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Clusters Containing Carbene Ligands. 2. The Transformation of a Secondary (Dimethylamino)carbene Ligand into a (Dimethylamino)carbyne Ligand by α-CH Bond Activation

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Pyrolysis of the carbene cluster complex $Os_3(CO)_{10}[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (1) in the absence of solvent at 200 °C results in the formation of the compounds $Os_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (2, 22%), $Os_3(CO)_{10}(\mu\text{-CNMe}_2)(\mu\text{-H})$ (3, 14%), $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-CNMe}_2)$ (4, 19%), $Os_6(CO)_{15}(\mu_3\text{-S})(\mu\text{-SPh})(\mu\text{-CNMe}_2)$ (5, 21%), and a red unidentified compound 6. Compounds 4 and 5 are new and were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For 4: space group $P2_1/c$, $a = 8.856$ (3) Å, $b = 8.945$ (4) Å, $c = 30.848$ (7) Å, $\beta = 92.22$ (2)°, $Z = 4$, $\rho_{calcd} = 2.76$ g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined (2806 reflections) to the final values of the residuals $R = 0.040$ and $R_w = 0.049$. The molecule consists of an open triangular cluster of three osmium atoms connected by two Os–Os bonds. The nonbonding Os–Os distance is bridged by a (dimethylamino)carbyne ligand, $CNMe_2$, and a benzenethiolato ligand. For 5: space group $P2_1/n$, $a = 10.601$ (2) Å, $b = 21.794$ (5) Å, $c = 15.256$ (2) Å, $\beta = 102.57$ (1)°, $Z = 4$, $\rho_{calcd} = 3.40$ g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined (4078 reflections) to the final values of the residuals $R = 0.047$ and $R_w = 0.050$. The molecule consists of a square-pyramidal cluster of five metal atoms. The square base contains a quadruply bridging sulfido ligand. A sixth metal atom bridges one edge of the square base, and a (dimethylamino)carbyne ligand bridges an adjacent edge. A benzenethiolato ligand bridges one of the metal–metal bonds to the edge-bridging osmium atom. It is believed that the carbyne ligands in 3, 4, and 5 were formed by an α-CH activation of the carbene ligand in 1.

Introduction

Although a wide range and diversity of mononuclear metal complexes containing heteronuclear carbene ligands have been prepared and studied,[1,2] there are relatively few examples of metal cluster compounds that contain these ligands.[3-12] Recently, we have shown that tertiary amines that contain methyl groups can serve as precursors to secondary (dialkylamino)carbene ligands in reactions with certain osmium carbonyl cluster compounds.[3,12] One of these complexes, $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-S})(\mu\text{-H})_2$, was found to be an active catalyst for transalkylation in tertiary amines.[3] In another, $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (1) we observed an unprecedented binuclear α-CH activation in the carbene ligand.[12] We have now found that the pyrolysis of 1 at 200 °C in the absence of solvent yields two new osmium clusters that contain (dimethylamino)carbyne ligands. The compounds have been characterized structurally, and the results of these studies are described in this report.

Experimental Section

General Procedures. Reagent grade solvents were dried over molecular sieves before use. $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (1) was prepared as previously described.[12] Infrared spectra were recorded on a Nicolet 5-DXB FT-IR spectrophotometer. A Brüker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Pyrolysis of Solid $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (1). 1 (50 mg, 0.0505 mmol) was placed in a glass tube. The tube was sealed under a vacuum and heated to 200 °C in a tube furnace for 5 min. The tube was then opened, and the residue was dissolved in a minimum amount of CH_2Cl_2. The solution was chromatographed by TLC on silica gel by using a 25/75, v/v, CH_2Cl_2/hexane solvent mixture. The following bands were separated: (1) $Os_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (2), 11 mg (22% yield); (2) yellow, $Os_3(CO)_{10}(\mu\text{-CNMe}_2)(\mu\text{-H})$ (3), 7.1 mg (14%); (3) yellow, $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-CNMe}_2)$ (4), 9.4 mg (19%); (4) red, $Os_6(CO)_{15}(\mu_3\text{-S})(\mu\text{-SPh})(\mu\text{-CNMe}_2)$ (5), 10.4 mg (21%); (6) a red compound, 6, (5.9 mg). IR (ν(CO), cm^{-1}, in hexane solvent): for 4, 2095 (w), 2060 (vs), 2046 (m), 2012 (s), 2003 (s), 1987 (m), 1967 (m); for 5, 2088 (w), 2066 (vs), 2056 (m), 2015 (s), 2005 (s), 1968 (w), 1954 (w), 1947 (w); for 6 2087 (w), 2062 (s), 2033 (m), 2023 (s), 2012 (vs), 2001 (m), 1983 (w), 1967 (w). ^1H NMR: for 4 (in CD_2Cl_2), δ 7.25 (m, 5 H), 3.86 (s, 6 H); for 5 (in $CDCl_3$), δ 7.45 (m, 5 H), 4.030 (s, 3 H), 4.024 (s, 3 H); for 6 (in CD_2Cl_2), δ 4.28 (s, 3 H), 4.08 (s, 3 H). Anal. Calcd for 4: C, 22.45; N, 1.38; H, 1.08. Found: C, 22.56; N, 1.11; H, 0.96. Anal. Calcd for 5: C, 16.38; N, 0.80; H, 0.62. Found: C, 16.27; N, 0.78; H, 0.42.

Crystallographic Analyses. Yellow crystals of 4 and red crystals of 5 suitable for X-ray diffraction measurements were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at −20 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections ob-

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[1] Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645.

