group protons is only 0.04 ppm downfield from that of 1 (with R = CH_3) reported previously.[3] In addition, only the signals of the bipyridyl protons are observed.

The structure as determined by X-ray analysis (Figure 1) is in accord with the IR and NMR spectroscopic evidence but reveals additional details, most notably an extremely distorted octahedral coordination geometry around the molybdenum atom, which is in part even more pronounced than that in 3.[7] Although complexes 3 and 4 crystallize in the same space group ($P\bar{1}$), the O–Mo–O angle of 110.20° is 7° wider than in 4; the C–Mo–C angle of 149.03° is 10° smaller than the Br–Mo–Br angle. These differences in the bond angles are caused by repulsions of the methyl groups by the two *cis*-oxygen atoms. Because of the negative inductive effect of the methyl groups, the charge density on the oxygen atoms in 4 is probably higher than in 3. However, the average Mo–O bond distances of 1.71 Å in 4 are within experimental error identical with those in 3. Table VI shows that the average Mo–C bond distances of 2.19 Å are slightly longer than bond lengths reported for methyl carbons bound to dinuclear Mo(II). However, they lie well within the range of 2.131–2.264 Å of previously reported $Mo–C_{aliphatic}$ bond lengths. Table VI contains additional structural data to facilitate further structural comparisons with other known molybdenum complexes. Bond distances and angles of the Mo(bpy) subunit are identical, within experimental error, for 3 and 4. The oxo groups are essentially coplanar with the bpy ligand; the dihedral angle between the bpy plane and the plane defined by O, O, Mo, N, N is 2.0°. It is of interest to note the systematic alternation of short and long C–C bonds in the bpy rings of 4. Presumably due to the lower resolution achieved, this phenomenon has not been observed in the structure of 3.[7] It was, however, reported previously for other aromatic rings containing heteroatoms.

In forthcoming papers of this series we will describe additional compounds of this type with emphasis on their relevance to catalysis and biocatalysis.

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Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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(7) R. H. Fenn, *J. Chem. Soc. A*, 1764 (1969).

(8) K. Wieghardt, W. Holzbach, E. Hofer, and J. Weiss, *Inorg. Chem.*, **20**, 343 (1981).

(9) C. A. Cliff, G. D. Fallon, B. M. Gatehouse, K. S. Murray, and P. J. Newman, *Inorg. Chem.*, **19**, 773 (1980).

(10) K. O. Hodgson and J. M. Berg, *Inorg. Chem.*, **19**, 2180 (1980).

(11) M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, **17**, 2338 (1978).

(12) F. Hug, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc. D*, 1079 (1971).

(13) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

Thermal and Photochemical Reactions of Dinuclear Metal Carbonyl Compounds with Metal Hydrides[1]

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The thermal or photochemical reaction of bis(tri-*n*-butylphosphine)hexacarbonyldicobalt, $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$, with tri-*n*-butyltin hydride, $HSn(n\text{-}Bu)_3$, leads to H_2 and $(n\text{-}Bu)_3SnCo(CO)_3P(n\text{-}Bu)_3$ as products. The rate law for the photochemical reaction and product distribution are consistent with a pathway involving loss of CO from the $Co(CO)_3P(n\text{-}Bu)_3\cdot$ radical following metal–metal bond rupture, oxidative addition of the H–Sn bond to the cobalt center, a hydrogen atom transfer from a second $HSn(n\text{-}Bu)_3$ to cobalt, and then a reductive elimination of H_2, as the pathway for reaction. A similar reaction pathway is indicated for reaction of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W) with $HSn(n\text{-}Bu)_3$ or $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with $HMo(CO)_3(\eta^5\text{-}C_5H_5)$. On the other hand reaction of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with $HMn(CO)_5$ leads to $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ and $Mn_2(CO)_{10}$ as products, suggesting a simple hydrogen atom transfer reaction between the $Mo(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ radical and $HMn(CO)_5$. The choice between the oxidative addition and hydrogen atom transfer pathways is determined by the donor M–H bond energy; a low M–H bond energy favors hydrogen atom transfer. On the basis of studies to date, the oxidative addition pathway, as described above, is the more common. Reaction of $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ with $HSn(n\text{-}Bu)_3$ leads to $(n\text{-}Bu)_3SnMo(CO)_3(\eta^5\text{-}C_5H_5)$ and H_2. The rate law is of the form $d(\text{product})/dt = \{k_a[HSn(n\text{-}Bu)_3]/(k_b + k_c[HSn(n\text{-}Bu)_3])\}[HMo(CO)_3(\eta^5\text{-}C_5H_5)]$. The rate law suggests the existence of a preequilibrium involving either a formyl intermediate, formed via a hydride migration, or a change in hapticity of the cyclopentadienyl ring to form a η^1-cyclopentadienyl intermediate.

We have recently reported the results of a study of the thermal or photochemical decomposition of cobalt tetracarbonyl hydride, $HCo(CO)_4$, which proceeds in accord with eq 1.[2] The kinetics behavior of the system is strongly

$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2 \qquad (1)$$

suggestive of a radical pathway involving $Co(CO)_4\cdot$ radicals as intermediates. The radical pathway proposed for reaction 1 can be generalized to describe the reaction of any dinuclear metal carbonyl compound with a metal or me-

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(2) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

talloid hydride, as shown in Scheme I. The metal carbonyl radicals that are essential intermediates in this process are formed in step 2, which is driven by either thermal or photochemical M–M bond homolysis. A key step in the overall mechanism is facile dissociation of CO from the $M(CO)_mL_n\cdot$ radical. Loss of CO from the 17-electron species results in formation of $M(CO)_{m-1}L_n$, a 15-electron species capable of undergoing oxidative addition reactions with suitable substrates. There are substantial experimental grounds for the proposal that CO loss is rapid in many 17-electron $M(CO)_mL_n\cdot$ species.[3-10] For example, recent experimental results suggest that dissociation of CO from $Mn(CO)_5\cdot$ occurs with a rate constant on the order of 100 s^{-1}.[10] Thus loss of CO competes with the recombination of $Mn(CO)_5\cdot$ radicals to reform $Mn_2(CO)_{10}$.

