Halide-Promoted Insertion of Carbon Monoxide into Osmium-μ-Methylene Bonds in Triosmium Clusters

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Abstract: The μ-CH_2 clusters [PPN][$Os_3(CO)_{10}$(μ-CH_2)(μ-X)] (**2**, X = Cl; **3**, X = Br; **4**, X = I; **5**, X = NCO) react with CO to give the μ-ketene clusters [PPN][$Os_3(CO)_{10}$(μ-CH_2CO)(μ-X)] (**6**, X = Cl; **7**, X = Br; **8**, X = I; **9**, X = NCO). However, these reactions are >10^2 faster than the corresponding reaction of $Os_3(CO)_{11}$(μ-CH_2) (**1**) with CO to give $Os_3(CO)_{12}$(μ-CH_2CO) (**10**), thus illustrating a significant halide-promoting effect on the μ-CH_2 → μ-CH_2CO conversion. The ability of the ketene ligand to accept the increased electron density created by the presence of the anionic X ligand appears to be the important factor in promoting this insertion. The methylene clusters **2–5** are in equilibrium with the ketene derivatives **6–9** at CO pressures of 0.2–0.8 atm, and equilibrium constants of 3.5 and 3.0 atm^{-1} have been derived for the **4** + CO ⇌ **8** and **5** + CO ⇌ **9** reactions, respectively. A labeling study has shown that it is one of the original cluster CO's that inserts to make the ketene ligand in **8**. Ketene clusters **6–9** are unstable when left under an atmosphere of CO, with **6–8** adding CO with loss of halide to give **10** whereas **9** adds one CO to give two isomers of [$Os_3(CO)_{11}$(μ-CH_2)(NCO)]⁻.

The insertion of carbon monoxide into metal–carbon bonds is a well-studied reaction and one which is involved in a number of catalytic and synthetic applications of organometallic complexes.[1] However, one aspect which is not well understood is the effect of halide and other anionic promoters on this reaction. Halides and anionic ligands in general have been shown to facilitate carbon–carbon bond formation in a number of homogeneous catalytic reactions of carbon monoxide. For example, in the $Ru_3(CO)_{12}$-catalyzed hydrogenation of CO, iodide promoters dramatically shift product selectivity from the C_1 products methanol and methylformate to the C_2 products ethylene glycol and ethanol, eq 1 and 2.[2-4] Iodide is also an important promoter

for the homologation of aliphatic carboxylic acids with ruthenium catalysts, eq 3.[5]

The published data thus imply that halides promote carbon–carbon bond formation, presumably by promoting a CO insertion step. Surprisingly, there have been no reported studies of discrete well-characterized compounds which model such a halide-promoting effect on CO insertion. Herein we describe such a halide effect on the insertion of CO into metal–(μ-methylene) bonds to give μ-ketene complexes.

We have previously described the insertion of CO into the Os–(μ-CH_2) bond in $Os_3(CO)_{11}$(μ-CH_2) (**1**), to give the μ-ketene complex $Os_3(CO)_{12}$(μ-CH_2CO), eq 4.[6]

We have since prepared a series of halide- and pseudohalide-substituted derivatives of **1** by the facile substitution reactions of eq 5.[7]

These complexes **2–5** also insert CO to give μ-ketene complexes with the X ligands accelerating the insertion rates by at least 10^2 when compared to the rate of CO insertion into **1**. These reactions are described herein with the experimental evidence indicating that the ability of the ketene ligand to accept the increased electron density created by the presence of the anionic X ligands is the important factor in promoting this insertion.[8]

Experimental Section

The complexes [PPN][$Os_3(CO)_{10}$(μ-CH_2)(μ-X)] (X = Cl, Br, I, and NCO) were prepared by published procedures.[7] Carbon monoxide (CP grade) was obtained from Matheson and used as received. ^{13}CO (99% ^{13}C) was obtained from the Monsanto Research Corp., Mound Laboratories, Columbus, OH. Solvents were dried and degassed by standard methods. All manipulations were conducted under prepurified N_2 with use of standard Schlenk and high-vacuum techniques. The [PPN]-[$Os_3(CO)_{10}$(μ-CH_2)(μ-X)] complexes are only mildly air sensitive and were handled and weighed in air. Infrared spectra were recorded on an IBM FT IR/32 spectrometer with 0.2 mm NaCl solution IR cells. NMR spectra were recorded on Bruker WP-200 Fourier transform and Varian

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(2) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419–7421.
(3) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508–6510.
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(6) (a) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 4104–4105. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. R. *J. Am. Chem. Soc.* **1984**, *106*, 4783–4789.

(7) (a) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics*, in press. (b) The isocyanate complex **5** results from the reaction [PPN]N_3 with **1**. (c) Although **2–5** are 50e⁻ clusters and thus require only two metal–metal bonds, the crystal structures of **4** and **5** show all metal–metal distances to be within or close to bonding values with the dibridged Os–Os distance the longest (ca. 3.1 Å).[7a] The structures of **2–5** are thus drawn here with dashed lines between the dibridged Os atoms to indicate the bonding uncertainty.
(8) A preliminary communication of part of this research has been published: Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 254.

