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Interaction of Iodine with a Hydridotriosmium Cluster Containing a Carboxamido Ligand: Crystal and Molecular Structure of a Dinuclear Carboxamido Complex and a Mononuclear Amine Complex

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The reaction of the hydridocarboxamidotriosmium cluster (μ-H)Os$_3$(CO)$_{10}$(μ-OCNHCHMe$_2$) (**1a**) with iodine is observed to give several di- or mononuclear osmium complexes in stepwise fashion. Reaction of **1a** with 2 equiv of I$_2$ gives the dinuclear compound (μ-I)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)I$_2$ (**2a**), along with the formation of *trans*-HIOs(CO)$_4$ (**5**-*trans*). Complex **5**-*trans* is unstable in CDCl$_3$, isomerizing to the cis form, **5**-*cis*. Complex **5**-*cis* is converted to the diiodo complex I$_2$Os(CO)$_4$ (**6**) with excess I$_2$. Reaction of (μ-H)Os$_3$(CO)$_{10}$(μ-OCNHCRMe$_2$) (R: H, **1a**; Me, **1b**) with 3 equiv of iodine in CH$_2$Cl$_2$/hexane gives the mononuclear amine compound Os(CO)$_3$(NH$_2$CRMe$_2$)I$_2$ (R: H, **4a**; Me, **4b**). Reactions of **1** with bromine give the bromine analogues of **2** and **4**. All products were characterized by spectroscopic methods. Single-crystal X-ray diffraction studies were carried out for complexes **2a** and **4b**. Crystals of **2a** are triclinic, $P\bar{1}$, with a = 7.573 (2) Å, b = 9.475 (1) Å, c = 14.084 (2) Å, α = 94.05 (1)°, β = 96.51 (2)°, γ = 90.49 (1)°, and Z = 2. The structure was refined to R = 0.0309 and R_w = 0.0221 for 4022 reflections. A carboxamido ligand bridges the two osmium centers, which are separated by 4.03 Å, indicating no metal-metal interaction. Crystals of **4b** are triclinic, $P\bar{1}$, with a = 6.742 (3) Å, b = 8.631 (3) Å, c = 12.835 (2) Å, α = 108.02 (2)°, β = 90.97 (2)°, γ = 100.47 (4)°, and Z = 2. The structure was refined to R = 0.0398 and R_w = 0.0391 for 2220 reflections. Three carbonyl ligands are in facial positions around the osmium atom. The Os–I$_{av}$ and Os–N distances are 2.735 (1) and 2.197 (9) Å, respectively.

Introduction

The reactivities and stabilities of metal clusters containing organic substrates have been under extensive investigation because of their possible roles in catalytic reactions.[1-9] The triosmium cluster system has drawn attention, since reactions with organic substrates can be followed by conventional spectroscopic techniques.[10,11] Triosmium cluster complexes containing a carboxamido ligand are readily prepared in relatively high yield by nucleophilic attack of a primary aliphatic amine at a terminal CO ligand[12-14] or by reaction of an NHR$^-$ anion with a carbonyl cluster having a labile ligand followed by protonation.[15] Little chemistry has thus far been explored on the chemical reactivity of these complexes, most possibly due to their high thermal stability. Thermolysis of carboxamido clusters to nitrene complexes could be observed only at relatively high temperatures.[16,17] Since iodide has been employed as a promoter in many catalytic[18-20] or stoichiometric reactions,[21-23] we were interested in the chemical behavior of a carboxamido cluster in the presence of I$_2$. On the assumption that all atoms are neutral, iodine could act as a one-electron-donor ligand if attached in a terminal position or could be considered as a three-electron donor if in a bridged bonding mode. We report here the isolation of new osmium complexes in the reactions of complex **1** with iodine and bromine.

Experimental Section

General Information. Solvents and reagents were of commercial reagent grade and were used without further purification unless otherwise noted. (μ-H)Os$_3$(CO)$_{10}$(μ-OCNHR) was prepared according to the literature method cited.[16] Although the cluster complexes were generally air stable, reactions, filtrations, and recrystallizations were routinely carried out under nitrogen atmosphere by using Schlenkware techniques or in a Vacuum Atmospheres Corp. nitrogen box equipped with a freezer. Chromatographic separations and handling of neutral complexes can be done in air if exposure is limited to a few hours. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer using a liquid cell equipped with CaF$_2$ windows. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300WB spectrometer and calibrated against internal residual CHCl$_3$ at δ = 7.24 for a proton. Mass spectra were obtained on a Jeol-JMS D300 mas spectrometer at the Taipei Regional Center for Instrumentation located at National Taiwan Normal University. Elemental analyses were performed by using a Perkin-Elmer 240C instrument at our department.

Reaction of (μ-H)Os$_3$(CO)$_{10}$(μ-OCNHR) with 2 equiv of Iodine. A quantity of (μ-H)Os$_3$(CO)$_{10}$(μ-OCNHCHMe$_2$) (**1a**) (293 mg, 0.31 mmol) was placed into a small Schlenk tube with 1 mL of CHCl$_3$ to dissolve the yellow solid. Under an atmosphere of N$_2$, this solution was treated with a 2-mL CHCl$_3$ solution of iodine (159 mg, 0.63 mmol) over a 20-min period at room temperature. The color of the solution changed from yellow to brown-purple. The solution was allowed to stand for 2.5 h, whereupon the brown color gradually faded to yellow. The solvent was removed at reduced pressure until only about 1 mL of solvent remained and white solid precipitated. After the yellow solution was decanted, the white powder was washed with cold pentane several times. The decanted yellow solution contained HOs(CO)$_4$I, whose characterization is described below. The white complex, (μ-I)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)I$_2$ (**2a**), is pure and is air stable as the solid. Yield: 186 mg, 58%. Single crystals of **2a** could be obtained from recrystallization by slowly diffusing

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[1] Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417.