Scheme I

$$M_2(CO)_{2m}L_{2n} \rightleftarrows 2M(CO)_mL_n\cdot \quad (2)$$

$$M(CO)_mL_n\cdot \rightleftarrows M(CO)_{m-1}L_n + CO \quad (3)$$

$$M(CO)_{m-1}L_n + HM'X_y \rightarrow M(CO)_{m-1}L_n(M'X_y)(H)\cdot \quad (4)$$

$$M(CO)_{m-1}L_n(M'X_y)(H)\cdot + HM'X_y \rightarrow M(CO)_{m-1}L_n(M'X_y)(H)_2 + M'X_y\cdot \quad (5)$$

$$M(CO)_{m-1}L_n(M'X_y)\ (H_2) \rightarrow M(CO)_{m-1}L_n(M'X_y) + H_2 \quad (6)$$

$$M(CO)_{m-1}L_n(M'X_y) + CO \rightarrow M(CO)_mL_n(M'X_y) \quad (7)$$

$$M(CO)_mL_n\cdot + M'X_y\cdot \rightarrow M(CO)_mL_n(M'X_y) \quad (8)$$

The $M(CO)_mL_n\cdot$ radical, once formed, can undergo reaction with a hydrogen atom source, $HM'X_y$, by either of two pathways. The more obvious one is simply a direct hydrogen atom transfer, as in eq 9. When this pathway

$$M(CO)_mL_n\cdot + HM'X_y \rightarrow HM(CO)_mL_n + M'X_y\cdot \quad (9)$$

is followed, the product of the reaction is a metal hydride. The alternative pathway, embodied in Scheme I, leads to evolution of H_2 and formation of the M–M′ bond. As a means of learning which of these alternative pathways is preferred in reactions of metal carbonyl compounds, we have examined the reaction of several dinuclear metal carbonyl compounds, $M_2(CO)_{2m}L_{2n}$, with tributyltin hydride, $HSn(n\text{-}Bu)_3$, under both thermal and photochemical conditions. Several related reactions have also been studied. Determination of the operative pathway for reaction is based on product determination and the kinetics of both the thermal and photochemical reactions.

Experimental Section

Materials. Hexane (Burdick and Jackson Laboratories) was passed over activated 6–12 mesh silica gel. Following this, it was distilled from benzophenone ketyl and stored over activated 4A molecular sieves in an inert atmosphere glovebox. Tetrahydrofuran (Aldrich), THF, was purified by the same procedure. Hexacarbonylbis(η^5-cyclopentadienyl)dimolybdenum, $[Mo(CO)_3Cp]_2$ (where Cp represents the η^5-cyclopentadienyl ligand), was obtained from Pressure Chemical Co. and purified by removing trace amounts of $Mo(CO)_6$ by sublimation (35 °C (1 mmHg)). IR for $[Mo(CO)_3Cp]_2$ in THF: 2010, 1955, 1912 cm^{-1} [lit.[11] (benzene): 2014, 1955, 1910 cm^{-1}]. $HSn(n\text{-}Bu)_3$ was obtained from Alfa Chemicals and used without further purification. The compound was stored under N_2 at 0 °C. $[W(CO)_3Cp]_2$,[12] $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$,[13] $HMo(CO)_3Cp$,[11] and $HMn(CO)_5$[14] were synthesized according to standard literature procedures. $HMo(CO)_3Cp$ was sublimed (70 °C (1 mmHg)) prior to use. $HW(CO)_3Cp$ was obtained as a gift from Dr. Daniel Foose. $HCo(CO)_3P(n\text{-}Bu_3)$ was prepared by acidifying a THF solution of $NaCo(CO)_3P(n\text{-}Bu)_3$ with glacial acetic acid. The solvent was removed under reduced pressure, leaving a mixture of $HCo(CO)_3P(n\text{-}Bu)_3$ and sodium acetate. The mixture remained under reduced pressure at 22 °C for 2 h to remove excess acetic acid. Hexane was added and sodium acetate was removed by filtration. The hexane solution was washed three times with 10 mL of water. IR bands (hexane): 2049, 1970 cm^{-1} [lit.[15] (hexane): 2045, 1968 cm^{-1}].

Photolysis Experiments. Photolysis with 366-nm wavelength radiation was carried out by using a Hanovia medium-pressure 200-W quartz mercury lamp. Wavelength selection was achieved by utilizing a standard filter solution.[16] Quartz photolysis cells approximately 15 cm in height with path lengths of 1.0 cm were used. Each cell was equipped with a stopcock and septum to allow sampling of the reaction mixture.

Photolysis using light of 500-nm wavelength was carried out with a high-pressure 1000-W xenon arc lamp. Filtering was accomplished by using an Oriel Corp. band-pass filter.