EM-360 NMR spectrometers. $Cr(acac)_3$ was added to all ^{13}C NMR samples as a shiftless relaxation agent.[9]

Reaction of [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] (X = Cl, Br, I) with CO To Give [PPN][Os_3(CO)_{10}(\mu-CH_2CO)(\mu-X)]. In a typical reaction, [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-I)] (0.030 g, 0.020 mmol) was placed in a 40-mL Schlenk flask under N_2, and 5.0 mL of dry CH_2Cl_2 was added via syringe. The solution was degassed by 3 freeze–pump–thaw cycles, and 1 atm of CO was admitted. This immediately produced a slight change in color from orange to light orange as [PPN][Os_3(CO)_{10}(\mu-CH_2CO)(\mu-I)] (8) formed. **8:** IR (CH_2Cl_2) 2082 (w), 2043 (s), 2027 (ms), 1993 (s), 1958 (m), 1551 (w) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 4.04 (d, 1 H, J_{HH} = 13.6 Hz), 3.89 (d, 1 H); ^{13}C NMR $(CDCl_3)$ δ 256.3 (s, CH_2CO), 30.5 (t, CH_2CO, J_{CH} = 125 Hz). Removal of the CO atmosphere from over solutions of **8** by evacuation or purging the sample with N_2 resulted in the immediate and quantitative regeneration of [PPN]-[Os_3(CO)_{10}(\mu-CH_2)(\mu-I)]. Complex **8** reacts further with CO over 14 h to give a 32% yield of $Os_3(CO)_{12}(\mu-CH_2CO)$,[6] based upon NMR integration with the phenyl protons of the PPN cation as an internal standard.

The complexes [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] (X = Cl, Br) reacted with CO in a similar fashion to give [PPN][Os_3(CO)_{10}(\mu-CH_2CO)(\mu-X)] (**6**, X = Cl; **7**, X = Br). **6:** IR (CH_2Cl_2) 2083 (w), 2045 (s), 2029 (m), 1990 (s), 1957 (m), 1556 (w) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 3.81 (d, 1 H, J_{HH} = 13.05 Hz), 3.06 (d, 1 H); ^{13}C NMR $(CDCl_3)$ δ 257.3 (s, CH_2CO), 35.3 (t, CH_2CO, J_{CH} = 126 Hz). **7:** IR (CH_2Cl_2) 2082 (w), 2043 (s), 2027 (m), 1993 (s), 1958 (m), 1554 (w) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 3.95 (d, 1 H, J_{HH} = 13.2 Hz), 3.40 (d, 1 H). Removal of the CO atmosphere from over solutions of **6** and **7** gave immediate regeneration of the starting complexes **2** and **3** but both slowly reacted with CO upon standing to lose the halide and form $Os_3(CO)_{12}(\mu-CH_2CO)$.

Reaction of PPN[Os_3(CO)_{10}(\mu-CH_2)(\mu-NCO)] with CO. PPN[Os_3-(CO)_{10}(\mu-CH_2)(\mu-NCO)] (0.030 g, 0.020 mmol) reacts with CO in a manner similar to the halide derivatives discussed above to give [PPN][Os_3(CO)_{10}(\mu-CH_2CO)(\mu-NCO)] (**9**). **9:** IR (CH_2Cl_2) 2193 (s, sh), 2080 (w), 2047 (s), 2030 (m), 1986 (s), 1956 (m) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 3.51 (d, 1 H, J_{HH} = 13.2 Hz), 2.80 (d, 1 H). Removal of the CO atmosphere from over solutions of **9** resulted in the immediate and quantitative regeneration of the precursor methylene complex **5**.

PPN[Os_3(CO)_{10}(\mu-CH_2CO)(\mu-NCO)] reacts further with CO with a half-life of approximately 30 min to give a mixture of two isomers of [PPN][Os_3(CO)_{11}(\mu-CH_2CO)(NCO)] (**11a** and **11b**) in a 1:1.3 ratio. IR (CH_2Cl_2) ν_{NCO} 2253 (m, br). ν_{CO} 2112 (mw), 2068 (s), 2043 (sh), 2031 (s), 1995 (m), 1979 (sh), 1956 (m), 1560 (vw), 1550 (w) cm^{-1}. **11a:** ^1H NMR $(CDCl_3)$ δ 3.10 (d, 1 H, J_{HH} = 6.7 Hz), 2.46 (d, 1 H). **11b:** ^1H NMR $(CDCl_3)$ δ 4.14 (d, 1.3 H, J_{HH} = 5.8 Hz), 2.52 (d, 1.3 H). **11a:** ^{13}C NMR $(CDCl_3)$ δ 240.7 (s, CH_2CO), 124.7 (s, NCO), 20.5 (t, CH_2CO, J_{CH} = 136 Hz). **11b:** ^{13}C NMR $(CDCl_3)$ δ 219.4 (s, CH_2CO), 124.0 (s, NCO), 50.9 (t, CH_2CO, J_{CH} = 132 Hz).