[2] Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049.

[3] Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508.

[4] Ugo, R.; Psaro, R. *J. Mol. Catal.* **1983**, *20*, 53.

[5] Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219.

[6] Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959.

[7] (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (b) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559.

[8] (a) Kaesz, H. D.; Knobler, C. B.; Andrews, M. A.; Van Buskirk, G.; Szostak, R.; Strouse, C. E.; Lin, Y. C.; Mayr, A. *Pure Appl. Chem.* **1982**, *54*, 131. (b) Kaesz, H. D.; Krone-Schmidt, W.; Sieber, W. J.; Boag, N. M.; Knobler, C. B. In *Homogeneous and Heterogeneous Catalysis*, Proceedings of the Fifth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Novosibirsk, July 15-19, 1986; Yermakov, Yu., Likholobov, V., Eds.; VNU Science Press: Utrecht, The Netherlands, 1986; pp 837-845.

[9] Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

[10] Adams, R. D.; Selegue, J. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 1032-1057.

[11] Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

[12] Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1201.

[13] Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1102.

[14] Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243.

[15] Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704.

[16] Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, C41.

[17] Lin, Y. C.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207.

[18] Forster, D. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1979; Vol. 17, p 255.

[19] Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508.

[20] Fakley, M. E.; Head, R. A. *Appl. Catal.* **1983**, *5*, 3.

[21] Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

[22] Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541.

[23] Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 254.

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hexane into saturated CH_2Cl_2 solution at low temperature. IR data (in CH_2Cl_2, cm^{-1}): 2122 (s), 2111 (s), 2047 (vs), 2012 (s), terminal CO absorptions; 1606 (m), 1510 (m), 1420 (m), amide absorptions. NMR data are as follows (in $CDCl_3$, δ). ^1H spectrum: 6.63 (d, 1 H, NH), 4.36 (m, 1 H, CH), 1.22 (d, 3 H, Me), 1.24 (d, 3 H, Me). ^{13}C spectrum: 209.57 (carboxamido carbon); 166.83, 166.00, 165.68, 163.64, 162.67, 161.85 (6 terminal carbonyls); 44.91 (CH); 22.77 (Me); 22.29 (Me). The mass spectrum shows a parent peak at *m/e* 1016. Anal. Calcd for $Os_2C_{10}H_8NI_3O_7$: C, 11.82; H, 0.79. Found: C, 11.90; H, 0.71.

Spectroscopic Identification of *trans* and *cis*-$HIOs(CO)_4$. Characterization of the decanted $CDCl_3$ yellow solution mentioned above is described below. The major species in this solution gives a strong peak at $\delta = -11.77$ in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, there is only one strong singlet at 167.96 ppm in the terminal CO region. The coupling constant J_{H-CO} of 5.36 Hz from the decoupling experiment clearly indicates the cis disposition of H and CO ligands. On the basis of the reaction stoichiometry and the spectroscopic data, this species is assigned as *trans*-$HIOs(CO)_4$ (**5**-*trans*). Complex **5**-*trans* disappears within 2 days in $CDCl_3$ solution, while the hydride peak at $\delta = -8.03$, assignable to a *cis*-$HIOs(CO)_4$ complex (**5**-*cis*), appeared and increased. The ^{13}C NMR spectrum of this species contains three peaks at 165.85 (CO, $J_{C-H} = 7.17$ Hz, 2 CO), 162.82 (CO, $J_{C-H} = 22.89$ Hz, 1 CO), and 161.11 ppm (CO, $J_{C-H} = 5.48$ Hz, 1 CO). This is again an unstable species; its absorptions slowly vanish over 1 week and are not replaced by any new peaks in the ^1H NMR spectrum. We could not isolate the trans isomer, since this decomposes on a silica gel column. The cis complex is the major isomer obtained from chromatographic separation, accompanied by the diiodo complex *cis*-$I_2Os(CO)_4$ (**6**), which is the final stable product. Formation of complex **6** could possibly be derived from the reaction of excess residual I_2 with **5**. The identity of complex **6** is confirmed by its IR, ^{13}C NMR, and mass spectra.[24] IR (in hexane, cm^{-1}): 2108 (m), 2100 (s), 2085 (m), 2049 (vs). ^{13}C NMR (in $CDCl_3$, ppm): 158.36, 155.78.