[2] Dotz, K. H.; Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Weinheim, West Germany, 1983. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

[3] Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

[4] Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615.

[5] Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679.

[6] Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926.

[7] Jensen, C. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 6969.

[8] Shapley, J. R.; Yeh, W. Y.; Churchill, M. R.; Li, Y. *Organometallics* **1985**, *4*, 1898.

[9] Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729.

[10] Adams, R. D.; Babin, J. E.; Kim, H. S. *Inorg. Chem.* **1986**, *25*, 4319.

[11] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[12] Adams, R. D.; Babin, J. E.; Kim, H. S. *Organometallics* **1986**, *5*, 1924.

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Table I. Crystallographic Data for Compounds 4 and 5

	4	5
(A) Crystal Data		
formula	$Os_3SO_{10}NC_{19}H_{11}$	$Os_6S_2O_{15}NC_{24}H_{11}$
temp, ±3 °C	23	23
space group	$P2_1/c$	$P2_1/n$
a, Å	8.856 (3)	10.601 (2)
b, Å	8.945 (4)	21.794 (5)
c, Å	30.848 (7)	15.256 (2)
β, deg	92.22 (2)	102.57 (1)
V, Å^3	2442 (1)	3440 (1)
M_r	1016	1759
Z	4	4
ρ_{calcd}, g/cm^3	2.76	3.40
(B) Measurement of Intensity Data		
radiation, Å	Mo Kα (0.710 69)	Mo Kα (0.710 69)
monochromator	graphite	graphite
detector aperture, mm		
horizontal	2.0	2.0
vertical	2.0	2.0
cryst faces	$0\bar{1}1,01\bar{1},10\bar{1}$ $\bar{1}01,0\bar{1}\bar{2},012$	$010,0\bar{1}1,0\bar{2}\bar{1}$ $10\bar{1},\bar{1}1\bar{1}$
cryst size, mm	0.078 × 0.143 × 0.149	0.105 × 0.220 × 0.240
cryst orientatn: directn; deg from ϕ axis	$[0\bar{1}1]$; 2.45	[010]; 52
reflctns measd	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ, deg	48	48
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°, A =	1.1	1.1
bkgd	$^1/_4$ scan time at each end of scan	$^1/_4$ scan time at each end of scan
ω-scan rate,[a] deg/min	4.0	4.0
no. of reflctns measd	4446	6045
data used ($F^2 \geq 3.0\sigma(F^2)$)	2806	4078
(C) Treatment of Data		
abs correctn	applied	applied
coeff, cm^{-1}	166.3	235.7
transmissn coeff		
max	0.349	0.399
min	0.132	0.189
no. of variables (refined)	307	233
p factor	0.04	0.02
final residues		
R_F	0.0403	0.0474
R_{wF}	0.0487	0.0503
esd of unit weight observn	1.468	2.108
largest shift/error		
value of final cycle	0.028	0.15
largest peak in final diff Fourier, e/Å^3	1.51	2.57

[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan etc. A maximum of three scans was permitted per reflection.

tained by using the diffractometer automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from Molecular Structure Corp., College Station, TX. Absorption corrections of a Gaussian integration type were done for both structures. Neutral atom scattering factors were calculated by the standard procedures.[13a] Anomalogous dispersion corrections were applied to all non-hydrogen atoms.[13b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

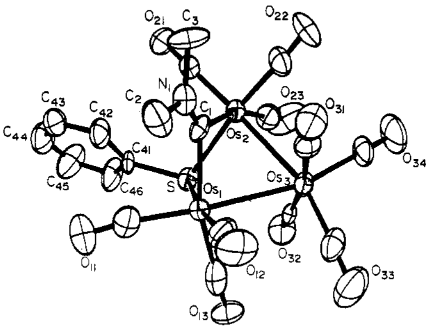

Figure 1. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}SPh)$ (4) showing 50% probability ellipsoids.

Table II. Positional Parameters and B(eq) for $Os_3(CO)_{10}(CNMe_2)(SPh)$ (4)

atom	x	y	z	B(eq), Å^2
Os1	0.292985 (70)	0.478427 (80)	0.888084 (20)	2.54 (3)
Os2	0.283235 (72)	0.826408 (83)	0.859857 (20)	2.68 (3)
Os3	0.238267 (69)	0.580446 (91)	0.800258 (20)	2.77 (3)
S	0.11928 (43)	0.68024 (54)	0.90648 (13)	2.8 (2)
O11	0.3558 (17)	0.3787 (21)	0.98171 (46)	6.2 (9)
O12	0.5096 (17)	0.2524 (18)	0.85206 (51)	6.0 (9)
O13	0.0216 (18)	0.2648 (19)	0.86941 (50)	6.3 (9)
O21	0.3430 (17)	1.0671 (18)	0.92719 (44)	5.3 (8)
O22	0.4960 (20)	0.9549 (22)	0.79499 (47)	7 (1)
O23	0.0039 (19)	0.9716 (20)	0.81493 (67)	8 (1)
O31	0.5853 (14)	0.5768 (20)	0.79491 (42)	5.2 (8)
O32	−0.0987 (13)	0.5973 (19)	0.82081 (42)	4.9 (7)
O33	0.1990 (22)	0.2647 (23)	0.76420 (55)	8 (1)
O34	0.1939 (19)	0.7733 (25)	0.71927 (48)	8 (1)
N1	0.5775 (15)	0.6731 (18)	0.89422 (42)	3.4 (7)
C1	0.4357 (16)	0.6697 (20)	0.88620 (46)	2.6 (7)
C2	0.6720 (24)	0.5520 (26)	0.90988 (64)	5 (1)
C3	0.6679 (19)	0.8116 (25)	0.88932 (76)	5 (1)
C11	0.3327 (21)	0.4264 (24)	0.94741 (66)	4 (1)
C12	0.4306 (24)	0.3341 (26)	0.86489 (62)	5 (1)
C13	0.1184 (27)	0.3394 (31)	0.87717 (61)	5 (1)
C21	0.3198 (20)	0.9788 (24)	0.90215 (57)	3.8 (9)
C22	0.4155 (23)	0.9066 (25)	0.81851 (59)	4 (1)
C23	0.1049 (22)	0.9167 (23)	0.83214 (60)	4 (1)
C31	0.4609 (22)	0.5813 (21)	0.79758 (55)	3.5 (9)
C32	0.0260 (18)	0.5905 (21)	0.81351 (44)	2.7 (7)
C33	0.2174 (20)	0.3891 (30)	0.77742 (60)	5 (1)
C34	0.2131 (20)	0.7029 (29)	0.74761 (58)	5 (1)
C41	0.1500 (18)	0.7341 (21)	0.96229 (43)	2.7 (7)
C42	0.2872 (20)	0.7638 (26)	0.98202 (52)	4 (1)
C43	0.3026 (22)	0.8034 (26)	1.02409 (55)	5 (1)
C44	0.1735 (25)	0.8297 (29)	1.04642 (61)	5 (1)
C45	0.0348 (23)	0.8175 (35)	1.02791 (69)	7 (1)
C46	0.0248 (21)	0.7648 (33)	0.98521 (55)	6 (1)