Rate of Reaction of 4 with CO. [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-I)] (**4**) (0.0746 g, 0.0487 mmol) was placed in a 100-mL three-necked round-bottom flask, and 2.50 mL of dry CH_2Cl_2 was added via syringe. The sample was degassed by 3 freeze–pump–thaw cycles, and 1 atm of a mixture of 25.5% CO and 74.5% H_2 (Matheson) was admitted to the stirred solution. Aliquots were removed at approximately 1-min intervals and the IR spectra recorded. The reaction was complete within 5 min to give an equilibrium mixture of the methylene complex **4** and the ketene complex **8**. In a separate experiment, complex **4** (0.0265 g, 0.0173 mmol) in 2.50 mL of dry CH_2Cl_2 was reacted with the same CO/H_2 gas mixture in a manner identical with that for the more concentrated sample. The reaction was complete within 2 min to give a mixture of **4** and **8**.

Reaction of [PPN][Os_3(CO)_{10}(\mu-CH_2CO)(\mu-I)] with ^{13}CO. [PPN]-[Os_3(CO)_{10}(\mu-CH_2)(\mu-I)] (0.159 g, 0.104 mmol) was placed in a 100-mL three-necked round-bottom flask under N_2, and 2.5 mL of dry CH_2Cl_2 was added via syringe. The solution was degassed by 3 freeze–pump–thaw cycles, and slightly more than 1 atm of 99% ^{13}CO was admitted. Samples were withdrawn in 15–20 min intervals into a 0.2-mm IR cell equipped with Luer lock fittings. The spectra initially showed only (ν_{12CO}) for the ketene ligand at 1551 cm^{-1}, but over the course of $\approx$1 h, this band decreased in intensity as a new band at 1517 cm^{-1} (ν_{13CO}) grew in.

Determination of K_{eq} for the $[Os_3(CO)_{10}(\mu-CH_2)(\mu-X)]^- \rightleftharpoons [Os_3-(CO)_{10}(\mu-CH_2CO)(\mu-X)]^-$ (X = I, NCO) Equilibria. The infrared spectrum of the appropriate [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] complex was recorded under various CO partial pressures as follows: A 100-mL three-necked round-bottom flask equipped with a gas adapter and rubber septum was first filled with the desired pressure of CO and then filled to a total pressure of $\approx$1.03 atm by adding dry prepurified N_2. Then 2.0 mL of a solution of [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] in dry CH_2Cl_2 (**4**,

8.22 $\times$ 10^{-3} M; **5**, 9.69 $\times$ 10^{-3} M) was added via syringe and the sample was allowed to stir for 5 min at 25 $\pm$ 1 °C. The IR spectrum of the solution was recorded in the absorbance mode. The spectrum of a slight impurity of $Os_3(CO)_{11}(\mu-CH_2)$ was subtracted from all sample spectra as necessary. For the **4 $\rightleftharpoons$ 8** equilibrium, appropriate fractions of the spectra recorded in the absence of CO (containing only [Os_3(CO)_{10}(\mu-CH_2)(\mu-I)]$^-$) and at a CO pressure of 1.034 atm (containing [Os_3-(CO)_{10}(\mu-CH_2)(\mu-I)]$^-$ and [Os_3(CO)_{10}(\mu-CH_2CO)(\mu-I)]$^-$ in a 20:80 ratio as separately determined by ^1H NMR integration) were computer added to simulate the spectra of the remaining samples as closely as possible. This allowed for the calculation of the concentrations of [Os_3(CO)_{10}(\mu-CH_2)(\mu-I)]$^-$ and [Os_3(CO)_{10}(\mu-CH_2CO)(\mu-I)]$^-$ and from these data the equilibrium constant. For the **5 $\rightleftharpoons$ 9** equilibrium, the concentrations of [Os_3(CO)_{10}(\mu-CH_2)(\mu-NCO)]$^-$ and [Os_3(CO)_{10}(\mu-CH_2CO)(\mu-NCO)]$^-$ were determined from the isocyanate absorbances at 2207 and 2193 cm^{-1}, respectively.

