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## Photochemical and Thermal Reactions of $\text{Co}_2(\text{CO})_8$ with $\text{Co}_2(\text{CO})_6(\text{phosphine})_2$ Compounds<sup>1</sup>

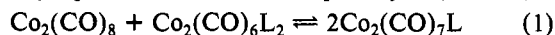
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Dicobalt octacarbonyl reacts photochemically with dicobalt hexacarbonyl bis(phosphine),  $\text{Co}_2(\text{CO})_6\text{L}_2$ , to yield a photostationary equilibrium consisting of  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_2(\text{CO})_6\text{L}_2$ , and  $\text{Co}_2(\text{CO})_7\text{L}$ . The approach to such an equilibrium follows first-order kinetics. The kinetics of the process and the photostationary-state equilibrium constant are consistent with homolytic metal-metal bond cleavage in all the dimers, followed by bimolecular recombinations of the radicals to yield the three possible dinuclear species. Thermal reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{Co}_2(\text{CO})_6\text{L}_2$  is slow in all cases except  $\text{L} = \text{P}(t\text{-Bu})_3$ , for which the reaction has a half-life of about 60 s. A mechanism involving electron transfer from the  $\text{Co}(\text{CO})_3\text{L}$  radical to  $\text{Co}_2(\text{CO})_8$  is proposed for this relatively fast reaction.

### Introduction

Photochemical homolysis of the metal-metal bond in dinuclear metal carbonyls has become a well-established route to formation of metal-centered carbonyl radicals.<sup>2</sup> It has been shown that for  $\text{Re}(\text{CO})_5$ ,  $\text{Mn}(\text{CO})_5$ , and  $\text{Co}(\text{CO})_4$  recombination occurs at close to diffusion-controlled rates.<sup>3,4</sup> However, significant reductions in recombination rates are observed for substituted metal-centered carbonyls.<sup>3,5-8</sup> For example, the recombination rate constant for  $\text{Co}(\text{CO})_4$  is greater by a factor of 5 than that for  $\text{Co}(\text{CO})_3\text{P}(n\text{-Bu})_3$ . If two different dinuclear carbonyl compounds,  $\text{M}-\text{M}$  and  $\text{M}'-\text{M}'$ , are photolyzed together such that nonselective metal-metal bond homolysis occurs, cross coupling of the radicals can result in formation of  $\text{M}-\text{M}'$ .<sup>9-11</sup> The kinetics of  $\text{M}-\text{M}'$  formation have not been reported. Because recombination rates of  $\cdot\text{M}$  and  $\cdot\text{M}'$  are not necessarily equivalent, and rates of bond homolysis may not be identical, a statistical product distribution in the photostationary states is not required. We report here our observations of the photochemical and thermal reactions of  $\text{Co}_2(\text{CO})_8$  with  $\text{Co}_2(\text{CO})_6\text{L}_2$  ( $\text{L} = \text{phosphine}$ ) as described by eq 1. Under continuous photolysis (366 nm) a



photostationary-state equilibrium is established within about

$10^3$  s. Except when  $\text{L} = \text{P}(t\text{-Bu})_3$ , the thermal dark reaction (22 °C) is exceedingly slow, contrary to previous reports.<sup>12,13</sup>

### 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 box. Dichloromethane (Aldrich),  $\text{CH}_2\text{Cl}_2$ , was distilled under  $\text{N}_2$  and stored over activated 4A molecular sieves. Dicobalt octacarbonyl (Pressure Chemical Co.),  $\text{Co}_2(\text{CO})_8$ , was sublimed (30 °C, 1 mmHg) prior to use.  $\text{Co}_2(\text{CO})_6\text{L}_2$ ,  $\text{L} = \text{P}(n\text{-Bu})_3$ ,  $\text{P}(t\text{-Bu})_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{CH}_3)_2\text{Ph}$ ,  $\text{P}(\text{CH}_3)\text{Ph}_2$  ( $\text{Ph} = \text{C}_6\text{H}_5$ ), was synthesized according to standard literature procedures.<sup>14</sup>