Reactions Involving Dinuclear Metal Carbonyl Compounds. In a typical experiment involving $HSn(n\text{-}Bu)_3$, $M_2(CO)_{2m}L_{2n}$ was weighed out by difference into a 25-mL Ray-sorb volumetric flask on a Mettler balance. The flask was purged with N_2, sealed, and taken into the glovebox. A known volume of $HSn(n\text{-}Bu)_3$ was added to the flask. The volumetric was filled to the mark with hexane. With minimal exposure to laboratory light the solution was transferred via syringe into a quartz photolysis tube wrapped in black plastic and then brought out of the glovebox. An initial IR spectrum was taken. The solution was the photolyzed (366 or 500 nm) and IR spectra recorded as a function of photolysis time.

To study the reactions of $[CpM(CO)_3]_2$ (M = Mo, W) it was necessary to employ a solvent other than hexane because of solubility limitations. THF was chosen because it afforded adequate solubility without reacting irreversibly with either the starting compounds or reaction intermediates.

In the reaction involving $HMn(CO)_5$, $M_2(CO)_{2m}L_{2n}$ was weighed by difference into a 25-mL Ray-sorb volumetric flask on a Mettler balance. The flask was purged with N_2, taken into the glovebox, and then filled to the mark with a 3.00×10^{-3} M hexane solution of $HMn(CO)_5$. An IR cell was filled, sealed, and brought out of the glovebox. After an initial IR scan the IR cell was placed in the photolysis beam. IR scans were recorded as a function of photolysis time. This procedure was also utilized in the photochemical reaction of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ with $HMo(CO)_3(\eta^5\text{-}C_5H_5)$.

Upon exposure to trace amounts of O_2, $HMn(CO)_5$ rapidly converts to $Mn_2(CO)_{10}$. IR cells filled in the box with a hexane solution of $HMn(CO)_5$ (3.00×10^{-3} M), brought out, and stored in the dark showed less than 1% decomposition after 48 h.

Reaction of Metal Carbonyl Hydrides with $HSn(n\text{-}Bu)_3$. In a typical experiment a known amount of $HMo(CO)_3Cp$ was added to a 250-mL volumetric flask in an inert atmosphere glovebox. The flask was filled to the mark with hexane. This solution was transferred to a 250-mL round-bottom flask covered with black plastic and sealed with a rubber septum. A known

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[3] Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

[4] (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) *Ibid.* 4246. (c) *Ibid.* 4908. (d) *Ibid.* 6042.

[5] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 947.

[6] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

[7] Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613.

[8] Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2982.

[9] Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6769.

[10] Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.

[11] Abramhamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 1003.

[12] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[13] Manning, A. *J. Chem. Soc. A* **1968**, 1135.

[14] Eisch, J. J.; King, R. B. *Organomet. Synth.* **1965**, *1*, 156.

[15] Spooncer, W. W.; Jones, A. C.; Slaugh, L. J. *J. Organomet. Chem.* **1969**, *18*, 327.

[16] Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.

volume of $HSn(n\text{-}Bu)_3$ was added to a 50-mL volumetric flask. The flask was filled to the mark with hexane. The solution was transferred to a brown amber bottle and sealed with a rubber septum. Several solutions of different $HSn(n\text{-}Bu)_3$ concentrations were made in a similar way. The reagents were brought out of the drybox and equilibrated at room temperature. The stopped-flow apparatus and data acquisition system utilized in these experiments have been described elsewhere.[8,17] Solution IR cells of 1.0-mm path lengths with NaCl windows were used. The rate of disappearance of $HMo(CO)_3Cp$ was determined by monitoring the IR absorbance at 2022 cm^{-1}.

A similar procedure was utilized in the reactions of $HW(CO)_3Cp$ or $HCo(CO)_3P(n\text{-}Bu)_3$ with $HSn(n\text{-}Bu)_3$.

Results

Thermal Reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$. The thermal reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$ in hexane results in formation of $Bu_3SnCo(CO)_3P(n\text{-}Bu)_3$, as shown in eq 10. Log plots of

$$Co_2(CO)_6[P(n\text{-}Bu)_3]_2 + 2HSn(n\text{-}Bu)_3 \rightarrow 2(n\text{-}Bu)_3SnCo(CO)_3P(n\text{-}Bu)_3 + H_2 \quad (10)$$

$Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ concentration vs. time are linear, indicating that the rate of product formation is first order in $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ concentration. Excellent first-order rate plots were obtained, with no variation in the pseudo-first-order rate constant with varying $HSn(n\text{-}Bu)_3$ concentration in the range 0.19–0.76 M. The observed rate constant at 35 °C is $(1.61 \pm 0.01) \times 10^{-5}\ s^{-1}$ and at 24 °C is $2.56 \pm 0.04 \times 10^{-6}\ s^{-1}$. Added CO ($\sim 2 \times 10^{-2}$ M) has a negligible effect on the reaction rate.

Photochemical Reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$. Photolysis (366 nm, 23 °C) of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ and $HSn(n\text{-}Bu)_3$ in hexane results in formation of $(n\text{-}Bu)_3SnCo(CO)_3P(n\text{-}Bu)_3$ as in eq 10.

The contribution of the thermal reaction to the loss of $Co_2(CO)_6[P(n\text{-}Bu_3)_2]_2$ during the photochemical reaction was subtracted from the data to obtain the net photochemical rate data. In the photochemical reaction $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ is the sole light absorber. The rate law describing the disappearance of $Co_2(CO)_6[P(n\text{-}Bu_3)_3]_2$ is given by eq 11. Φ_d is the disappearance quantum yield,

$$-d[Co_2(CO)_6L_2]/dt = \Phi_d I_a \quad (11)$$

defined at the number of moles of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ converted into products per einstein of photons absorbed. I_a is the light flux absorbed by $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$. The absorption of incident light is essentially total with the path length utilized in the photochemical experiments.

