supply oxidizing equivalents to generate Co(IV) on which the O–O bond is assembled. In these reactions the role of Ru(III) is in contrast to recently described systems in which Ru(II)/(IV) couples, etc. effect inner-sphere water oxidation.

Acknowledgment. We are indebted to Drs. Mark A. Andrews and Tony Chang, who made the IR and NMR measurements and whose comments have been extremely helpful. We also thank Ms. Elinor Norton, who performed analyses for ruthenium. This work was performed at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. $Ru(bpy)_2(bpyO)^{2+}$, 90912-91-7; $Ru(bpy)_3^{3+}$, 18955-01-6; Co, 7440-48-4; H_2O, 7732-18-5.

Supplementary Material Available: Method for chemiluminescence yield calibration and rate constants for $Ru(bpy)_3^{3+}$ reduction at pH 7 as a function of Ru(III) and Ru(II) concentrations (5 pages). Ordering information is given on any current masthead page.

Trinuclear Osmium Clusters as Models for Intermediates in CO Reduction Chemistry. 2. Conversion of a Methylene into a Ketene Ligand on a Triosmium Cluster Face

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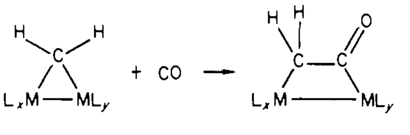
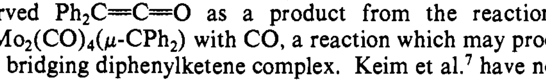
Abstract: The bridging methylene complex $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (**3**) reacts with CO to give the new ketene complex $Os_3(CO)_{12}(\eta^2\text{-}(C,C),\mu_2\text{-}CH_2CO)$ (**4**) in high yield. Complex **4** has been spectroscopically as well as structurally characterized. It crystallizes in the space group $P2_1/n$, with $a = 9.414$ (2) Å, $b = 15.369$ (3) Å, $c = 13.940$ (4) Å, $\beta = 107.9$ (2)°, $V = 1918.6$ (7) Å,[3] and $Z = 4$. Least-squares refinement of the 3015 reflections with $(F_o)^2 > 3\sigma(F_o)^2$ converged to $R = 0.033$ and $R_w = 0.034$. The ketene ligand is incorporated into a triosmacyclopentanone ring and bridges between two Os atoms that are not joined by a metal–metal bond. Bond angles imply sp^3 and sp^2 hybridization for the CH_2 and CO carbon atoms, respectively. Complex **4** reacts with H_2O and CH_3OH to yield CH_3COOH and CH_3COOCH_3, respectively, along with $Os_3(CO)_{12}$. Reaction of **4** with H_2 yields CH_3CHO and the clusters $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$. The formation of **4** can be partially reversed to **3** by heating in vacuo, although the thermal instability and moisture sensitivity of **4** preclude quantitative recovery of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Carbon-13 labeling experiments show that the ketene carbonyl derives from one of the original cluster carbonyls rather than from the added CO. The possible relevance of the $\mu\text{-}CH_2 \rightarrow \mu\text{-}CH_2CO$ conversion to the mechanism of formation of C_2-oxygenated products during CO reduction catalysis is discussed.

A large number of methylene-bridged transition-metal compounds have been prepared, and their chemistry is under active investigation.[2] However, one important reaction that has not been well-documented for this class of compounds is the insertion of CO into a metal–methylene bond to yield a coordinated ketene, eq 1. Such reaction may be of relevance to the mechanism for chain growth during CO reduction over heterogeneous catalysts where surface-bound methylene ligands are believed important.[3] In particular, the CO insertion into a metal–methylene bond to give a surface ketene ligand could be an important step in the formation of C_2-oxygenated products. Such reaction has been suggested by Ichikawa et al.[4a] to play an important role in the high-yield formation of ethanol from CO/H_2 over certain $Rh/ZrO_2/SiO_2$ and $Rh/TiO_2/SiO_2$ catalysts, eq 2. Recent isotopic tracer experiments on ethanol synthesis from CO/H_2 by Takeuchi and Katzer[4b] also indicate that this product forms via CO insertion into a surface-methylene bond as indicated in eq 2.



(1)



(2)

A few mononuclear carbene complexes have been shown to insert or add CO to give complexes containing ketene ligands.[5] Only recently has evidence been obtained for similar reactions with polynuclear μ-carbene complexes. Curtis and Messerle[6] observed $Ph_2C{=}C{=}O$ as a product from the reaction of $Cp_2Mo_2(CO)_4(\mu\text{-}CPh_2)$ with CO, a reaction which may proceed via a bridging diphenylketene complex. Keim et al.[7] have noted that $Fe_2(CO)_8(\mu\text{-}CH_2)$ reacts with methanol and ethanol in the presence of CO to yield the corresponding acetates and presented evidence that these reactions proceed through the unstable bridging ketene complex **1**, eq 3. Lin et al.[8] recently reported insertion

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[1] (a) The Pennsylvania State University. (b) The University of Delaware.

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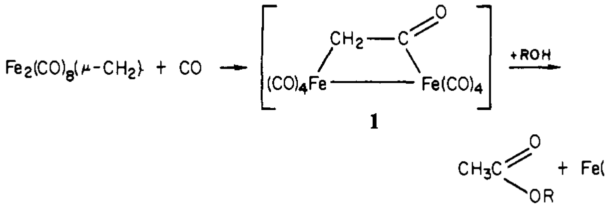
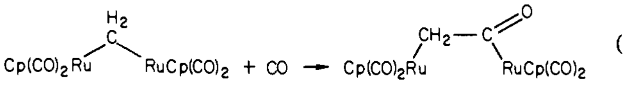


(3)

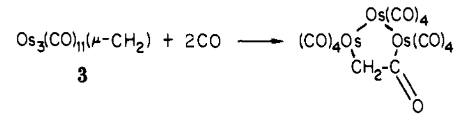
of CO into the Ru-CH$_2$ bond of Cp$_2$Ru$_2$(CO)$_4$(μ-CH$_2$) to give the bridging ketene complex **2**, eq 4. This complex was spectroscopically but not structurally characterized.



(4)

2

We describe herein the reaction of Os$_3$(CO)$_{11}$(μ-CH$_2$) (**3**) with CO to give the stable ketene derivative Os$_3$(CO)$_{12}$(η^2-(C,C),μ_2-CH$_2$CO), hereafter abbreviated as Os$_3$(CO)$_{12}$(μ-CH$_2$CO) (**4**), eq 5.[9] This complex has been fully characterized by a single-crystal X-ray diffraction study which gives the first structural parameters for a polynuclear ketene complex of any type.[10] Also described are the reactivity properties of **4**, including its reactions with H$_2$ and nucleophiles and its loss of CO to regenerate Os$_3$(CO)$_{11}$(μ-CH$_2$). Important IR spectroscopic data which could prove useful in the search for ketenes on metal surfaces is also tabulated.



