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Stepwise C−H Cleavage of Two Methyl Groups of a Pentamethylcyclopentadienyl Ligand on a Tetraosmium Cluster

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Pyrolysis of $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) in solution at 50 °C afforded $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**1**). The clusters $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**2**), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**3**), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**4**) have been isolated from the pyrolysis of **1** above 90 °C. Each tetrahedral cluster has been structurally characterized by X-ray crystallography and thereby provides a unique series of structures that depict the stepwise C−H activation of two methyl groups of a C_5Me_5 ligand on a metal cluster. The series also allows a comparison of Os−Os lengths of Os_4, $Os_4(\mu\text{-}H)$, $Os_4(\mu\text{-}H)_2$, and $Os_4(\mu\text{-}H)_3$ units in a closely related series of clusters. Crystallographic data for compound **1**: space group, *Pcmn*; $a = 8.852(1)$ Å, $b = 14.821(2)$ Å, $c = 19.054(2)$ Å; $R = 0.019$, 1813 observed reflections. For compound **2**: space group, $P2_1/c$; $a = 9.924(1)$ Å, $b = 17.051(3)$ Å, $c = 15.020(3)$ Å, $\beta = 101.81(1)°$, $R = 0.031$, 2934 observed reflections. For compound **3**: space group, *Pbca*; $a = 14.254(2)$ Å, $b = 16.214(2)$ Å, $c = 21.735(3)$ Å, $R = 0.038$, 2197 observed reflections. For compound **4**: space group: $P2_1/n$; $a = 9.655(1)$ Å, $b = 16.380(2)$ Å, $c = 14.842(1)$ Å, $\beta = 92.66(1)°$, $R = 0.030$, 2822 observed reflections.

Introduction

The pentamethylcyclopentadienyl ligand, $\eta^5\text{-}C_5Me_5$ (Cp*), is a widely used ligand in organometallic chemistry because of its exceptional steric and electronic properties.[1] We have recently described the synthesis of $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (**5**) by the addition of $Cp^*Os(CO)_2(H)$ to $Os_3(CO)_{10}(cyclooctene)_2$. The unexpected butterfly arrangement of metal atoms in **5** was attributed in part to the strong donor properties of the Cp* ligand.[2]

In the preparation of the precursor $Cp^*Os(CO)_2(H)$, by the reaction of C_5Me_5H with $Os_3(CO)_{12}$ at 200 °C,[3] a small amount of a crystalline byproduct was isolated. Subsequent analysis of the compound by X-ray diffraction and NMR spectroscopy revealed it to be $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**4**), that is, a product in which C−H cleavage of two methyl groups of the C_5Me_5 ligand had apparently occurred on a tetranuclear metal unit. The C−H cleavage of a single methyl group of a C_5Me_5 ligand in a mononuclear or dinuclear complex is common,[4,5] and there are examples where C−H activation of two methyl groups has been observed.[6,7] Of the latter examples, only one involves a cluster compound.[7]

Herein we report a rational synthesis of **4** by the careful pyrolysis of **5**. Furthermore, intermediates in the reaction of $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**1**) and $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**2**) have been isolated and structurally characterized, thereby providing a unique series of structures that illustrate the stepwise C−H activation of two methyl groups of a C_5Me_5 ligand on a metal cluster. Also isolated, in trace amounts, in the pyrolysis of **5** was $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**3**), the structure of which has been determined and is reported here.

Experimental Section

Standard Schlenk techniques were employed in the syntheses. Solvents were rigorously dried and stored under nitrogen before use. The cluster $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ was prepared by

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(1) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. (b) Campbell, P. H.; Chiu, N. W. K.; Deugan, K.; Miller, I. J.; Sorensen, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 6404. (c) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (d) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *94*, 5087. (e) King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. (f) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1. (g) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (h) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (i) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892. (j) Wolzanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (k) Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6389. (l) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1. (m) Marks, T. J. *Science* **1982**, *217*, 989. (n) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533. (o) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101. (p) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291. (q) Elschenbroich, C.; Salzer, A. *Organometallics. A Concise Introduction*; VCH: New York, 1989, p 47.

(2) Wang, W.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1993**, *12*, 3079.

(3) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095.

(4) For example: (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (d) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818. (e) Hashimoto, H.; Tobita, H.; Ogino, H. *Organometallics* **1993**, *12*, 2182. (f) Fan, L.; Turner, M. L.; Hursthouse, M. B.; Abdul Malik, K. M.; Gusev, O. V.; Maitlis, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 385. (g) Gusev, O. V.; Sergeev, S.; Saez, I. M.; Maitlis, P. M. *Organometallics* **1994**, *13*, 2059.

(5) Bottomley, F.; Egharevba, G. O.; Lin, I. J. B.; White, P. S. *Organometallics* **1984**, *4*, 550.

(6) (a) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945. (b) Pattiasina, J. W.; Hissink, C. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 7758. (c) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (d) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

(7) He, X.-D.; Chaudret, B.; Lahoz, F.; Lopez, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 958.

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the literature method.[2] Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer. NMR spectra were recorded on a Bruker WM400 spectrometer. The $^{13}C\{^1H\}$ NMR spectrum was obtained on a sample that had been ^{13}CO-enriched (~35%). Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (1). A round-bottom flask fitted with a Teflon valve was charged with $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (20 mg, 0.016 mmol) and CH_2Cl_2 (20 mL). The flask and contents were cooled to −196 °C and evacuated; the solution was degassed with three freeze−pump−thaw cycles. The sealed flask was heated at 50 °C for 8 h. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel (1.2 × 20 cm). Elution with hexane/CH_2Cl_2 (3/1) gave an orange band from which **1** (14 mg, 72%) was isolated as air-stable, orange crystals: IR (CH_2Cl_2) ν(CO) 2083 (s), 2056 (vs), 2024 (vs), 2003 (sh), 1995 (m), 1937 (m), 1814 (m, br), 1773 (sh) cm^{-1}; ^1H NMR (CD_2Cl_2, room temperature) δ 2.11 (s, 15H), −20.71 (s, 1H). Anal. Calcd for $C_{21}H_{16}O_{11}Os_4$: C, 20.93; H, 1.34. Found: C, 21.05, H, 1.30.

Preparation of $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (2), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (3), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (4). The pyrolysis of **1** always gave **4** as the major product. Below 90 °C, the reaction was slow (as determined by IR spectroscopy); above ~110 °C, the reaction produced mainly **4**. Because of their similar solubilities, clusters **2** and **4** could not be separated completely by chromatography. For these reasons, the yield of **3** was insufficient to allow for a microanalysis, and samples of **2** always contained trace amounts of **4** and were also not microanalyzed.

Method 1: A flask with **1** (25 mg, 0.021 mmol), CH_2Cl_2 (7 mL), and hexane (20 mL) was cooled to −196 °C and evacuated; the solvent mixture was degassed with three freeze−pump−thaw cycles. The sealed flask was heated at 94 °C for 3 d. The solvent was then removed on the vacuum line and the remaining solid chromatographed on silica gel. Elution with hexane/CH_2Cl_2 (7/1, v/v) gave a yellow band from which 15 mg of a mixture of **2** and **4** was obtained (the ratio **2**/**4** was approximately 1/3 after further recrystallization from CH_2Cl_2/hexane). Further elution with hexane/CH_2Cl_2 (3/1) gave an orange band from which 8 mg of a mixture of **1** and **3** (in an approximate 1/1 ratio) was obtained. Spectroscopic properties and the crystal used in the X-ray study of **2** were obtained from samples manually separated from **4**.