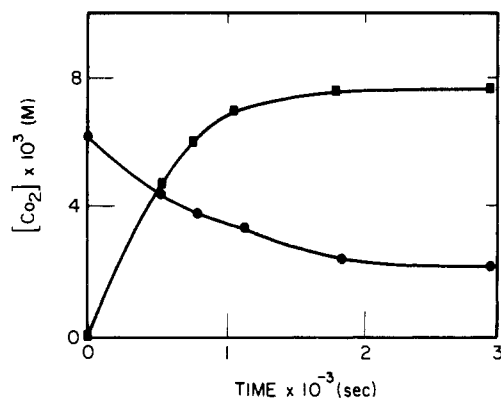
**Thermal Experiments.** Due to the extreme light sensitivity of the reaction mixture, all manipulation must be carried out under red light. In a typical experiment known amounts of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$  were added to a 25-mL Ray-sorb volumetric flask in an inert-atmosphere glovebox. Following addition of solvent, the solution was transferred into a quartz tube previously covered with black plastic. The tube was equipped with a stopcock and septum to allow sampling of the reaction mixture. The tube was brought out of the glovebox, purged with CO that was first passed through glass columns packed with 4A molecular sieves and activated manganese oxide, and then placed in a constant-temperature bath ( $25 \pm 1$  °C) in the dark. After equilibration an initial IR spectrum was taken. IR spectra were then recorded as a function of time. Care was taken during IR sampling to avoid exposure of the reaction mixture to stray light. A germanium filter was placed in the source beam in front of the IR cell to block UV and visible light originating from the Nernst glower.

The reaction of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6[\text{P}(t\text{-Bu})_3]_2$  was observed with use of a simple stopped-flow apparatus, described elsewhere.<sup>15,16</sup>

**Photochemical 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<sup>17</sup> to isolate the 366-nm line. Quartz photolysis

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**Figure 1.** Change in the  $\text{Co}_2(\text{CO})_8$  (●) and  $\text{Co}_2(\text{CO})_7\text{L}$  (■) concentrations as a function of photolysis (366 nm) time. The solid lines represent calculated values based on numerical fitting (Table II).

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. The reagents were mixed and handled as described above. An initial IR spectrum was taken after the quartz tubes (wrapped in black plastic) were removed from the glovebox. The plastic was removed, and the solution was photolyzed (366 nm); IR spectra were taken of samples removed following various photolysis times.

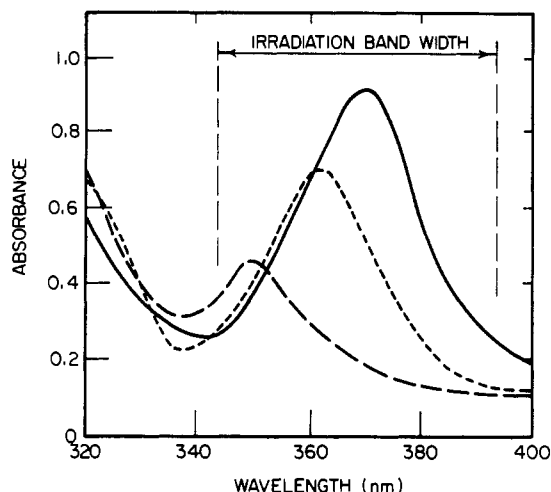
### Results

**Thermal Reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{Co}_2(\text{CO})_6\text{L}_2$ .** The reactions of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$  ( $\text{L} = \text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{CH}_3)_2\text{Ph}$ ,  $\text{P}(t\text{-Bu})_3$ ) at 25 °C under 1 atm of CO results in the formation of  $\text{Co}_2(\text{CO})_7\text{L}$  (eq 1). When  $\text{L} = \text{P}(n\text{-Bu})_3$ , the thermal equilibrium constant at 25 °C is about 20. In the case of  $\text{P}(n\text{-Bu})_3$  and  $\text{P}(\text{CH}_3)_2\text{Ph}$  the rate of product formation is very slow. For example, with initial  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$  concentrations of  $2.5 \times 10^{-3}$  M, only about 5% reaction was observed after 5 days. However, for  $\text{L} = \text{P}(t\text{-Bu})_3$  the reaction half-life, with initial  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6[\text{P}(t\text{-Bu})_3]_2$  concentrations of  $3.0 \times 10^{-3}$  M, is approximately 60 s.