Results

Reaction of PPN[Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] (X = Cl, Br, I, and NCO) with CO To Give μ-Ketene Clusters. Each of the clusters [PPN][Os_3(CO)_{10}(\mu-CH_2)(\mu-X)] (X = Cl, Br, I, NCO) reacts rapidly with CO to give the spectroscopically characterized μ-ketene clusters **6–9**, eq 6. These reactions with 1 atm of CO are

6. X = Cl
7. X = Br
8. X = I
9. X = NCO
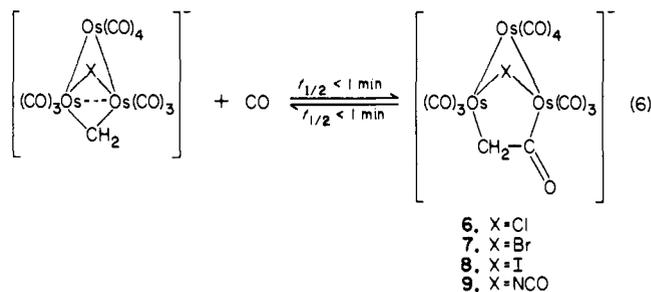
complete within 1 min by IR spectroscopy, with the rate apparently limited by dissolution of CO into the CH_2Cl_2 solvent. At lower CO pressures, the rate is noticeably slowed; at P_{CO} = 0.255 atm, the reaction required $\sim$5 min for equilibrium to be obtained. When the CO atmosphere was removed from over the ketene clusters **6–9**, rapid loss of CO occurred to reform the precursor μ-CH_2 compounds. Also, at lower CO pressure (<1 atm) IR data showed the μ-CH_2 and μ-CH_2CO clusters to be in equilibrium, and the pressure dependence of this equilibrium (see below) indicates that only one CO is taken up in forming complexes **6–9**.

Clusters **6–9** have been characterized spectroscopically, since their instability precluded their isolation. The spectroscopic data for complexes **6–9** are sufficiently similar so as to imply similar structures for all four compounds. Infrared spectra of the complexes in CH_2Cl_2 solutions show a weak band in the 1551–1561 cm^{-1} spectral region assigned to the ketene ν_{CO} vibration, in addition to metal carbonyl bands in the 2085–1988 cm^{-1} region. The ketene ν_{CO} bands for complexes **6–9** are within the range of ν_{CO} reported for anionic η^1-acyl complexes of triosmium clusters (1542–1609 cm^{-1})[10] and are indicative of negative charge localization on the ketene oxygen atom, eq 7. This is also in-

dicated by the facile alkylation of the ketene carbonyl oxygen by reagents such as $[(CH_3)_3O][BF_4]$.[11] The terminal carbonyl bands of the ketene clusters **6–9** are shifted to higher energy by 8–16
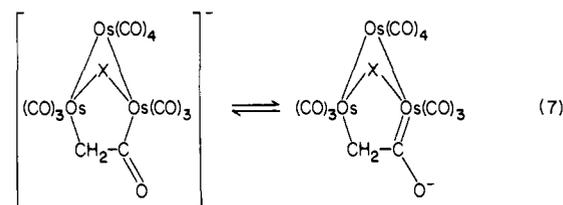
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(11) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L., unpublished results.

Halide-Promoted Insertion of CO into Bonds

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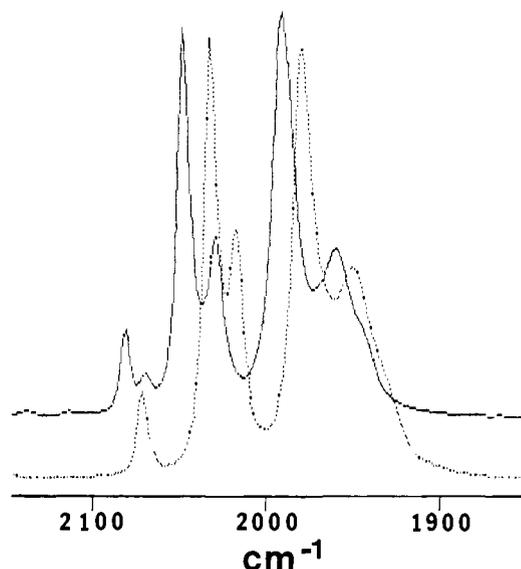
Figure 1. IR spectra of the terminal carbonyl region for [PPN][Os₃-$(CO)_{10}(\mu$-CH₂CO)(μ-NCO)] (—) and [PPN][Os₃(CO)₁₀(μ-CH₂)(μ-NCO)] (- - -) in CH₂Cl₂ solution.

Table I. Equilibria Data for the $4 + CO \rightleftharpoons 8$ and $5 + CO \rightleftharpoons 9$ Reactions in CH₂Cl₂ Solutions[a]

P_{CO}, atm	[1], M	[4], M	[8], M	K_{eq}
0.149	0.36×10^{-3}	4.96×10^{-3}	3.04×10^{-3}	4.1
0.300	0.63×10^{-3}	4.03×10^{-3}	3.83×10^{-3}	3.2
0.446	0.81×10^{-3}	3.02×10^{-3}	4.53×10^{-3}	3.4
0.597	0.90×10^{-3}	2.63×10^{-3}	4.87×10^{-3}	3.1
1.03		ratio 4:8 =	19.8:80.2	3.9
				av 3.5

P_{CO},[c] atm	[5], M	[9], M	K_{eq}
0.153	6.00×10^{-3}	3.46×10^{-3}	3.8
0.300	5.18×10^{-3}	4.55×10^{-3}	2.9
0.446	4.24×10^{-3}	4.77×10^{-3}	2.5
0.589	3.58×10^{-3}	5.42×10^{-3}	2.6
			av 3.0

[a] 25 ± 1 °C. [b] By ¹H NMR integration. [c] [1] ≈ 0 M in these experiments.

cm⁻¹ compared to the spectra of the bridging methylene precursors, Figure 1, also implying some degree of charge localization on the ketene ligand.