Reaction of 1 with 3 equiv of Iodine. In a 50:50 hexane/dichloromethane mixture (10 mL) was dissolved 132 mg (0.14 mmol) of (μ-H)$Os_3(CO)_{10}$(μ-$OCNHCHMe_2$) (**1a**). To this mixture was added, at room temperature, 10 mL of a freshly prepared iodine/CH_2Cl_2 solution containing 0.42 mmol of I_2. The purple I_2 color faded in about 17 h. The IR spectrum of the solution indicated the complete consumption of the starting material. Silica gel was added to this solution and the solvent stripped off, leaving behind a dry coated powder. This was placed at the top of a dry-packed silica gel column. Elution with CH_2Cl_2 gave two yellow bands: the fast moving band is complex **6** and the slow moving one is identified as $Os(CO)_3[NH_2CHMe_2]I_2$ (**4a**). The isolated yield of **4a** was 74 mg. IR (in hexane, cm^{-1}): 2012 (s), 2039 (s), 2110 (s). NMR data are as follows (in CD_3COCD_3, ppm). ^1H: 4.65 (s, 2 H, NH, at 3.68 ppm when in $CDCl_3$), 3.44 (m, 1 H, CH), 1.36 (d, 6 H, 2 CH_3). ^{13}C: 168.73, 165.62 (terminal carbonyls); 53.94 (CH); 23.69 (Me). Mass spectral data, *m/e*: 589 (parent peak), 530 (P − NH_2CHMe_2), 502 (P − CO − NH_2CHMe_2), 474 (P − 2CO − NH_2CHMe_2), 447 (P − 3CO − NH_2CHMe_2), 462 (P − I), 434 (P − I − CO), 402 (P − I − NH_2CHMe_2), 373 (P − I − CO − NH_2CHMe_2), 307 (P − 2I − CO). Anal. Calcd for $OsC_6H_9NI_2O_3$: C, 12.22; H, 1.53. Found: C, 12.30; H, 1.40. $Os(CO)_3[NH_2CMe_3]I_2$ (**4b**) (58 mg) could be prepared similarly from the reaction of $HOs_3(CO)_{10}(OCNHCMe_3)$ (**1b**) (104 mg, 0.17 mmol) with 3 equiv of I_2. IR (in hexane, cm^{-1}): 2011 (s), 2039 (s), 2111 (s). ^1H NMR data (in CD_3COCD_3, ppm): 4.74 (s, 2 H, NH), 1.46 (s, 9 H, CH_3). Mass spectral data, *m/e*: 603 (parent peak) and fragmentation peaks.

Reaction of 1a with Bromine. Reaction of **1a** with 2 equiv of bromine was carried out in a manner similar to that for the reaction of **1a** with 2 equiv of iodine. A dinuclear complex, (μ-Br)$Os_2(CO)_6$(μ-$OCNHCHMe_2$)Br_2, was characterized by spectroscopic methods. ^1H NMR (in $CDCl_3$, ppm): 6.62 (d, br, 1 H, NH), 4.37 (m, 1 H, CH), 1.22 (d, 3 H, Me), 1.24 (d, 3 H, Me). IR data (in $CHCl_3$, cm^{-1}): 2130 (m), 2119 (m), 2082 (vs), 2054 (s), 2037 (m), 2012 (w) (terminal CO absorptions); 1600 (m), 1514 (w) (amide absorptions).

X-ray Crystallography. Single crystals of **2a** were subjected to a preliminary photographic examination. This suggested the space group $P1$ or $P\bar{1}$. The centrosymmetric choice was suggested by the *E* statistics, where *E* is defined as

$$|E(hkl)|^2 = \{[K^2|F(hkl)|^2]/\epsilon\}\sum_{j=1}^{N} g_j^2$$

where *K* is the scale factor associated with $|F(hkl)|$, ϵ is a factor depending upon the crystal class and its value for triclinic space groups is always 1, and g_j is the temperature-corrected atomic scattering factor.[25a] The centrosymmetric choice was confirmed by all subsequent developments during structure solution and refinement. A crystal with approximate dimensions of 0.12 × 0.20 × 0.30 mm was mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. These data were measured with Mo Kα (λ = 0.7107 Å) radiation on an automated Nonius CAD-4 diffractometer. The calculated density for **2a** is 3.367 g/cm^3. Diffracted intensities were measured with $2\theta-\omega$ scans with a scan width of $2(0.7 + 0.35 \tan\theta)°$ and a variable scan rate of 20/16 to 20/3 deg/min. The three standard reflections (−2,1,8), (2,5,−1), and (3,2,−5), measured after every 97 reflections, showed a small decrease with time; no correction was made. An analytical absorption correction was applied to the data with use of a linear absorption coefficient of 172.97 cm^{-1} for Mo Kα radiation, and the transmission factors were between 0.51 and 1.0. A total of 5827 reflections with $2\theta < 60°$ were measured.

Table I. Crystal and Intensity Collection Data for $Os_2(CO)_6(CONHCHMe_2)I_3$ and $Os(CO)_3I_2(NH_2CMe_3)$

mol formula	$C_{10}H_8NO_7I_3Os_2$	$C_7H_{11}NO_3I_2Os$
mol wt	1016	603
space group	$P\bar{1}$	$P\bar{1}$
a, Å	7.573 (2)	6.742 (3)
b, Å	9.475 (1)	8.631 (3)
c, Å	14.084 (2)	12.835 (2)
α, deg	94.05 (1)	108.02 (2)
β, deg	96.51 (2)	90.97 (2)
γ, deg	90.49 (1)	100.47 (4)
V, Å^3	1000.25 (4)	696.24 (4)
ρ(calcd), g cm^{-3}	3.367	2.863
Z	2	2
cryst dimens, mm	0.12 × 0.2 × 0.3	0.1 × 0.2 × 0.12
abs coeff μ (Mo Kα), cm^{-1}	172.97	172.9
temp, °C	rm temp	rm temp
radiation	Mo Kα, λ = 0.7107 Å	Mo Kα, λ = 0.7107 Å
2θ range, deg	0–60	0–53
scan speed, deg min^{-1}	20/16 to 20/3	20/16 to 20/3
scan type	$2\theta/\omega$	$2\theta/\omega$
scan width, deg	$2(0.7 + 0.35 \tan\theta)$	$2(0.7 + 0.35 \tan\theta)$
total no. of reflcns	5827	2881
no. of unique reflcns ($I_0 > 3\sigma(I_0)$)	4022	2220
total no. of variables	209	128
std refcns	(−2,1,8), (2,5,−1), (3,2,−5)	(−3,0,0), (0,−4,0), (0,0,−6)
variation	$\pm3\sigma$, ±2%	$\pm3\sigma$, ±2%
R	0.0309	0.0398
R_w	0.0221	0.0391
ΔF, e/Å^3	<1.45, Os2	<0.20, I