Method 2: A similar reaction to that described above was carried out except that a temperature of 115−120 °C and a reaction time of 42 h were employed. Chromatography as above gave pure **3** (~2 mg, ~10%) and **4** (14 mg, 82%). There was no evidence for **2** in the IR spectrum of the reaction solution. Compound **2**: IR (CH_2Cl_2) ν(CO) 2097 (w), 2079 (s), 2040 (vs), 2012 (vs), 1999 (m), 1967 (sh), 1964 (m), 1937 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.75 (t, J_{HH} = 0.7 Hz, 2H), 2.34 (s, 6H), 1.53 (s, 6H), −16.88 (s, 2H). **Compound 3**: IR (CH_2Cl_2) ν(CO) 2078 (s), 2035 (vs) 2003 (vs), 1993 (sh), 1974 (m), 1951 (w, sh), 1904 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.78 (s, 2H), 2.21 (s, 6H), 1.14 (s, 6H). Compound **4**: IR (CH_2Cl_2) ν(CO) 2097 (s), 2053 (vw), 2023 (vs), 2012 (s), 1999 (m), 1966 (vw), 1938 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.89 (s, 3H), 1.82 (d, J_{HH} = 8 Hz, 2H), 1.68 (d, J_{HH} = 8 Hz, 2H), 1.49 (s, 6H), −17.46 (s, 2H), −19.70 (s, 1H); $^{13}C/^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 4/1) δ 186.0 (2C), 174.4 (2C, J_{CH} = 13 Hz), 172.0 (1C), 171.8 (2C), 164.8 (2C, J_{CH} = 13 Hz). Anal. Calcd for $C_{19}H_{16}O_9Os_4$: C, 19.86; H, 1.41. Found: C, 20.04; H, 1.45.

X-ray Analysis of 1−4. In each case a crystal was mounted on an Enraf Nonius diffractometer and intensity data collected with the use of graphite-monochromated Mo Kα radiation. Because of the crystal shape of **1**, an azimuth position for which minimum absorption was determined from the shape and mounting of the crystal was used for the intensity data collection. 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 (2 h for **3**) of acquisition time, varied randomly up to ±2% (**1**, **3**, **4**) and ±3% (**2**) during the data collection process. Background measurements were made by extending the scan width by 25% on each side of the scan. Absorption corrections calculated by Gaussian integration (and carefully checked against ψ-scan measurements) were applied to the measured intensity data. Data reduction included the small corrections for intensity scale variation and for Lorentz and polarization effects.

The positions of the Os atoms were determined by direct methods. 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 attached carbon atom. The coordinates of carbon atoms with attached hydrogen atoms were linked so that the derived coordinates included contributions from derivatives from the appropriate atom sites. In each case an extinction parameter was required in the refinement. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme, based on counting statistics, was adopted for which $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Complex scattering factors for neutral atoms[8] were used in the calculation of structure factors. The final least-squares refinement included coordinates for all non-hydrogen atoms (the methyl hydrogen atoms were linked to the appropriate carbon atoms), anisotropic thermal parameters for the osmium atoms, isotropic thermal parameters for the carbonyl carbon atoms, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to carbon atoms. Oxygen atoms were refined anisotropically except in **3**. The outer-ring carbon atoms of the Cp* ligand were given anisotropic thermal parameters in **1** and **2**, and isotropic thermal parameters in **3**, while the ring carbon atoms were given anisotropic thermal parameters in **1** and isotropic thermal parameters in **2** and **3**. The final refinement of **4** included one thermal parameter for the ring carbon atoms, one for both C(6) and C(10), and one for both C(7) and C(9). The coordinates and isotropic thermal parameter of the hydride ligand in **1** were refined; the hydrides in **2** and **4** were included as fixed contributions in the final refinement. The programs used for data reduction, structural solution, and initial refinement were from the NRCVAX[9] crystal structure system. The program suite CRYSTALS[10] was employed in the final refinement. All computations were carried out on a MicroVAX-II computer. Crystallographic data are summarized in Table 1. Final fractional coordinates for the non-hydrogen atoms and hydride ligands of **1**, **2**, **3**, and **4** are given in Tables 2, 4, 6, and 8, respectively, and bond length and angle data are in Table 3, 5, 7, and 9, respectively.

Placement of the Hydride Ligands. Compound 1. Immediately before the final refinement a low angle ($0 < (\sin\theta)/\lambda \leq 0.35$ Å^{-1}) difference map revealed that the largest peak (with electron density 0.35(7) e Å^{-3}) was on the mirror-symmetry plane 1.7 Å from Os(1) and Os(1′). The hydride ligand was therefore placed in that position and the coordinates and isotropic thermal parameter were refined. The relatively long Os(1)−Os(1′) distance [2.938(1) Å] and large Os(1′)−Os(1)−C(13) angle [113.4(2)°] also supported the view that the hydride ligand bridged Os(1) and Os(1′). Calculations for the hydride ligand in different bridging modes with the HYDEX[11] program indicated that a hydride ligand bridging

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[8] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, p 99 (present distributor Kluwer Academic: Dordrecht, The Netherlands).

[9] Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L. NRCVAX−An Interactive Program System for Structural Analysis. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[10] Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1985.

Table 1. Summary of Crystal Data and Details of Intensity Collection for $(\eta^5\text{-}C_5Me_5)Os_4(\mu\text{-}H)(CO)_{11}$ (1), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (2), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (3), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (4)

	1	2	3	4
formula	$C_{21}H_{16}O_{11}Os_4$	$C_{20}H_{16}O_{10}Os_4$	$C_{21}H_{14}O_{11}Os_4$	$C_{19}H_{16}O_9Os_4$
fw	1205.1	1177.1	1203.1	1149.1
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*Pcmn*	$P2_1/c$	*Pbca*	$P2_1/n$
a, Å	8.852(1)	9.924(1)	14.254(2)	9.655(1)
b, Å	14.821(2)	17.051(3)	16.214(2)	16.380(2)
c, Å	19.054(2)	15.020(3)	21.735(3)	14.842(1)
β, deg		101.81(1)		92.66(1)
V, Å^3	2499.8	2487.7	5023	2344.7
2θ range of unit cell, deg	29−44	29−38	28−38	31−48
Z	4	4	8	4
D_{calc}, g cm^{-3}	3.202	3.143	3.182	3.255
μ(Mo Kα), cm^{-1}	203.47	204.38	202.51	216.79
cryst size, mm	0.016 × 0.25 × 0.27	0.11 × 0.30 × 0.17	0.048 × 0.11 × 0.11	0.13 × 0.27 × 0.28
transmission coeff range[a]	0.054−0.73	0.076−0.19	0.087−0.40	0.019−0.12
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan range (2θ), deg	3−45	3−48	3−45	3−48
scan width (ω), deg	$1.0 + 0.35 \tan\theta$	$0.90 + 0.35 \tan\theta$	$0.85 + 0.35 \tan\theta$	$0.95 + 0.35 \tan\theta$
scan rate (ω), deg min^{-1}	0.92−5.5	0.82−5.5	0.78−5.5	0.87−5.5
no. of unique rflns	2290	3889	3264	3633
no. of obsd rflns[b]	1813	2934	2197	2822
no. of variables	149	234	167	189
R[c]	0.019	0.031	0.038	0.030
R_w[d]	0.021	0.039	0.047	0.041
k[d]	0.00005	0.00006	0.0016	0.00006
GOF[e]	1.2	2.1	0.92	2.4
extinction	0.41(2)	0.106(12)	0.79(7)	0.316(16)
*F*000	2135.12	2079.13	4254.25	2023.14