When  $\text{L} = \text{P}(n\text{-Bu})_3$  and  $\text{P}(\text{CH}_3)_2\text{Ph}$ , the reactions must be carried out with added CO in solution to suppress decomposition of  $\text{Co}_2(\text{CO})_8$ , which, without added CO, occurs more rapidly than  $\text{Co}_2(\text{CO})_7\text{L}$  formation;<sup>18,19</sup>  $\text{Co}_4(\text{CO})_{12}$  is the product.

**Photochemical Reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{Co}_2(\text{CO})_6\text{L}_2$ .** Irradiation (366 nm) of a hexane or  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$ , typically,  $5.0 \times 10^{-3}$  M in each, leads to an approach to a photostationary state according to equilibrium 1. The reaction proceeds smoothly for  $\text{L} = \text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{O}i\text{Pr})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{CH}_3)_2\text{Ph}$ , and  $\text{P}(\text{CH}_3)\text{Ph}_2$ . In all cases the equilibrium lies somewhat to the right and is attained within 1 h under a constant photon flux (22 °C). The results of a typical experiment for  $\text{L} = \text{P}(n\text{-Bu})_3$  are illustrated in Figure 1. Initial  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$  concentrations were  $5.8 \times 10^{-3}$  M. Equilibrium concentrations, estimated from the intensities of CO stretching absorptions in the IR spectrum, were  $2.05 \times 10^{-3}$  M for  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$  and  $7.48 \times 10^{-3}$  M for  $\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$ . Equilibrium concentrations of all components were determined only for  $\text{L} = \text{P}(n\text{-Bu})_3$ ; in all other cases the IR bands for one or more species could not be sufficiently distinguished from other bands to permit accurate estimates of concentrations.

The rate of  $\text{Co}_2(\text{CO})_7\text{L}$  formation for  $\text{L} = \text{P}(n\text{-Bu})_3$  or  $\text{P}(\text{O}i\text{Pr})_3$  was determined quantitatively by monitoring the



**Figure 2.** UV absorption spectra of  $\text{Co}_2(\text{CO})_8$  (---),  $\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$  (-·-), and  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$  (—) and the irradiation bandwidth employed in the photochemical experiments.

**Table I.** Absorption Maxima for  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$ , and  $\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$

compd	$\lambda_{\text{max}}$ , nm	$\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$
$\text{Co}_2(\text{CO})_8$	350	8 400
$\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$	363	13 600
$\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$	370	21 500

decrease in IR absorbance at  $2045\text{ cm}^{-1}$  due to  $\text{Co}_2(\text{CO})_8$ . Under a constant photon flux the disappearance of  $\text{Co}_2(\text{CO})_8$  followed first-order kinetics. The reaction was carried out in hexane for  $\text{L} = \text{P}(n\text{-Bu})_3$ . In the case of  $\text{L} = \text{P}(\text{O}i\text{Pr})_3$ ,  $\text{CH}_2\text{Cl}_2$  was utilized due to the low solubility of  $\text{Co}_2(\text{CO})_6[\text{P}(\text{O}i\text{Pr})_3]_2$  in alkanes. It has been reported that  $\text{CH}_2\text{Cl}_2$  can act as a Cl atom donor in the presence of some metal-centered carbonyl radicals.<sup>10,20,21</sup> However, photolysis (366 nm) of  $\text{Co}_2(\text{CO})_8$  or  $\text{Co}_2(\text{CO})_6[\text{P}(\text{O}i\text{Pr})_3]_2$  in  $\text{CH}_2\text{Cl}_2$  for 3 h resulted in negligible change in either carbonyl concentration.

### Discussion

The UV absorption spectra of  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$ , and  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$  and the irradiation bandwidth employed in the photochemical experiments are shown in Figure 2. The absorption maxima and molar extinction coefficients are listed in Table I. By analogy with other well-characterized dinuclear metal carbonyls, the absorption maximum at 363 nm due to  $\text{Co}_2(\text{CO})_7\text{P}(n\text{-Bu})_3$  is assigned to the  $\sigma \rightarrow \sigma^*$  transition of the Co-Co bond.<sup>9,10,22,23</sup> A similar assignment is made for the absorption maximum at 370 nm due to  $\text{Co}_2(\text{CO})_6[\text{P}(n\text{-Bu})_3]_2$ .  $\text{Co}_2(\text{CO})_8$  exists in solution as a mixture of bridged and nonbridged isomers, in rapid equilibrium.<sup>24–27</sup> Comparable concentrations of bridged and unbridged forms are present at room temperature. The 350-nm absorption (Figure 2) has been assigned to the  $\sigma \rightarrow \sigma^*$  transition of the Co-Co bond in the nonbridged isomer.<sup>23,28</sup>

