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Photochemical Ligand Dissociation, Electron Transfer, and Metal–Metal Bond Cleavage of Phosphine-Substituted Cobalt Carbonyl Complexes

Marlis F. Mirbach* and Manfred J. Mirbach

Universitat Duisburg, Fachbereich 6, 4100 Duisburg, West Germany

Richard W. Wegman*

Union Carbide Corporation, South Charleston, West Virginia 25303

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The major photochemical reactions of $[Co(CO)_3L_2][Co(CO)_4]$ are initiated by photolysis of the cation $Co(CO)_3L_2^+$. Upon photolysis $Co(CO)_3L_2^+$ loses a ligand, either CO or L (L = tributylphosphine), to give $Co(CO)_2L_2^+$ and $Co(CO)_3L^+$ which will react with $Co(CO)_4^-$ to give $Co_2(CO)_6L_2$ and $Co_2(CO)_7L$, with excess L to give $Co(CO)_2L_3^+$ and $Co(CO)_3L_2^+$, and with H_2 to give $HCo(CO)_2L_2$ and $HCo(CO)_3L$, respectively. The neutral complex $Co_2(CO)_6L_2$ is photostable in the absence of phosphine. With an excess of L it undergoes either photosubstitution to $Co_2(CO)_5L_3$ and $Co_2(CO)_4L_4$ or disproportionation to $[Co(CO)_2L_3][Co(CO)_4]$ (major) and $[Co(CO)_3L_2][Co(CO)_3L]$, depending on the nature of the solvent (hexane or methanol, respectively). Electron-transfer and radical reactions are responsible for the observed products.

Introduction

Photosubstitution of a mononuclear metal carbonyl $M(CO)_nL_X$ typically proceeds via photoinduced ligand loss followed by reaction of the coordinatively unsaturated intermediate with a nucleophile.[1] In some instances photosubstitution proceeds via an electron-transfer mechanism.[2] In the case of dinuclear metal carbonyls photolysis can result in ligand loss or cleavage of the metal–metal bond.[3,4]

We have studied and compared the photochemistry of the ionic complexes $[Co(CO)_3L_2][Co(CO)_4]$ and $[Co(CO)_3L_2](OAc)$ and the neutral dinuclear complex $Co_2(CO)_6L_2$ (L = tributylphosphine) in the presence of potential ligands like CO, H_2, and L. We have found that all three photoreactions, namely, ligand dissociation, electron transfer, and metal–metal bond cleavage can be studied in this system. This is of interest because $[Co(CO)_3L_2][Co(CO)_4]$ has been shown to be the photoactive catalyst precursor in the photochemical hydroformylation of olefins in methanol solution.[5]

Table I. Spectroscopic Data of Cobalt Carbonyl Complexes[a]

compd	IR, cm^{-1} (ϵ)[a]	UV, nm (ϵ)[a]	solv
$Co(CO)_3L_2^+$	2000 (3000), 1992	245 (80 000)	MeOH
$Co(CO)_4^-$	1905 (5000)	255 (6300)[c]	MeOH
$Co_2(CO)_6L_2$	1972, 1953 (10 200)	365 (25 000)[c]	MeOH
	1950 (18 000)[g]	370 (21 500)[h]	hexane
$Co_2(CO)_7L$	1992[b]	360	MeOH
	1993 (8200)[g]	362 (13 600)[h]	hexane
$Co(CO)_2L_3^+$	1953, 1942[d]		
$HCo(CO)_3L$	1975 (3500)[e]		MeOH
	1968 (3500)[g]		hexane
$HCo(CO)_2L_2$	1905[e]		MeOH
$AcO\text{-}Co(CO)_2L_2$	1915[f]		MeOH
$Co_2(CO)_5L_3$	1945, 1750[h]		hexane
$Co_2(CO)_4L_4$	1917, 1719[j]		hexane

[a] Only strong bands are listed, which are relevant for the described experiments; in M^{-1} cm^{-1}. [b] Compared with a separately prepared authentic sample. [c] In H_2O, from ref 14. [d] Assigned in analogy to the corresponding triethyl phosphine complex.[9] [e] Compare ref 11 and 20. [f] Assigned in analogy to $ICo(CO)_2L_2$.[7] [g] From ref 21. [h] From ref 14. [i] From ref 9. [j] From ref 22.

Results

$[Co(CO)_3L_2][Co(CO)_4]$. The yellow ionic complex ($L = P(Bu)_3$) is insoluble in nonpolar solvent but readily dissolves in methanol dissociating into the cation $Co(CO)_3L_2^+$ and anion $Co(CO)_4^-$. Photolysis (25 °C, 366 nm) of $[Co(CO)_3L_2][Co(CO)_4]$ in methanol under Ar results in the neutral species $Co_2(CO)_6L_2$ and $Co_2(CO)_7L$ (eq 1).

$$[Co(CO)_3L_2][Co(CO)_4] \xrightarrow{h\nu} Co_2(CO)_6L_2\ (70\%) + Co_2(CO)_7L\ (30\%) \quad (1)$$

$$\Phi \approx 0.2$$

$Co_2(CO)_6L_2$ is also obtained in the absence of light when $[Co(CO)_3L_2][Co(CO)_4]$ is heated to 60 °C in nonpolar solvents,[6] electrolyzed,[7] or treated with amine oxide. The photochemical reaction is suppressed by CO; at 25 °C and 50 atm of CO the quantum yield is about one-tenth the value observed in Ar.