The inequivalent methylene protons of complexes 6–9 appear as two doublets in the ¹H NMR spectra in the δ 2.80–4.10 spectral region with similar 13–14 Hz J_{HH} coupling. Carbon-13 NMR spectra of complexes 6 and 8 show the ketene carbonyls at δ 257.3 and 256.3, respectively, within the range reported for metal acyl complexes (δ 240–350).[12] The CH₂ groups of complexes 6 and 8 appear as triplets at δ 35.3 and 30.5 with $J_{CH} = 126$ and 125 Hz, respectively.

The isocyanate cluster 9 shows a strong, sharp ν_{NCO} band at 2193 cm⁻¹ which implies that this ligand is in a bridging rather than terminal position, in agreement with the structure shown in eq 6. Gladfelter et al.[13] have pointed out that bridging NCO ligands generally show strong, sharp ν_{NCO} bands whereas broad bands are found when these are bound in a terminal fashion.

Determination of the Equilibrium Constants for the μ-CH₂ $\rightleftharpoons$ μ-CH₂CO Reactions. An equilibrium between the methylene clusters 2–5 and their ketene derivatives 6–9 can be observed by IR and ¹H NMR monitoring of the reactions under reduced CO pressures (0.2–0.8 atm). The relative amounts of the complexes

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(13) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774–1779.

present are pressure dependent, and computer simulation of IR spectra at different CO pressures gave the concentrations and equilibrium constants set out in Table I. The equilibrium constants were calculated by assuming that only one CO is taken up in the methylene-to-ketene conversion, and as the data in Table I indicates, consistent sets of constants were obtained at the different pressures by using this assumption. An assumption of two CO's per methylene-to-ketene conversion gave equilibrium constants which varied from 5.19 to 27.7 for the $X = I^-$ complex, implying that this assumption cannot be correct.

Slow Further Reaction of the μ-Ketene Clusters with CO. Although the reactions of eq 6 to form the ketene clusters 6–9 proceed smoothly, the latter were unstable when left under a CO atmosphere for prolonged periods. The isocyanate cluster 9 was most reactive and added one CO to give a 1:1.3 mixture of isomeric terminal NCO clusters 11a and 11b with $t_{1/2} \approx 30$ min, eq 8.
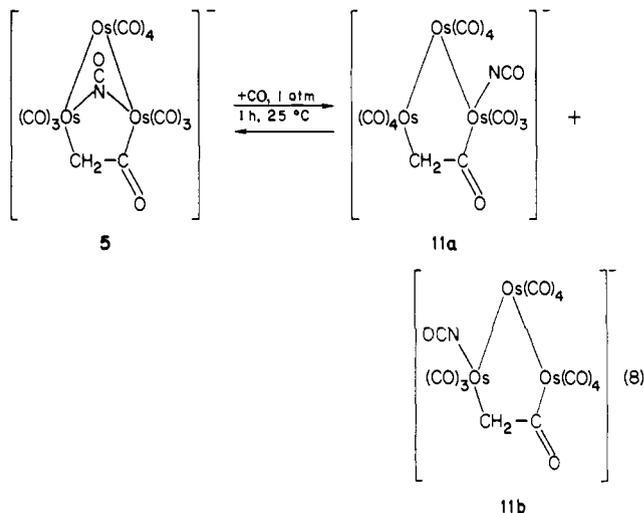
These clusters 11a and 11b readily lose CO to give quantitative regeneration of the precursor methylene complex 5. The halide clusters behaved similarly except that they slowly and irreversibly lost the halide ligand with addition of CO to give 10 and [PPN]X with $t_{1/2} \approx 4$ h for each, eq 9.
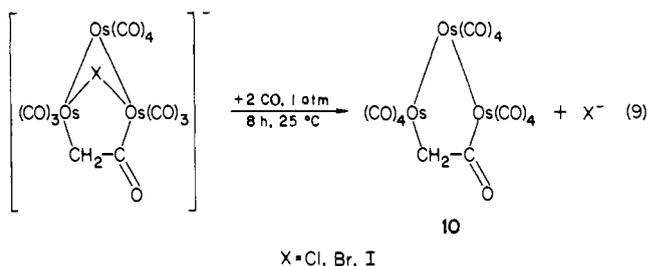
The [PPN][Os₃(CO)₁₁(μ-CH₂CO)(NCO)] clusters 11a and 11b have been spectroscopically characterized, but they were insufficiently stable to isolate because of their tendency to lose CO. The infrared spectrum of the 11a,b product mixture showed two weak ketene carbonyl vibrations at 1560 and 1550 cm⁻¹, in the same spectral region as was seen for the ketene clusters 6–9. A broad NCO stretch at 2253 cm⁻¹ was also apparent, indicative of terminal coordination of this ligand.[13]