Plots of $Co_2(CO)_6[P(n\text{-}Bu_3)_3]_2$ concentration as a function of photolysis time are linear, as predicted by eq 11. I_a was measured by using potassium ferrioxolate actinometry.[16,20] The calculated Φ_d values range from 0.06 to 0.18 and increase as the square of $HSn(n\text{-}Bu)_3$ concentration, as illustrated in Figure 1.

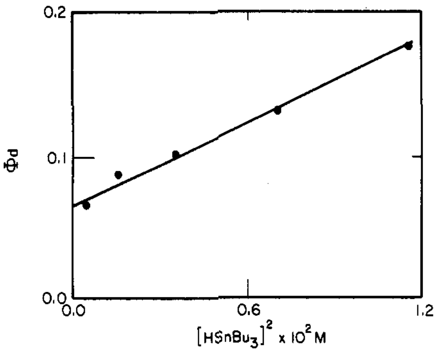

Figure 1. Variation in disappearance quantum yield Φ_d with $[HSn(n\text{-}Bu)_3]^2$ in reaction with $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$.

The fact that the graph does not exhibit a zero intercept at zero concentration of hydride may be due to photochemical decomposition of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$. Photolysis (366 nm, 23 °C, 90 min) of hexane solution of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (3.00×10^{-3} M) that have been degassed via several freeze–pump–thaw cycles results in some loss of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$. Decomposition is generally between 1 and 2% of the original $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ concentration. Photolysis of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ solutions prepared in the inert atmosphere glovebox results in slightly larger loss. The decomposition product, a green-brown solid, was not identified. When $HSn(n\text{-}Bu)_3$ is present at low concentrations, the decomposition reaction may contribute significantly to the loss in $Co_2(CO)_6]P(n\text{-}Bu)_3]_2$ concentration. In this case a plot of Φ_d vs. $HSn(n\text{-}Bu)_3$ would not yield a zero intercept.

Addition of CO inhibits the rate of photochemical reaction with $HSn(n\text{-}Bu)_3$. Two samples with identical $HSn(n\text{-}Bu)_3$ (1.01×10^{-1} M) and $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (3.01×10^{-3} M) concentrations in hexane were photolyzed with a constant light flux. One sample was sealed under 1 atm of N_2; the second was saturated with CO ($\sim 1 \times 10^{-2}$ M) prior to photolysis. A zero-order rate plot for each sample gave $\Phi_d I_a$ equal to 5.0×10^{-8} and $2.5 \times 10^{-8}\ M\ s^{-1}$ for the N_2 and CO samples, respectively.

In summary, the photochemical reaction is zero order in $Co_2CO_6[P(n\text{-}Bu)_3]_2$ concentration, second-order in $HSn(n\text{-}Bu)_3$ concentration, and inversely dependent on the CO concentration.

Photochemical Reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HMn(CO)_5$. Photolysis (366 nm, 30 min, 24 °C) of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (2.0×10^{-3} M) and $HMn(CO)_5$ (3.0×10^{-3} M) in hexane results in formation of $Mn_2(CO)_{10}$ and $(CO)_5MnCo(CO)_3P(n\text{-}Bu)_3$. Prolonged photolysis results in formation of species which were not identified. The effect of added CO or variation in $HMn(CO)_5$ concentration was not investigated. The thermal reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (23 °C) with $HMn(CO)_5$ proceeds at a negligible rate at room temperature.

Photochemical Reaction of $[M(CO)_3Cp]_2$ with $HSn(n\text{-}Bu)_3$. The photochemical reaction (366 or 500 nm) of $[M(CO)_3Cp]_2$ (M = Mo, W) with $HSn(n\text{-}Bu)_3$ in THF results in formation of $Cp(CO)_3MSn(n\text{-}Bu)_3$ according to eq 12. The thermal reaction (24 °C) of $HSn(n\text{-}Bu)_3$

$$[M(CO)_3Cp]_2 + 2HSn(n\text{-}Bu)_3 \xrightarrow{h\nu} 2(n\text{-}Bu)_3SnM(CO)_3Cp + H_2 \quad (12)$$

with $[M(CO)_3Cp]_2$ proceeds at negligible rate.[21] By contrast photolysis times of less than 2 h are required for quantitative conversion of reactants into products. Prolonged photolysis at 366 nm results in decomposition of $(n\text{-}Bu)_3SnM(CO)_3Cp$. The reaction described by eq 12 was followed by monitoring the change in absorbance of the 2010- or 1956-cm^{-1} band due to $[M(CO)_3Cp]_2$ as a function of photolysis time. Under photolysis in the presence of

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[17] Bellus, P. Ph.D. Thesis, University of Illinois, Urbana-Champaign, 1980.

[18] Adamson, A. W. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds., Wiley: New York, 1975; Chapter 10.

[19] Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970; Chapter 2.

[20] (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 519. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

[21] Bradley, G. F.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1974**, 264.

excess $HSn(n\text{-}Bu)_3$, the rate of product formation does not follow a simple rate law. The rate of product formation increases with increasing initial $HSn(n\text{-}Bu)_3$ concentration, but a precise order in $HSn(n\text{-}Bu)_3$ concentration was not determined. Added CO ($\sim 10^{-2}$ M) has negligible effect on the rate.