Both compounds crystallized in the monoclinic crystal system. Systematic absences in the data allowed identification of the space group $P2_1/c$ for 4 and the space group $P2_1/n$ for 5. The coordinates of the metal atoms for both analyses were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. For 4 all non-hydrogen atoms were refined by using anisotropic thermal parameters. For 5 only atoms larger than oxygen were refined anisotropically. Hydrogen atom positions for both structures were calculated by assuming idealized tetrahedral or planar sixfold geometry. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The largest peaks in the final difference Fourier syntheses were small residuals proximate to the metal atoms. They are believed to be chemically insignificant. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

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(13) *International Tables for X-ray Crystallography*; Vol. IV: Birmingham, England, 1975; Kynoch: (a) Table 2.2B, pp 99–101, (b) Table 2.3.1, pp 149–150.

Table III. Intramolecular Distances (Å) for $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}CNMe_2)$ (4)[a]

atom	atom	dist	atom	atom	dist
Os1	C11	1.91 (2)	O12	C12	1.10 (2)
Os1	C12	1.93 (2)	O13	C13	1.11 (3)
Os1	C13	2.00 (3)	O21	C21	1.12 (2)
Os1	C1	2.13 (2)	O22	C22	1.12 (2)
Os1	S	2.453 (5)	O23	C23	1.13 (2)
Os1	Os3	2.882 (1)	O31	C31	1.11 (2)
Os2	C22	1.90 (2)	O32	C32	1.14 (2)
Os2	C21	1.91 (2)	O33	C33	1.19 (3)
Os2	C23	1.94 (2)	O34	C34	1.09 (2)
Os2	C1	2.09 (2)	N1	C1	1.27 (2)
Os2	S	2.459 (4)	N1	C2	1.44 (2)
Os2	Os3	2.885 (1)	N1	C3	1.49 (2)
Os3	C33	1.86 (3)	C41	C42	1.36 (2)
Os3	C32	1.94 (2)	C41	C46	1.37 (2)
Os3	C34	1.96 (2)	C42	C43	1.35 (2)
Os3	C31	1.98 (2)	C43	C44	1.38 (3)
S	C41	1.80 (1)	C44	C45	1.34 (3)
O11	C11	1.15 (2)	C45	C46	1.40 (3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Results

Pyrolysis of solid $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ (1) at 200 °C in a sealed glass tube resulted in the formation of five products. Two of these were the previously known compounds $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (2)[5] and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$[3] (3). They were identified by their characteristic IR and ^1H NMR spectra. Compound 3 was also characterized structurally.[14] Two of the remaining three compounds are new. They are $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}SPh)$ (4) and $Os_6(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}CNMe_2)(\mu\text{-}SPh)$ (5). The third compound red 6 has not yet provided crystals suitable for a diffraction analysis and is thus structurally unidentified. All the products were characterized by IR and ^1H NMR spectroscopies. Compounds 4 and 5 were also characterized structurally by single-crystal X-ray diffraction analyses.

Description of the Structure of 4. An ORTEP drawing of the molecular structure of 4 is shown in Figure 1. Positional parameters are listed in Table II. Interatomic distances and angles are listed in Tables III and IV, respectively. The structure of 4 consists of an open triangular cluster of three osmium atoms that contains two metal–metal bonds. It is similar in structure to the compound $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ (7) which has been structurally characterized.[15] The two metal–metal bonds in 4 are nearly identical, Os(1)–Os(3) = 2.882 (1) Å and Os(2)–Os(3) = 2.885 (1) Å, but are significantly longer than those found in 7, 2.815 (3) and 2.823 (3) Å. The nonbonding osmium–osmium separation, Os(1)···Os(2) = 3.233 (1) Å, is bridged by a benzenethiolato ligand and a (dimethylamino)carbyne ligand, $CNMe_2$. The osmium–sulfur distances Os(1)–S = 2.453 (5) Å and Os(2)–S = 2.459 (4) Å are slightly longer than those found in $Os_3(CO)_{10}(\mu\text{-}SEt)(\mu\text{-}H)$ (8), 2.39 (1) and 2.41 (1) Å.[15] The (dimethylamino)carbyne ligand is structurally similar to those found in the compounds $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (9)[12] and $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (10).[16] The nitrogen atom is planar, and the carbon atom is bonded symmetrically to the two os-