The ¹H and ¹³C NMR spectra of the 11a,b mixture showed resonances attributed to the two isomers in a 1:1.3 intensity ratio. The methylene protons of both complexes are inequivalent and appeared as two sets of two doublets in the ¹H NMR spectrum: 11a, δ 3.10 (d), 2.46 (d); 11b, δ 4.14 (d), 2.52 (d). The ¹³C NMR spectrum of the 11a,b mixture showed resonances assigned to the ketene carbonyls (11a, δ 240.7; 11b, δ 219.4), the isocyanate carbons (11a, δ 124.7; 11b, δ 124.0), and the methylene carbons (11a, δ 20.5 (t, $J_{CH} = 136$ Hz); 11b, δ 50.9 (t, $J_{CH} = 132$ Hz)).

The ¹³C NMR data also imply that the structures of 11a and 11b are those shown in eq 8. The ketene carbonyl resonance of 11b at δ 219.4 is in exactly the same location as that observed
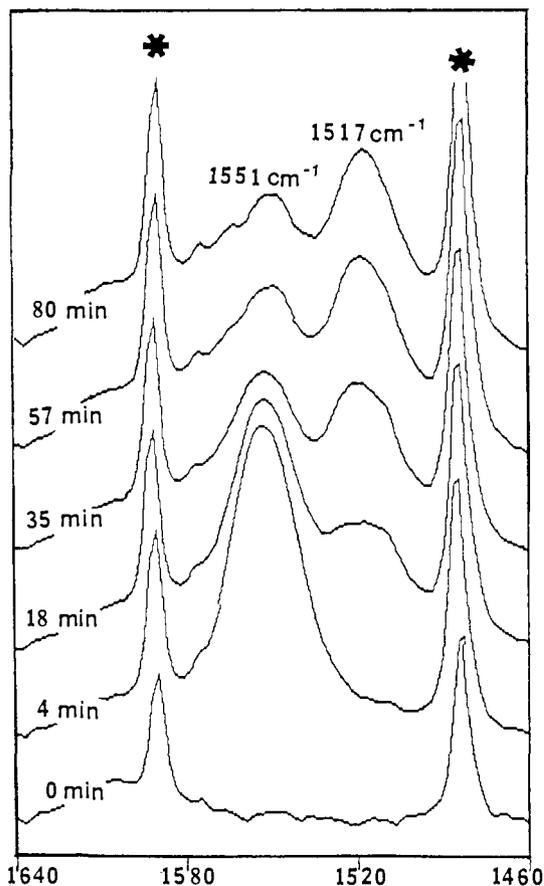
Figure 2. IR spectra recorded during the reaction of [PPN][Os₃-(CO)₁₀(μ-CH₂)(μ-I)] with 99% ¹³CO in CH₂Cl₂ solution. Vibrations at 1590 and 1483 cm⁻¹ marked with an asterisk are due to the PPN cation.

for the ketene carbonyl in $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$,[6] consistent with the formulation of this isomer as the one in which the ketene carbonyl is not adjacent to the isocyanate ligand. In contrast, the ketene carbonyl resonance of **11a** (δ 240.7) is shifted significantly downfield, implying that the isocyanate ligand and the ketene carbonyl are attached to the same metal in this isomer. Conversely, the methylene resonance of **11a** (δ 20.5) is in the normal range (cf. $Os_3(CO)_{11}(\mu\text{-}CH_2CO)$, δ 32.8) whereas that of **11b** (δ 50.9) is shifted downfield, consistent with it being adjacent to the isocyanate ligand.

Reaction of PPN[Os₃(CO)₁₀(μ-CH₂)(μ-I)] with ¹³CO. Infrared spectra recorded during the reaction of **4** with ¹³CO have shown that the CO that ends up in the ketene ligand is one of the original cluster carbonyls and not the added CO. This is evidenced by the exposure of **4** to ¹³CO which immediately gave **8** with a ketene ν_{12CO} at 1551 cm⁻¹, in the same location as from the reaction of **4** with ¹²CO. However, slow incorporation of ¹³CO into the ketene ligand did occur over ≈1 h as evidenced by a gradual decrease in intensity of the 1551-cm⁻¹ band and growth of a ν_{13CO} band at 1517 cm⁻¹ (Figure 2).

