

the antibonding CH-O transition-state orbital.

The general conclusion is that the CH activation process has associated with it two important bonding interactions, a CH  $\sigma$  donation bond to the closed-shell oxygen anion and its antibonding counterpart which correlates with the OH  $\sigma^*$  orbital. Photoexcitation of an electron from the latter orbital activates the hydrogen transfer process by increasing the net bond order by  $1/2$  in the transition state. The products are the same with and without photoactivation, consisting in coordinated OH<sup>-</sup> and H<sub>2</sub>CO and reduced molybdenum oxide.

The three-center  $\sigma$  donation activation phenomenon has previously been studied theoretically on various metal and metal oxide surfaces.<sup>7</sup> In the case of metals, the antibonding acetylene<sup>7a</sup> and propylene<sup>7b</sup> CH-M, water<sup>7c,d</sup> OH-M, and ClH-M<sup>7e</sup> orbitals donate their electrons into the partially filled conduction bands; this results in low dehydrogenation barriers. In the case of water OH-O<sup>7c,f</sup> and ClH-O<sup>7e</sup> hydrogen transfer on oxides, an electron is transferred back to OH or Cl to yield hydroxide and chloride anions, again lowering the activation barriers. Whether these and other AH bonds can be photoactivated will depend on the details of the electronic structures and the lifetimes of the electron-hole pairs. It is probable that the mechanism described here will be found to be common.

**Acknowledgment.** We are grateful to the National Science Foundation for supporting this work through a grant to the Materials Research Laboratory at Case Western Reserve University and to the Standard Oil Co. (OH) for computing support. Thanks are extended to Dr. L. E. Firment for providing a copy of ref 1 prior to publication.

(7) (a) Anderson, A. B.; Mehandru, S. P. *Surf. Sci.* **1984**, *136*, 398. (b) Anderson, A. B.; Kang, D. B.; Kim, Y. *J. Am. Chem. Soc.* **1984**, *106*, 6597. (c) Anderson, A. B. *Surf. Sci.* **1981**, *105*, 159. (d) Anderson, A. B.; Ray, N. K. *J. Phys. Chem.* **1982**, *86*, 488. (e) Debnath, N. C.; Anderson, A. B. *J. Vac. Sci. Technol.* **1982**, *21*, 945. (f) Debnath, N. C.; Anderson, A. B. *Surf. Sci.* **1983**, *128*, 61.

## Halide-Promoted Insertion of CO into Bridging-Methylene Ligands in Triosmium Clusters

Eric D. Morrison and Gregory L. Geoffroy\*

Department of Chemistry  
The Pennsylvania State University  
University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, The University of Delaware  
Newark, Delaware 19716

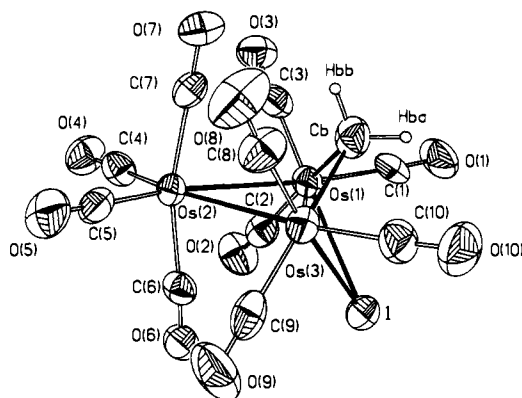
Received August 20, 1984

Halides are important promoters in various homogeneously catalyzed reactions of carbon monoxide, including methanol<sup>1</sup> and acetic acid<sup>2</sup> carbonylations and the reduction of CO to oxygenated products.<sup>3</sup> One important effect of halides, and ionic promoters in general, is to facilitate carbon-carbon bond formation. In the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed hydrogenation of CO, for example, iodide promoters dramatically shift product selectivity from methanol to ethylene glycol and ethanol,<sup>3</sup> products that presumably arise via a CO insertion step. One possible conclusion that can be drawn from the published data is that halides promote this insertion. However, there are no reported studies of discrete well-characterized compounds that model such an accelerating effect on a

(1) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255-268.

(2) Knifton, J. F. *J. Mol. Catal.* **1981**, *11*, 91-106.

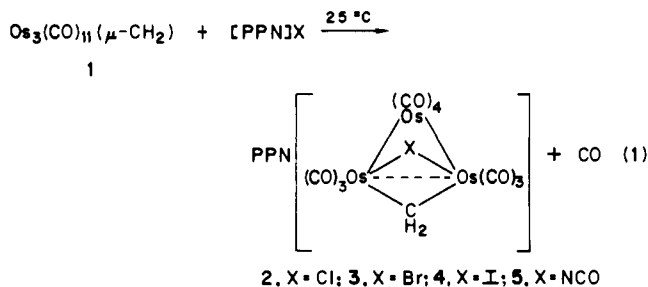
(3) (a) Dombeck, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508-6510. (b) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959-3961.