3

4

(5)

Experimental Section

The complex Os$_3$(CO)$_{11}$(μ-CH$_2$) was prepared by published procedures.[11] Carbon monoxide (CP grade) was obtained from Matheson or Airco (grade 2.3) and used as received. ^{13}CO (90% ^{13}C) was obtained from the Monsanto Research Corp., Mound Laboratories, Columbus, OH. Solvents used were dried and degassed by standard methods. All manipulations, unless otherwise specified, were conducted under prepurified N$_2$ with use of standard Schlenk and high vacuum line techniques. Infrared spectra were obtained on Perkin-Elmer Model 580 IR and IBM FT IR/32 spectrometers with 0.5- and 0.2-mm NaCl solution cells or KBr pellets. NMR spectra were recorded on Bruker WP-200 Fourier Transform and Varian EM-360 NMR spectrometers. Cr(acac)$_3$ was added to all ^{13}C NMR samples as a shiftless relaxation agent.[12] Electron impact mass spectra were obtained by R. J. Hale at the Tennessee Eastman Co., Kingsport, TN. Gas chromatography was conducted with use of a 1400 series Varian Aerograph FID gas chromatograph with 1 m × $^1/_8$ in. Porapak Q, 12 ft. × $^1/_8$ in. Poropak N, and 10 ft. × $^1/_8$ in. 10% carbowax columns. GC/MS spectra were recorded on a Finnegan 3200 GC/MS equipped with a Finnegan 6000 data system with a 6 ft. × $^1/_8$ in. Poropak QS column.

Preparation of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) (4). Os$_3$(CO)$_{11}$(μ-CH$_2$) (0.514 g, 0.576 mmol) in 2.5 mL of CH$_2$Cl$_2$ (distilled from BaO in vacuo) was placed in a 50-mL Schlenk flask, and 1 atm of CO was admitted. After the mixture was stirred for 9.0 h, a yellow-orange solution with a yellow precipitate of Os$_3$(CO)$_{12}$ was obtained. The solvent and volatile products were removed by vacuum distillation and collected in a trap cooled to liquid nitrogen temperature. Fresh CH$_2$Cl$_2$ (~4.0 mL) was distilled into the reaction flask, and the solution filtered to removed Os$_3$(CO)$_{12}$ (0.0923 g, 0.102 mmol, 17.7%). Solvent was removed from the filtrate to yield crude yellow Os$_3$(CO)$_{12}$(μ-CH$_2$CO) (**4**) (0.415 g, 0.48 mmol, 76%). This was recrystallized by dissolution in 3.0 mL of CH$_2$Cl$_2$ followed by addition of 6.0 mL of hexane. When the solution was cooled to ca. −50 °C, buff colored microcrystals of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) deposited. These were collected by decanting the solvent under N$_2$ and washing with cold (0 °C) hexanes to give **4** in 39% yield (0.214 g, 0.226 mmol). Anal. Calcd for C$_{14}$H$_2$O$_{13}$Os$_3$: C, 17.71; H, 0.21. Found: C, 17.89; H, 0.38. GC/MS analysis of the volatile distillate from above showed the presence of diketene (*m/e* 84 (M$^+$), 56 (M$^+$ − CO), 42 (M$^+$ − CH$_2$CO)). Quantitation by GC (Poropak Q, $^1/_8$ in. × 1 m; CH$_2$Cl$_2$ solvent; temperature programmed 70 °C → 190 °C at 8 °C/min) showed the formation of diketene in 3% yield.

Decomposition of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) in vacuo. Os$_3$(CO)$_{12}$(μ-CH$_2$CO) (~0.010 g, 0.011 mmol) in ca. 2 mL of CDCl$_3$ was placed in a 5-mm degassable NMR tube and its ^{1}H NMR spectrum obtained. The tube was subsequently evacuated by 3 freeze–pump–thaw cycles, sealed, and then immersed in a water bath at 60–64 °C. After 0.5 h, the sample was removed and a second ^{1}H NMR spectrum recorded. This showed that Os$_3$(CO)$_{11}$(μ-CH$_2$) was present in 8% yield based upon the Os$_3$(CO)$_{12}$(μ-CH$_2$CO) consumed (~97%) by comparison of the integrated NMR peak intensities of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) and Os$_3$(CO)$_{11}$(μ-CH$_2$) to those of the residual CHCl$_3$ protons in the solvent.

Reaction of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) with H$_2$. Os$_3$(CO)$_{12}$(μ-CH$_2$CO) (35 mg, 0.037 mmol) in 1.0 mL of CDCl$_3$ was placed in a 5-mm NMR tube inside a carefully dried Parr Model 4564 pressure reactor and pressurized with 1800 psi of ultrapure hydrogen (Matheson, 99.999%) and allowed to react for 5 days. After the pressure was released, the ^{1}H NMR spectrum of the CDCl$_3$ solution showed resonances due to acetic acid (δ 5.2 (br s, 1 H), δ 2.08 (s, 3 H)), acetaldehyde (δ 9.08 (q 1 H, J = 2.9 Hz), δ 2.20 (d, 3 H)), and unreacted Os$_3$(CO)$_{12}$(μ-CH$_2$CO). Chromatography of the solution gave three major fractions: H$_2$Os$_3$(CO)$_{10}$ (ν_{CO} 2077 s, 2065 s, 2028 vs, 2012 s, 1990 m cm^{-1} (lit.[13a] ν_{CO} 2112 vw, 2076 s, 2063 m, 2026 s, 2011 s, 1989 w, 1973 vw, 1957 vw cm^{-1})), Os$_3$(CO)$_{12}$, and H$_4$Os$_4$(CO)$_{12}$ (ν_{CO} 2090 m, 2070 s, 2020 s, 1999 m cm^{-1} (lit.[13a] ν_{CO} 2086 m, 2069 s, 2022 s, 2000 m cm^{-1})). Integration showed the acetyl protons of acetic acid (δ 2.08) and acetaldehyde (δ 2.20) to be present in a 4.03:1 ratio. The combined yield of these two products was 96% based on the amount of Os$_3$(CO)$_{12}$(μ-CH$_2$CO) reacted (65%) by integration with CH$_2$Cl$_2$ as the internal standard. Both products were also identified by GC retention times. The ^{1}H NMR resonance of H$_2$Os$_3$(CO)$_{10}$ at δ −11.46 accounted for >75% of the integrated intensity of all hydride resonances.

Reaction of Os$_3$(CO)$_{11}$(μ-CH$_2$) with CH$_3$OH/CO. Os$_3$(CO)$_{11}$CH$_2$ (0.030 g, 0.034 mmol) in 1.5 mL of CDCl$_3$ was placed in a 20-mL Schlenk flask, and 0.100 mL of a 0.67 M solution of CH$_3$OH in CDCl$_3$ was added via syringe. The solution was stirred under 1 atm of CO for 9 h to yield a light yellow solution and a yellow precipitate of Os$_3$(CO)$_{12}$. The volatile products were removed by vacuum distillation. IR analysis of the residue showed only Os$_3$(CO)$_{12}$ present. Methyl acetate was identified in the distillate by comparison of its IR spectrum (ν_{CO} 1735 cm^{-1}) to that of an authentic sample, and methyl acetate was the only compound observed in the ^{1}H NMR spectrum of the distillate. In a separate experiment conducted in a sealed NMR tube, integration with CH$_2$Cl$_2$ as an internal standard in the CDCl$_3$ solvent showed methyl acetate to be formed in 105 ± 10% yield.

