $\delta$  174.4) showed a well-defined coupling (of 8.6 Hz) to  $\text{H}_A$  (i.e., the hydride ligand between Os(2) and Os(3)); the signal at  $\delta$  176.8 was broadened, which suggested an unresolved coupling to  $\text{H}_A$ . When  $\text{H}_A$  was decoupled, however, two of the signals showed well-resolved coupling to  $\text{H}_B$ , i.e.,  $\delta$  175.5 ( $J_{\text{H-C}} = 7.2$  Hz) and 171.4 ( $J_{\text{H-C}} = 6.8$  Hz). The most reasonable positions for the second hydride are either across the hinge (Os(1)–Os(3)) bond or across the Os(1)–Os(4) bond. If it were in the latter position, it would be expected to show couplings similar to that of  $\text{H}_A$  since the sites each occupy are similar (cis C–H couplings are assumed negligible). This was not observed, and we therefore believe the second hydride ligand is located along the hinge bond. This assignment is supported by the homonuclear nuclear Overhauser effect that the hydrides exhibit.<sup>23</sup> Of the previously mentioned butterfly clusters,  $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2]^+$  (**4**),<sup>12</sup>  $[\text{Re}_4(\mu\text{-H})_5(\text{CO})_{14}]^-$ ,<sup>13</sup> and  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}[\text{P}(\text{C}_6\text{H}_{11})_3]$  (**5**)<sup>15</sup> also have a hydride along the hinge bond. With the location of the second hydride ligand along the hinge bond, the following signals in the  $^{13}\text{C}$  NMR spectrum of **1** may be tentatively assigned:  $\delta$  176.8 (C(22)), 175.5 (C(11)), 174.4 (C(33)), 171.4 (C(31)). Besides the coupling to  $\text{H}_B$ , the assignment of C(31) (and hence C(11)) was made on the basis that the environment of C(31) is most different from those of the other carbonyls in the molecule (adjacent to the  $\text{Os}(\mu\text{-H})\text{Os}(\text{PMe}_3)$  unit); this should give rise to the signal at highest field.

The usual lengthening<sup>17</sup> of the hinge Os–Os bond due to the bridging hydride apparently does not occur in **1**. This has, however, been observed before in butterfly clusters. For example, in **5** the hinge Os–Os distance is 2.869 (1) Å,<sup>15</sup> in **4** it is 2.937 (2) Å compared with distances of 3.130 (2) and 3.145 (2) Å for the Os–Os bonds of the other  $\text{Os}(\mu\text{-H})\text{Os}$  groups in the cluster.<sup>12</sup> A neutron diffraction study of  $\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}\text{I}$  revealed the Os–Os bond length of the hinge  $\text{Os}(\mu\text{-H})\text{Os}$  unit to be 2.927 (2) Å whereas the Os–Os lengths of the other  $\text{Os}(\mu\text{-H})\text{Os}$  units were 3.055 (1) Å.<sup>24</sup> It may be that there is a lengthening, but unbridged hinge Os–Os bonds are shorter than 2.877 Å, the Os–Os

distance in  $\text{Os}_3(\text{CO})_{12}$ ,<sup>25</sup> usually taken to represent the length of an Os–Os single bond. For example, in  $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2$  the length of the unbridged hinge Os–Os bond is 2.773 (2) Å.<sup>14</sup> In  $\text{Os}_4(\text{CO})_{14}$ , which has a distorted tetrahedral framework, the Os–Os bond between the two  $\text{Os}(\text{CO})_3$  fragments has a length of 2.763 (1) Å.<sup>26</sup>

**Comparison of Planar and Butterfly Clusters.** As mentioned in the Introduction,  $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$  has a planar structure.<sup>2</sup> Other 62-electron clusters that have only terminal ligands and an essentially planar array of four metal atoms are  $[\text{Re}_4(\text{CO})_{16}]^{2-}$ ,<sup>27</sup>  $\text{HOs}_3\text{Re}(\text{CO})_{15}$ ,<sup>28</sup>  $\text{Os}_4(\text{CO})_{15}$ ,<sup>29</sup> and  $(\eta^5\text{-C}_5\text{Me}_5)\text{-IrOs}_3(\text{CO})_{11}$ .<sup>29</sup> There are a number of planar tetranuclear clusters with edge bridging or face bridging (non-hydrogen) ligands.<sup>11,30</sup> Because the requirements of these bridging ligands may dictate the structure adopted, these molecules will not be considered here. For the same reason, the many butterfly clusters with a ligand bridging the wing-tip metal atoms<sup>11</sup> will also not be considered.

It is apparent that, when the planar clusters mentioned above are compared to butterfly clusters with only hydride bridges, the planar clusters have at least one hinge metal atom with four terminal ligands. Although seven-coordinate, the metal atom in question may be regarded as pseudooctahedral coordinate with the seventh bond capping an edge of the octahedron. On the other hand, in the butterfly clusters both hinge metal atoms have only three terminal ligands and, once again, each metal has pseudooctahedral coordination, if it is assumed there is a bent metal–metal bond along the hinge. From the data available, it therefore appears that, in the absence of bridging ligands other than hydride ligands, 62-electron metal clusters adopt a butterfly configuration if both hinge metal atoms have three terminal ligands but a planar geometry if there is at least one hinge atom with four terminal ligands.

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**Supplementary Material Available:** Tables of hydrogen atom coordinates and anisotropic thermal parameters for **1** (1 page); listing of observed and calculated structure factors for **1** (18 pages). Ordering information is given on any current masthead page.

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