IR absorptions due to a species other than $Cp(CO)_3MSn(n\text{-}Bu)_3$ were detected in the reaction mixture during photolysis. A weak band at 2025 cm^{-1} (M = Mo) or 2029 cm^{-1} (M = W) appears shortly after start of photolysis. The absorption eventually loses intensity and is absent by the end of the reaction. Photolysis (366 or 500 nm of a THF solution of $[M(CO)_3Cp]_2$ (3.0×10^{-3} M) without added $HSn(n\text{-}Bu)_3$ results in growth of absorptions at these same frequencies, with concurrent loss in bands due to $[M(CO)_3Cp]_2$. Storing the reaction mixture in the dark results in loss of absorptions due to the transient, with concurrent recovery of the $[M(CO)_3Cp]_2$ absorption.

Photochemical Reaction of $[Mo(CO)_3Cp]_2$ with $HMo(CO)_3Cp$. Photolysis (366 nm, 23 °C, 1 atm of N_2) of a hexane solution of $HMo(CO)_3Cp$ (3.1×10^{-3} M) and $[Mo(CO)_3Cp]_2$ (1.0×10^{-3} M) results in formation of $[Mo(CO)_3Cp]_2$. These results suggest reaction 13, where

$$2HMo(CO)_3Cp \xrightarrow[366\ \text{nm}]{[\text{cat}]} [Mo(CO)_3Cp]_2 + H_2 \quad (13)$$

[cat] is $[Mo(CO)_3Cp]_2$. The rate of reaction, determined quantitatively by monitoring the IR absorption at 2022 cm^{-1} due to $HMo(CO)_3Cp$, is second order in $HMo(CO)_3Cp$ concentration. The effect of added CO was not investigated.

Photochemical Reaction of $[Mo(CO)_3Cp]_2$ with $HMn(CO)_5$. Photolysis (500 nm, 24 °C, 1 atm of N_2) of $[CpMo(CO)_3]_2$ (1.0×10^{-3} M) and $HMn(CO)_5$ (3.00×10^{-3} M) in hexane results in formation of $HMo(CO)_3Cp$ and $Mn_2(CO)_{10}$. There was no evidence of $Cp(CO)_3MoMn(CO)_5$ in the IR spectrum of the reaction medium.[22] These results indicate that the reaction proceeds as

$$[CpMo(CO)_3]_2 + 2HMn(CO)_5 \xrightarrow{h\nu} 2HMo(CO)_3Cp + Mn_2(CO)_{10} \quad (14)$$

Thermal Reaction of $HCo(CO)_3P(n\text{-}Bu)_3$ with $HSn(n\text{-}Bu)_3$. The thermal reaction of $HCo(CO)_3P(n\text{-}Bu)_3$ with $HSn(n\text{-}Bu)_3$ was studied because of its possible intermediacy in the photochemical reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$. The thermal reaction (22 °C, 1 atm of N_2) of $HCo(CO)_3P(n\text{-}Bu)_3$ (3.50×10^{-3} M) with $HSn(n\text{-}Bu)_3$ in hexane results in formation of $Bu_3SnCo(CO)_3P(n\text{-}Bu)_3$. The rate of product formation was determined by monitoring the decrease in absorbance at 2048 cm^{-1} due to $HCo(CO)_3P(n\text{-}Bu)_3$. Log plots of $HCo(CO)_3P(n\text{-}Bu)_3$ concentration vs. time are linear, indicating that the rate is first order in $HCo(CO)_3P(n\text{-}Bu)_3$ concentration. The observed pseudo-first-order rate constant, k_{obsd}, is 8.6×10^{-5} and 4.3×10^{-5} s^{-1} for initial $HSn(n\text{-}Bu)_3$ concentrations of 8.20×10^{-2} and 3.45×10^{-2} M, respectively. With the assumption that the reaction is first order in $HSn(n\text{-}Bu)_3$ concentration, the apparent second-order rate constant is approximately 1.2×10^{-3} M^{-1} s^{-1}.

The Thermal Reaction of $HM(CO)_3Cp$ with $HSn(n\text{-}Bu)_3$. The reaction of $HM(CO)_3Cp$ with $HSn(n\text{-}Bu)_3$ was studied due to its possible intermediacy in the photochemical reaction of $[M(CO)_3Cp]_2$ with $HSn(n\text{-}Bu)_3$. The thermal reaction (22 °C, 1 atm of N_2) of $HW(CO)_3Cp$ (2.99×10^{-3}) with $HSn(n\text{-}Bu)_3$ (5.6×10^{-2} M) in hexane proceeds at a negligible rate. Under the same conditions reaction of the molybdenum analogue results in slow formation of $Cp(CO)_3MoSn(n\text{-}Bu)_3$.

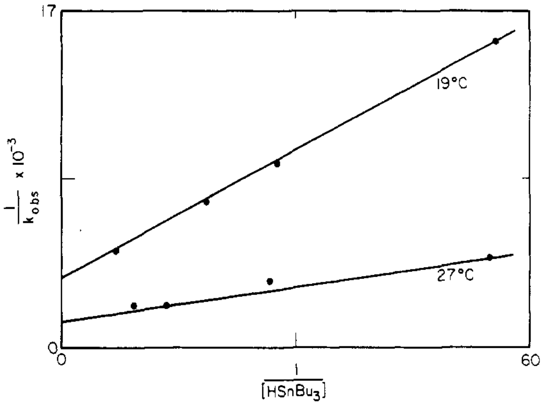

Figure 2. k_{obsd}^{-1} vs. $[HSn(n\text{-}Bu)_3]^{-1}$ for reaction of $HMo(CO)_3Cp$ with $HSn(n\text{-}Bu)_3$ at 23 °C.