Photolysis of $[Co(CO)_3L_2][Co(CO)_4]$ with an equimolar amount of L results in the formation of $Co_2(CO)_6L_2$ and

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(1) For summaries see: (a) Strohmeier, W. *Angew. Chem.* **1964,** *76,* 873. (b) Wrighton, M. S. *Chem. Rev.* **1974,** *74,* 401. (c) Wrighton, M. S.; Geoffroy, G. L. "Organometallic Photochemistry"; Academic Press: New York, 1979. (d) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982,** *21,* 113.

(2) For examples see: Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981,** *103,* 5238. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *Ibid.* **1982,** *104,* 3034.

(3) (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. (b) Poë, A. *Transition Met. Chem. (Weinheim, Ger.)* **1982,** *7,* 65.

(4) (a) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978,** *100,* 4095. (b) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *Ibid.* **1980,** *102,* 6248. (c) Forbus, N. P.; Brown, T. L. *Inorg. Chem.* **1981,** *20,* 4343.

(5) (a) Mirbach, M. J.; Mirbach, M. F.; Saus, A.; Topalsavoglou, N.; Phu, T. N. *J. Am. Chem. Soc.* **1981,** *103,* 7590. (b) Mirbach, M. J.; Mirbach, M. F.; Saus, A.; Topalsavoglou, N.; Phu, T. N. *Ibid.* **1981,** *103,* 7594. (c) Mirbach, M. J.; Topalsavoglou, N.; Phu, T. N.; Mirbach, M. F.; Saus, A. *Angew. Chem.* **1981,** *93,* 391; *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 3381.

(6) (a) McCleverty, J. A.; Davison, A.; Wilkinson, G. *J. Chem. Soc.* **1965,** 389. (b) Manning, A. R. *J. Chem. Soc. A.* **1968,** 1135. (c) Szabo, P.; Fekete, L.; Bor, G.; Nagy-Magos, Z.; Marko, L. *J. Organomet. Chem.* **1968,** *12,* 245.

(7) Mirbach, M. F.; Gurtler, O., to be published separately.

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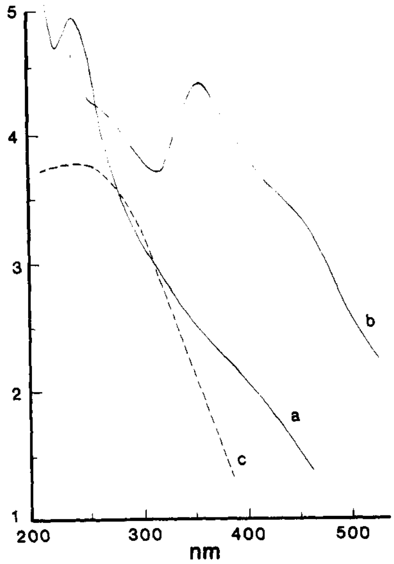


Figure 1. UV absorption spectra of (a) $[Co(CO)_3L_2]^+$ and (b) $Co_2(CO)_6L_2$ in methanol and (c) $[Co(CO)_4]^-$ in water (from ref 19; L = tributylphosphine).

the ionic complex $[Co(CO)_2L_3][Co(CO)_4]$ (eq 2).[8] With a 10-fold excess of L, $[Co(CO)_2L_3][Co(CO)_4]$ is the only product.

$$[Co(CO)_3L_2][Co(CO)_4] + L \xrightarrow{h\nu} Co_2(CO)_6L_2\ (80\%) + [Co(CO)_2L_3][Co(CO)_4]\ (20\%) \quad (2)$$

The substituted hydrides $HCo(CO)_3L$ and $HCo(CO)_2L_2$ are the principal products when $[Co(CO)_3L_2][Co(CO)_4]$ is photolyzed under 55 atm of H_2. Overlapping reactant product IR bands precluded accurate quantitative determination of $HCo(CO)_2L_2$.

$[Co(CO)_3L_2](OAc)$. The electronic absorption spectra of cation $Co(CO)_3L_2^+$ and anion $Co(CO)_4^-$ are qualitatively similar with maxima at 245 and 255 nm, respectively. The extinction coefficient of $Co(CO)_3L_2^+$, however, is much higher than that of $Co(CO)_4^-$ (compare Figure 1 and Table I). Upon irradiation most of the light is therefore absorbed by the cation. Thus, it is very probable that the photochemical reactions of $[Co(CO)_3L_2][Co(CO)_4]$ result from photolysis of $Co(CO)_3L_2^+$. To test this hypothesis the complex $[Co(CO)_3L_2](OAc)$ was prepared, which allowed the investigation of the photochemical reactions of $Co(CO)_3L_2^+$ without the disturbing influence of the anion $Co(CO)_4^-$.