Table IV. Intramolecular Bond Angles (deg) for $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}CNMe_2)$ (4)[a]

atom	atom	atom	angle
C11	Os1	C12	95.5 (8)
C11	Os1	C13	97.0 (8)
C11	Os1	C1	97.7 (8)
C11	Os1	S	93.0 (6)
C11	Os1	Os3	175.6 (6)
C12	Os1	C13	91.0 (9)
C12	Os1	C1	98.2 (7)
C12	Os1	S	171.1 (6)
C12	Os1	Os3	87.1 (6)
C13	Os1	C1	161.7 (8)
C13	Os1	S	90.5 (7)
C13	Os1	Os3	86.4 (6)
C1	Os1	S	78.1 (4)
C1	Os1	Os3	78.4 (4)
S	Os1	Os3	84.3 (1)
C22	Os2	C21	95.5 (8)
C22	Os2	C23	93.4 (8)
C22	Os2	C1	96.2 (7)
C22	Os2	S	169.7 (7)
C22	Os2	Os3	86.2 (6)
C21	Os2	C23	96.8 (8)
C21	Os2	C1	97.1 (7)
C21	Os2	S	93.9 (5)
C21	Os2	Os3	175.8 (6)
C23	Os2	C1	162.3 (8)
C23	Os2	S	89.4 (6)
C23	Os2	Os3	87.0 (6)
C1	Os2	S	78.7 (4)
C1	Os2	Os3	78.9 (4)
S	Os2	Os3	84.1 (1)
C33	Os3	C32	92.3 (7)
C33	Os3	C34	101 (1)
C33	Os3	C31	94.2 (8)
C33	Os3	Os1	94.3 (6)
C33	Os3	Os2	162.5 (6)
C32	Os3	C34	93.9 (7)
C32	Os3	C31	169.8 (6)
C32	Os3	Os1	86.9 (4)
C32	Os3	Os2	86.6 (5)
C34	Os3	C31	92.6 (7)
C34	Os3	Os1	164.4 (7)
C34	Os3	Os2	96.3 (7)
C31	Os3	Os1	84.8 (5)
C31	Os3	Os2	84.9 (5)
Os1	Os3	Os2	68.18 (3)
C41	S	Os1	110.2 (6)
C41	S	Os2	110.3 (6)
Os1	S	Os2	82.3 (1)
C1	N1	C2	127 (2)
C1	N1	C3	122 (2)
C2	N1	C3	111 (1)
N1	C1	Os2	133 (1)
N1	C1	Os1	127 (1)
Os2	C1	Os1	100.0 (6)
O11	C11	Os1	172 (2)
O12	C12	Os1	179 (2)
O13	C13	Os1	177 (2)
O21	C21	Os2	179 (2)
O22	C22	Os2	178 (2)
O23	C23	Os2	178 (2)
O31	C31	Os3	177 (2)
O32	C32	Os3	179 (1)
O33	C33	Os3	177 (2)
O34	C34	Os3	177 (2)
C42	C41	C46	117 (1)
C42	C41	S	125 (1)
C46	C41	S	117 (1)
C43	C42	C41	122 (2)
C42	C43	C44	118 (2)
C45	C44	C43	123 (2)
C44	C45	C46	117 (2)
C41	C46	C45	122 (2)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

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(14) Adams, R. D.; Babin, J. E., unpublished results.

(15) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* 1977, *140*, 297.

(16) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* 1976, *15*, 1843.

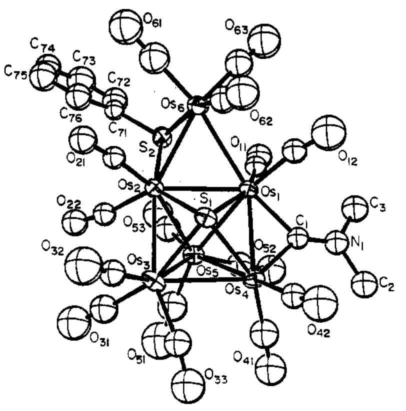

Figure 2. An ORTEP diagram of $Os_6(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}SPh)(\mu\text{-}CNMe_2)$ (5) showing 50% probability thermal ellipsoids.

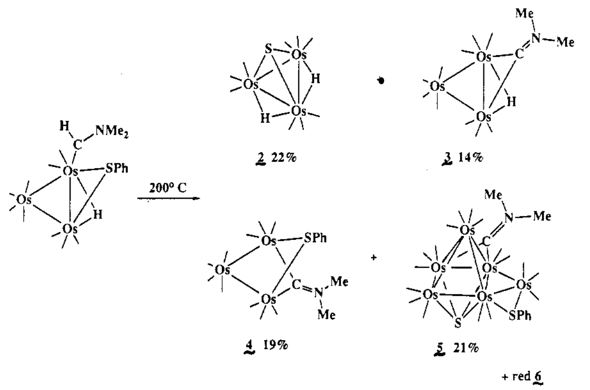

Figure 3. A summary of the products obtained from pyrolysis of $Os_3(CO)_{10}[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ (1).