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

Table 2. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å × 10^4) for $(\eta^5\text{-}C_5Me_5)Os_4(\mu\text{-}H)(CO)_{11}$ (1)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	2728.0(3)	3491.2(2)	238.6(1)	297
Os(3)	484.1(4)	2500	−426.0(2)	313
Os(4)	3386.1(4)	2500	−1021.8(2)	264
O(0)	5837(5)	3753(4)	−537(3)	491
O(11)	1711(6)	5251(3)	−438(3)	548
O(12)	335(6)	3650(4)	1375(3)	528
O(13)	5205(6)	4295(4)	1162(3)	636
O(31)	−851(5)	4094(3)	−1208(3)	494
O(32)	−2165(8)	2500	581(4)	586
C(0)	4676(7)	3370(4)	−539(4)	350(15)
C(11)	2101(8)	4588(5)	−184(4)	411(17)
C(12)	1187(8)	3579(5)	927(4)	455(17)
C(13)	4292(8)	4004(5)	807(4)	448(18)
C(31)	−357(7)	3491(4)	−915(4)	376(15)
C(32)	−1178(12)	2500	203(6)	437(24)
C(1)	2086(10)	2500	−2099(5)	309
C(2)	3024(8)	3279(4)	−2038(4)	364
C(3)	4570(7)	2964(5)	−2015(3)	357
C(4)	507(11)	2500	−2386(6)	438
C(5)	2538(8)	4238(4)	−2137(4)	513
C(6)	5958(8)	3560(6)	−2077(4)	556
H(1′1)	3293(152)	2500	596(74)	1165(501)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-}C_5Me_5)Os_4(\mu\text{-}H)(CO)_{11}$ (1)

	Bond Lengths		
Os(1)−Os(1′)[a]	2.938(1)	Os(3)−C(31)	1.892(7)
Os(1)−Os(3)	2.776(1)	Os(3)−C(32)	1.90(1)
Os(1)−Os(4)	2.875(1)	Os(4)−C(0)	1.952(6)
Os(3)−Os(4)	2.808(1)	Os(1)−H(1′1)	1.69(7)
Os(1)−C(0)	2.280(6)		
Os(1)−C(11)	1.897(7)	C−O)	1.13(1)−1.17(1)
Os(1)−C(12)	1.896(8)	$(C-C)_{ring}$	1.38(1)−1.45(1)
Os(1)−C(13)	1.915(7)	$(C-C_{Me})$	1.50(1)−1.52(1)
	Bond Angles		
Os(3)−Os(1)−Os(1′)[a]	58.051(6)	Os(3)−Os(4)−Os(1)	58.46(1)
Os(4)−Os(1)−Os(1′)[a]	59.271(6)	C(11)−Os(1)−Os(1′)[a]	149.0(2)
Os(4)−Os(1)−Os(3)	59.57(1)	C(11)−Os(1)−Os(3)	92.9(2)
Os(1)−Os(3)−Os(1′)[a]	63.90(2)	C(12)−Os(1)−Os(1′)[a]	93.9(2)
Os(1)−Os(4)−Os(1′)[a]	61.46(1)	C(13)−Os(1)−Os(1′)[a]	113.4(2)
Os(4)−Os(3)−Os(1)	61.96(1)	Os(1)−Os(1′)[a]−H(1′1)	29(4)

[a] These are symmetry equivalent atoms by the operation of (*x*, 0.5 − *y*, *z*).

Os(1) and Os(1′) had the minimum “site energy” in agreement with the refined position.

Compound 2. The integration of the peaks and the triplet observed for the methylene group due to the coupling with the hydride ligands in the ^{1}H NMR spectrum suggested the existence of two equivalent hydride ligands. The low-angle difference map revealed the two largest peaks with electron density 0.67(13) e Å^{-3} [1.6 Å from Os(2) and 2.0 Å from Os(3)] and 0.53(13) e Å^{-3} [1.3 Å from Os(1) and 1.8 Å from Os(3)]. The HYDEX calculations also showed two sites with a minimum “site energy” arrangement that were near the indicated positions but had more reasonable distances from the appropriate Os atoms. After considering the evidence, the two hydride ligands were placed in the positions calculated with the HYDEX program.

Compound 4. Tne ^{1}H NMR spectrum showed two peaks at δ −17.46 (2H) and −19.70 (1H). No clear evidence for the hydride positions was, however, obtained from the low-angle difference map. The ^{13}C NMR spectrum revealed two doublets at δ 174.35 (2C) and 164.84 (2C). This evidence suggested that the two equivalent hydride ligands, H(12) and H(13), bridge Os(1)−Os(2) and Os(1)−Os(3), respectively [with H(12) coupling to C(12) and H(13) coupling to C(13)]; the other hydride ligand, H(23), bridges Os(2)−Os(3) [and couples to C(22) and C(32)]. Calculations with the HYDEX program indicated that hydride ligands bridging Os(1)−Os(2), Os(1)−Os(3), and Os(2)−Os(3) gave a minimum “site energy”arrangement. Prior to their inclusion in the refinement, a Fourier difference map revealed that the electron density at the proposed sites were0.6(3), 0.2(3), and 0.3(3) e Å^{-3}, respectively [compared to a peak of 1.7(3) e Å^{-3} 1.1 Å from Os(2)]. The three hydride ligands were therefore placed in the positions calculated with the HYDEX program.

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(11) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

Table 4. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å × 10^4) for (η^5,η^1-$C_5Me_4CH_2$)$Os_4(\mu$-$H)_2(CO)_{10}$ (2)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	3759.1(5)	5483.2(3)	1549.2(4)	342
Os(2)	2875.3(5)	4974.3(3)	3061.9(4)	363
Os(3)	3976.3(5)	6564.4(3)	2995.0(4)	318
Os(4)	1202.2(5)	6173.0(3)	1999.7(3)	284
O(11)	4856(12)	6553(8)	219(9)	738
O(12)	6184(11)	4384(7)	1813(9)	691
O(13)	2125(13)	4377(7)	117(9)	657
O(21)	1331(15)	4491(8)	4546(10)	828
O(22)	5592(12)	4353(7)	4124(9)	678
O(23)	2079(13)	3448(7)	2043(9)	735
O(31)	6440(12)	6723(9)	4539(9)	734
O(32)	5048(13)	7846(8)	1963(10)	854
O(41)	−398(11)	4666(7)	1617(9)	675
O(42)	1195(11)	6478(8)	12(7)	577
C(11)	4381(15)	6169(10)	714(10)	487(39)
C(12)	5247(14)	4789(9)	1697(10)	436(36)
C(13)	2707(16)	4788(10)	656(11)	575(44)
C(21)	1918(17)	4705(11)	3984(12)	624(46)
C(22)	4523(17)	4559(10)	3710(11)	589(44)
C(23)	2379(15)	4044(10)	2415(11)	525(41)
C(31)	5521(16)	6659(10)	3952(11)	541(41)
C(32)	4580(15)	7382(9)	2376(10)	484(39)
C(41)	316(14)	5211(9)	1787(10)	439(36)
C(42)	1350(14)	6291(9)	773(10)	418(35)
C(1)	1522(13)	7215(8)	3063(9)	369(32)
C(2)	959(14)	7492(9)	2179(10)	434(36)
C(3)	−335(14)	7129(9)	1829(10)	448(37)
C(4)	−638(13)	6625(8)	2513(9)	382(33)
C(5)	523(14)	6639(9)	3262(10)	435(35)
C(6)	2823(14)	7362(9)	3664(10)	470
C(7)	1564(15)	8137(9)	1715(11)	549
C(8)	−1383(15)	7363(9)	1003(10)	515
C(9)	−1955(15)	6215(12)	2494(13)	715
C(10)	470(19)	6326(13)	4208(11)	724
H(31)	5015	5961	2420	500
H(32)	3316	5867	3698	500

Results and Discussion

(η^5-C_5Me_5)$Os_4(\mu$-$H)(CO)_{11}$ (1). Cluster **1** was prepared by the method depicted in eqs 1[2] and 2. The cluster was isolated as air-stable, orange crystals.

$$Os_3(CO)_{10}(COE)_2 + Cp^*Os(CO)_2(H) \xrightarrow{0\ °C} \underset{\mathbf{5}}{Cp^*Os_4(\mu\text{-}H)(CO)_{12}} \quad (1)$$

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

$$Cp^*Os_4(\mu\text{-}H)(CO)_{12} \xrightarrow{50\ °C} \underset{\mathbf{1}}{Cp^*Os_4(\mu\text{-}H)(CO)_{11}} \quad (2)$$

The crystal structure of **1** (Figure 1) reveals a tetrahedral metal core, with six metal−metal bonds, as expected from polyhedral skeletal electron pair theory (PSEPT) for a 60-electron metal cluster compound.[12] (The precursor compound, **5**, has a butterfly arrangement of metal atoms with five metal−metal bonds.[2]) Molecule **1** contains a crystallographic mirror plane that passes through the Os(3) and Os(4) atoms and the midpoint of the Os(1)−Os(1′) vector. All the available evidence indicates the hydride ligand bridges the Os(1)−Os(1′) vector. Further discussion of the location of the hydride ligands and the Os−Os lengths in **1** and the other clusters (**2**−**4**) described here is postponed to a later section of this paper.