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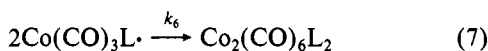
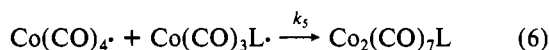
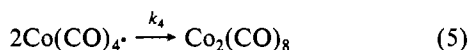
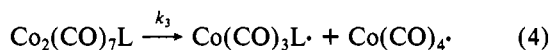
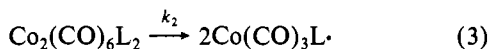
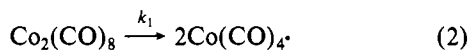
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The overall lower absorption of Co<sub>2</sub>(CO)<sub>8</sub> within the irradiation bandwidth compared to those for Co<sub>2</sub>(CO)<sub>6</sub>[P(*n*-Bu)<sub>3</sub>]<sub>2</sub> and Co<sub>2</sub>(CO)<sub>7</sub>P(*n*-Bu)<sub>3</sub>, as illustrated in Figure 2, is a consequence of the bridged–nonbridged equilibrium. The wavelength of the absorption maximum due to Co<sub>2</sub>(CO)<sub>7</sub>P(*n*-Bu)<sub>3</sub> falls between the values for Co<sub>2</sub>(CO)<sub>8</sub> and Co<sub>2</sub>(CO)<sub>6</sub>[P(*n*-Bu)<sub>3</sub>]<sub>2</sub>. A similar observation has been made for Mn<sub>2</sub>(CO)<sub>10</sub> and its mono- and disubstituted phosphine derivatives.<sup>10</sup>

The broad-band photolysis centered at 366 nm (Figure 2) results in nonselective photochemical homolysis of the metal–metal bonds of Co<sub>2</sub>(CO)<sub>8</sub>, Co<sub>2</sub>(CO)<sub>7</sub>L, and Co<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub>. The photostationary equilibrium is best accounted for in terms of the processes of Scheme I. Scheme I is general for all L and may be applicable to similar reactions involving other dinuclear metal carbonyl compounds.<sup>9,10,22</sup> *k*<sub>1</sub>–*k*<sub>3</sub> are the photochemical rate constants (defined below) for Co–Co bond homolysis. The bimolecular recombinations of ·Co(CO)<sub>4</sub> or ·Co(CO)<sub>6</sub>L result in formation of Co<sub>2</sub>(CO)<sub>8</sub> or Co<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub>, respectively. Rate constants *k*<sub>4</sub> and *k*<sub>6</sub> have the values 4.2 × 10<sup>8</sup> and 9.1 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>29</sup> Cross coupling of ·Co(CO)<sub>4</sub> and ·Co(CO)<sub>3</sub>L results in formation of Co<sub>2</sub>(CO)<sub>7</sub>L.

### Scheme I



Scheme I accounts for the observed photostationary-state equilibrium. The photostationary state is established when the overall rates of photochemical Co–Co bond cleavage equal the rates of Co–Co bond formation. When this condition is met, and when Scheme I is used, eq 8–10 apply. The

$$-d[\text{Co}_2(\text{CO})_8]/dt = k_1[\text{Co}_2(\text{CO})_8] - k_4[\text{Co}(\text{CO})_4 \cdot]^2 = 0 \quad (8)$$

$$-d[\text{Co}_2(\text{CO})_7\text{L}]/dt = k_3[\text{Co}_2(\text{CO})_7\text{L}] - k_5[\text{Co}(\text{CO})_3\text{L} \cdot][\text{Co}(\text{CO})_4 \cdot] = 0 \quad (9)$$

$$-d[\text{Co}_2(\text{CO})_6\text{L}_2]/dt = k_2[\text{Co}_2(\text{CO})_6\text{L}_2] - k_6[\text{Co}(\text{CO})_3\text{L} \cdot]^2 = 0 \quad (10)$$

photostationary equilibrium constant is given by eq 11. *k*<sub>1</sub>–*k*<sub>3</sub>

$$K_{\text{eq}} = \frac{[\text{Co}_2(\text{CO})_7\text{L}]^2}{[\text{Co}_2(\text{CO})_8][\text{Co}_2(\text{CO})_6\text{L}_2]} = \left( \frac{k_5^2}{k_4 k_6} \right) \left( \frac{k_1 k_2}{k_3^2} \right) \quad (11)$$

are the photochemical first-order rate constants defined as shown in eq 12–14.