Table V. Positional Parameters and B(eq) for $Os_6(CO)_{15}S(CNMe_2)(SPh)$ (5)

atom	x	y	z	B(eq), Å^2
Os1	0.878487 (82)	0.119033 (40)	0.276606 (54)	2.28 (3)
Os2	0.659389 (79)	0.108231 (40)	0.346009 (51)	2.13 (3)
Os3	0.667095 (87)	−0.020502 (42)	0.333182 (57)	2.65 (4)
Os4	0.889101 (86)	−0.005464 (42)	0.259907 (56)	2.49 (4)
Os5	0.655525 (84)	0.054763 (43)	0.178070 (52)	2.49 (4)
Os6	0.814784 (86)	0.206896 (43)	0.401650 (58)	2.73 (4)
S1	0.84553 (49)	0.04510 (25)	0.39364 (32)	2.3 (2)
S2	0.62347 (52)	0.20967 (27)	0.28782 (36)	2.7 (2)
O11	0.8200 (17)	0.21880 (88)	0.1401 (11)	5.0 (4)
O12	1.1485 (21)	0.1617 (11)	0.3657 (14)	6.9 (5)
O21	0.6196 (16)	0.11781 (79)	0.5353 (10)	4.1 (3)
O22	0.3715 (17)	0.08466 (86)	0.2842 (11)	4.7 (4)
O31	0.3874 (23)	−0.0583 (11)	0.2663 (14)	7.5 (6)
O32	0.6501 (20)	−0.0465 (10)	0.5259 (14)	6.9 (5)
O33	0.7508 (19)	−0.1506 (10)	0.2970 (13)	6.3 (5)
O41	0.8489 (20)	−0.1002 (10)	0.1134 (13)	6.4 (5)
O42	1.1244 (20)	−0.06710 (98)	0.3701 (13)	6.3 (5)
O51	0.4929 (27)	−0.0499 (14)	0.0824 (18)	10.3 (8)
O52	0.7907 (21)	0.0668 (10)	0.0235 (14)	6.7 (5)
O53	0.4631 (23)	0.1505 (11)	0.0904 (15)	7.6 (6)
O61	0.7149 (20)	0.2716 (10)	0.5461 (14)	6.7 (5)
O62	1.0360 (19)	0.15593 (92)	0.5457 (12)	5.6 (4)
O63	0.9685 (22)	0.3146 (11)	0.3611 (14)	7.3 (5)
N1	1.0608 (19)	0.06682 (95)	0.1598 (12)	3.8 (4)
C1	0.9810 (21)	0.0617 (11)	0.2130 (14)	2.9 (4)
C2	1.1208 (25)	0.0122 (13)	0.1287 (16)	4.4 (6)
C3	1.0996 (27)	0.1255 (13)	0.1290 (17)	4.8 (6)
C11	0.8470 (22)	0.1824 (11)	0.1973 (15)	3.3 (5)
C12	1.0397 (24)	0.1522 (12)	0.3322 (15)	3.6 (5)
C21	0.6405 (21)	0.1167 (11)	0.4622 (14)	2.9 (4)
C22	0.4814 (24)	0.0876 (11)	0.3057 (15)	3.5 (5)
C31	0.4941 (28)	−0.0455 (14)	0.2894 (18)	4.9 (6)
C32	0.6558 (22)	−0.0373 (11)	0.4501 (15)	3.5 (5)
C33	0.7272 (24)	−0.0990 (13)	0.3111 (16)	4.1 (5)
C41	0.8651 (28)	−0.0617 (14)	0.1709 (19)	5.2 (6)
C42	1.0345 (23)	−0.0459 (11)	0.3253 (14)	3.3 (5)
C51	0.5569 (33)	−0.0077 (16)	0.1225 (21)	6.5 (8)
C52	0.7319 (26)	0.0609 (13)	0.0858 (17)	4.6 (6)
C53	0.5284 (28)	0.1135 (14)	0.1263 (18)	5.1 (6)
C61	0.7523 (29)	0.2474 (15)	0.4883 (19)	5.5 (7)
C62	0.9488 (24)	0.1734 (12)	0.4907 (16)	3.8 (5)
C63	0.9107 (28)	0.2744 (14)	0.3799 (18)	5.0 (6)
C71	0.4926 (20)	0.2493 (10)	0.3196 (13)	2.8 (4)
C72	0.4331 (27)	0.2923 (14)	0.2575 (18)	5.0 (6)
C73	0.3284 (32)	0.3254 (17)	0.2752 (21)	6.8 (8)
C74	0.2906 (27)	0.3201 (14)	0.3520 (18)	5.0 (6)
C75	0.3460 (28)	0.2758 (14)	0.4124 (19)	5.4 (7)
C76	0.4494 (26)	0.2432 (13)	0.3965 (17)	4.5 (6)

Table VI. Intramolecular Distances (Å) for $Os_6(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}SPh)(\mu\text{-}CNMe_2)$ (5)[a]

atom	atom	dist	atom	atom	dist
Os1	C11	1.82 (2)	Os5	C52	1.78 (3)
Os1	C12	1.88 (3)	Os5	C51	1.81 (4)
Os1	C1	2.04 (2)	Os5	C53	1.90 (3)
Os1	S1	2.486 (5)	Os6	C61	1.83 (3)
Os1	Os4	2.730 (1)	Os6	C63	1.86 (3)
Os1	Os2	2.764 (1)	Os6	C62	1.89 (2)
Os1	Os5	2.874 (1)	Os6	S2	2.366 (5)
Os1	Os6	2.885 (1)	S2	C71	1.79 (2)
Os2	C21	1.84 (2)	O11	C11	1.17 (3)
Os2	C22	1.91 (2)	O12	C12	1.17 (3)
Os2	S2	2.382 (6)	O21	C21	1.18 (2)
Os2	S1	2.385 (5)	O22	C22	1.14 (3)
Os2	Os6	2.729 (1)	O31	C31	1.14 (3)
Os2	Os5	2.807 (1)	O32	C32	1.19 (3)
Os2	Os3	2.815 (1)	O33	C33	1.18 (3)
Os3	C32	1.85 (2)	O41	C41	1.20 (3)
Os3	C33	1.88 (3)	O42	C42	1.14 (3)
Os3	C31	1.89 (3)	O51	C51	1.23 (4)
Os3	S1	2.390 (5)	O52	C52	1.25 (3)
Os3	Os4	2.836 (1)	O53	C53	1.13 (3)
Os3	Os5	2.860 (1)	O61	C61	1.17 (3)
Os4	C41	1.81 (3)	O62	C62	1.17 (3)
Os4	C42	1.87 (2)	O63	C63	1.14 (3)
Os4	C1	1.98 (2)	N1	C1	1.30 (3)
Os4	S1	2.450 (5)	N1	C3	1.45 (3)
Os4	Os5	2.840 (1)	N1	C2	1.48 (3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