Intensity data were reduced, and 4022 reflections with $F_o > 3\sigma(F_o)$ were retained as observed and used in all subsequent calculations. The procedures for the data collection are similar for crystals of **4b**. Crystallographic data and other pertinent information for both crystals are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data were corrected for absorption by the empirical ω-scan method. The heavy-atom positions were obtained by Patterson synthesis. The structure of complex **2a** was refined in space group $P\bar{1}$ to convergence. All hydrogen atoms of the complex were located form the difference Fourier map (with single-bond distances in the range 0.9–1.15 Å), and they were included in the final refinement cycle. Anisotropic thermal parameters were used for all non-hydrogen atoms. For **2a**, the maximum electron density in the final difference Fourier map is 1.45 e Å^{-3} near Os2. The structure of complex **4b** was refined in space group $P\bar{1}$ to convergence. The absorption correction was also applied with transmission factors between 0.75 and 1.0. All hydrogen atoms in the structure were located from the difference Fourier map; the maximum electron density in the final difference Fourier map is 0.2 e Å^{-3} near I. The discrepancy indices, $R = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, are listed in Table I. The programs used for computing were the NRCC SDP PDP-11 Package.[25b] Final atomic coordinates, isotropic thermal parameters, and selected bond distances and bond angles for **2a** and **4b** are listed in Tables II–V, re-

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(24) (a) Hales, L. A. W.; Irving, R. J. *J. Chem. Soc. A* **1967**, 1389. (b) Hales, L. A. W.; Irving, R. J. *J. Chem. Soc. A* **1967**, 1932.

(25) (a) Ladd, M. F. C.; Palmer, R. A. *Structure Determination by X-Ray Crystallography*; Plenum: New York, 1985; p 296. (b) Gabe, E. J.; Lee, F. L. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, C339.

Table II. Positional Parameters and Isotropic Thermal Parameters for $(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$

	x	*y*	*z*	B_{eq}[a] Å^2
Os1	0.30849 (5)	0.35570 (1)	0.15513 (2)	2.44 (1)
Os2	0.04184 (1)	0.02500 (1)	0.21123 (2)	2.10 (1)
I1	0.09996 (10)	0.55496 (8)	0.23169 (6)	4.85 (5)
I2	−0.23153 (9)	0.16159 (8)	0.32021 (5)	1.34 (4)
I3	0.01372 (8)	0.19307 (7)	0.09228 (4)	3.00 (3)
C1	0.2899 (12)	0.4529 (11)	0.0138 (6)	3.7 (5)
C2	0.5036 (11)	0.4715 (11)	0.2066 (6)	3.5 (6)
C3	0.4557 (11)	0.2156 (10)	0.0994 (6)	3.0 (5)
C4	−0.1405 (11)	−0.1031 (10)	0.1707 (6)	3.4 (5)
C5	0.0545 (12)	−0.0822 (10)	0.3499 (6)	3.1 (5)
C6	0.2444 (12)	−0.0684 (11)	0.1946 (7)	3.8 (5)
C7	0.2200 (10)	0.1757 (10)	0.3198 (6)	2.9 (5)
C8	0.3547 (14)	0.2927 (13)	0.4781 (7)	5.5 (8)
C9	0.4539 (14)	0.2233 (14)	0.5570 (8)	6.3 (9)
C10	0.2500 (17)	0.4124 (13)	0.5111 (8)	6.8 (9)
O1	0.2815 (9)	0.5125 (8)	−0.0210 (5)	5.7 (5)
O2	0.6139 (0)	0.5487 (8)	0.2380 (5)	5.0 (5)
O3	0.5353 (8)	0.1364 (8)	0.0615 (5)	1.9 (5)
O4	−0.2474 (8)	−0.1745 (8)	0.1309 (5)	4.8 (1)
O5	0.0576 (10)	−0.1454 (8)	0.4162 (5)	5.1 (5)
O6	0.3528 (9)	−0.1184 (8)	0.1680 (5)	5.6 (5)
O7	0.3180 (7)	0.2638 (7)	0.2836 (1)	3.2 (3)
N	0.2448 (10)	0.1902 (10)	0.4156 (6)	4.6 (5)
HN	0.1697	0.1163	0.4522	6.3
H8	0.4522	0.3351	0.4636	6.3
H91	0.5232	0.1336	0.5254	6.3
H92	0.5461	0.3007	0.5940	6.3
H93	0.3616	0.1838	0.6014	6.3
H101	0.1668	0.3822	0.5642	6.3
H102	0.3460	0.4920	0.5419	6.3
H103	0.1662	0.4526	0.4517	6.3

[a] $B_{eq} = {}^{8}/_{3}\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Positional Parameters and Isotropic Thermal Parameters for $Os(CO)_3(NH_2CMe_3)I_2$

	x	*y*	*z*	B_{eq},[a] Å^2
Os	0.99154 (7)	0.45240 (6)	0.2367 (4)	2.33 (2)
I1	0.6623 (1)	0.4913 (1)	0.1270 (1)	3.92 (5)
I2	0.9259 (2)	0.6922 (1)	0.4226 (1)	3.90 (5)
N	0.785 (1)	0.283 (1)	0.302 (1)	3.0 (5)
O1	1.068 (2)	0.202 (1)	0.024 (1)	5.8 (7)
O2	1.359 (1)	0.419 (2)	0.360 (1)	7.2 (9)
O3	1.227 (1)	0.732 (1)	0.167 (1)	4.7 (5)
C1	1.033 (2)	0.294 (2)	0.106 (1)	3.6 (7)
C2	1.217 (2)	0.429 (2)	0.314 (1)	4.1 (7)
C3	1.143 (2)	0.628 (2)	0.192 (1)	2.9 (6)
C4	0.737 (2)	0.095 (2)	0.259 (1)	3.6 (7)
C5	0.925 (2)	0.029 (2)	0.254 (1)	4.1 (8)
C6	0.597 (2)	0.040 (2)	0.340 (1)	4.8 (8)
C7	0.618 (2)	0.046 (1)	0.148 (1)	4.5 (8)
HN1	0.637	0.318	0.297	3.5
HN2	0.835	0.315	0.387	3.5
H51	1.014	0.063	0.193	5.4
H52	0.888	−0.105	0.193	8.0
H53	1.007	0.074	0.326	8.6
H61	0.454	0.093	0.333	9.1
H62	0.676	0.084	0.416	5.8
H63	0.570	−0.088	0.314	6.3
H71	0.481	0.095	0.147	3.7
H72	0.574	−0.075	0.124	6.6
H73	0.700	0.082	0.088	4.2