**Figure 1.** ORTEP drawing of **4**. Relevant bond distances (Å) and angles (deg): Os1-Os3, 3.112 (1); Os1-Os2, 2.927 (1); Os2-Os3, 2.934 (1); Os1-I, 2.863 (1); Os3-I, 2.844 (1); Os1-Cb, 2.145 (14); Os3-Cb, 2.180 (13); Os1-Cb-Os3, 92.0 (5); Os1-I-Os3, 66.1 (1).

CO insertion reaction. We describe herein such a halide effect on the insertion of CO into metal-( $\mu$ -methylene) bonds to give  $\mu$ -ketene complexes.

The starting point for these studies are the [PPN][Os<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -CH<sub>2</sub>)( $\mu$ -X)] clusters **2-5** (PPN = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>). These rapidly form (1-10 min) in 89-97% yield upon reaction of Os<sub>3</sub>(CO)<sub>11</sub>( $\mu$ -CH<sub>2</sub>) (**1**)<sup>4</sup> with the appropriate PPN halide salts<sup>5</sup> in CH<sub>2</sub>Cl<sub>2</sub> or reaction of **1** with [PPN]N<sub>3</sub> in acetone/THF to give **5** (eq 1). Such reactivity is unusual for coordinatively saturated



osmium clusters, although Lavigne and Kaesz recently reported a similar facile substitution with Ru<sub>3</sub>(CO)<sub>12</sub> which gives [PPN][Ru<sub>3</sub>( $\mu$ -Cl)(CO)<sub>10</sub>] upon reaction with [PPN]Cl.<sup>6</sup> Clusters **2-5** have been spectroscopically characterized,<sup>7</sup> with the chloro, iodo, and isocyanato derivatives **2**, **4**, and **5** further defined by X-ray crystallographic studies. The three structures are similar with that of **4** shown in Figure 1.<sup>8</sup> These clusters have 50 valence electrons, two more than the required 48e<sup>-</sup> for a closed triangular cluster.<sup>9</sup> However, all metal-metal distances are within or close to bonding values, with the dibridged Os-Os distances being somewhat longer than the nonbridged Os-Os distances, as summarized in the figure caption. Also, the Os-CH<sub>2</sub>-Os angle of 92.0 (5)<sup>o</sup> in **4** is the largest reported angle for this ligand bridging two

(4) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559-2564.

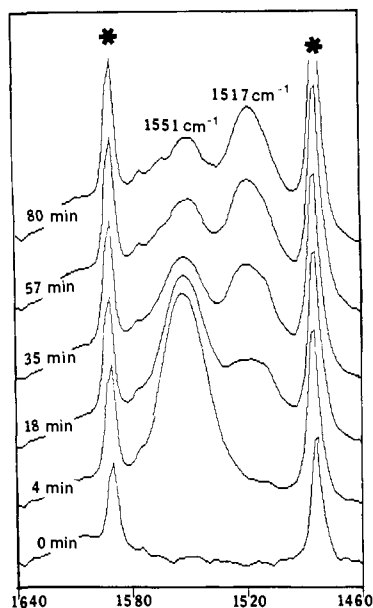
(5) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *31*, 645-650.

(6) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647-4648.

(7) Satisfactory C and H analyses were obtained for **2-5**. **2**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 2072 (w), 2030 (s), 2016 (m s), 1977 (s), 1949 (m), 1935 (sh); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.70 (d, 1 H, *J* = 8.6 Hz), 2.92 (d, 1 H). **3**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 2070 (w), 2029 (s), 2018 (m s), 1979 (s), 1950 (m), 1933 (sh); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.81 (d, 1 H, *J* = 8.55 Hz), 3.19 (d, 1 H). **4**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 2072 (w), 2027 (s), 2018 (m s), 1979 (s), 1950 (m), 1933 (sh); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.83 (d, 1 H, *J* = 8.01 Hz), 3.58 (d, 1 H). **5**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 2207 (s sh), 2070 (w), 2031 (s), 2016 (m s), 1977 (s), 1948 (m s), 1930 (sh); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.38 (d, 1 H, *J* = 8.06 Hz), 2.79 (d, 1 H).