mium atoms, Os(1)–C(1) = 2.13 (2) Å and Os(2)–C(1) = 2.09 (2) Å. The C(1)–N(1) bond distance of 1.27 (2) Å is indicative of a partial multiple bonding between these atoms. The central osmium atom Os(3) has four carbonyl ligands. Os(1) and Os(2) each have three. The cluster contains an approximate reflection plane (not crystallographically imposed) passing through the atoms Os(3), C(1), N(1), S, and the plane of the phenyl ring. Thus, the methyl groups of the carbyne ligand are equivalent and appear as a single resonance in the ^1H NMR spectrum, δ 3.86.

Description of the Structure of 5. An ORTEP drawing of the molecular structure of 5 is shown in Figure 2. Positional parameters are listed in Table V. Interatomic distances and angles are listed in Tables VI and VII, respectively. This compound contains six osmium atoms. Five of these are arranged in the form of a square-pyramidal cluster that contains a quadruply bridging sulfido ligand across the square base. The sixth osmium atom Os(6) bridges the pair of osmium atoms Os(1)–Os(2) of the square base of the cluster. This Os_6S portion of 5 is very similar to that found for the compound $Os_6(CO)_{16}(\mu_4\text{-}$

Table VII. Intramolecular Bond Angles (deg) for $Os_6(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}SPh)(\mu\text{-}CNMe_2)$ (5)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C11	Os1	C12	91 (1)	C32	Os3	S1	87.6 (7)	Os2	Os5	Os1	58.22 (3)
C11	Os1	C1	101 (1)	C32	Os3	Os2	97.0 (8)	Os4	Os5	Os3	59.66 (3)
C11	Os1	S1	159.4 (7)	C32	Os3	Os4	129.5 (7)	Os4	Os5	Os1	57.07 (3)
C11	Os1	Os4	134.2 (7)	C32	Os3	Os5	155.6 (8)	Os3	Os5	Os1	87.96 (3)
C11	Os1	Os2	105.8 (7)	C33	Os3	C31	91 (1)	C61	Os6	C63	93 (1)
C11	Os1	Os5	90.6 (7)	C33	Os3	S1	110.0 (8)	C61	Os6	C62	90 (1)
C11	Os1	Os6	84.3 (7)	C33	Os3	Os2	159.2 (8)	C61	Os6	S2	98 (1)
C12	Os1	C1	86 (1)	C33	Os3	Os4	72.1 (8)	C61	Os6	Os2	108 (1)
C12	Os1	S1	100.4 (7)	C33	Os3	Os5	109.2 (7)	C61	Os6	Os1	166 (1)
C12	Os1	Os4	111.9 (8)	C31	Os3	S1	159.1 (9)	C63	Os6	C62	95 (1)
C12	Os1	Os2	128.1 (7)	C31	Os3	Os2	105.7 (9)	C63	Os6	S2	105.3 (9)
C12	Os1	Os5	170.7 (7)	C31	Os3	Os4	136.0 (8)	C63	Os6	Os2	152.2 (8)
C12	Os1	Os6	76.5 (7)	C31	Os3	Os5	90.5 (8)	C63	Os6	Os1	101.0 (8)
C1	Os1	S1	96.7 (6)	S1	Os3	Os2	53.8 (1)	C62	Os6	S2	158.3 (8)
C1	Os1	Os4	46.2 (6)	S1	Os3	Os4	55.1 (1)	C62	Os6	Os2	103.2 (8)
C1	Os1	Os2	135.3 (6)	S1	Os3	Os5	82.2 (1)	C62	Os6	Os1	88.4 (7)
C1	Os1	Os5	85.1 (6)	Os2	Os3	Os4	87.21 (4)	S2	Os6	Os2	55.2 (1)
C1	Os1	Os6	161.6 (6)	Os2	Os3	Os5	59.28 (3)	S2	Os6	Os1	79.5 (1)
S1	Os1	Os4	55.8 (1)	Os4	Os3	Os5	59.82 (3)	Os2	Os6	Os1	58.92 (3)
S1	Os1	Os2	53.7 (1)	C41	Os4	C42	93 (1)	Os2	S1	Os3	72.2 (1)
S1	Os1	Os5	80.3 (1)	C41	Os4	C1	103 (1)	Os2	S1	Os4	107.4 (2)
S1	Os1	Os6	82.3 (1)	C41	Os4	S1	156 (1)	Os2	S1	Os1	69.1 (1)
Os4	Os1	Os2	90.36 (4)	C41	Os4	Os1	138 (1)	Os3	S1	Os4	71.7 (1)
Os4	Os1	Os5	60.84 (3)	C41	Os4	Os3	103 (1)	Os3	S1	Os1	109.5 (2)
Os4	Os1	Os6	137.88 (4)	C41	Os4	Os5	91 (1)	Os4	S1	Os1	67.2 (1)
Os2	Os1	Os5	59.67 (3)	C42	Os4	C1	97 (1)	C71	S2	Os6	113.9 (7)
Os2	Os1	Os6	57.73 (3)	C42	Os4	S1	92.9 (7)	C71	S2	Os2	114.7 (8)
Os5	Os1	Os6	112.65 (4)	C42	Os4	Os1	117.8 (7)	Os6	S2	Os2	70.2 (2)