[a] $B_{eq} = {}^{8}/_{3}\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

spectively. Final values of the anisotropic thermal parameters, complete bond distances and bond angles, and observed and calculated structure factors are available as supplementary material.

Table IV. Selected Interatomic Distances (Å) for $(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$ and $Os(CO)_3(NH_2CMe_3)I_2$

$(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$			
Os1–I1	2.7148 (9)	Os1–I3	2.7279 (8)
Os1–C2	1.878 (8)	Os1–C3	1.923 (8)
Os2–I2	2.7309 (9)	Os2–I3	2.7469 (8)
Os2–C5	1.854 (9)	Os2–C6	1.95 (1)
Os1–C1	1.867 (9)	Os1–O7	2.056 (5)
Os2–C4	1.980 (8)	Os2–C7	2.102 (7)
C1–O1	1.14 (1)	C2–O2	1.14 (1)
C3–O3	1.09 (1)	C6–O6	1.04 (1)
C4–O4	1.12 (1)	C5–O5	1.14 (1)
C7–O7	1.28 (1)	C7–N	1.34 (1)
C8–C10	1.47 (1)	C8–N	1.45 (1)
C8–C9	1.47 (1)		
$Os(CO)_3(NH_2CMe_3)I_2$			
Os–I1	2.735 (1)	Os–I2	2.736 (1)
Os–C1	1.87 (1)	Os–C2	1.88 (1)
N–C4	1.52 (1)	O1–C1	1.17 (1)
O2–C2	1.15 (1)	C4–C5	1.48 (2)
C4–C6	1.54 (1)	Os–N	2.197 (9)
Os–C3	1.91 (1)	O3–C3	1.11 (1)
C4–C7	1.52 (1)		

Table V. Selected Bond Angles (deg) for $(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$ and $Os(CO)_3(NH_2CMe_3)I_2$

$(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$			
I1–Os1–I3	89.79 (2)	I1–Os1–C1	88.2 (3)
I1–Os1–C2	86.9 (2)	I1–Os1–C3	179.3 (2)
I1–Os1–O7	86.7 (1)	I3–Os1–C1	92.5 (2)
I3–Os1–C2	175.8 (2)	I3–Os1–C3	90.2 (2)
I3–Os1–O7	88.2 (1)	C1–Os1–C2	89.9 (3)
C1–Os1–C3	91.1 (4)	C1–Os1–O7	174.8 (3)
C2–Os1–C3	93.2 (3)	C2–Os1–O7	89.0 (3)
C3–Os1–O7	94.0 (3)	I2–Os2–I3	91.22 (2)
I2–Os2–C4	87.0 (2)	I2–Os2–C5	86.2 (3)
I2–Os2–C6	117.4 (2)	I2–Os2–C7	89.2 (2)
I3–Os2–C4	88.3 (2)	I3–Os2–C5	177.3 (2)
I3–Os2–C6	89.6 (2)	I3–Os2–C7	88.6 (2)
C4–Os2–C5	92.1 (3)	C1–Os2–C6	95.5 (3)
C4–Os2–C7	174.9 (3)	C5–Os2–C6	93.0 (1)
C5–Os2–C7	90.6 (3)	C6–Os2–C7	88.1 (3)
Os1–I3–Os2	95.77 (2)	Os1–C1–O1	178.9 (7)
Os1–C2–O2	175.5 (9)	Os1–C3–O3	177.2 (7)
Os2–C4–O4	177.9 (7)	Os2–C5–O5	177.6 (8)
Os2–C6–O6	179.9 (2)	Os2–C7–O7	126.7 (5)
Os2–C7–N	122.3 (6)	O7–C7–N	111.0 (6)
C9–C8–C10	113.0 (8)	C9–C8–N	111 (1)
C10–C8–N	111.5 (9)	Os1–O7–C7	135.1 (4)
C7–N–C8	129.1 (8)		
$Os(CO)_3(NH_2CMe_3)I_2$			
I1–Os–I2	90.66 (4)	I1–Os–N	88.0 (2)
I1–Os–C1	87.3 (4)	I1–Os–C2	178.9 (4)
I1–Os–C3	86.5 (3)	I2–Os–N	84.3 (2)
I2–Os–C1	177.5 (4)	I2–Os–C2	88.2 (4)
I2–Os–C3	87.2 (3)	N–Os–C1	97.0 (4)
N–Os–C2	92.0 (4)	N–Os–C3	169.9 (4)
C1–Os–C2	93.8 (6)	C1–Os–C3	91.3 (5)
C2–Os–C3	93.3 (5)	Os–N–C4	127.8 (8)
Os–C1–O1	176.0 (1)	Os–C2–O2	177.0 (1)
Os–C3–O3	178.0 (1)	N–C4–C5	110.0 (1)
N–C4–C6	106 (1)	N–C4–C7	106 (1)
C5–C4–C6	112 (1)	C5–C4–C7	113 (1)
C6–C4–C7	109 (1)		