Reaction of Os$_3$(CO)$_{12}$(μ-CH$_2$) with H$_2$O/CO. Os$_3$(CO)$_{11}$CH$_2$ (0.0592 g, 0.066 mmol) in 8 mL of THF was placed in a 20-mL Schlenk flask, and 0.100 mL of a 6.67 M solution of H$_2$O in THF was added via syringe. The solution was stirred for 14 h under 1 atm of CO to yield a light yellow solution and a yellow microcrystalline precipitate of Os$_3$(CO)$_{12}$. The solution was filtered through glass wool and Celite. The IR spectrum of the supernatant liquid showed Os$_3$(CO)$_{12}$ to be the only organometallic product. Acetic acid in the supernatant liquid was identified by comparison of its infrared spectrum (ν_{CO} 1753, 1728 cm^{-1}) to that of an authentic sample. The yield of acetic acid in the supernatant liquid was determined to be 103 ± 5% by titration with standardized NaOH. In a separate experiment, Os$_3$(CO)$_{11}$(μ-CH$_2$) (0.00995 g, 0.011 mmol) in 0.5 mL of THF-d_8 was placed in a 5-mm NMR tube and 3.00 μL of H$_2$O (0.166 mmol) and 2.0 μL of CH$_2$Cl$_2$ (as an internal standard) were added via microliter syringe. After the reaction had proceeded for 48 h under 1 atm of CO, ^{1}H NMR indicated that no Os$_3$(CO)$_{11}$(μ-CH$_2$)

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[9] A preliminary account of this research has appeared: Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4104.

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Table I. Crystal and Refinement Data for $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (**4**)

Crystal Parameters			
formula	$Os_3C_{14}H_2O_{13}$	a, Å	9.414 (2)
formula wt	948.6	b, Å	15.369 (3)
cryst system	monoclinic	c, Å	13.940 (4)
space group	$P2_1/n$	β, deg	107.9 (2)
ρ(calcd), g cm^{-3}	3.28	V, Å	1918.6 (7)
temp, °C	23	Z	4
cryst dimens, mm	0.11 × 0.14 × 0.31		

Measurement of Intensity Data	
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
μ, cm^{-1}	209.3
scan speed, deg/min	variable 3–15
scan width, deg	$1.6 + \Delta(\alpha_1 - \alpha_2)$
2θ scan range, deg	$4 < 2\theta < 52$
scan technique	θ–2θ
data collected	$\pm h, k, l$
no. of independent refln collected	3331
no. with $(F_o)^2 > 3\sigma(F_o)^2$	3015
std reflns	3197 (3% decay, corrected)
weighting factor, g	0.0009 (fixed)
RF	0.0332
RwF	0.0342
GOF	1.053

remained and CH_3CO_2H was present in 87 ± 10% yield based on reacted $Os_3(CO)_{11}(\mu\text{-}CH_2)$. No other products were observed.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CD_3CN/CH_3OH. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (0.035 g, 0.039 mmol) in 1.0 mL of $CDCl_3$ was placed in a 5-mm NMR tube, and 5.0 μL of CH_3OH (0.123 mmol) and 30.0 μL of CD_3CN (0.540 mmol) were added via syringe. After 1 week at 22 °C, the ^1H NMR spectrum showed no $Os_3(CO)_{11}(\mu\text{-}CH_2)$ present and $CH_3CO_2CH_3$ as the only observable product. The IR spectrum of the solution also indicated the presence of $CH_3CO_2CH_3$ (ν_{CO} 1735 cm^{-1}) and $Os_3(CO)_{11}(CD_3CN)$ (ν_{CO} 2053 s, 2040 s, 2020 s, 2008 vs, 1985 sh (lit.[13b] ν_{CO} 2052 s, 2040 s, 2020 m, 2000 vs, 1984 sh, 1981 m, 1969 vw, 1960 vw)).

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with $H_2O/CH_3OH/CO$. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ 0.0580 g, 0.0650 mmol) was placed in a 20-mL Schlenk flask, and 0.5 mL of a 1.37 M solution of H_2O in THF-d_8 and 0.5 mL of a 1.37 M solution of CH_3OH in THF-d_8 were added. The mixture was frozen and evacuated. Carbon monoxide was admitted to the evacuated flask to a pressure of 1 atm. The solution was stirred for 16 h, and the volatile products were removed by vacuum distillation to dryness. The ^1H NMR spectrum of the distillate showed the acetyl protons of acetic acid and methyl acetate to be present in a ratio of 0.99:1.

Reaction of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ with H_2O/CH_3OH. $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (0.0479 g, 0.0505 mmol) was placed in a 20-mL Schlenk flask under N_2, and 30 μL of a 50:50 molar mixture of H_2O and CH_3OH and 1 g of THF-d_8 were added. This mixture was divided into two portions and each placed in 5-mm NMR tubes. One was sealed under ~2.5 atm of CO and the other was sealed under N_2. These were turned upside down so the $Os_3(CO)_{12}$ precipitate produced would remain in the top and the reaction was allowed to continue for 24 h. NMR analysis showed formation of acetic acid and methyl acetate in ratios of 2.46:1 under CO and 2.04:1 under N_2.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with $^{13}CO/CH_3OH$. A sample of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (0.030 g, 0.0336 mmol) which was ~25% ^{13}C enriched in all carbons, prepared from ~25% ^{13}C enriched $Os_3(CO)_{12}$, in 4 mL of $CDCl_3$ was placed in a 20-mL Schlenk flask and 0.100 mL of a 1.33 M solution of CH_3OH in $CDCl_3$ was added via syringe. The solution was stirred under 1 atm of 90% ^{13}CO for 14 h, yielding a light yellow solution and a yellow microcrystalline precipitate of $Os_3(CO)_{12}$. The solution was filtered through glass wool and Celite into a 10-mm NMR tube. To this was added 2 mg of $Cr(acac)_3$ as a relaxation agent.[12] The ^{13}C NMR spectrum was recorded with an inverse-gated pulse sequence with a pulse width of 7.0 s to ensure that the recorded integrals for the observed nuclei were unaffected by their relaxation times. The ^{13}C NMR spectrum showed the carbonyl (δ 171.6) and methyl (δ 20.7) signals of the methyl acetate product to have relative integrals of 1.06:1. Carbon-13 satellites for the methyl and carbonyl resonances indicate that the ratio of methyl acetate labeled *only at the carbonyl carbon* to methyl acetate *labeled only at the methyl carbon* was 0.87:1.

In a separate experiment, $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (0.067 g, 0.076 mmol) in 4 mL of CH_2Cl_2 was placed in a 20-mL Schlenk flask, and 15 μL of MeOH was added via syringe. The solution was allowed to stir under 90% ^{13}CO for 14 h, and the volatile products were removed by vacuum distillation. Infrared examination of the organic carbonyl region showed only $\nu_{^{12}CO}$ for methyl acetate at 1735 cm^{-1}, and no $\nu_{^{13}CO}$ at 1698 cm^{-1} for ^{13}C-methyl acetate was observed.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (**4**)