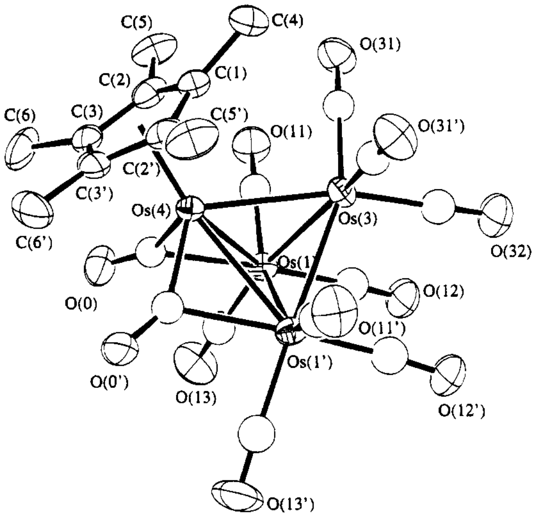

Figure 1. Molecular structure of [η^5-C_5Me_5]$Os_4(\mu$-$H)(CO)_{11}$ (**1**).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (η^5,η^1-$C_5Me_4CH_2$)$Os_4(\mu$-$H)_2(CO)_{10}$ (2)

	Bond Lengths		
Os(1)−Os(2)	2.739(1)	Os(2)−C(23)	1.87(2)
Os(1)−Os(3)	2.823(1)	Os(3)−C(31)	1.88(2)
Os(1)−Os(4)	2.997(1)	Os(3)−C(32)	1.84(2)
Os(2)−Os(3)	2.932(1)	Os(3)−C(6)	2.15(1)
Os(2)−Os(4)	2.898(1)	Os(4)−C(41)	1.86(2)
Os(3)−Os(4)	2.928(1)	Os(4)−C(42)	1.89(1)
Os(1)−C(11)	1.91(2)	C(1)−C(6)	1.44(3)
Os(1)−C(12)	1.87(1)		
Os(1)−C(13)	1.93(2)	(C−O)	1.13(3)−1.18(3)
Os(2)−C(21)	1.89(2)	$(C-C)_{ring}$	1.41(3)−1.47(3)
Os(2)−C(22)	1.86(2)	$(C-C_{Me})$	1.44(3)−1.53(3)
	Bond Angles		
Os(3)−Os(1)−Os(2)	63.62(2)	Os(2)−Os(4)−Os(1)	55.34(2)
Os(4)−Os(1)−Os(2)	60.48(2)	Os(3)−Os(4)−Os(1)	56.89(2)
Os(4)−Os(1)−Os(3)	60.33(2)	Os(3)−Os(4)−Os(2)	60.44(2)
Os(3)−Os(2)−Os(1)	59.59(2)	C(11)−Os(1)−Os(2)	160.3(5)
Os(4)−Os(2)−Os(1)	64.18(2)	C(11)−Os(1)−Os(3)	97.0(5)
Os(4)−Os(2)−Os(3)	60.30(2)	C(12)−Os(1)−Os(2)	94.6(4)
Os(2)−Os(3)−Os(1)	56.79(2)	C(12)−Os(1)−Os(3)	112.8(4)
Os(4)−Os(3)−Os(1)	62.78(2)	C(13)−Os(1)−Os(2)	99.3(5)
Os(4)−Os(3)−Os(2)	59.26(2)		

A feature of interest in the structure of **1** is the presence of an asymmetrically bridging carbonyl ligand between Os(4) and Os(1), and Os(4) and Os(1′) [Os(4)−C(0) = 1.95(1) Å; Os(1)−C(0) = 2.28(1) Å]. Bridging carbonyl ligands are comparatively rare in the carbonyl clusters of osmium.[13-16] The infrared spectrum of **1** in CH_2Cl_2 exhibits bands at 1814 and 1773 cm^{-1} consistent with the presence of bridging carbonyl ligands.

A second feature of interest is the displacement of one methyl carbon atom [C(4)] 0.52 Å out of the plane of the central carbon ring of the C_5Me_5 ligand. The next largest displacement of this type observed in the clusters described here is 0.32 Å [C(10) in molecule **2**]; the

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(12) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437. (d) Owen, S. M. *Polyhedron* **1988**, *7*, 253. (e) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990. (f) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall: New Jersey, 1990.

(13) (a) Adams, R. D. *Polyhedron* **1985**, *4*, 2003. (b) Adams, R. D.; Horváth, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

(14) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(15) Adams, R. D.; Selegue, J. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 4, p 967.

(16) Vargas, M. D.; Nichols, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.

Table 6. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å × 10^4) for (η^5,η^1−$C_5Me_4CH_2$)$Os_4(CO)_{11}$ (3)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	4285.9(6)	4037.3(5)	1909.6(3)	312
Os(2)	5283.1(6)	2668.3(5)	1557.4(3)	331
Os(3)	3363.1(6)	2555.5(5)	1713.1(3)	293
Os(4)	4081.4(5)	3439.6(5)	645.9(3)	286
O(11)	2962(16)	5511(14)	1979(9)	939(61)
O(12)	4429(13)	3807(11)	3291(7)	676(48)
O(13)	6028(14)	5113(11)	1922(7)	717(48)
O(21)	6089(16)	1145(14)	919(9)	952(63)
O(22)	5566(13)	2052(11)	2851(7)	662(47)
O(23)	7163(13)	3514(11)	1462(7)	681(47)
O(31)	4077(13)	791(12)	1505(7)	694(48)
O(32)	1932(12)	3823(10)	2141(7)	583(42)
O(33)	2738(11)	1785(9)	2894(6)	487(37)
O(41)	6021(14)	3199(11)	147(7)	697(48)
O(42)	4416(12)	5278(11)	687(7)	622(44)
C(11)	3470(17)	4945(15)	1970(10)	569(62)
C(12)	4425(18)	3898(16)	2747(11)	581(65)
C(13)	5373(17)	4679(15)	1912(9)	483(56)
C(21)	5763(18)	1757(16)	1156(11)	602(66)
C(22)	5502(17)	2297(15)	2352(10)	515(61)
C(23)	6436(20)	3230(16)	1495(10)	617(66)
C(31)	3946(15)	1522(13)	1537(8)	387(49)
C(32)	2571(16)	3456(13)	1967(8)	428(50)
C(33)	2959(13)	2090(11)	2432(7)	278(43)
C(41)	5343(16)	3257(13)	413(9)	422(52)
C(42)	4319(15)	4569(13)	770(9)	394(50)
C(1)	2690(14)	2714(11)	554(8)	308(45)
C(2)	2555(15)	3583(12)	414(8)	351(47)
C(3)	3106(14)	3754(13)	−128(9)	389(50)
C(4)	3622(15)	3045(13)	−303(8)	371(48)
C(5)	3393(16)	2388(14)	132(9)	443(54)
C(6)	2267(15)	2238(12)	1059(8)	394(50)
C(7)	1806(17)	4129(15)	657(10)	563(62)
C(8)	3049(16)	4564(14)	−467(10)	499(57)
C(9)	4208(16)	2948(15)	−853(9)	509(60)
C(10)	3674(18)	1514(16)	39(10)	616(67)

displacements of the other methyl carbon atoms from the carbon ring plane in clusters **1**−**4** are in the range 0.13−0.22 Å. The bending C(4) in **1** [and C(10) in **2**] can be attributed to the steric interaction of the methyl group with the nearest carbonyls. This close proximity of methyl groups to adjacent osmium atoms is no doubt responsible for the facile intramolecular C−H cleavage reactions that **1** undergoes, which are described below.