Results and Discussion

The transformations observed in this work are summarized in Scheme I. The dinuclear osmium complex with one bridging I and two cis terminal ligands, $(\mu\text{-I})Os_2(CO)_6(\mu\text{-OCNHCHMe}_2)I_2$ (**2a**), was fully characterized by a single-crystal X-ray diffraction study, which is described below. Careful NMR monitoring of the initial stage of the reaction of **1a** with iodine indicates that the reaction stoichiometry is 1:2. The IR spectrum of **2a** shows four absorption peaks in the terminal CO stretching region, and in addition, absorption peaks at 1606 (m), 1510 (m), and 1420 cm^{-1} in the amide region are also observed. The band at 1420 cm^{-1} could be due to the absorption of the N—C stretching of the amide group.[26] The peak at 1606 cm^{-1} could be assigned as the amide I and II bands corresponding to C═O stretching and

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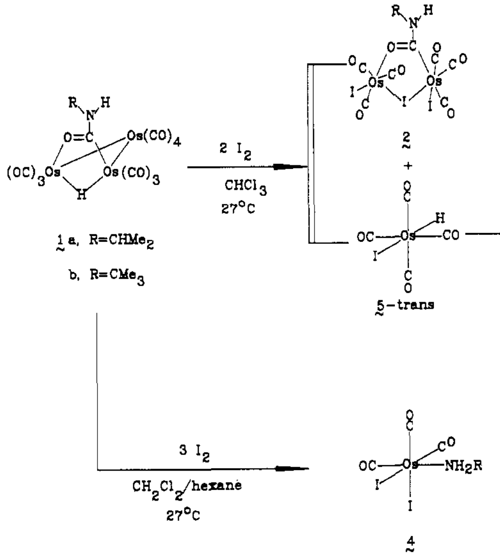
[26] Bellamy, L. J. *Advances in Infrared Group Frequencies*; Chapman and Hall: London, 1975; pp 238–250.

Scheme I



NH bending. This is about 80 cm^{-1} lower than that of the dilute primary amide solution.[27] By contrast, no absorption could be detected in this amide region for the bridged carboxamido group in the triosmium cluster complex **1a**. Six terminal carbonyl ligands are detected in the ^{13}C NMR spectrum of **2a**, with the absorption peak assignable to the carboxamido carbon occurring at 209.57 ppm. The mass spectrum of **2a** shows the parent peak at m/e 1016 as well as fragmentation assignable to M − CO$^+$.

Under the reaction conditions, the μ-η^2-carboxamido ligand exhibits higher stability than the Os(CO)$_4$ group, also bridging the same two osmium atoms despite the fairly strong Os–Os bond.[28] The bridging iodine is a three-electron-donor ligand; therefore, no metal–metal bond is expected between the two osmium atoms of **2a**. This is confirmed by the single-crystal structure determination described below.

The fragmentation product *trans*-HIOs(CO)$_4$ (**5**-*trans*) is also observed in the reaction of complex **1a** with 2 equiv of iodine, as is required by the stoichiometry. The ^{1}H NMR spectrum of this product shows a hydride peak at $\delta = -11.77$. The ^{13}C NMR spectrum shows only one peak at 167.96 ppm. On the basis of the symmetry, the mononuclear complex *trans*-HIOs(CO)$_4$ (**5**-*trans*) is assumed. A cis coupling between H and the C of a cis CO, $J_{C-H} = 5.36$ Hz, is observed. Complex **5**-*trans* is unstable in solution and, over 2 days, transforms to a new hydride complex that gives a peak at $\delta = -8.04$, assigned as *cis*-HIOs(CO)$_4$ (**5**-*cis*). Three J_{C-H} coupling constants are observed in the ^{13}C NMR spectrum: 22.89 Hz for the trans and 7.17 and 5.48 Hz for the two cis carbonyls, respectively. Complex **5**-*cis* is also unstable and eventually transforms into the *cis*-diiodo complex I$_2$Os(CO)$_4$ (**6**)[24] with the excess I$_2$ in the system. An attempt to isolate **5**-*trans* by column chromatography led to its transformation first to **5**-*cis* and then to **6**.

Exclusive formation of *trans*-HIOs(CO)$_4$ in the early stage of the reaction deserves some comment: this is the kinetically controlled product, since it isomerizes to **5**-*cis* in solution. Cleavage of the Os–Os bonds could possibly occur simultaneously with the formation of *trans*-HIOs(CO)$_4$ with certain regiospecificity.

Reaction of 1a with 3 equiv of I$_2$ in a 50% CH$_2$Cl$_2$/n-hexane solution caused a complete cleavage of the trinuclear cluster, to yield the mononuclear amine complexes Os(CO)$_3$(NH$_2$R)I$_2$ (R: CHMe$_2$, **4a**; *t*-Bu, **4b**). Complexes **4a** and **4b** were characterized by IR, NMR, and mass spectra, and complex **4b** was also characterized by a single-crystal X-ray diffraction study. In the ^{1}H NMR spectra, change of the NH$_2$ absorption peak in CDCl$_3$ from 6.63 ppm in the carboxamido dinuclear complex to 3.68 ppm in the mononuclear complex is significant; in **4**, the nitrogen atom is attached directly to the more electropositive metal atom instead of to an electron-withdrawing carbonyl group. Only two absorption peaks are observed in the terminal CO region in the ^{13}C NMR spectrum, indicating the presence of a reflection plane. There are examples for this type of transformation, namely, from carbamoyl to amine ligand.[27] The other major product isolated by column chromatography is the diiodo complex **6**.