$$k_1 = \Phi_8 I_8 S / V[\text{Co}_2(\text{CO})_8] \quad (12)$$

$$k_2 = \Phi_6 I_6 S / V[\text{Co}_2(\text{CO})_6\text{L}_2] \quad (13)$$

$$k_3 = \Phi_7 I_7 S / V[\text{Co}_2(\text{CO})_7\text{L}] \quad (14)$$

The Φ values represent the quantum yields for formation of diffusively separated radicals. Each *I*S/*V* represents the number of photons per unit volume per unit time absorbed by

Table II. Optimal Rate Constants Utilized for Computer Modeling of Reaction Scheme 1<sup>a</sup>

rate constant	value	rate constant	value
<i>k</i> <sub>1</sub> <sup>b</sup>	2.71 × 10 <sup>-3</sup> s <sup>-1</sup>	<i>k</i> <sub>4</sub> <sup>c</sup>	4.2 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup>
<i>k</i> <sub>2</sub> <sup>b</sup>	2.71 × 10 <sup>-3</sup> s <sup>-1</sup>	<i>k</i> <sub>5</sub> <sup>d</sup>	7.1 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup>
<i>k</i> <sub>3</sub> <sup>b</sup>	2.71 × 10 <sup>-3</sup> s <sup>-1</sup>	<i>k</i> <sub>6</sub> <sup>c</sup>	9.1 × 10 <sup>7</sup> M <sup>-1</sup> s <sup>-1</sup>

<sup>a</sup> Initial Co<sub>2</sub>(CO)<sub>8</sub> and Co<sub>2</sub>(CO)<sub>6</sub>[P(*n*-Bu)<sub>3</sub>]<sub>2</sub> concentrations equal 5.80 × 10<sup>-3</sup> M. <sup>b</sup> Based on the observed rate of disappearance of Co<sub>2</sub>(CO)<sub>8</sub>; we assume the same rate of metal–metal bond cleavage for all three dinuclear compounds. <sup>c</sup> Reference 29. <sup>d</sup> *k*<sub>5</sub> varied to obtain optimal fit.

the corresponding metal carbonyl. The absorbed photon fluxes per unit time for each species are given by eq 15–17, where

$$I_8 = I_0(1 - e^{-2.303D}) \frac{\epsilon_8 I [\text{Co}_2(\text{CO})_8]}{D} \quad (15)$$

$$I_6 = I_0(1 - e^{-2.303D}) \frac{\epsilon_6 I [\text{Co}_2(\text{CO})_6\text{L}_2]}{D} \quad (16)$$

$$I_7 = I_0(1 - e^{-2.303D}) \frac{\epsilon_7 I [\text{Co}_2(\text{CO})_7\text{L}]}{D} \quad (17)$$

the ε values are weighted average molar extinction coefficients and *D* = *l*(ε<sub>8</sub>[Co<sub>2</sub>(CO)<sub>8</sub>] + ε<sub>6</sub>[Co<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub>] + ε<sub>7</sub>[Co<sub>2</sub>(CO)<sub>7</sub>L]). With the assumption that *e*<sup>-2.303*D*</sup> is negligible

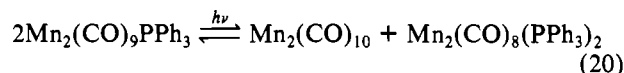
$$\frac{k_1 k_2}{k_3^2} = \left( \frac{\epsilon_8 \epsilon_6}{\epsilon_7^2} \right) \left( \frac{\Phi_8 \Phi_6}{\Phi_7^2} \right) \quad (18)$$

substituting eq 18 into eq 11 gives

$$\frac{[\text{Co}_2(\text{CO})_7\text{L}]_{\text{eq}}^2}{[\text{Co}_2(\text{CO})_8]_{\text{eq}}[\text{Co}_2(\text{CO})_6\text{L}_2]_{\text{eq}}} = \left( \frac{k_5^2}{k_4 k_6} \right) \left( \frac{\epsilon_8 \epsilon_6}{\epsilon_7^2} \right) \left( \frac{\Phi_8 \Phi_6}{\Phi_7^2} \right) \quad (19)$$