The reaction of $HMo(CO)_3Cp$ with $HSn(n\text{-}Bu)_3$ was studied under condition of excess $HSn(n\text{-}Bu)_3$. The reactions were carried out at 23 °C and under an N_2 atmosphere. The rate of product formation, described by eq 15, was determined quantitatively by monitoring the decrease in IR absorbance at 2022 cm^{-1} due to $HMo(CO)_3Cp$.

$$-d[HMo(CO)_3Cp]/dt = k_{obsd}[HMo(CO)_3Cp] \quad (15)$$

The reactants were mixed via a conventional stopped-flow apparatus mounted into an IR spectrometer. Pseudo-first-order rate plots are linear for at least 3 half-lives. The pseudo-first-order rate constant, k_{obsd}, increases with increasing $HSn(n\text{-}Bu)_3$ concentration, but not linearly. Plotting the data as $1/k_{obsd}$ vs. $1/[HSn(n\text{-}Bu)_3]$ results in a straight line, as illustrated in Figure 2. It is noteworthy that added CO (2×10^{-2} M) has negligible effect on the reaction rate with the $HSn(n\text{-}Bu)_3$ concentrations utilized.

Discussion

Reactions of $M_2(CO)_{2m}L_{2n}$ with $HM'X_y$. The results described above clearly show that the most commonly observed reaction course in reactions of $M_2(CO)_{2m}L_{2n}$ with hydride $HM'X_y$ is consistent with Scheme I. The 17-electron metal carbonyl radicals are produced by either photochemical or thermal homolysis of the metal–metal bond (eq 2). The radical undergoes the succession of steps 3–5, involving rapid CO loss, oxidative addition at the 15-electron intermediate, and a final hydrogen atom transfer to produce a coordinatively saturated dihydride that reductively eliminates H_2 and then adds CO to form the observed products.

The primary evidences for the pathway described by Scheme I are the observed products $M(CO)_mL_nM'X_y$ and H_2. In addition, the kinetics results are generally consistent with this scheme. In particular, in the photochemical reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$, the proposed reaction scheme can accommodate the observations if it assumed that step 5 is rate determining. The rate of product formation is then given by eq 16, where

$$\frac{d[Co(CO)_3PR_3SnR_3]}{dt} = k_5[HSnR_3][HCoSnR_3(CO)_2PR_3] \quad (16)$$

R = n-Bu. With the usual steady-state assumptions regarding intermediates, the disappearance quantum yield for $CO_2(CO)_6[P(n\text{-}Bu)_3]_2$ can be expressed as in eq 17.

$$\Phi_d = \left(\frac{\phi}{2I_ak_1}\right)^{1/2} \frac{k_2k_3k_4[HSnR_3]^2}{2k_{-2}k_{-3}[CO]} \quad (17)$$

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[22] Cotton, F. A. *Discuss. Faraday Soc.* **1969**, *47*, 79.

Here ϕ is the quantum efficiency for photochemical production of diffusively separated $Co(CO)_3PR_3\cdot$ radicals. For the range of $HSn(n\text{-}Bu)_3$ concentrations utilized, Φ_d values are in the range of 0.1 (Figure 1). The expected second-order dependence on $[HSn(n\text{-}Bu)_3]$ and inverse dependence on [CO] were observed.

The proposed mechanism requires that steps 3–5 occur rapidly in competition with the hydrogen atom transfer (eq 9). Because such a reaction might be expected to be quite rapid even when the overall free energy change is positive, it is important to investigate the possibility that $HCo(CO)_3P(n\text{-}Bu)_3$ is an intermediate in the overall reaction, which could be formulated as

$$Co_2(CO)_6[P(n\text{-}Bu)_3]_2 \underset{k_r}{\overset{h\nu}{\rightleftarrows}} 2Co(CO)_3P(n\text{-}Bu)_3\cdot \quad (18)$$

$$Co(CO)_3P(n\text{-}Bu)_3\cdot + HSn(n\text{-}Bu)_3 \xrightarrow{k_2} HCo(CO)_3P(n\text{-}Bu)_3 + \cdot Sn(n\text{-}Bu)_3 \quad (19)$$

$$HSn(n\text{-}Bu)_3 + HCo(CO)_3P(n\text{-}Bu)_3 \xrightarrow{k_h} (n\text{-}Bu)_3SnCo(CO)_3P(n\text{-}Bu)_3 + H_2 \quad (20)$$

No evidence for $HCo(CO)_3P(n\text{-}Bu)_3$ in the reaction medium during reaction was seen. Because the IR absorbance at 1990 cm^{-1} due to this hydride has an extinction coefficient of 3.5×10^3 M^{-1} cm^{-1}, we can confidently expect to observe concentrations on the order of 10^{-4} M in a 1-mm cell. The steady-state concentration of $HCo(CO)_3P(n\text{-}Bu)_3$ for the reaction pathway described by eq 18–20 is given by eq 21. In a typical photochemical reaction, $I_a\Phi_d \approx 3$

$$[HCo(CO)_3P(n\text{-}Bu)_3] = 2I_a\Phi_d/k_h[HSn(n\text{-}Bu)_3] \quad (21)$$

$\times 10^{-8}$ s^{-1}, $[HSn(n\text{-}Bu)_3] \approx 7 \times 10^{-2}$ M. As previously noted, the apparent second-order rate constant for step 20 is 1.2×10^{-3} M^{-1} s^{-1}. The values suggest a steady-state concentration on the order of 8×10^{-4} M, which should have been easily detectable. Thus the alternative pathway embodied in steps 18–20 is ruled out.