[μ,η^5,η^1-$C_5Me_4CH_2$]$Os_4(\mu\text{-}H)_2(CO)_{10}$ (2) and [μ,η^5,η^1-C_5Me_4]$Os_4(CO)_{11}$ (3). These clusters were isolated in low yield from the pyrolysis of **1** above 90 °C (eq 3).

$$\mathbf{1} \xrightarrow{>90\ °C} \underset{\mathbf{2}}{[C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}} + \underset{\mathbf{3}}{[C_5Me_4CH_2]Os_4(CO)_{11}} \qquad (3)$$

Furthermore, samples of **2** contained [μ_3,η^5,η^1,η^1-$C_5Me_3(CH_2)_2$]$Os_4(\mu\text{-}H)_3(CO)_9$ (**4**), the final product of the pyrolysis of **1** at these temperatures. For these reasons, the characterization of **2** and **3** relied mainly on X-ray diffraction (the single crystal used for the X-ray diffraction study of **2** was selected manually from a sample containing both **2** and **4**).

The structures of **2** (Figure 2) and **3** (Figure 3) reveal that both contain a $C_5Me_4CH_2$ ligand that is η^5 bound to one osmium atom and η^1 bound to a second osmium atom of a tetrahedral Os_4 skeleton via the CH_2 unit. In other words, **2** and **3** result from the C−H average of a methyl group in the precursor cluster **1** and are examples of cluster-assisted ligand transformations.[17] Both **2** and **3** maintain 60-electron counts by elimination of CO in **2** and elimination of H_2 in **3**. The Os-C(CH_2) bond lengths in **2** and **3** are equal within experimental error [2.15(1) Å in **2**, 2.17(2) Å in **3**]; these lengths, not unexpectedly, are significantly longer than the Os−C

Table 7. Selected Bond Angles (Å) and Angles (deg) for (η^5,η^1-$C_5Me_4CH_2$)$Os_4(CO)_{11}$ (3)

	Bond Lengths		
Os(1)−Os(2)	2.745(1)	Os(3)−C(31)	1.91(2)
Os(1)−Os(3)	2.772(1)	Os(3)−C(32)	1.93(2)
Os(1)−Os(4)	2.927(1)	Os(3)−C(33)	1.83(2)
Os(1)−C(11)	1.88(3)	Os(3)−C(6)	2.17(2)
Os(1)−C(12)	1.85(2)	Os(4)−C(41)	1.89(2)
Os(1)−C(13)	1.87(2)	Os(4)−C(42)	1.88(2)
Os(2)−Os(3)	2.764(1)	C(1)−C(6)	1.47(3)
Os(2)−Os(4)	2.902(1)		
Os(2)−C(21)	1.85(3)	(C−O)	1.13(2)−1.21(3)
Os(2)−C(22)	1.85(2)	$(C-C)_{ring}$	1.42(3)−1.46(3)
Os(2)−C(23)	1.88(3)	$(C-C_{Me})$	1.47(3)−1.51(3)
Os(3)−Os(4)	2.913(1)		
	Bond Angles		
Os(3)−Os(1)−Os(2)	60.12(3)	Os(4)−Os(3)−Os(1)	61.93(3)
Os(4)−Os(1)−Os(2)	61.45(3)	Os(4)−Os(3)−Os(2)	61.43(3)
Os(4)−Os(1)−Os(3)	61.39(3)	Os(2)−Os(4)−Os(1)	56.17(3)
Os(3)−Os(2)−Os(1)	60.43(3)	Os(3)−Os(4)−Os(1)	56.68(3)
Os(4)−Os(2)−Os(1)	62.38(3)	Os(3)−Os(4)−Os(2)	56.75(3)
Os(4)−Os(2)−Os(3)	61.81(3)	C(11)−Os(1)−Os(2)	166.6(7)
Os(2)−Os(3)−Os(1)	59.45(3)	C(11)−Os(1)−Os(3)	113.3(7)
C(12)−Os(1)−Os(2)	96.9(8)		
C(13)−Os(1)−Os(2)	91.3(7)		
C(13)−Os(1)−C(12)	88.7(10)		

Table 8. Fractional Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å × 10^4) for (η^5,η^1,η^1-$C_5Me_3(CH_2)_2$)$Os_4(\mu\text{-}H)_3(CO)_9$ (4)

atom	*x*	*y*	*z*	*U*(iso)
Os(1)	876.9(5)	9653.0(3)	2450.3(3)	280
Os(2)	805.5(5)	7891.5(3)	2407.6(3)	270
Os(3)	−1029.8(5)	8832.4(3)	3561.8(3)	287
Os(4)	−1566.2(5)	8767.2(3)	1601.4(3)	267
O(11)	3293(13)	10360(7)	3550(8)	674
O(12)	−618(13)	11276(6)	2435(7)	607
O(13)	2503(12)	9938(6)	786(6)	560
O(21)	2880(15)	6759(7)	3310(7)	676
O(22)	2103(15)	7550(8)	614(7)	593
O(31)	−381(13)	8704(6)	5556(6)	570
O(32)	−3068(15)	10175(7)	3864(8)	730
O(41)	−2857(13)	10439(6)	1368(7)	533
O(42)	48(11)	8974(6)	−92(6)	469
C(11)	2367(17)	10111(9)	3129(10)	465(36)
C(12)	−60(14)	10655(8)	2411(8)	353(30)
C(13)	1876(16)	9825(8)	1379(9)	396(32)
C(21)	2084(16)	7205(9)	2996(9)	433(34)
C(22)	1670(17)	7682(9)	1268(9)	467(36)
C(31)	−702(15)	8749(8)	4806(9)	396(32)
C(32)	−2296(18)	9661(10)	3737(10)	528(40)
C(41)	−2312(16)	9829(9)	1491(9)	437(35)
C(42)	−469(14)	8918(7)	564(8)	327(29)
C(1)	−2695(15)	7878(7)	2545(8)	368(14)
C(2)	−3684(14)	8308(8)	1973(8)	368(14)
C(3)	−3395(14)	8105(8)	1025(8)	368(14)
C(4)	−2254(14)	7556(8)	1053(8)	368(14)
C(5)	−1824(15)	7404(8)	1962(8)	368(14)
C(6)	−2591(15)	7863(8)	3541(8)	418(23)
C(7)	−4870(16)	8795(8)	2273(9)	513(22)
C(8)	−4362(16)	8323(9)	221(9)	513(22)
C(9)	−1718(16)	7133(8)	250(9)	513(22)
C(10)	−710(14)	6875(8)	2287(9)	418(23)
H(32)	74	7912	3537	500
H(21)	2019	8749	2611	500
H(31)	325	9625	3631	500

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(17) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York 1990, p 201.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Os_4(\mu\text{-}H)_3(CO)_9$ (4)