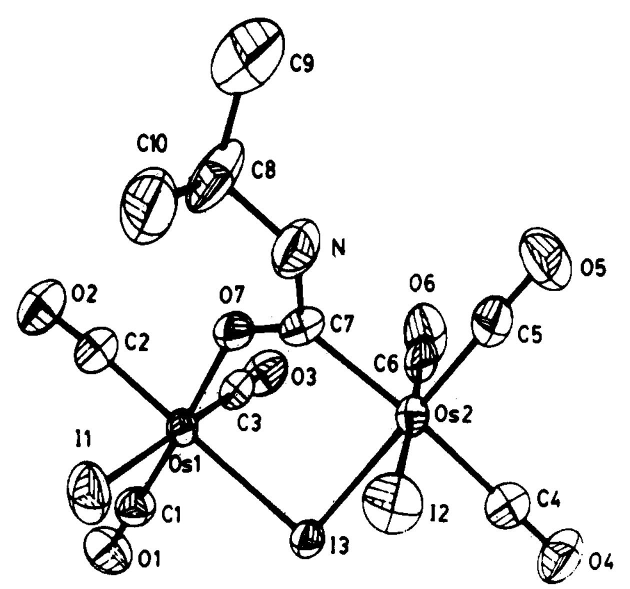


Figure 1. ORTEP drawing of (μ-I)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)I$_2$.

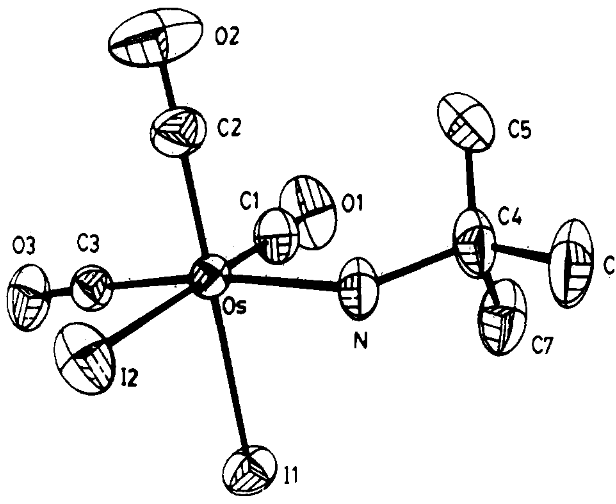


Figure 2. ORTEP drawing of Os(CO)$_3$(NH$_2$CMe$_3$)I$_2$.

The behavior of the reaction of **1** with bromine is somewhat similar to that of iodine. Reaction with 2 equiv of bromine in chloroform also yields a dinuclear osmium complex, (μ-Br)Os$_2$(CO)$_6$(μ-OCNHCHMe$_2$)Br$_2$. Its transformation pathway basically follows that of the iodine system. However, a greater excess of the Br$_2$ is needed in order to produce the final mononuclear complex Os(CO)$_3$(NH$_2$R)Br$_2$.

Crystal Structures of 2a and 4b. The structures of complexes **2a** and **4b** were determined by single-crystal X-ray diffraction studies. Both crystals consist of discrete molecular units. ORTEP drawings of the molecular complexes **2a** and **4b** are shown in Figures 1 and 2, respectively. Selected interatomic distances and their estimated standard deviations (esd's) are collected in Table IV. Selected bond angles with esd's are listed in Table V. In complex **2a**, two osmium metal centers, each with three terminal carbonyl ligands, are bridged by both a μ-η^2-carboxamido ligand and an iodine atom. Pseudooctahedral geometry is observed around both metals. For **2a**, the metal atoms are separated by 4.03 Å, indicating no metal–metal interaction, and none is expected by the EAN rule. When two metals are bridged by a carboxamido ligand and a one-electron-donor ligand, i.e. hydride, such as that

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[27] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

[28] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

in (μ-H)$Os_3(CO)_{10}$(μ-OCNHR), the M-M separation is found to be in the range 2.6-3.0 Å. In those cases, there should be an M-M bond according to the EAN rule. In complex **2a**, where the bridging iodine should be considered as a three-electron donor, no M-M bond is required in order to conform to the EAN rule. One could reasonably expect a longer M-M separation. The Os1-O7 and Os2-C7 distances are 2.056 (5) and 2.102 (7) Å, respectively. The Os-C(CO) distances are somewhat longer for two CO ligands trans to the terminal iodine ligand (1.92, 1.95 Å); the longest (1.98 Å), however, is observed for the CO trans to the carboxamido carbon atom. The carboxamido ligand shows partial double-bond character for both C=O (1.28 Å) and CN (1.34 Å) bonds, similar to many other complexes of the same type. For complex **4b**, pseudooctahedral geometry is again observed, exemplified by the cis interligand bond angle within the range 84.3 (2)-97.0 (4)° around the osmium metal. The three CO ligands are arranged in a facial configuration, with a somewhat longer Os-C distance for the CO trans to the amine ligand. The longer Os-N separation (2.197 (9) Å) than Os-C_{av} (1.89 (1) Å) clearly indicates the π-acid character of the CO ligand. The Os-I separations, 2.735 (1) and 2.736 (1) Å, are normal bonding Os-I distances.

Acknowledgment. This work was supported by the National Science Council, Republic of China.

Registry No. **1a**, 113600-31-0; **1b**, 113600-36-5; **2a**, 113600-32-1; **4a**, 113600-34-3; **4b**, 113600-35-4; *trans*-**5**, 113600-33-2; *cis*-**5**, 113666-89-0; **6**, 17632-05-2; (μ-Br)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)Br_2, 113600-37-6; I_2, 7553-56-2; OHCNHCHMe$_2$, 16741-46-1; OHCNHCMe$_3$, 2425-74-3.