If it is assumed that a preequilibrium, eq 2, is established in the thermal reaction, the rate law for the *thermal* reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$ is of the form

$$\frac{-d[Co_2(CO)_6(PR_3)_2]}{dt} = \frac{\kappa[HSnR_3]_2[Co_2(CO)_6(PR_3)_2]^{1/2}}{[CO]} \quad (22)$$

where κ incorporates all constants. This is not in accord with the observations. Rather, the first-order dependence on $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ and lack of dependence on $[HSn(n\text{-}Bu)_3]$ or [CO] suggests that the forward process in eq 2 is rate determining. Added support for this hypothesis comes from the observation that the rate constant for reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $SnCl_2$ in THF,[23,24] extrapolated to 25 °C, is 5×10^{-6} s^{-1}, in reasonable agreement with our value of 2.3×10^{-6} s^{-1} for reaction of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ with $HSn(n\text{-}Bu)_3$ in hexane. The rate-determining step in the reaction with $SnCl_2$ is postulated to be metal–metal bond rupture. (The reaction was observed to be light-sensitive, consistent with light-induced metal–metal bond rupture.)

It has been well established that irradiation of $[CpM(CO)_3]_2$ (M = Mo, W) compounds at 366 or 500 nm results in efficient homolysis of the metal–metal bond. Furthermore, rapid loss of CO from $CpM(CO)_3\cdot$ has been invoked to account for the efficient radical chain substitution of $CpM(CO)_3H$.[7] Thus both the observed reaction products, $CpM(CO)_3Sn(n\text{-}Bu)_3 + H_2$, and previously observed characteristics of the radical intermediate point to Scheme I as the mechanism of the photochemical reaction between $[CpM(CO)_3]_2$ and $HSn(n\text{-}Bu)_3$. The alternate pathway

$$CpM(CO)_3\cdot + HSn(n\text{-}Bu)_3 \rightarrow CpM(CO)_3H + Sn(n\text{-}Bu)_3\cdot \quad (23)$$

$$CpM(CO)_3H + HSn(n\text{-}Bu)_3 \rightarrow H_2 + CpM(CO)_3Sn(n\text{-}Bu)_3 \quad (24)$$

is ruled out by the observation that reaction 24 under thermal conditions is too slow to account for the observed overall rate. (Neither hydride absorbs significantly at either 366 or 500 nm in comparision with the dinuclear compound.)

Two aspects of these reaction systems are noteworthy. First, there is no evident inhibition of the overall reaction by added CO, as observed in the analogous reaction involving $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$. Secondly, a transient IR absorbance is seen during reaction. We propose that this transient is due to $Cp_2M_2(CO)_5THF$, formed as

$$[CpM(CO)_3]_2 \rightleftarrows 2CpM(CO)_3\cdot \quad (25)$$

$$CpM(CO)_3 \rightleftarrows CpM(CO)_2 + CO \quad (26)$$

$$CpM(CO)_2 + THF \rightarrow CpM(CO)_2THF\cdot \quad (27)$$

$$CpM(CO)_2THF\cdot + CpM(CO)_3\cdot \rightarrow Cp_2M_2(CO)_5THF \quad (28)$$

Added CO does not alter the observed overall rate because the CO does not compete effectively with the much more abundant THF for reaction with $CpM(CO)_2$.

Assignment of the transient absorption to $Cp_2M_2(CO)_5THF$ is consistent with the observation of the same IR absorbance upon irradiation of $[CpM(CO)_3]_2$ alone in THF. The THF-containing species disappears in time as the more weakly bound THF is replaced by CO. (One might have expected to observe a second THF-containing species, $Cp_2M_2(CO)_4(THF)_2$. However, disubstituted species $Cp_2M_2(CO)_4L_2$, where L is a phosphine, are not readily formed, presumably because of steric factors.[25,26] It seems likely that $Cp_2M_2(CO)_4(THF)_2$ is similarly disfavored; however, our evidence on this point is not conclusive.)

The photochemical reaction of $[CpMo(CO)_3]_2$ with $CpMo(CO)_3H$ is apparently entirely analogous to the photochemical decomposition of $HCo(CO)_4$, catalyzed by $Co_2(CO)_8$. These reactions proceed in accord with Scheme I. By contrast the photochemical reaction of $[CpMo(CO)_3]_2$ with $HMn(CO)_5$, producing $CpMo(CO)_3H$ and $Mn_2(CO)_{10}$ as products, appears to proceed via the direct hydrogen atom transfer (eq 9) to yield $HCpMo(CO)_3$. The difference in reaction pathways can be related to the fact that the H–Mn bond energy in $HMn(CO)_5$ is expected to be about 200 kJ mol^{-1},[27] as compared with 293 kJ mol^{-1} for the H–Sn bond energy.[28] With the assumption of an order of bond enthalpies H–Sn > H–Mo > H–Mn, the H atom transfer step involving the initially formed metal carbonyl radical is exothermic for the reaction with $HMn(CO)_5$ and endothermic for reaction with $HSn(n\text{-}Bu)_3$. Thus, only in the former reaction is the H atom transfer step competitive with CO loss followed by oxidative addition. The fact that reaction between $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ and $HMn(CO)_5$ appears to proceed via Scheme I

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[23] Barrett, P. F.; Poë, A. J. *J. Chem. Soc. A* **1968**, 429.