Bond Lengths			
Os(1)−Os(2)	2.887(1)	Os(3)−C(31)	1.86(1)
Os(1)−Os(3)	2.864(1)	Os(3)−C(32)	1.85(2)
Os(1)−Os(4)	2.997(1)	Os(3)−C(6)	2.19(1)
Os(2)−Os(3)	2.955(1)	Os(4)−C(41)	1.89(1)
Os(2)−Os(4)	2.912(1)	Os(4)−C(42)	1.93(1)
Os(3)−Os(4)	2.934(1)	C(1)−C(6)	1.48(2)
Os(1)−C(11)	1.87(1)	C(5)−C(10)	1.45(2)
Os(1)−C(12)	1.87(1)		
Os(1)−C(13)	1.92(2)	(C−O)	1.10(2)−1.15(2)
Os(2)−C(21)	1.86(1)	$(C-C)_{ring}$	1.42(2)−1.48(2)
Os(2)−C(22)	1.95(2)	$(C-C_{Me})$	1.45(2)−1.52(2)
Os(2)−C(10)	2.22(1)		

Bond Angles			
Os(3)−Os(1)−Os(2)	61.84(2)	Os(4)−Os(3)−Os(1)	62.24(2)
Os(4)−Os(1)−Os(2)	59.29(2)	Os(4)−Os(3)−Os(2)	59.27(2)
Os(4)−Os(1)−O(3)	60.02(2)	Os(2)−Os(4)−Os(1)	58.47(2)
Os(3)−Os(2)−Os(1)	58.69(2)	Os(3)−Os(4)−Os(1)	57.73(2)
Os(4)−Os(2)−Os(1)	62.24(2)	Os(3)−Os(4)−Os(2)	60.73(2)
Os(4)−Os(2)−Os(3)	60.00(2)	C(11)−Os(1)−Os(2)	115.4(4)
Os(2)−Os(3)−Os(1)	59.47(2)	C(12)−Os(1)−Os(4)	92.4(4)
C(13)−Os(1)−Os(2)	98.1(4)	C(21)−Os(2)−Os(3)	116.5(4)
C(13)−Os(1)−Os(4)	98.0(4)	C(22)−Os(2)−Os(1)	100.6(4)
C(21)−Os(2)−Os(1)	125.4(4)	C(22)−Os(2)−Os(4)	95.2(4)

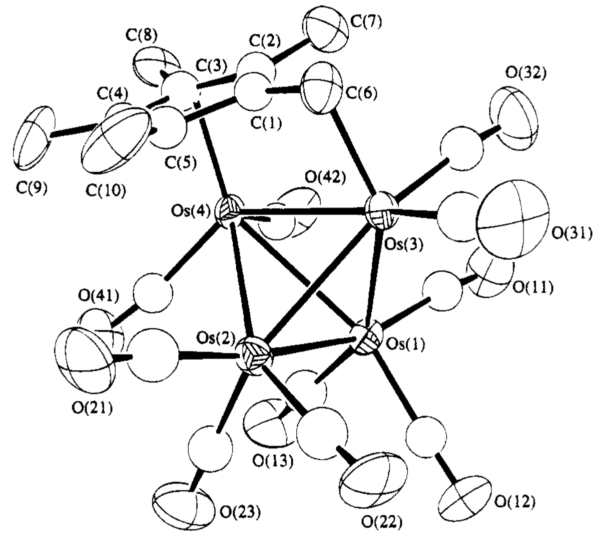

Figure 2. Molecular structure of $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2)]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**2**).

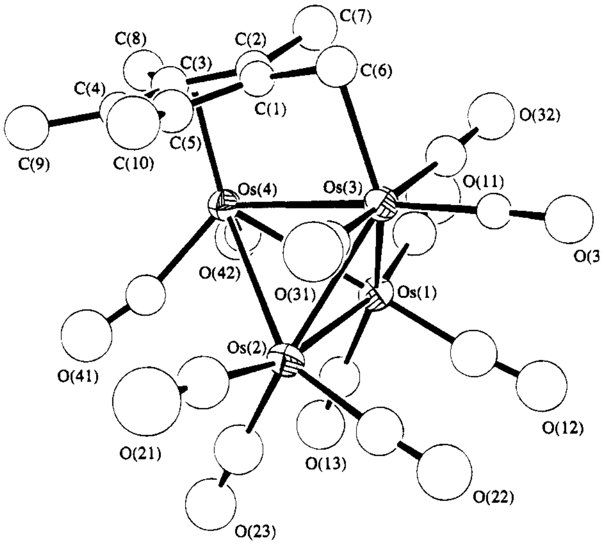

Figure 3. Molecular structure of $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**3**).

lengths to the carbonyls in the clusters. In $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5H_2Et(CHMe)(CO)]Os_3(\mu\text{-}H)(CO)_8$ the Os−C length to the CHMe substituent is 2.194(14) Å.[18]

The available evidence indicates the hydrides in **2** bridge the Os(1)−Os(3) and Os(2)−Os(3) bonds. In solution, the $[C_5Me_4CH_2]Os(CO)_2$ moiety probably oscillates with respect to the rest of the cluster such that the hydride ligands are rendered chemically equivalent; consistent with this view is that **2** exhibits just one sharp resonance (at δ −16.88) in the hydride region of the ^1H NMR spectrum. The ^1H NMR signal of the CH_2 unit at δ 2.75 is a triplet attributed to a small coupling (J_{HH} = 0.7 Hz) to the equivalent hydride ligands that is not resolved in the hydride resonance. A small coupling between a bridging hydride ligand and a CH unit in an osmium carbonyl cluster has been observed previously.[19]

In **2**, the carbonyl ligands of the $[\eta^5\text{-}C_5Me_4CH_2]Os(CO)_2$ unit have only weak semibridging interactions with other Os atoms in the cluster [Os(1)−C(42) = 2.80(2), Os(2)−C(41) = 2.88(2) Å] and therefore only one metal−metal bond is required for Os(4) to have an 18-electron configuration. For a 60-electron cluster such as **2**, six metal−metal bonds are expected. This suggests that the three metal−metal interactions of the $[\eta^5\text{-}C_5Me_4CH_2]Os(CO)_2$ unit of **2** with the rest of the cluster are comprised of one nondative and two dative metal−metal bonds, that is, this unit contributes five electrons to the metal−metal bonding of the metal skeleton. That some metal−metal bonds in osmium carbonyl clusters should be considered as dative bonds was first suggested by John et al.[20] We have proposed that dative bonds are present in some osmium clusters[21,22] and furthermore have reported a number of stable dinuclear complexes that contain unbridged dative metal−metal bonds in which an 18-electron osmium compound acts as the donor.[23] (Analogous iron and ruthenium compounds do not form such complexes.) The ability of osmium to form strong dative (donor−acceptor) metal−metal bonds may explain in part why osmium, and not iron and ruthenium, forms so many high nuclearity metal carbonyl cluster compounds. For reasons discussed previously,[2,22] a strong donor ligand such as $[C_5Me_4(CH_2)]$ would be expected to stabilize the donor−acceptor metal−metal bonds believed present in **2**.

A similar conclusion regarding the metal−metal bonding in **2** may be reached by using PSEPT. Twelve cluster bonding electrons are required for a tetrahedron (a *nido* trigonal bipyramid). In **2**, of these 12 electrons, two are provided by the hydride ligands, four from the two $Os(CO)_3$ units, and one or two from the $Os(CO)_2$-

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[18] Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291.

[19] For example: Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

[20] John, G. R.; Johnson, B. F. G.; Lewis, J., *J. Organomet. Chem.* **1979**, *181*, 143.

[21] (a) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 294. (b) Einstein, F. W. B.; Johnston, V. J.; Ma, A. K.; Pomeroy, R. K. *Organometallics* **1990**, *9*, 52.

[22] (a) Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *Organometallics* **1990**, *9*, 2754. (b) Wang, W.; Batchelor, R. J.; Einstein, F. W. B.; Lu, C.-Y.; Pomeroy, R. K. *Organometallics* **1993**, *12*, 3598. (c) Wang, W.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1994**, *13*, 1114.