Discussion

The most significant finding of this study is the accelerating effect of the X ligands on the CO insertion reaction in the methylene-to-ketene conversion, an observation that supports the suggestion of a similar ligand effect in the halide promoted synthesis gas reactions mentioned in the introduction.[2–5] The reactions of CO with clusters **2–5** to give the ketene clusters **6–9** (eq 6) are complete in less than 1 min, with the rate apparently limited by dissolution of CO into the solvent. This is in marked contrast to the rate of reaction of the parent cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (**1**) with CO to give the ketene cluster $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$, a reaction that requires 4 h to go to completion.[6] *The halide and NCO ligands thus accelerate the CO insertion step by a factor of at least 10^2.* Another significant effect of the X ligands is that

Scheme I
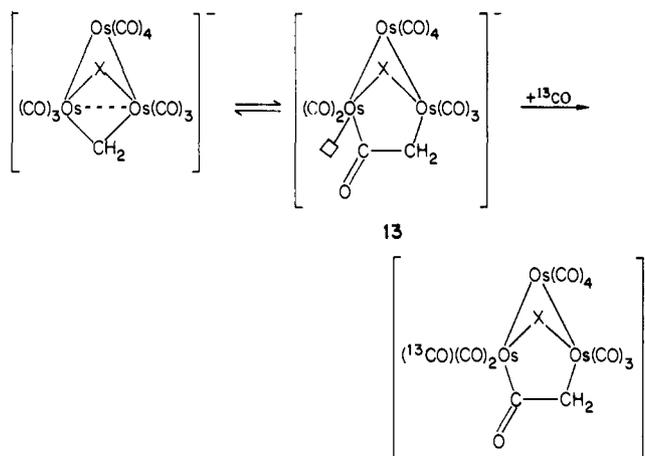
they also promote deinsertion, a reaction that $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ does not readily undergo.[6]

In order to properly address the question of the basis for the halide-promoting effect we must first consider the mechanism of the reaction and the nature of the resultant ketene complex. The ¹³CO-labeling experiment described above clearly shows that one of the original cluster carbonyls is initially incorporated into the ketene ligand and not the added CO. Thus any mechanism involving insertion of exogenous CO into the metal–methylene bond can be excluded. The most reasonable mechanism which fits the experimental data is that shown in Scheme I in which the precursor methylene cluster is in equilibrium with the coordinatively unsaturated ketene intermediate **13**. The latter subsequently adds exogenous CO to give the final product. A similar mechanism was previously indicated for the $Os_3(CO)_{11}(\mu\text{-}CH_2)$ to $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ conversion.[6]

The spectroscopic data clearly imply that the ketene ligands in complexes **6–9** are strongly electron withdrawing. Upon forming the ketene clusters, the terminal carbonyl ν_{CO} *pattern* remains the same but the bands shift to higher energy by 8–16 cm⁻¹ (Figure 1), implying a net withdrawal of electron density from the cluster by the ketene ligand. Also, the low ν_{CO} vibrations of the ketene ligands at 1550–1560 cm⁻¹ imply substantial buildup of electron density on the ketene carbonyl as does the facile alkylation of this oxygen by reagents such as $[(CH_3)_3O]^+$.[11]

We believe that the ability of the ketene π-system to accept electron density from the cluster is an important factor in the promotion of CO insertion by the anionic ligands. Increased negative charge on the cluster is a clear result of substitution of one of the original cluster carbonyls by anionic ligands, as evidenced by the upfield shift of the ¹H NMR μ-CH₂ resonances of the bridging methylene clusters **2–5** (δ 2.5–4.0)[7] compared to those of neutral unsubstituted $Os_3(CO)_{11}(\mu\text{-}CH_2)$ at δ 7.75 and 6.47[14] and a corresponding 30–50 cm⁻¹ red-shift in the ν_{CO} vibrations of the metal carbonyls.[7,14] The additional electron density on the cluster can apparently be better stabilized by the electron-withdrawing ketene ligand than by the methylene ligand, thus providing a driving force for formation of the ketene clusters. The mechanism of conversion of clusters **2–5** to their ketene derivatives **5–9** shown in Scheme I and the similar mechanism indicated for the **1** to $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ reaction involve a pre-equilibrium step between the initial μ-CH₂ clusters and coordinatively unsaturated ketene intermediates such as **13**. The latter are then scavenged by CO to give the final μ-ketene products. Additional electron density in the starting μ-CH₂ cluster as in **2–5** would cause this pre-equilibrium to lie further to the right, increasing the concentration of **13** and resulting in more rapid rates of reaction for these clusters with CO.

The equilibrium constants determined for the methylene-to-ketene conversions for the X = I⁻ and NCO⁻ complexes were not

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significantly different, implying that the negative charge on the cluster is more important than the nature of the X ligand. This in turn implies that the major effect of the X ligands is simply to supply the cluster with additional electron density.

In the halide-promoted catalytic reactions cited in the introduction, CO insertion into metal–alkyl bonds to give acyl complexes must be important reaction steps. The basis for the halide-promoted insertions in these reactions is likely the same as

for our methylene-to-ketene conversions since acyl ligands should be better electron acceptors than alkyl ligands. They thus better stabilize the extra electron density provided by the halide ligands, and the alkyl $\rightleftharpoons$ acyl equilibrium is shifted to the right.