atom	x	y	z	U
Os(1)	3533 (1)	1275 (1)	639 (1)	31 (1)[a]
Os(2)	3173 (1)	1312 (1)	2659 (1)	31 (1)[a]
Os(3)	4824 (1)	3084 (1)	908 (1)	29 (1)[a]
O	6392 (7)	1855 (5)	3372 (5)	45 (3)[a]
Ck(1)	5111 (11)	2139 (7)	2915 (6)	36 (3)[a]
Ck(2)	4984 (11)	3035 (6)	2527 (6)	37 (3)[a]
Hk(2a)	4099	3291	2611	37
Hk(2b)	5841	3365	2902	37
O(1)	3959 (10)	1289 (5)	−1435 (5)	65 (4)[a]
O(2)	2361 (12)	−586 (5)	450 (7)	87 (5)[a]
O(3)	6774 (8)	644 (5)	1655 (6)	55 (3)[a]
O(4)	360 (8)	2020 (6)	18 (6)	56 (3)[a]
O(5)	1141 (8)	2932 (6)	2183 (6)	58 (3)[a]
O(6)	3250 (9)	1377 (6)	4866 (6)	69 (4)[a]
O(7)	5405 (9)	−230 (5)	3180 (6)	64 (4)[a]
O(8)	334 (9)	159 (7)	1895 (7)	82 (4)[a]
O(9)	4772 (8)	3169 (5)	−1301 (5)	54 (3)[a]
O(10)	6160 (10)	4896 (5)	1260 (7)	76 (4)[a]
O(11)	8012 (8)	2306 (6)	1544 (6)	62 (3)[a]
O(12)	1701 (8)	3891 (5)	485 (6)	56 (3)[a]
C(1)	3814 (12)	1297 (7)	−656 (7)	45 (4)[a]
C(2)	2785 (13)	109 (7)	537 (7)	53 (4)[a]
C(3)	5579 (12)	888 (6)	1296 (7)	39 (4)[a]
C(4)	1534 (11)	1772 (7)	240 (7)	39 (4)[a]
C(5)	1871 (12)	2330 (7)	2324 (8)	43 (4)[a]
C(6)	3241 (11)	1375 (7)	4044 (7)	41 (4)[a]
C(7)	4591 (12)	331 (7)	2981 (7)	45 (4)[a]
C(8)	1390 (12)	566 (7)	2188 (8)	46 (4)[a]
C(9)	4735 (11)	3097 (6)	−508 (7)	38 (4)[a]
C(10)	5661 (12)	4213 (7)	1151 (8)	49 (4)[a]
C(11)	6819 (12)	2581 (7)	1315 (7)	42 (4)[a]
C(12)	2797 (11)	3561 (6)	606 (7)	38 (4)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal and Molecular Structure of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$. Crystals of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ were grown by slow evaporation of a CH_2Cl_2/cyclohexane solution at 4 °C under N_2. A suitable crystal was affixed to a glass fiber such that the long crystal dimension was perpendicular to the beam. Diffraction data were collected on a Nicolet R3 diffractometer controlled by a Data General Nova 4 computer. Lattice parameters were obtained from the least-squares fit of angular settings of 25 well-centered reflections, $25° \leq 2\theta \leq 30°$. The data collection and refinement procedures used were as previously reported;[14a] pertinent details are provided in Table I. The systematic absences uniquely identified the space group as $P2_1/n$. Lorentz and polarization corrections were applied to the data, but no satisfactory absorption correction could be obtained (see below). The atomic coordinates for the three Os atoms were obtained from the E map with the highest combined figures of merit generated by the direct-methods routine SOLV ($E_{min} = 1.8$, $E_{ref} = 0.6$), and the remaining non-hydrogen atoms were obtained from a difference map phased by the three Os atoms. Further refinement of a model containing an empirical (ψ-scan) absorption correction[14b] and all non-hydrogen atoms proved impossible as all of the carbon atoms of the terminal carbonyl groups were severely displaced toward the Os atoms along the approximate Os–C–O vectors while leaving the Os and O atoms in chemically reasonable locations. Only after removal of the correction for absorption was a normal refinement possible. With the incorporation of hydrogen atoms in fixed, idealized positions (d(C–H) = 0.96 Å), the refinement process smoothly converged to the residuals reported in Table I. The final difference map revealed no unusual features (highest peak = 0.883 e$^-$/Å^3). An inspection for trends in the values of F_o *vs.* F_c, Miller indices, parity groups, and sin θ showed that the omission of an absorption correction had not produced systematic errors in the data.

Refinement by blocked cascade, least-squares methods minimized the value of $\sum W\Delta^2$ ($\Delta = |F_o| - |F_o|$); $W^{-1} = \sigma^2(F + gF^2)$; $R_F = \sum|\Delta|/\sum|F_o|$; $RwF = \sum(|\Delta|w^{1/2})/(|F_o|w^{1/2})$; GOF = $[\sum w(\Delta^2)/N_{obsd} - N_{par})]^{1/2}$.

During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ terms. Final positional

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(14) (a) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327. (b) Thirty-six step ψ-scan data, av max/min I = 1.21.

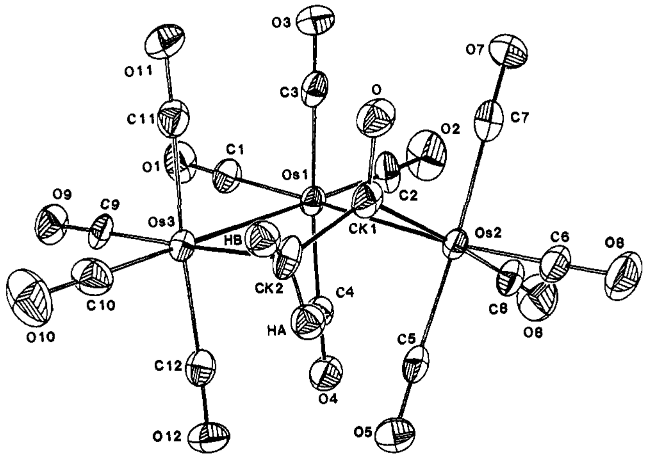
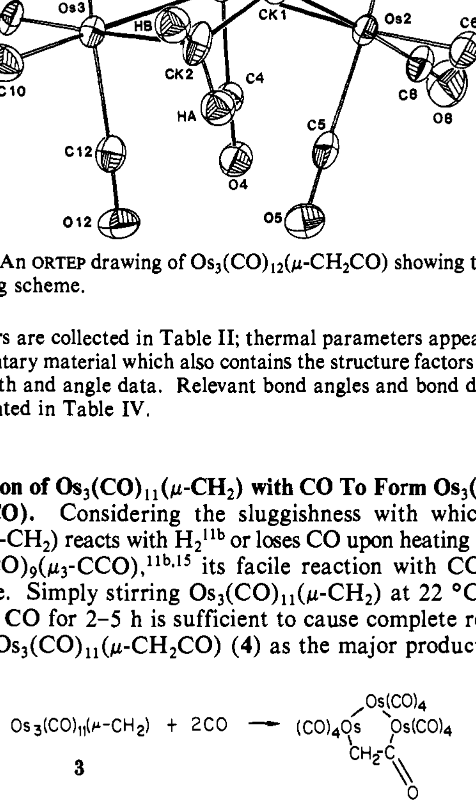


Figure 1. An ORTEP drawing of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ showing the atom numbering scheme.

parameters are collected in Table II; thermal parameters appear in the supplementary material which also contains the structure factors and full bond length and angle data. Relevant bond angles and bond distances are presented in Table IV.

Results

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CO To Form $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$. Considering the sluggishness with which $Os_3(CO)_{11}(\mu\text{-}CH_2)$ reacts with H_2[11b] or loses CO upon heating to form $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$,[11b,15] its facile reaction with CO is remarkable. Simply stirring $Os_3(CO)_{11}(\mu\text{-}CH_2)$ at 22 °C under 1 atm of CO for 2–5 h is sufficient to cause complete reaction to form $Os_3(CO)_{11}(\mu\text{-}CH_2CO)$ (4) as the major product, eq 6.