C21	Os2	C22	92 (1)	C42	Os4	Os3	113.2 (7)	C1	N1	C3	123 (2)
C21	Os2	S2	103.0 (7)	C42	Os4	Os5	173.4 (7)	C1	N1	C2	121 (2)
C21	Os2	S1	91.2 (7)	C1	Os4	S1	99.5 (6)	C3	N1	C2	116 (2)
C21	Os2	Os6	78.8 (7)	C1	Os4	Os1	48.0 (6)	N1	C1	Os4	137 (2)
C21	Os2	Os1	129.7 (7)	C1	Os4	Os3	138.2 (6)	N1	C1	Os1	137 (2)
C21	Os2	Os5	160.0 (7)	C1	Os4	Os5	87.1 (6)	Os4	C1	Os1	85.8 (8)
C21	Os2	Os3	100.2 (7)	S1	Os4	Os1	57.0 (1)	O11	C11	Os1	173 (2)
C22	Os2	S2	91.9 (8)	S1	Os4	Os3	53.2 (1)	O12	C12	Os1	167 (2)
C22	Os2	S1	131.1 (8)	S1	Os4	Os5	81.6 (1)	O21	C21	Os2	174 (2)
C22	Os2	Os6	140.7 (7)	Os1	Os4	Os3	91.35 (4)	O22	C22	Os2	169 (2)
C22	Os2	Os1	138.7 (7)	Os1	Os4	Os5	62.09 (3)	O31	C31	Os3	176 (3)
C22	Os2	Os5	77.9 (7)	Os3	Os4	Os5	60.51 (3)	O32	C32	Os3	178 (2)
C22	Os2	Os3	77.5 (7)	C52	Os5	C51	90 (1)	O33	C33	Os3	172 (2)
S2	Os2	S1	134.7 (2)	C52	Os5	C53	91 (1)	O41	C41	Os4	178 (3)
S2	Os2	Os6	54.6 (1)	C52	Os5	Os2	140.7 (9)	O42	C42	Os4	175 (2)
S2	Os2	Os1	81.8 (1)	C52	Os5	Os4	83.1 (9)	O51	C51	Os5	178 (3)
S2	Os2	Os5	94.3 (1)	C52	Os5	Os3	139.0 (9)	O52	C52	Os5	177 (2)
S2	Os2	Os3	154.7 (1)	C52	Os5	Os1	85.0 (9)	O53	C53	Os5	172 (3)
S1	Os2	Os6	87.5 (1)	C51	Os5	C53	92 (1)	O61	C61	Os6	177 (3)
S1	Os2	Os1	57.1 (1)	C51	Os5	Os2	129 (1)	O62	C62	Os6	176 (2)
S1	Os2	Os5	83.4 (1)	C51	Os5	Os4	103 (1)	O63	C63	Os6	176 (3)
S1	Os2	Os3	54.0 (1)	C51	Os5	Os3	83 (1)	C76	C71	C72	118 (2)
Os6	Os2	Os1	63.35 (3)	C51	Os5	Os1	159 (1)	C76	C71	S2	128 (2)
Os6	Os2	Os5	119.93 (4)	C53	Os5	Os2	88.1 (8)	C72	C71	S2	114 (2)
Os6	Os2	Os3	141.46 (4)	C53	Os5	Os4	164.8 (9)	C71	C72	C73	119 (3)
Os1	Os2	Os5	62.11 (3)	C53	Os5	Os3	128.9 (8)	C74	C73	C72	122 (3)
Os1	Os2	Os3	91.07 (4)	C53	Os5	Os1	108.5 (9)	C73	C74	C75	119 (3)
Os5	Os2	Os3	61.16 (3)	Os2	Os5	Os4	87.28 (3)	C76	C75	C74	119 (3)
C32	Os3	C33	95 (1)	Os2	Os5	Os3	59.56 (3)	C71	C76	C75	122 (3)
C32	Os3	C31	91 (1)								

[a] Estimated standard deviations in the least significant figure are given in parentheses.

$S)(\mu_3\text{-}S)$ (11).[17] A benzenethiolato ligand, SPh, bridges the Os(2)–Os(6) metal–metal bond between the bridging osmium atom and Os(2) in the square base. The Os(2)–Os(6) distance 2.729 (1) Å is significantly shorter than the bond to the other basal osmium atom, Os(1)–Os(6) = 2.885 (1) Å. The difference is probably due to the presence of the bridging benzenethiolato ligand. A (dimethylamino)carbyne ligand bridges the osmium atoms Os(1) and Os(4) in the base of the square pyramid. This metal–metal bond, Os(1)–Os(4) = 2.730 (1) Å, is also relatively short, 2.730 (1) Å, presumably due to the presence of the bridging ligand. The osmium–osmium and osmium–sulfur distances in the square pyramid span a wide range, at 2.730 (1)–2.874 (1) Å and 2.385 (5)–2.486 (5) Å, respectively. Similar ranges were observed for the Os–Os and Os–S distances in 11.[17] In both cases the longest bonds involve the atom Os(1), Os(1)–Os(5) = 2.874 (1) Å and Os(1)–S(1) = 2.486 (5) Å. The increased lengths of these bonds may be due to steric crowding about Os(1) which is eight-coordinate. The methyl groups on the carbyne ligand are inequivalent and appear as two closely spaced singlets, δ 4.030 and 4.024 in the ^1H NMR spectrum.