The photostationary equilibrium constant is given by the right-hand side of eq 19.<sup>30</sup> The disappearance quantum yields are likely to be very similar; the last term in eq 19 can be set equal to 1.<sup>9,21,22</sup> However, the effective values of ε for the different species over the range of wavelengths represented by the irradiation source (Figure 2) differ substantially. As an approximation the ε values required can be taken as those for λ<sub>max</sub> (Table I).

With use of the observed values for *k*<sub>4</sub> and *k*<sub>6</sub>, and the observed equilibrium concentrations, *k*<sub>5</sub> can be calculated, if all Φ values are assumed to be equal. The resulting value of *k*<sub>5</sub> is 7 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>, close to that for *k*<sub>4</sub>, the rate constant for formation of Co<sub>2</sub>(CO)<sub>8</sub>. Continuous photolysis (366 nm) of Mn<sub>2</sub>(CO)<sub>9</sub>PPh<sub>3</sub> results in formation of Mn<sub>2</sub>(CO)<sub>10</sub> and Mn<sub>2</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)<sub>2</sub> according to eq 20.<sup>10</sup> With use of data



obtained from that work and eq 19 the photostationary-state equilibrium constant for reaction 20 is calculated to be 8.8. This value is similar to that observed for reaction 1.

The rate equations for reactions 2–7 for L = P(*n*-Bu)<sub>3</sub> were numerically integrated by using an algorithm for the numerical integration of “stiff” differential equations.<sup>31</sup> The input parameters utilized in the computer study are listed in Table II.

(29) Olsen, R. J.; Wegman, R. W.; Brown, T. L., unpublished observations.

(30) Adamson, A. W. In “Concepts of Inorganic Photochemistry”; Adamson, A. W.; Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 10.  
(31) Stabler, R. N.; Chesick, J. P. *Int. J. Chem. Kinet.* 1978, 10, 461.

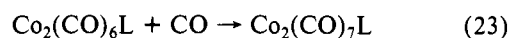
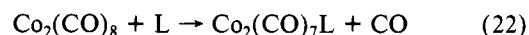
In keeping with the assumption of nonselective photoinduced Co-Co bond homolysis, we assumed the photochemical first-order rate constants  $k_1$ - $k_3$  to be equal, at a value that reproduces the observed pseudo-first-order behavior. Numerical values for  $k_4$  and  $k_6$  were obtained from flash photolysis experiments.<sup>29</sup> The recombination rate constant,  $k_5$ , was varied from  $1.0 \times 10^8$  to  $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . An optimal fit with the observed rate data, as illustrated in Figure 1, was achieved with  $k_5$  equal to  $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , close to the value derived from eq 19.

It is noteworthy that the approach to a photostationary state is first order in  $[\text{Co}_2(\text{CO})_8]$  when  $\text{L} = \text{P}(n\text{-Bu})_3$ . This behavior results from the strong internal filter effect created by the presence of  $\text{Co}_2(\text{CO})_7\text{L}$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$  in addition to  $\text{Co}_2(\text{CO})_8$ .<sup>32,33</sup>