[23] (a) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854; (b) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030. (c) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

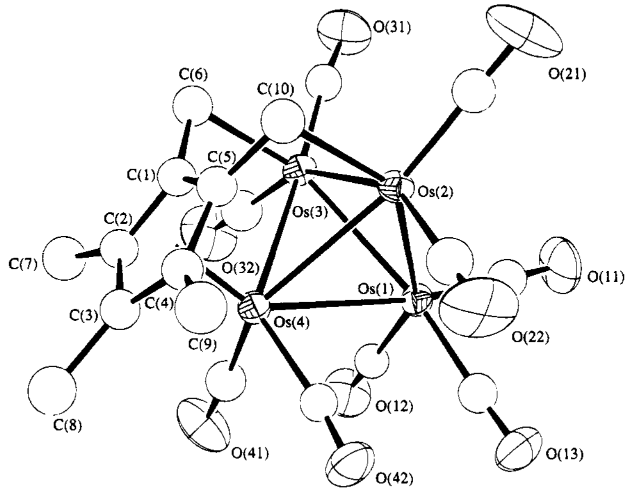


Figure 4. Molecular structure of $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-H})_3(CO)_9$ (**4**).

$(CH_2C_5Me_4)$ unit, depending upon the bonding of the $CH_2C_5Me_4$ substituent to the osmium in question (see below). The Os atom [Os(4)] of the $Os(CO)_2(\eta^5\text{-}C_5H_4\text{-}CH_2)$ is therefore required to donate five or four electrons to cluster bonding, that is, Os(4) is a net electron donor compared to the other metal atoms in **2**. Similar descriptions are possible for clusters **1**, **3**, and **4** although the presence of semibridging carbonyl ligands makes the descriptions less precise.

$[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-H})_3(CO)_9$ (4). Cluster **4** was formed in excellent yield by the prolonged pyrolysis of **1** at 115–120 °C, presumably via the

$$\mathbf{1} \xrightarrow[\text{[2]}]{115-120\ ^\circ\text{C}} \underset{\mathbf{4}}{[C_5Me_3(CH_2)_2]Os_4(\mu\text{-H})_3(CO)_9} \qquad (4)$$

intermediacy of **2** (eq 4). It was also formed in low yield by the reaction of $Os_3(CO)_{12}$ with a large excess of C_5Me_5H in heptane at 200 °C. Cluster **4** appeared stable under the latter reaction conditions. It was isolated as a yellow-brown, air-stable crystalline solid.

The crystal structure of **4** (Figure 4) reveals a $C_5Me_3(CH_2)_2$ ligand that is η^5 bound to one osmium atom of a tetrahedral Os_4 cluster with adjacent CH_2 units each η^1 bound to other osmium atoms of the cluster [Os(2)–C(10) = 2.22(1) Å; Os(3)–C(6) = 2.19(1) Å]. Bond length data and calculations with the HYDEX program[11] indicate the hydride ligands bridge each of the Os–Os vectors of the Os(1)Os(2)Os(3) triangle.

As can be seen from Figure 4, cluster **4** has an approximate mirror plane that passes through Os(1) and Os(4) and the midpoint of the Os(2)–Os(3) [and C(1)–C(5)] vector. The ^1H and $^{13}C\{^1H\}$ NMR data for **4** indicate that the cluster has the same structure (with a mirror plane) in solution as found in the solid state. Two signals in a 6:3 ratio in the ^1H NMR spectrum at δ 1.49 and 2.89 are assigned to the chemically different methyl groups; doublets in a 2:2 ratio at δ 1.68 and 1.82 are assigned to the chemically different (inner and outer) protons of the CH_2 groups; the two resonances in a 2:1 ratio at δ −17.46 and −19.70 are assigned to the chemically different hydride ligands. The $^{13}C\{^1H\}$ NMR spectrum of ^{13}CO-enriched **4** exhibits five signals in the carbonyl region in a 2:2:1:2:2 ratio and, furthermore, two of the signals are split into doublets in the ^1H-coupled ^{13}C NMR spectrum. This data is therefore not only consistent with the solid-state structure butalso with the view that the hydride and carbonyl ligands in **4** are stereochemically rigid in solution at room temperature, on the NMR time scale.

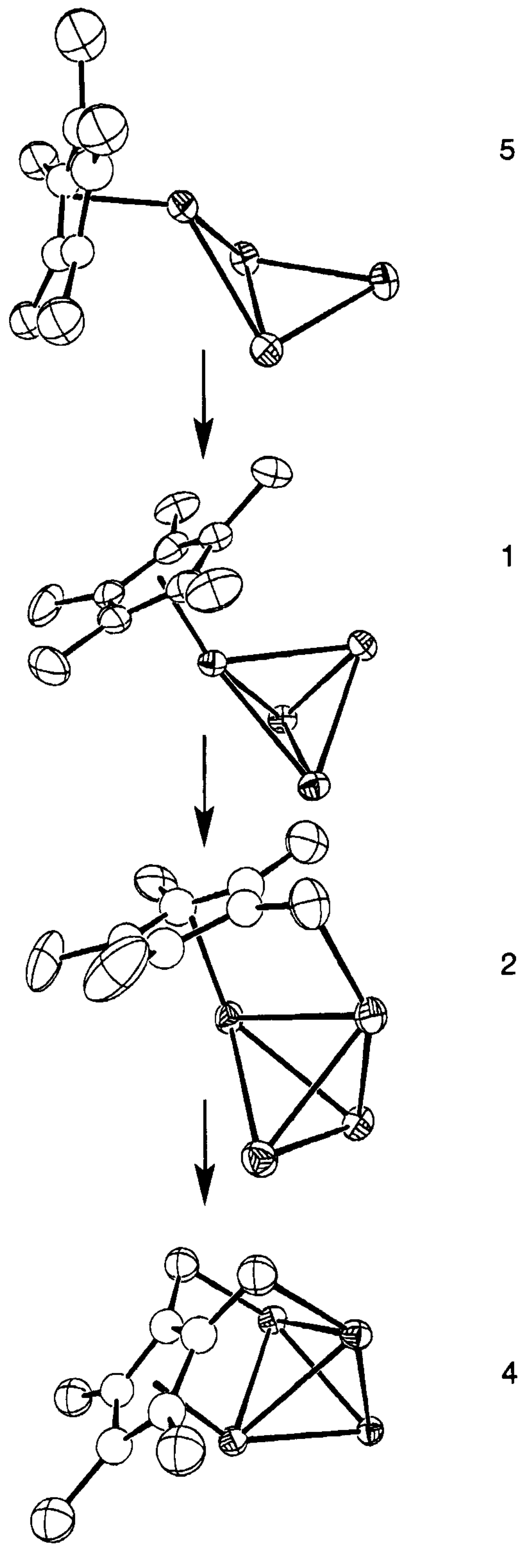
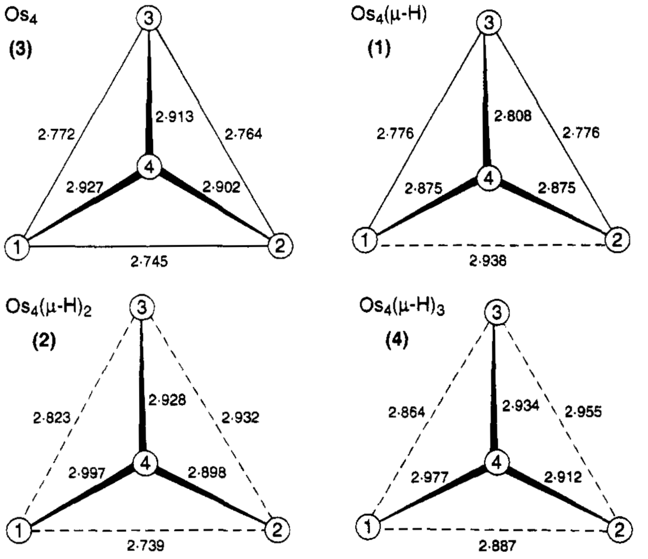


Figure 5. ORTEP drawings of the Os_4 core and cyclopentadienyl ligand for the **5** → **1** → **2** → **4** transformation.