3 4 (6)

The reaction involves addition of 2CO's to 3; data summarized below indicate that an original cluster CO goes into the ketene ligand and two exogenous CO's add to become cluster carbonyls. This reaction also yields a significant quantity of $Os_3(CO)_{12}$ (18%). The latter likely results from reaction of an intermediate, unsaturated ketene complex with adventitious moisture in the CO (see below), or possibly by loss of free ketene from an intermediate ketene cluster. Diketene (*m/e* 84) was indeed detected by GC/MS in the volatile products of the reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CO, and its yield was determined by GC to be 3%. The isolated ketene complex $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ is relatively stable in the presence of CO as it yields only a trace of $Os_3(CO)_{12}$ over a 24-h period. The moisture sensitivity of 4 does not permit chromatographic purification, and it must be isolated by fractional crystallization. Complex 4 appears not to be O_2 sensitive, but it does react with H_2O to give acetic acid and $Os_3(CO)_{12}$ (see below).

Formation of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (4) from the methylene complex 3 is partially reversible, although the instability of 4 precludes its quantitative recovery. Thus, when a $CDCl_3$ solution of 4 is heated to 60–64 °C for 30 min under reduced pressure, the methylene-proton resonances of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ appear at ~8% of their expected intensity based on the amount of 4 consumed, eq 7. This observation is in accord with Arce and

$$\underset{4}{Os_3(CO)_{12}(\mu\text{-}CH_2CO)} \xrightarrow[30\ \text{min}]{60\text{–}64\ °\text{C, } \textit{in vacuo}} 2CO + \underset{3}{Os_3(CO)_{11}(\mu\text{-}CH_2)} \quad (7)$$

Deeming's[16] recent preparation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ from the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with ketene, a synthesis which likely proceeds through a ketene complex which readily de-inserts.

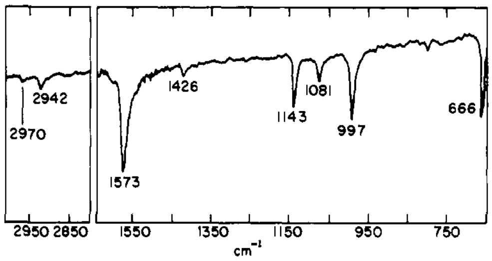


Figure 2. IR spectrum of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ in a KBr disk in the 3000–2800- and 1800–600-cm^{-1} spectral regions.

Table III. Vibrational Frequencies of the μ-CH_2CO Ligand in Complex 4

mode	ν, cm^{-1}	mode	ν, cm^{-1}
antisymmetric C–H stretch	2970 (vw)	CH_2 wag	1143 (m)
symmetric C–H stretch	2942 (w)	CH_2 twist	1081 (w)
C–O stretch	1573 (s)	CH_2 rock	997 (m)
CH_2 deformation	1426 (w)	Os–C stretch	666 (m)

Spectroscopic Characterization of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$. An ORTEP drawing of 4 (see below) is shown in Figure 1, and the spectroscopic data are consistent with the determined structure. Complex 4 shows an electron impact mass spectrum with a parent ion at *m/z* 948 and a strong fragment ion at *m/z* 906, consistent with loss of the CH_2CO ligand from the parent. Fragment ions corresponding to the subsequent, successive loss of 12 CO's are also present. The ^1H NMR spectrum of 4 shows a broad singlet at δ 2.77 ($\nu_{1/2}$ 11 Hz) attributed to the two methylene protons. The crystal structure of 4, Figure 1, shows that the methylene protons are not equivalent. Thus the single resonance implies rapid exchange of the protons by inversion of the Os_3C_2 ring or an accidental chemical shift equivalence of the protons. The ^{13}C NMR spectrum of 4 shows an acyl resonance at 219.4 s which is only slightly upfield of the normal metal acyl range (δ 240–350).[17] The ketene CH_2 ^{13}C NMR resonance at δ 32.8 (t) falls within the usual range for sp^3-hybridized methylene carbons adjacent to carbonyls (δ 27–46),[18] and this carbon couples to the methylene protons with J = 136 Hz. The integrated intensity ratio of the δ 32.8 (t) and 219.4 (s) resonances is 1.22:1. The Os carbonyls appear in the δ 165–185 spectral range.[19]

The IR spectrum of 4 in the metal carbonyl region shows bands at 2107 s, 2071 s, 2054 sh, 2046 sh, and 2020 m cm^{-1}, consistent with the presence of terminal but not bridging CO's. The remainder of the spectrum in the 3000–2800- and 1800–600-cm^{-1} regions is shown in Figure 2. Specific band assignments for the ketene ligand appear in Table III. Such data could prove useful in identifying the presence of ketene ligands on metal surfaces. Similar IR analyses of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and other μ-CH_2 clusters have been employed to substantiate claims of observations of surface-bound methylene ligands.[20–22] The ketene ν_{CO} stretch of 4 appears as a relatively intense band at 1573 cm^{-1} and falls within the range characteristic of metal acyls. The antisymmetric and symmetric C–H stretches are weak but fall in the usual region at 2970 and 2942 cm^{-1}. They compare to the corresponding C–H

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(15) (a) Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1981**, *1*, 214. (b) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Ibid.* **1983**, *2*, 185.

(16) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364.

(17) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; pp 147–149.

(18) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 128–150.

(19) δ 181.2, 180.0, 178.3, 170.0, 169.6, 169.0, 165.0, 164.8.

(20) Oxton, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1982**, 719.

(21) Backx, C.; Willis, R. F. *Chem. Phys. Lett.* **1978**, *53*, 471.

(22) George, P. M.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc.* **1983**, *105*, 1393.

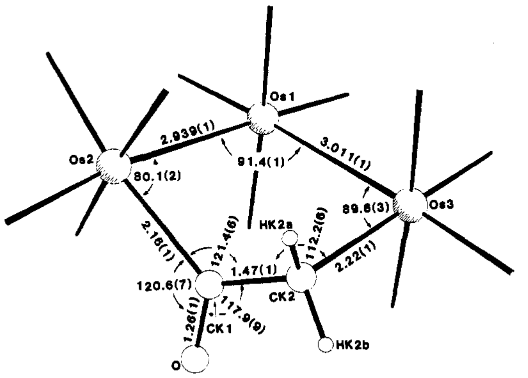

Figure 3. A drawing showing the central metallacycle in $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ giving relevant bond angles and distances. Carbonyl positions are depicted as vectors to the carbon atoms.

stretches of the parent $Os_3(CO)_{11}(\mu\text{-}CH_2)$ complex at 2990 vw and 2949 w cm^{-1}.[20] The remainder of the band assignments given in Table III were derived by comparison to the assigned spectrum of $Os_3(CO)_{11}(\mu\text{-}CH_2)$[20] since the band patterns and relative intensities are similar for the two compounds. However, none of these bands can be expected to be "pure" vibrations and are surely admixtures of several fundamentals.

Structural Characterization of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$. An ORTEP drawing of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ is shown in Figure 1, and relevant bond angles and bond lengths are listed in Table IV. The molecule appears best described as a triosmacyclopentanone derivative, and an expanded view of the Os_3CH_2CO core of the molecule which illustrates this point is shown in Figure 3. The angles about the ketene carbonyl carbon (Ck(1)) closely approximate 120° as expected for an sp^2-hybridized carbon, and the 1.26 (1) Å carbonyl (Ck(1)–O) bond length is only slightly longer than the 1.23 (1) Å length which is typical of organic carbonyls.[23] Likewise the angles about the methylene carbon (Ck(2)) are close to the 109.5° value expected for a tetrahedral sp^3 carbon. The carbon–carbon distance (1.470 (14) Å) within the ketene ligand is close to the typical carbon–carbon single-bond distance for carbons adjacent to carbonyls (1.52 Å[23]). It is thus somewhat inappropriate to refer to this compound as a ketene complex, even though it contains the CH_2CO ligand, since the bond lengths and angles and the indicated carbon hybridizations are not those of free ketene. The coordination at each Os center is essentially octahedral, and the two Os–Os bond lengths fall within the range found for other Os–Os single bonds.[24] The Os(2)- -Os(3) distance of 4.259 (2) Å clearly indicates that these two atoms are not directly bound to each other.