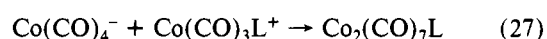
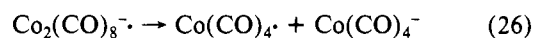
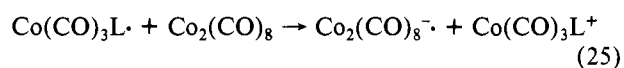
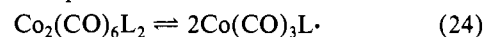
Except for the case of  $\text{L} = \text{P}(t\text{-Bu})_3$  the thermal reactions of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$  are extremely slow. No attempt was made to study the kinetics of the thermal reactions in detail. It is tempting to suggest that the thermal reaction proceeds via a mechanism analogous to Scheme I with steps 2-4 proceeding by thermal bond homolysis. The equilibration in such a case is rate limited by the slower rate of metal-metal bond rupture in  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_6\text{L}_2$ . Certain thermal reactions involving dinuclear cobalt carbonyl compounds have been postulated to occur via Co-Co bond homolysis.<sup>34,35</sup> The slow rates of thermal equilibration for L other than  $\text{P}(t\text{-Bu})_3$  are not inconsistent with what is known of this process in  $\text{Co}_2(\text{CO})_8$  and the  $\text{Co}_2(\text{CO})_6\text{L}_2$  compound involved. However, the very rapid rate of equilibration of  $\text{Co}_2(\text{CO})_8$  with  $\text{Co}_2(\text{CO})_6[\text{P}(t\text{-Bu})_3]_2$  is inconsistent with this mechanism. Co-Co bond rupture in  $\text{Co}_2(\text{CO})_6[\text{P}(t\text{-Bu})_3]_2$  is likely to be comparatively rapid as a result of steric strain created by the

phosphine ligands.<sup>36</sup> In that event, Co-Co bond rupture in  $\text{Co}_2(\text{CO})_8$  would be rate determining. However, equilibration occurs at a rate much faster than the estimated rate of metal-metal bond homolysis in  $\text{Co}_2(\text{CO})_8$ .<sup>37</sup>

A process involving rate-determining loss of L from  $\text{Co}_2(\text{CO})_6\text{L}_2$ , eq 21-23, can also be ruled out. The kinetics of the



reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{P}(t\text{-Bu})_3$  have recently been studied.<sup>38</sup> The results show that the reaction is too slow to account for the present results. Our observations can be accommodated by a postulated rapid electron-transfer process, as shown in eq 24-27. The slow process in this mechanism could be either



step 24 or step 25. There is precedent for an electron-transfer process such as 25 in the reactions of  $\text{Co}_2(\text{CO})_8$  with phosphines.<sup>37,38</sup> Steps 26 and 27 would be expected to be rapid.<sup>39</sup>

**Registry No.**  $\text{Co}_2(\text{CO})_8$ , 10210-68-1;  $\text{Co}_2(\text{CO})_6(\text{P}(n\text{-Bu})_3)_2$ , 14911-28-5;  $\text{Co}_2(\text{CO})_6(\text{P}(t\text{-Bu})_3)_2$ , 70623-28-8;  $\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2$ , 21118-36-5;  $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$ , 1010-27-1;  $\text{Co}_2(\text{CO})_6(\text{P}(\text{CH}_3)_2\text{Ph})_2$ , 21407-17-0;  $\text{Co}_2(\text{CO})_6(\text{P}(\text{CH}_3)\text{Ph}_2)_2$ , 31224-11-0;  $\text{Co}_2(\text{CO})_7(\text{P}(n\text{-Bu})_3)$ , 19298-62-5;  $\text{Co}_2(\text{CO})_7(\text{P}(\text{CH}_3)_2\text{Ph})$ , 83746-88-7;  $\text{Co}_2(\text{CO})_7(\text{P}(\text{OPh})_3)$ , 19298-61-4.

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## Imine Formation and Stability and Interligand Condensation with Cobalt(III) 1,2-Ethanediamine Complexes

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The isolation of imine complexes formed by the condensation of acetaldehyde with Co(III) 1,2-ethanediamine complexes is described. In one instance two such acetaldehyde moieties condense relatively stereospecifically. The X-ray crystal structures of this product and another acetaldehyde product derived from the  $\Delta$ -[Co(en)<sub>2</sub>((S)-Tyr)]<sup>2+</sup> ion are also described. The results indicate something of the reactivity and stability of such coordinated imines and have implications for the manner in which macrocyclic ligands are formed on metal ions.

### Introduction

The reactions that occur between carbonyl compounds and amines or amine derivatives in the presence of metal ions have been widely exploited and form the basis of many quite ex-

tensive studies in inorganic chemistry.<sup>1,2</sup> One of the simplest reactions of this kind is the so-called "Curtis reaction" between acetone and nickel(II) ethylenediamine complexes, the ultimate products being the very well-known macrocyclic diimine ligand complexes **1** and **2**. Several intermediates, including isopropylidene amine ligand complexes such as **3**, have been

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