(8) **4** crystallizes in the space group  $P\bar{1}$  with *a* = 12.978 (3) Å, *b* = 13.131 (3) Å, *c* = 14.074 (4) Å,  $\alpha$  = 90.21 (2)<sup>o</sup>,  $\beta$  = 96.40 (2)<sup>o</sup>,  $\gamma$  = 90.63 (2)<sup>o</sup>, *V* = 2383 (10) Å<sup>3</sup>, and *Z* = 2. Least-squares refinement of the 4429 reflections with *F*<sub>o</sub> > 3 $\sigma$ (*F*<sub>o</sub>) gave convergence to *R* = 0.041 and *R*<sub>w</sub> = 0.038.

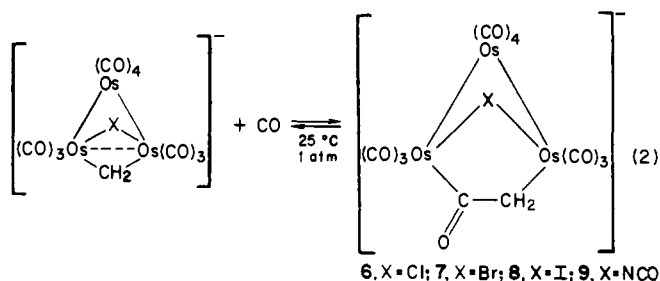
(9) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305-5315.



**Figure 2.** IR spectra recorded during the reaction of  $\text{PPN}[\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-I})]$  with 99%  $^{13}\text{CO}$  in  $\text{CH}_2\text{Cl}_2$  solution. Bands at 1590 and  $1483\text{ cm}^{-1}$  marked with an asterisk are due to the PPN cation.

metals joined by a metal-metal bond,<sup>10</sup> but it is much less than the corresponding angles found in the few structures in which a  $\mu\text{-CH}_2$  ligand is unsupported by a metal-metal bond.<sup>11</sup> This large angle implies the presence of some degree of strain in this dibridged unit. The spectroscopic data of  $2 \rightarrow 5$  are consistent with the determined structures showing inequivalent methylene protons (see Figure 1) as two doublets in the  $^1\text{H}$  NMR  $\delta$  2.5–4.0 spectral region with  $J_{\text{HH}} = 8\text{--}10\text{ Hz}$ .<sup>7</sup>

When clusters  $2\text{--}5$  are placed under 1 atm of CO at  $25\text{ }^\circ\text{C}$ , they rapidly react to give the spectroscopically characterized  $\mu\text{-ketene}$  clusters  $6\text{--}9$ <sup>12</sup> (eq 2). The  $^{13}\text{C}$  NMR spectrum of ketene

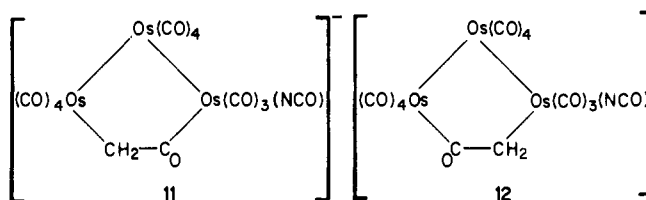


complex **8** ( $\text{X} = \text{I}$ ) shows a singlet at  $\delta$  256.3 for the ketene carbonyl and a triplet at  $\delta$  30.5 ( $J_{\text{CH}} = 125\text{ Hz}$ ) for the ketene methylene. In the  $^1\text{H}$  NMR spectrum the  $\mu\text{-CH}_2$  protons are inequivalent and appear as doublets at  $\delta$  4.04 and 3.89 with  $J_{\text{HH}} = 13.6\text{ Hz}$ . This complex also shows a weak  $\nu_{\text{CO}}$  at  $1551\text{ cm}^{-1}$  due to the ketene carbonyl. IR monitoring has shown that the reactions of eq 2 are complete in less than 1 min, with the rate apparently limited by dissolution of CO into the  $\text{CH}_2\text{Cl}_2$  solvent. This is in marked contrast to the rate of reaction of the parent

cluster **1** with CO to give the ketene cluster  $\text{Os}_3(\text{CO})_{12}(\mu\text{-CH}_2\text{CO})$  (**10**), a reaction that requires 4 h to go to completion.<sup>13</sup> 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 lies in the reversibility of the insertion, a reaction that **10** does not readily undergo.<sup>13</sup> When the CO atmosphere was removed from over the ketene clusters **6–9**, rapid loss of CO occurred to reform the precursor  $\mu\text{-CH}_2$  compounds. An equilibrium between **4** and **8** can actually be observed under reduced CO pressure.  $^1\text{H}$  NMR and IR monitoring shows the presence of both **4** and **8** when the CO pressure is between 0.2–0.8 atm, and the relative amounts of these are pressure dependent. Computer simulation of IR spectra at different CO pressures gave an equilibrium constant of  $3.4\text{ atm}^{-1}$  for the reaction  $4 + \text{CO} = 8$  at  $25\text{ }^\circ\text{C}$ . The pressure dependence of the reaction also showed that only one CO was incorporated in the  $4 \rightarrow 8$  conversion as indicated in eq 2.