Table IV. Relevant Bond Lengths (Å) and Bond Angles (deg) in $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (**4**)

	Bond Lengths		
Os(1)–Os(2)	2.939 (1)	Os(1)–Os(3)	3.011 (1)
Os(1)–C(1)	1.905 (11)	Os(1)–C(2)	1.915 (11)
Os(1)–C(3)	1.953 (10)	Os(1)–C(4)	1.947 (10)
Os(2)–Ck(1)	2.162 (10)	Os(2)–C(5)	1.954 (11)
Os(2)–C(6)	1.913 (11)	Os(2)–C(7)	1.971 (10)
Os(2)–C(8)	1.971 (11)	Os(3)–Ck(2)	2.218 (9)
Os(3)–C(9)	1.949 (10)	Os(3)–C(10)	1.893 (11)
Os(3)–C(11)	1.947 (11)	Os(3)–C(12)	1.964 (10)
O–Ck(1)	1.256 (11)	Ck(1)–Ck(2)	1.470 (14)
	Bond Angles		
Os(2)–Os(1)–Os(3)	91.4	Os(2)–Os(1)–C(1)	177.5 (3)
Os(3)–Os(1)–C(1)	86.1 (3)	Os(2)–Os(1)–C(2)	86.6 (3)
Os(3)–Os(1)–C(2)	177.0 (3)	C(1)–Os(1)–C(2)	95.8 (5)
Os(2)–Os(1)–C(3)	86.9 (3)	Os(3)–Os(1)–C(3)	85.5 (3)
C(1)–Os(1)–C(3)	92.6 (5)	C(2)–Os(1)–C(3)	92.1 (4)
Os(2)–Os(1)–C(4)	83.1 (3)	Os(3)–Os(1)–C(4)	89.5 (3)
C(1)–Os(1)–C(4)	97.3 (4)	C(2)–Os(1)–C(4)	92.6 (5)
C(3)–Os(1)–C(4)	168.6 (4)	Os(1)–Os(2)–Ck(1)	80.1 (2)
Os(1)–Os(2)–C(5)	92.0 (3)	Ck(1)–Os(2)–C(5)	90.2 (4)
Os(1)–Os(2)–C(6)	171.7 (3)	Ck(1)–Os(2)–C(6)	92.2 (4)
C(5)–Os(2)–C(6)	91.4 (5)	Os(1)–Os(2)–C(7)	86.2 (3)
Ck(1)–Os(2)–C(7)	86.2 (4)	C(5)–Os(2)–C(7)	176.2 (5)
C(6)–Os(2)–C(7)	90.0 (4)	Os(1)–Os(2)–C(8)	90.4 (3)
Ck(1)–Os(2)–C(8)	170.5 (4)	C(5)–Os(2)–C(8)	88.8 (4)
C(6)–Os(2)–C(8)	97.3 (4)	C(7)–Os(2)–C(8)	94.5 (4)
Os(1)–Os(3)–Ck(2)	89.6 (3)	Os(1)–Os(3)–C(9)	89.7 (3)
Ck(2)–Os(3)–C(9)	178.1 (4)	Os(1)–Os(3)–C(10)	177.0 (3)
Ck(2)–Os(3)–C(10)	87.4 (4)	C(9)–Os(3)–C(10)	93.3 (5)
Os(1)–Os(3)–C(11)	89.2 (3)	Ck(2)–Os(3)–C(11)	86.1 (4)
C(9)–Os(3)–C(11)	92.1 (4)	C(10)–Os(3)–C(11)	90.1 (5)
Os(1)–Os(3)–C(12)	89.4 (3)	Ck(2)–Os(3)–C(12)	89.3 (4)
C(9)–Os(3)–C(12)	92.5 (4)	C(10)–Os(3)–C(12)	91.1 (4)
C(11)–Os(3)–C(12)	175.2 (5)	Os(2)–Ck(1)–O	120.6 (7)
Os(2)–Ck(1)–Ck(2)	121.4 (6)	O–Ck(1)–Ck(2)	117.9 (9)
Os(3)–Ck(2)–Ck(1)	112.2 (6)	Os(3)–Ck(2)–Hk(2a)	108.6 (3)
Ck(1)–Ck(2)–Hk(2a)	108.4 (6)	Os(3)–Ck(2)–Hk(2b)	108.5 (3)
Ck(1)–Ck(2)–Hk(2b)	109.6 (5)		

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2CO)$ with H_2. Herrmann et al.[5a] have shown that the diphenylketene complex $Cp(CO)_2Mn(Ph_2C{=}C{=}O)$ reacts with H_2 at 750 atm, 50 °C, to yield a mixture of 2,2-diphenylacetaldehyde and 2,2-diphenylethanol. Since such hydrogenation is of relevance to the intermediacy of surface-bound ketenes during CO reduction chemistry, a similar reaction was examined for $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ (**4**). Hydrogenation of **4** at 1800 psi of H_2 pressure, 23 °C, proceeds slowly to yield mainly the products shown in eq 8. In addition, 35%

$$Os_3(CO)_{12}(\mu\text{-}CH_2CO) + H_2 \xrightarrow{\text{4 days}} CH_3CHO + CH_3CO_2H + H_4Os_4(CO)_{12} + H_2Os_3(CO)_{10} + Os_3(CO)_{12} \quad (8)$$

of unreacted **4** was present after 5 days under H_2 pressure. Although acetaldehyde was produced in 19% yield, the major and only other organic product detected was acetic acid in 77% yield. The latter probably derives from reaction of the ketene complex with adventitious moisture present in the pressure reactor or H_2 gas even though the former was carefully dried and high-purity H_2 was used. Consistent with this is the observation of $Os_3(CO)_{12}$ as the major organometallic product. Acetic acid and $Os_3(CO)_{12}$ readily form when $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ is exposed to H_2O (see below).

Reaction of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ with H_2O and CH_3OH. The ketene complex **4** reacts with both of these reagents over a period of several hours to yield acetic acid and methyl acetate respectively eq 9 and 10. Although no attempt was made to quantitate these

$$Os_3(CO)_{12}(\mu\text{-}CH_2CO) + H_2O \rightarrow CH_3CO_2H + Os_3(CO)_{12} \quad (9)$$

$$Os_3(CO)_{12}(\mu\text{-}CH_2CO) + CH_3OH \rightarrow CH_3CO_2CH_3 + Os_3(CO)_{12} \quad (10)$$

reactions, both ^{1}H NMR and IR data imply these products to form in >95% yield. The reaction of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ with H_2O accounts for the instability of the complex in air and the difficulty in purifying it by chromatography. Competitive experiments in which $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ was allowed to react with a 1:1 mixture of H_2O and CH_2OH under CO and N_2 atmospheres gave ratios of CH_3CO_2H to $CH_3CO_2CH_3$ of 2.46 (under CO) and 2.04 (under N_2), implying that reaction of **4** with H_2O is faster than that with MeOH in both cases.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CO/H_2O, CO/CH_3OH, and CH_3CN/CH_3OH. The bridging methylene complex $Os_3(CO)_{11}(\mu\text{-}CH_2)$ reacts with H_2O and CH_3OH extremely slowly, requiring several days for any detectable reaction with either of these reagents. However, when placed under a CO atmosphere, reaction with either H_2O or CH_3OH occurs on essentially the same time scale as the reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CO to produce the ketene complex **4**. The products of the former two

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(23) "Tables of Interatomic Distances and Configurations in Molecules and Ions"; Sutton, L. E., Ed.; The Chemical Society: London, 1958; Special Publication No. 11.