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(17) Adams, R. D.; Horváth, I. T.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 1533.

Discussion

It is known that the pyrolysis of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$, in the absence of solvent at 200 °C, results in the elimination of benzene and the formation of a variety of higher nuclearity sulfido osmium carbonyl cluster compounds.[18] It was hoped that benzene elimination from **1** would lead to higher nuclearity clusters that contain carbene ligands.

The results of this study are summarized in Figure 3. The formation of compounds **2** and **5** confirms the loss of a phenyl group (benzene formation was not established), but no products containing carbene ligands were obtained. Compounds **3**–**5** each contain a bridging (dimethylamino)carbyne ligand. It is believed that the carbyne ligand was formed by an α-activation of the C–H bond of the carbene ligand. This transformation has been observed in the pyrolysis of **1** in solutions.[12] The formation of compounds **2**–**4** has involved a variety of ligand eliminations from **1**, presumably by competing reactions. Mechanistic details are not available at this time. Compound **5** is the only higher nuclearity product that was characterized, although it is suspected that red **6** is also a higher nuclearity species. Compound **5** is electron-precise and has adopted a cluster shape that is analogous to that of compound **11**. The mechanism of the formation of **5** is not clear at this time, but it seems that it could have been formed by a combination of **4** with an SOs_3 species.

The synthesis of high nuclearity carbene clusters is proving to be a great challenge. There is, to date, only one report of carbene-containing clusters in which the metal nuclearity is higher than three.[10] The high reactivity of carbene ligands on transition-metal clusters, and their propensity for transformation to carbyne ligands, as described in this report and previously, may be a major impediment in their synthesis.

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Registry No. 1, 106499-78-9; 2, 38979-82-7; 3, 63373-87-5; 4, 109637-86-7; 5, 109669-11-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters for compounds 4 and 5 (6 pages); listings of observed and calculated structor factor amplitudes for 4 and 5 (46 pages). Ordering information is given on any current masthead page.

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[18] Adams, R. D.; Horvâth, I. T.; Mathur, P.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1078.

Coordination Chemistry of Methyl Iodide

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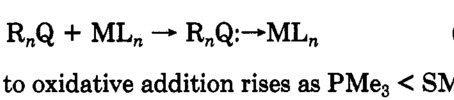
The complex $[IrH_2(IMe)_2(PPh_3)_2]SbF_6$ (**1**) contains two iodomethane groups coordinated via the iodine atoms. The Ir–I–C angles are 105.5 (4) and 108.2 (5)°. The coordinated iodomethane is activated toward nucleophilic attack at the carbon atom by NEt_3, the rate of which is enhanced by 10^4–10^5-fold relative to free MeI. Removing the hydride ligands with $t\text{-BuCH}{=}CH_2$ leads to oxidative addition to give $[MeIr(\mu\text{-I})(PPh_3)_2]_2$ (**2**). Crystal structures of **1** and **2** were determined.

Introduction

Main-group alkyls QR_n (Q = element of groups 15–17), such as PMe_3, SMe_2, and IMe, can in principle bind to a transition metal either with oxidative addition of the Q–C bond to the metal (eq 1) or via a lone pair on Q (eq 2).



$$R_nQ + ML_n \longrightarrow R_{n-1}Q{-}\overset{\overset{\textstyle R}{|}}{M}L_n \qquad (1)$$

$$R_nQ + ML_n \rightarrow R_nQ{:}{\rightarrow}ML_n \qquad (2)$$

The tendency to oxidative addition rises as $PMe_3 < SMe_2 < IMe$, and examples involving P–C cleavage in phosphines are rather rare. On the other hand, the tendency to bind via a lone pair falls as $PMe_3 > SMe_2 > IMe$, and no crystallographically authenticated example of an iodocarbon complex was known until our first report[1] in this area some years ago.

The origin of the trend found for oxidative addition may lie in the progressive lowering of the Q–C σ^* level as Q goes from P to I. As this happens, oxidative addition, either by attack of the metal at the Q–C σ^* or by single electron transfer into the Q–C σ^*, becomes easier. The trend in binding via Q is probably a result of the decreasing basicity of the lone pair(s) on Q as we go from P to I.

An earlier report[2] of the existence of an iodomethane complex was not confirmed[3] by a crystallographic study. We therefore felt we should determine the crystal structure of our complex. We and others have also reported cases of bromo–,[4] chloro–,[4a,5] and fluorocarbon[6] binding to transition metals, and even I_2 is now known to bind.[7]

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[1] Crabtree, R. H.; Faller, J. W. Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361–66.

[2] Lawson, D. N.; Osborn, J. A.; Wilkinson, G. W. *J. Chem. Soc. A* **1966**, 1733.

[3] (a) Troughton, P. G. H.; Skapski, A. *Chem. Commun.* **1968**, 575–6. Skapski, A. personal communication, 1985. Siedle A. R.; Newmark, R. A.; Pignolet, L. H. *Organometallics* **1984**, *3*, 855–9.

[4] (a) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638–40. (b) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* **1985**, 43.

[5] Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214; **1980**, *35B*, 985.

[6] Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559. Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Susa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261. Rust, P. M.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *103*, 3206. Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482.

0276-7333/87/2306-2241$01.50/0