Supplementary Material Available: For the structure determinations of (μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)I_2 and $Os(CO)_3(NH_2CMe_3)I_2$, tables of anisotropic thermal parameters and complete interatomic distances and bond angles (4 pages); listings of calculated and observed structure factors (57 pages). Ordering information is given on any current masthead page.

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Thermal and Photochemical Reactions of $Ru_3(CO)_{12}$ Adsorbed onto Porous Vycor Glass

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$Ru_3(CO)_{12}$ physisorbs onto porous Vycor glass, PVG, without disruption or significant distortion of the complex. UV photolysis in vacuo and thermolysis at $T < 100$ °C lead to oxidative addition of a surface silanol group and quantitative formation of (μ-H)$Ru_3(CO)_{10}$(μ-OSi$_{surf}$). The activation energies for formation of (μ-H)$Ru_3(CO)_{10}$(μ-OSi$_{surf}$), 6.2 ± 0.4 kcal/mol, and regeneration of $Ru_3(CO)_{12}$ in the presence of CO, 5.1 ± 0.4 kcal/mol, suggest that these species are in dynamic equilibrium on the glass surface. The photoinduced oxidative addition is independent of excitation wavelength and occurs with a quantum yield of $(1.6 \pm 0.3) \times 10^{-2}$ with 350-nm excitation. The photochemistry of the adsorbed complex is interpreted within the current solution phase model where the specificity of the reaction arises not from chemical factors but from the rigidity and low dimensionality of the support.

Introduction

Interest in organometallic chemistry arises not only from the interdisciplinary nature of the chemistry, but the practical applications of these complexes in catalysis. Ruthenium complexes, for example, have been recognized as active catalysts of a number of transformations.[1-7] An alternative to homogeneous catalysis is to bind a potentially active reagent to a support, i.e., assemble a hybrid system.[8-10] $Ru_3(CO)_{12}$ physisorbs onto alumina and silica with the metal framework intact, and the adsorbed complex thermally decomposes to mononuclear species.[11] Basset and co-workers report that thermal activation of $Ru_3(CO)_{12}$ on silica gel leads to oxidative addition of a silanol group.[12] The grafted cluster, $HRu_3(CO)_{10}$(OSi), decomposes at ≥100 °C to form aggragated metal particles covered with CO and a Ru(II) carbonyl species. On high surface area supports under H_2, thermal decomposition of $Ru_3(CO)_{12}$ at 350-400 °C yields small metal particles with a crystallite size of 15-20 Å that exhibit enhanced activity and selectivity in the hydrogenolysis of straight-chain hydrocarbon to methane.[13]

With few exceptions, the catalytic activity of Ru complexes, whether in homogeneous[1-7] or heterogeneous[8-18] systems, requires high temperatures and pressures. Consequently, there is an interest in the photochemical reactivity of these complexes. Photoactivation offers a route to catalytic intermediates under less stringent conditions and, since the thermal and photochemical reactions of $Ru_3(CO)_{12}$ differ,[19] the possibility of new reactive intermediates.

The photochemistry of $Ru_3(CO)_{12}$ in fluid solution has been interpreted in terms of cleavage of a Ru-Ru bond[20] and formation of an isomeric form of the ground state.[21] In a recent, extensive

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(1) Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1978**, *145*, 189.
(2) Sanchez-Delgado, R. A.; deOchoa, O. L. *J. Mol. Catal.* **1979**, *6*, 303-5.
(3) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229-41.
(4) Castiglioni, M.; Milone, L.; Osella, D.; Vagilio, G. A.; Valle, M. *Inorg. Chem.* **1976**, *15*, 394-6.
(5) Knifton, J. F. *J. Mol. Catal.* **1980**, *11*, 91-105.
(6) King, R. B.; King, A. D.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75-83.
(7) Johnson, T. H.; Siegle, L. A.; Chaffin, J. K. *J. Mol. Catal.* **1980**, *9*, 307-11.
(8) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109-48.
(9) Ichikawa, M. *CHEMTECH* **1982**, 674-80.
(10) Basset, J. M.; Choplin, A. J. *J. Mol. Catal.* **1983**, *21*, 95-108.
(11) Kuznetsov, V. L.; Bell, A. T.; Yermakov, Y. I. *J. Catal.* **1980**, *65*, 374-9.
(12) Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M.; Zanderighi, G.; Sourisseau, C. *Polyhedron* **1983**, *2*, 119.
(13) Simpson, A. F.; Whyman, R. *J. Organomet. Chem.* **1981**, *213*, 157.
(14) Smith, A. K.; Theolier, A.; Basset, J. M.; Ugo, R.; Commereuc, D.; Chauvin, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2590-1.
(15) Verdonck, J. J.; Jacobs, P. A.; Uytterhoven, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 181.
(16) Goodwin, J. G.; Naccache, C. *J. Mol. Catal.* **1982**, *14*, 259.
(17) Sanchez-Delgado, R. A.; Duran, I.; Monfort, J.; Rodriguez, E. *J. Mol. Catal.* **1981**, *11*, 193-203.
(18) Zecchina, A.; Guglielminotti, E.; Bossi, A.; Camia, M. *J. Catal.* **1982**, *74*, 225, 240, 266.
(19) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1975**, 876; *J. Organomet. Chem.* **1974**, *67*, C75-6.
(20) Wrighton, M. S. *Ann. N.Y. Acad. Sci.* **1980**, Vol *333*, 188-207.
(21) Malito, J.; Markiewicz, S.; Poe, A. *Inorg. Chem.* **1982**, *21*, 4335-7.

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