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

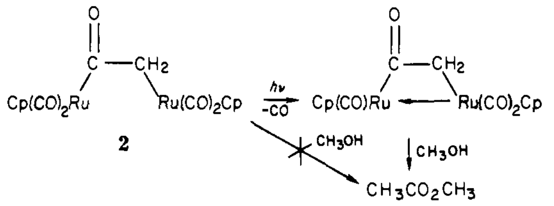
reactions are acetic acid and methyl acetate, along with $Os_3(CO)_{12}$, eq 11 and 12. A quantitative titration of the CH_3CO_2H formed

$$Os_3(CO)_{11}(\mu\text{-}CH_2) + CO/H_2O \rightarrow Os_3(CO)_{12} + CH_3CO_2H \quad (11)$$

$$Os_3(CO)_{11}(\mu\text{-}CH_2) + CO/CH_3OH \rightarrow Os_3(CO)_{12} + CH_3CO_2CH_3 \quad (12)$$

via reaction 11 showed that the yield of CH_3CO_2H was 103 ± 5% based on the amount of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ consumed. NMR integrations (see Experimental Section) also showed both of these reactions to be essentially quantitative.

One likely pathway to the products shown in eq 11 and 12 is the in situ formation of **4**, which as discussed above reacts in a similar fashion with H_2O and CH_3OH. However, a competitive experiment in which $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was allowed to react with a 1:1 H_2O/CH_3OH mixture in the presence of CO gave a 0.99:1 acetic acid/methyl acetate product ratio, which is significantly different from the 2.46:1 ratio obtained in a similar experiment with **4** (see above). This implies the formation of an intermediate ketene complex en route to **4** which is much less selective in its reactions with these nucleophiles than is **4**. The decreased selectivity toward these nucleophiles of the intermediate ketene complex may likely be due to its being coordinatively unsaturated. Lin et al.[8] have examined the reactivity of the ketene complex **2** with methanol and have concluded that an open coordination site is required for its reaction to yield $CH_3CO_2CH_3$, eq 13.



(13)

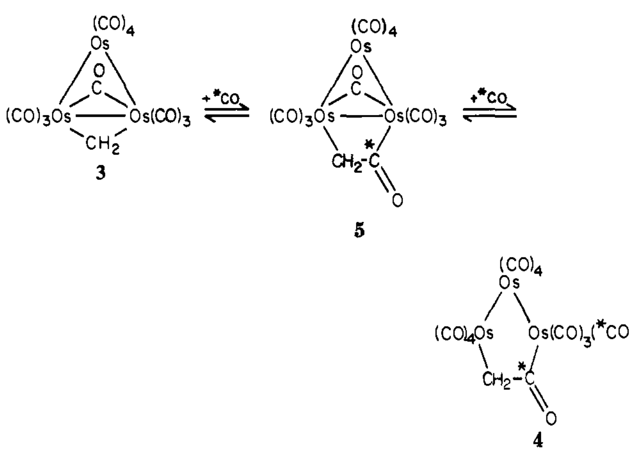
$Os_3(CO)_{11}(\mu\text{-}CH_2)$ also reacts with CH_3OH in the presence of CD_3CN, with no CO present. This reaction requires 7 days to go to completion, and the products are methyl acetate and $Os_3(CO)_{11}(CD_3CN)$, eq 14. The latter complex was identified

$$Os_3(CO)_{11}(\mu\text{-}CH_2) + CH_3OH \xrightarrow{CD_3CN} CH_3CO_2CH_3 + Os_3(CO)_{11}(CD_3CN) \quad (14)$$

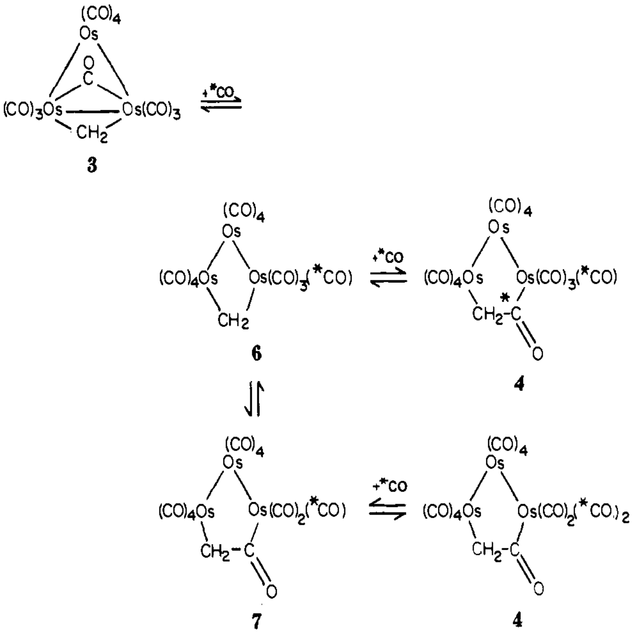
in the product mixture by comparison of its IR spectrum to literature data.[13b] This reaction is obviously not stoichiometric since the expected cluster product would be $Os_3(CO)_{10}(CD_3CN)_2$, but it may proceed through an intermediate ketene/CD_3CN complex such as $[Os_3(CO)_{10}(CD_3CN)(CH_2CO)]$ which is rapidly scavenged by CH_3OH.

Mechanism of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ Formation from $Os(CO)_{11}(\mu\text{-}CH_2)$. In order to probe the mechanism of $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ formation, the reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with ^{13}CO in the presence of CH_3OH was examined. A 25% ^{13}C enriched sample of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, equally enriched in all carbons, was exposed to ^{13}CO (90%) in a $CDCl_3$ solution containing CH_3OH, and $CH_3CO_2CH_3$ was produced. The ^{13}C NMR spectrum of this solution showed that the carbonyl and methyl carbons of the methyl acetate were equally enriched in ^{13}C, implying that both were bound to the original cluster. Since these carbons derive from the ketene ligand, this observation implies that one of the original cluster CO's inserts into an Os–(μ-CH_2) bond to give the ketene and that exogeneous CO is *not* incorporated into this ligand. If the ketene ligand and hence the methyl acetate produced in the above experiment had incorporated external CO, a 4:1 ^{13}C NMR intensity ratio for the carbonyl and methyl resonances of methyl acetate would have been observed. The conclusion that exogeneous CO is not incorporated into the ketene ligand is also supported by IR monitoring of a reaction of unenriched $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with ^{13}CO in the presence of CH_3OH. All of the $CH_3CO_2CH_3$ produced in this experiment showed a $\nu_{^{12}CO}$ stretch at 1735 cm^{-1}, and there was no evidence for the $\nu_{^{13}CO}$ stretch of $CH_3{}^{13}CO_2CH_3$ at 1698 cm^{-1}.