[24] Barrett, P. F. *Can. J. Chem.* **1974**, *52*, 3773.

[25] Haines, R. J.; Nyholm, R. J.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43.

[26] Strohmeier, W. S. *Angew. Chem.* **1964**, *76*, 873.

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

[28] Jackson, R. *J. Organomet. Chem.* **1979**, *166*, 17.

suggests that the Co–H bond energy in $HCo(CO)_3P(n\text{-}Bu)_3$ may not be as high as the H–Mn bond energy in $HMn(CO)_5$.

Thermal Reaction of $HM(CO)_3Cp$ with $HSn(n\text{-}Bu)_3$. The thermal reaction between $HW(CO)_3Cp$ and $HSn(n\text{-}Bu)_3$ is too slow at room temperature to admit of measurement. By contrast $HMo(CO)_3Cp$ reacts with $HSn(n\text{-}Bu)_3$ to form $CpMo(CO)_3Sn(n\text{-}Bu)_3$. The fact that there is no observed inhibition of rate by added CO and other aspects of the observed kinetics suggest a pathway of the form

$$HMo(CO)_3Cp \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A \qquad (29)$$

$$A + HSn(n\text{-}Bu)_3 \xrightarrow{k_2} B \qquad (30)$$

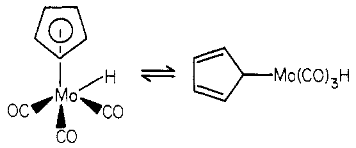
$$B \rightarrow H_2 + CpMo(CO)_3Sn(n\text{-}Bu)_3 \qquad (31)$$

With the assumption of a steady-state concentration for A, the rate law is of the form of eq 15, where

$$k_{obsd} = \frac{k_1k_2[HSn(n\text{-}Bu)_3]}{k_{-1} + k_2[HSn(n\text{-}Bu)_3]} \qquad (32)$$

A graph of k_{obsd}^{-1} vs. $[HSn(n\text{-}Bu)_3]^{-1}$ should be linear, as observed (Figure 2). The slope and y intercept are k_{-1}/k_1k_2 and k_1^{-1}, respectively. When the data is utilized from Figure 2, $k_1 = 2.5 \times 10^{-4}$ s^{-1} and k_{-1}/k_2 equals 6.2×10^{-2} M at 19 °C. At 27 °C $k_1 = 6.7 \times 10^{-4}$ s^{-1} and $k_{-1}/k_2 = 3.5 \times 10^{-2}$ M.

Species A of eq 29 could be a formyl intermediate, $(HCO)Mo(CO)_2Cp$, the result of a hydrogen atom migration. This coordinatively unsaturated species could then undergo oxidation addition of $HSn(n\text{-}Bu)_3$, followed by reductive elimination. In reactions thought to proceed via formyl intermediates the formyl species has not been observed or trapped. Although stable formyl compounds are known,[29-31] none have been prepared by direct H atom transfer. There has thus been some skepticism regarding the importance of H atom migration in carbonyl hydrides. An alternative for A is a change in the effective coordination number of the Cp ring to yield an η^3-C_5H_5 or η^1-C_5H_5 intermediate.[32,33] A shift to the η^1 mode of binding would constitute a significant reduction in steric requirements in addition to generating coordinative unsaturation at the metal center.



The present studies do not admit of a distinction between these alternative pathways. However, it is noteworthy that the reaction is much faster for the molybdenum compound than for its tungsten analogue. Since the M–H bond energies should vary in the order W–H > Mo–H, the comparative reactivity is consistent with the hydride migration pathway. It should be noted that, whichever pathway is involved, it is not the one followed in simple substitution, which occurs much more rapidly via a radical chain pathway.[7]

Summary. The most important result from this work has been to show that the reaction Scheme I is quite general. The additional observations made here add to the credibility of the mechanism as a model for the thermal and photochemical decompositions of $HCo(CO)_4$ as autocatalyzed by $Co_2(CO)_8$.[2] In addition the results show that a competing simpler pathway involving simple hydrogen atom transfer to a metal carbonyl radical can operate when the M–H bond in the hydrogen donor is sufficiently weak.

Registry No. $HSn(n\text{-}Bu)_3$, 688-73-3; $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$, 14911-28-5; $HMn(CO)_5$, 16972-33-1; $[Mo(CO)_3Cp]_2$, 12091-64-4; $[W(CO)_3Cp]_2$, 12091-65-5; $HMo(CO)_3Cp$, 12176-06-6; $HCo(CO)_3P(n\text{-}Bu)_3$, 20161-43-7; $HW(CO)_3Cp$, 12128-26-6; $Bu_3SnCo(CO)_3P(n\text{-}Bu)_3$, 79255-77-9; $Mn_2(CO)_{10}$, 10170-69-1; $(n\text{-}Bu)_3SnMo(CO)_3Cp$, 59296-12-7; $(n\text{-}Bu)_3SnW(CO)_3Cp$, 79255-78-0; $NaCo(CO)_3P(n\text{-}Bu)_3$, 29477-05-2; $(CO)_5MnCo(CO)_3P(n\text{-}Bu)_3$, 79255-79-1.

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(29) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.

(30) Johnson, B. F. G.; Kelly, R. L.; Lewis, J.; Thornback, J. R. *J. Organomet. Chem.* **1980**, *190*, C91.

(31) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503.

(32) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2517.

(33) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154.