Comparison of the Structures of 1–4. The important structural transformations described here are summarized in Figure 5. The structures **1**–**3** provide an unprecendented structural depiction of the CH activation of two methyl substituents of a C_5Me_5 ligand

Chart 1



in a cluster compound. The series of structures reportedhere also provides a unique opportunity to compare the bond lengths of tetrahedral Os_4, $Os_4(\mu\text{-}H)$, $Os_4(\mu\text{-}H)_2$, and $Os_4(\mu\text{-}H)_3$ units in a closely related series of clusters. These lengths are shown diagrammatically in Chart 1 (the solid and dashed lines represent Os–Os bonds that are believed unbridged and hydride-bridged, respectively). As can be seen, the lengths may be divided into three groups: hydride-bridged Os–Os bonds, unbridged Os–Os bonds that do not involve Os(4) (to which the cyclopentadienyl ligand is coordinated), and Os–Os bonds that do involve Os(4).

The six lengths of the first type range from 2.739(1) to 2.776(1) Å, which is significantly shorter than 2.877(3) Å, the average Os–Os length in $Os_3(CO)_{12}$,[24] and which is usually taken as representative of an Os–Os single bond length in osmium carbonyl cluster compounds. It has, however, been found that Os–Os bond lengths in more condensed, higher nuclearity clusters of osmium are often shorter than 2.877 Å.[15,16,25] This can be attributed in part to the fewer terminal ligands on the osmium atoms in such clusters and consequently the fewer steric repulsions between these terminal ligands. The short bonds in clusters **1**–**4** are consistent with this view.

The six Os–Os vectors in **1**–**4** believed bridged by a hydride ligand range in length from 2.823(1) to 2.955(1) Å. In trinuclear carbonyl clusters of osmium, Os–Os distances of $Os(\mu\text{-}H)Os$ linkages are usually much longer than 2.877 Å:[26] a distance of 3.00 ± 0.05 Å is typical for such lengths.[14,15] The Os–Os lengths of the $Os(\mu\text{-}H)Os$ linkages in **1**–**4** would therefore not, if each molecule were considered in isolation, be considered significantly lengthened. But as discussed above, the comparable unbridged Os–Os distances in these clusters are some 0.1 Å shorter than 2.877 Å, so the Os–Os distances of the $Os(\mu\text{-}H)Os$ groups in these tetranuclear clusters do indeed represent a significant lengthening. In the tetrahedral cluster $Os_4(\mu\text{-}H)_4(CO)_{12}$, the twounbridged Os–Os bonds have a mean length of 2.817 (2) Å whereas the H-bridged bonds have a mean length of 2.964 (2) Å.[27] Also pertinent is that the neutron diffraction study of the tetrahedral cluster $Os_4(\mu\text{-}H)_3(\mu\text{-}CHCHPh)(CO)_{11}$ reveals that one of the short OsOs edges [of length 2.787(3) Å] is bridged by a hydride ligand whereas one of the long OsOs edges [of length 1.942(3) Å] is unbridged.[28]

As can be seen from Chart 1, if the Os–Os bonds lengths of **1** are excluded from the discussion, the Os–Os bonds that involve Os(4) range in length from 2.898(1) to 2.997(1) Å. This lengthening may be in part attributed to the higher coordination number of Os(4) (it may be regarded as eight coordinate in these clusters). It may also be because some of the metal–metal bonds are weak dative bonds. We and others have previously observed a long metal–metal bond in a cluster compound that is believed to be a dative bond.[2,29,30]

The metal–metal bonds in **1** that involve Os(4) are shorter than expected [Os(1)–Os(4) = Os(1′)–Os(4) = 2.875 (1) Å, Os(1′) ≡ Os(2); Os(3)–Os(4) = 2.808 (1) Å]. As mentioned above, there appears to be a considerable steric interaction of one of the methyl groups of the C_5Me_5 ligand with two of the carbonyl ligands on Os(3). This might be expected to lengthen the Os(3)–Os(4) bond, and yet this is by far the shortest Os–Os bond that involves Os(4) in the molecules **1**–**4**. The reason for the shortness of this bond is uncertain, although it is noted that, of the clusters considered here, **1** is the only cluster in which the cyclopentadienyl ligand is bound solely in the η^5 mode. It may be that the requirements of the μ,η^5,η^1 (or $\mu_3,\eta^5,\eta^1,\eta^1$) mode of bonding of the cyclopentadienyl ligand lengthen the metal–metal bonds that involve Os(4) in **2**–**4**. The shorter Os–Os bonds to Os(4) in **1** may explain why the carbonyls on Os(4) in this cluster have the strongest bridging interactions with other metal atoms in the cluster.

For the $C_5Me_4CH_2$ ligand, besides the η^5,η^1 mode of coordination, there is the possibility that the coordination should be considered as η^4,η^2, that is, the $C_5Me_4CH_2$ should be considered as a fulvene unit with monoene and diene groups.[4,5,31] The distances of the η^2-bound osmium atom to the internal carbon atom of the olefin unit in the fulvene formulation are short: the Os(3)–C(1) distance is 2.70(2) in **2** and 2.71(2) Å in **3**; in **4** the comparable distances are 2.66(2) Å [Os(3)–C(1)] and 2.71(2) Å [Os(2)–C(5)]. Although these distances probably indicate some bonding interaction, we nevertheless believe the η^5,η^1 (or η^5,η^1,η^1) description more accurately describes the bonding of the cyclopentadienyl ligand in these clusters. The C–C ring distances for the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ groups are all equal within experimental error, and the $C\text{–}C(CH_2)$ lengths

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[24] Churchill, M. R.; DeBoer, B. G.; Inorg. *Chem.* **1977**, *16*, 878.

[25] Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161.

[26] (a) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. (b) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (c) Elliot, D. J.; Vittal, J. J.; Puddephatt, R. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chem.* **1992**, *31*, 1247.

[27] Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 1728.

[28] Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Rouse, K. D. *J. Chem. Soc., Dalton Trans.* **1981**, 788.

[29] Lu, C.-Y.; Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *Inorg. Chem.*, **1989**, *28*, 4212.

[30] (a) Bruce, M. I.; Williams, M. L. *J. Organomet. Chem.* **1985**, *282*, C11. (b) Adams, R. D.; Wang, S. *Organometallics* **1987**, *6*, 739.

[31] (a) Bandy, J. A.; Mtetwa, V. S. B.; Prout, K.; Green, J. C.; Davies, C. E.; Green, M. L. H.; Hazel, N. J.; Izquierdo, A.; Martin-Polo, J. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2037. (b) Blake, A. J.; Dyson, P. J.; Johnson, B. F. G.; Reed, D.; Shephard, D. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1347.

are notsignificantly shorter than the corresponding C−C(CH_3) distances in these molecules. Both data are consistent with the η^5,η^1 formulation. Furthermore, the H−H coupling of the inequivalent protons of the CH_2 units of **4** of 8 Hz is more consistent with sp^3 hybridization at these carbons.[32] The analysis of the bonding of the $C_5Me_4CH_2$, and $C_5Me_3(CH_2)_2$ fragments in these clusters is similar to that previously carried out for $(Cp^*Ti)_2(\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$, a molecule that contains a $C_5Me_4CH_2$ bridging two metal atoms and believed bonded to the two atoms in an η^5,η^1 fashion.[5]

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Supplementary Material Available: Tables of fractional coordinates and isotropic temperature factors for the hydrogen atoms, additional bond lengths and angles, and anisotropic temperature factors for **1**−**4** (21 pages). Ordering information is given on any masthead page.

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[32] Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980, p 41.