Scheme I



Scheme II



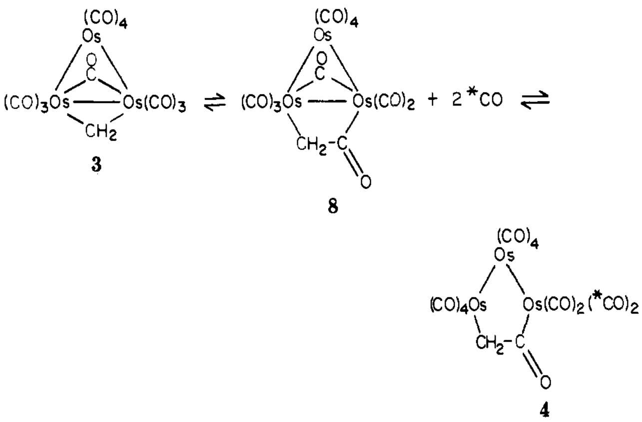
Discussion

There is growing evidence that indicates that CO can readily insert into a metal–(μ-CH_2) bond to give a ketene ligand. Although the $Os_3(CO)_{11}(\mu\text{-}CH_2) \rightarrow Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ transformation described herein has led to the first structurally characterized polynuclear ketene complex from such a reaction, earlier work by Keim et al.[7] indicated that $Fe_2(CO)_8(\mu\text{-}CH_2)$ reacts with CO to give the reactive ketene complex shown in eq 3, and Lin et al.[8] recently reported that CO inserts into the Ru–(μ-CH_2) bond of $Cp_2Ru_2(CO)_4(\mu\text{-}CH_2)$ to give the spectroscopically but not structurally characterized ketene complex in eq 4.

The mechanism by which the $Os_3(CO)_{11}(\mu\text{-}CH_2) \rightarrow Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ conversion occurs is of obvious interest. Three possibilties can be envisaged. The first of these, Scheme I, involves insertion of exogenous CO (*CO) into one of the Os–carbon bonds of the μ-CH_2 ligand to give a ketene complex such as **5**; complex **4** would derive from **5** by addition of a second *CO at one of the metals. However, the ^{13}CO-labeling experiments described in the Results and Experimental sections clearly indicate that the ketene carbonyl in **4** derives from one of the original cluster carbonyls and *not* from exogeneous CO. Thus the mechanism of Scheme I is excluded.

Exogeneous CO could add to one Os to yield a μ-CH_2 cluster such as **6** in Scheme II in which the bridging methylene ligand

Scheme III



is not supported by a metal–metal bond. A few examples of complexes which have methylene ligands bridging two metals not joined by a metal–metal bond are now known.[8,25] The latter intermediate could insert exogenous CO into the Os–(μ-CH$_2$) bond or could insert one of the original cluster CO's into this bond and subsequently add *CO to give the ketene product **4**. The former path is not consistent with the ^{13}CO-labeling experiment which shows that exogenous CO is not incorporated into the ketene ligand, whereas the latter pathway cannot be excluded.

Alternatively, the μ-CH$_2$ cluster **3** could be in equilibrium with a coordinatively unsaturated ketene cluster such as **8** formed by insertion of one of the original cluster CO's into the Os(μ-CH$_2$) bond, Scheme III. Addition of two molecules of exogenous *CO to the Os atoms of this intermediate would give **4**. This mechanism is, of course, consistent with the ^{13}CO-labeling experiment.

The data do not allow us to distinguish between the lower path of Scheme II or that given in Scheme III. If the former mechanism were operative, one might expect some ^{13}CO to be incorporated into the ketene ligand since the immediate precursor to this species possesses one of its 12 CO's labeled with ^{13}C. No such incorporation was observed, but that alone does not rule out this mechanism since ^{13}CO/^{12}CO site exchange on the cluster could be much slower than CO insertion and the insertion step could be stereospecific such that only an original cluster CO is incorporated. It should be noted that the lower mechanism of Scheme II is consistent with the results of Lin et al.,[8] who observed CO insertion into the Ru–(μ-CH$_2$) bond of Cp$_2$Ru$_2$(CO)$_4$(μ-CH$_2$) in which no Ru–Ru bond is present.

Our experimental data do indicate that a cluster-bound ketene intermediate of some type is formed en route to **4**; recall the H$_2$O/CH$_3$OH competition experiments in which Os$_3$(CO)$_{12}$(μ-CH$_2$CO) gave a 2.46:1 ratio of the CH$_3$CO$_2$H and CH$_3$CO$_2$CH$_3$ products from these reagents under a CO atmosphere whereas Os$_3$(CO)$_{11}$(μ-CH$_2$) + CO gave a 1:1 ratio. This implies the formation of a reactive ketene intermediate from the latter combination of reagents which is much less selective in its reactions with these nucleophiles then is the ketene cluster **4**. The structure of such an intermediate is not known, although its decreased selectivity toward the nucleophiles H$_2$O and CH$_3$OH may be due to the presence of an open coordination site in this species.

Another important question concerns the reactivity of the ketene ligand in Os$_3$(CO)$_{12}$(μ-CH$_2$CO). Does the ligand resemble free ketene in its chemistry or is it substantially stabilized by incorporation into the cluster? We have not extensively explored this aspect of **4**, but the crystal structure indicates that free ketene-like reactivity should not be expected since the ligand hybridization is substantially different. Ketene itself reacts with nucleophiles such as H$_2$O and CH$_3$OH to give acetic acid and methyl acetate.[26] Complex **4** also reacts in a similar manner, but at a much attenuated rate, requiring several hours for complete reaction to occur. Ketene also reacts readily with EtOH to give ethyl acetate, but complex **4** does not react with this reagent at a detectable rate.

The insertion of CO into a metal–(μ-CH$_2$) bond is of potential relevance to CO reduction chemistry over heterogeneous catalysts. Ichikawa et al.[4] have directly invoked such a reaction step in their proposed mechanism for the selective formation of CH$_3$CH$_2$OH over certain Rh/ZrO$_2$/SiO$_2$ and Rh/TiO$_2$/SiO$_2$ catalysts as have Takeuchi and Katzer[4b] to explain isotopic tracer results for the Rh-catalyzed reduction of CO to ethanol. The formation of surface methylene ligands during CO reduction chemistry has been widely discussed in the catalytic literature,[3,27-30] and the insertion of CO into these could also account for chain growth via ketene intermediates. Indeed, in early work, Blyholder and Emmett[28,29] carried out experiments in which they studied the decomposition of ^{14}C-labeled ketene over Fischer–Tropsch catalysts during CO/H$_2$ reduction. With ketene labeled with ^{14}C at the methylene carbon they observed ^{14}C incorporation into the hydrocarbon products *with the radioactivity per mole of product approximately constant*, showing little dependence on the number of carbon atoms in the molecules. They concluded that surface methylenes *initiate* chain growth, but with chain growth *propagated by CO addition*. However, Brady and Pettit[3d,e] have argued on the basis of somewhat similar experiments using CH$_2$N$_2$ that hydrocarbon synthesis occurs through oligomerization of surface methylene and methyl groups and that CO insertion is not required.

It is not our intent to enter into the controversy concerning the role of surface methylenes during CO reduction but to simply point out that there is now organometallic precedent for the insertion of CO into M–(μ-CH$_2$) bonds to give ketene ligands and that such reactions could be important and should be considered in mechanistic discussions of CO reduction chemistry. Perhaps the spectroscopic data reported herein for **4**, particularly the IR data in Figure 2 and Table III, will aid the search for surface-bound ketene ligands.

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Supplementary Material Available: Tables of anisotropic temperature factors and structure factors for **4** (22 pages). Ordering information is given on any current masthead page.

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