Formation of Glycol Monoacetates in the Oxidation of Olefins Catalyzed by Metal Nitro Complexes: Mono- vs. Bimetallic System

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Abstract: The oxidation of terminal olefins by bis(acetonitrile)chloronitropalladium(II) (**1**) in acetic acid leads to a mixture of glycol monoacetate isomers as the main products. Various amounts of ketones and unsaturated acetates are also formed. The rate of formation and the yield of glycol monoacetate decrease with increasing chain length. Cyclic olefins yield no glycol monoacetates. Replacement of acetic acid by stronger or sterically hindered carboxylic acids completely eliminates the formation of glycol monocarboxylates. Introduction of oxygen converts this stoichiometric reaction into a catalytic system. Our studies, including those carried out with complex **1** labeled with ^{18}O in the nitro ligand, suggest that the glycol monoacetates and most of the ketones are the product of oxygen atom transfer from the nitro group, while the unsaturated acetates are the result of a Wacker-type reaction. In the glycol monoacetate, the ^{18}O label is found exclusively in the acetate group. A mechanism which is in agreement with the above observations as well as a comparison of the above reaction with the oxidation of olefins by nitrate ions in the presence of palladium(II) salts is offered. The formation of glycol monoacetates in the monometallic system represented by complex **1** is to be compared with the results obtained in the bimetallic systems consisting of a combination of py(TPP)CoNO$_2$ and either (CH$_3$CN)$_2$PdCl$_2$ or Pd(OAc)$_2$. In the latter systems, ketones or vinyl acetates are found as the predominant products. This fact underlines the difference between the mono- and bimetallic systems and strongly argues against alternative mechanisms involving nitro group transfer from cobalt to palladium before the olefin oxidation takes place. Additional evidence underlining the difference between these two systems is presented.

In the last 3 years, a novel approach has been developed for the specific oxidation of olefins.[1-6] The importance of this approach lies in the fact that it yields, for the first time, nonradical and nonperoxidic olefin epoxidation.[2,4,6] The principal step in this oxidation involves oxygen transfer from a nitro ligand to a coordinated olefin. Two basic systems have been discovered. The first published examples were of a bimetallic system (eq 1) in which the nitro ligand and the reacting olefin are bound to two different metal centers.[1-4] The second case is represented by a

$$M\text{-}NO_2 + X_nM^1\text{-}\Vert^R \longrightarrow M\text{-}NO + X_nM^1 + RCH\overset{O}{-}CH_2 \quad (1)$$
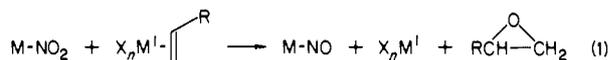
monometallic catalyst in which the nitro ligand and the reacting olefin are coordinated to the same metal (eq 2).[4-6] Only the

$$M\overset{NO_2}{\underset{\Vert}{\diagdown}}{}_R \longrightarrow M\text{-}NO + RCH\overset{O}{-}CH_2 \quad (2)$$
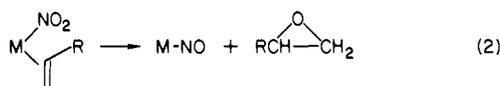
bimetallic system consisting of L(TPP)CoNO$_2$ and thallium(III) salts epoxidizes simple aliphatic olefins such as propylene and 1-octene to the corresponding epoxides as the main product.[2] With the monometallic system, only certain cyclic olefins and, to a lesser extent, isobutylene are converted to the corresponding epoxides.[6c]

Recently, it was suggested that the bi- and monometallic systems may react via an identical intermediate formed by migration of the nitro ligand from the cobalt nitro complex to the metal on which the olefin is activated (eq 3). Only then would

$$M\text{-}NO_2 + XM^1\text{-}\text{-}\Vert^R \longrightarrow M\text{-}X + M^1\overset{NO_2}{\underset{\Vert}{\diagdown}}{}_R \quad (3)$$
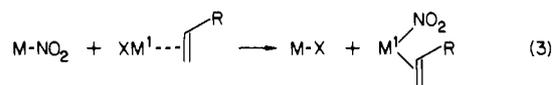
the olefin be oxidized.[7] Such a suggestion has far-reaching implications for the further development of these metal nitro-catalyzed oxidations. For this reason, a study was undertaken to examine this mechanistic possibility. The results of that study are presented herein and support the existence of both the mono- and bimetallic mechanisms for these reactions. Additional evidence against the suggested conversion of the bi- into the monometallic system comes from our work on oxidation of olefins by metal nitro complexes in protic solvents such as acetic acid. We have reported that, in acetic acid, the oxidation of ethylene by the bimetallic system (L(TPP)CoNO$_2$ + Pd(OAc)$_2$) affords only vinyl acetate.[1] No oxygen transfer products have been detected. This reflects the fact that acetate ion effectively competes with the nitro ligand, which is expected to be an extremely weak

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