Clusters **6–9** were unstable when left under a CO atmosphere for several hours. The  $\mu\text{-NCO}$  ketene cluster **9** reversibly added an additional carbonyl to give a 1:1.3 mixture of isomeric terminal NCO clusters **11** and **12**.<sup>14</sup> The halide clusters **6–8** slowly lost



the halide ligand and added CO to give **10**. The presence of the terminal NCO ligands in **11** and **12** is indicated by the broad IR band at  $2253\text{ cm}^{-1}$ .<sup>15</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of this mixture shows two sets of ketene resonances at  $\delta$  240.7 ( $\text{CH}_2\text{CO}$ , **11**), 219.4 ( $\text{CH}_2\text{CO}$ , **12**), 50.9 ( $\text{CH}_2\text{CO}$ , **12**), and 20.5 ( $\text{CH}_2\text{CO}$ , **11**).

IR monitoring of the reaction of **4** with  $^{13}\text{CO}$  (Figure 2) has 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  $^{13}\text{CO}$  which immediately gave **8** with a ketene  $\nu_{^{13}\text{CO}}$  band at  $1551\text{ cm}^{-1}$ , in the same location as from the reaction of **4** with  $^{12}\text{CO}$ . However, slow incorporation of  $^{13}\text{CO}$  into the ketene ligand did occur over  $\sim 1\text{ h}$  as evidenced by a gradual decrease in intensity of the  $\nu_{^{12}\text{CO}}$   $1551\text{-cm}^{-1}$  band and growth of a  $\nu_{^{13}\text{CO}}$  band at  $1517\text{ cm}^{-1}$ .

The most significant finding of this study is the  $10^2$  accelerating effect of the X ligands on the CO insertion reaction, an observation that supports the suggestion of a similar halide effect in the halide-promoted synthesis gas reactions.<sup>2,3</sup> Whether the effect of the anionic ligand is to promote a methylene = ketene pre-equilibrium or to facilitate associative formation of reactive intermediates via opening of the M–X–M bridge is not known. This aspect is currently under exploration, and the results will be reported in full at a later time.

**Acknowledgment.** We thank the Department of Energy, Office of Basic Energy Sciences for support of this research, the Engelhard Co. for a loan of Os metal, and the SOHIO Co. for a fellowship award.

**Supplementary Material Available:** Tables of X-ray diffraction data for  $\text{PPN}[\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-I})]$  (5 pages). Ordering information is given on any current masthead page.

(10) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159–263.  
 (11) (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679–1680. (b) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 614–616. (c) Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (d) McKeer, I. R.; Cowie, M. *Inorg. Chim. Acta* **1982**, *65*, L107–L109.

(12) **6**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2083 (w), 2045 (s), 2029 (m s), 1990 (s), 1957 (m), 1556 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.81 (d, 1 H,  $J = 13.05\text{ Hz}$ ), 3.06 (d, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  257.3 (s,  $\text{CH}_2\text{CO}$ ), 35.3 (t,  $\text{CH}_2\text{CO}$ ,  $J_{\text{CH}} = 126\text{ Hz}$ ). **7**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2083 (w), 2045 (s), 2029 (m s), 1993 (s), 1958 (m), 1554 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.95 (d, 1 H,  $J = 13.17\text{ Hz}$ ), 3.40 (d, 1 H). **8**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2082 (w), 2043 (s), 2027 (m s), 1993 (s), 1958 (m), 1551 (w). **9**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2193 (s sh), 2080 (w), 2047 (s), 2030 (m s), 1986 (s), 1956 (m), 1561 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.51 (d, 1 H,  $J = 13.17\text{ Hz}$ ), 2.80 (d, 1 H).

(13) (a) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4104–4105. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783–4789.

(14) IR ( $\text{CH}_2\text{Cl}_2$ ) 2253 (m br), 2112 (m w), 2068 (s), 2043 (sh), 2031 (s), 1995 (m), 1979 (sh), 1956 (m), 1560 (vw), 1550 (w).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): **11**,  $\delta$  3.10 (d, 1 H,  $J_{\text{HH}} = 6.68\text{ Hz}$ ), 2.46 (d, 1 H); **12**,  $\delta$  4.14 (d, 1 H,  $J_{\text{HH}} = 5.82\text{ Hz}$ ), 2.52 (d, 1 H).

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