Irradiation of a methanol solution of $[Co(CO)_3L_2](OAc)$ leads to a new IR absorption band at 1915 cm^{-1} which we tentatively assign to $AcO-Co(CO)_2L_2$ by analogy to the corresponding iodide complex.[9] $AcO-Co(CO)_2L_2$ is rapidly converted to the starting material under 50 atm of CO in the dark (eq 3). Similarly, $AcO-Co(CO)_2L_2$ reacts rapidly with excess L to generate $Co(CO)_2L_3^+$. Photolysis of $[Co(CO)_3L_2](OAc)$ with a large excess of L yields only $Co(CO)_2L_3^+$, presumably via steps 3 and 4. The photochemical reaction is inhibited by added CO as expected by the back-reaction in step 3.

$$[Co(CO)_3L_2](OAc) \underset{50\ \text{atm CO}}{\overset{h\nu}{\rightleftharpoons}} AcO-Co(CO)_2L_2 + CO \quad (3)$$

$$AcO-Co(CO)_2L_2 + L \rightarrow Co(CO)_2L_3^+ + OAc^- \quad (4)$$

Photolysis of $[Co(CO)_3L_2](OAc)$ under 50 atm of H_2 gives $HCo(CO)_3L$ and $HCo(CO)_2L_2$ in about a 1:1 molar ratio. This reaction is markedly inhibited by added CO (H_2, 50 atm; CO, 50 atm), and the ratio of hydrides is changed to 9:1 in favor of $HCo(CO)_3L$. In the presence of excess $P(Bu)_3$ and at 50 atm H_2 formation of $HCo(CO)_3L$ is not observed but instead a mixture of $HCo(CO)_2L_2$ (35%) and $[Co(CO)_2L_3^+]$ (65%) is obtained.

$Co_2(CO)_6L_2$. In the absence of any potential ligand $Co_2(CO)_6L_2$ is fairly photostable. Decomposition occurs upon prolonged irradiation as evidenced by some loss of starting material. The decomposition products, which do not display IR absorptions in the CO stretching region, were not identified.

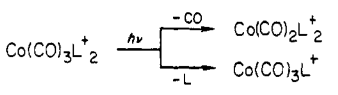
Photolysis of $Co_2(CO)_6L_2$ under 80 atm H_2 yielded only $Co_2(CO)_6L_2$; there was no evidence of the hydrides $HCo(CO)_3L$ or $HCo(CO)_2L_2$ being formed.

Irradiation of $Co_2(CO)_6L_2$ in the presence of excess L yields products that vary according to the solvent employed. In the case of methanol $[Co(CO)_2L_3][Co(CO)_4]$ is the principal product along with a minor amount of the ionic complex $[Co(CO)_3L_2][Co(CO)_3L]$. In hexane the neutral species $Co_2(CO)_5L_3$ and $Co_2(CO)_4L_4$ are formed, the reaction being inhibited by added CO.

Discussion

Photochemistry of $[Co(CO)_3L_2][Co(CO)_4]$. The ionic complex $[Co(CO)_3L_2][Co(CO)_4]$ is completely dissociated in methanol as judged from conductivity measurements and its IR spectrum.[10] The fraction of UV light absorbed by the cation $Co(CO)_3L_2^+$ within the irradiation band width employed is at least an order of magnitude greater than that of the anion $Co(CO)_4^-$. This, and the fact that the photoproducts are similar to those observed with $[Co(CO)_3L_2](OAc)$, suggests that $Co(CO)_3L_2^+$ is the photoactive species.

In order to account for the observed products, the primary photochemical reaction of $Co(CO)_3L_2^+$ must involve both CO and L dissociation (eq 5 and 6). In the absence of nucleophiles the coordinatively unsaturated 16-electron species $Co(CO)_2L_2^+$ and $Co(CO)_3L^+$ react with their counterion. For instance, with $Co(CO)_4^-$ the dinuclear compounds $Co_2(CO)_6L_2$ and $Co_2(CO)_7L$ are generated (eq 7 and 8). Since $Co_2(CO)_6L_2$ and $Co_2(CO)_7L$ are formed in a 70:30 ratio, CO dissociation (eq 5) appears to be favored by a ratio of 7:3 over loss of L.



(5)

(6)

$$Co(CO)_2L_2^+ + Co(CO)_4^- \rightarrow Co_2(CO)_6L_2 \quad (7)$$

$$Co(CO)_3L^+ + Co(CO)_4^- \rightarrow Co_2(CO)_7L \quad (8)$$

In the presence of added L photolysis of $[Co(CO)_3L_2][Co(CO)_4]$ results in the formation of $[Co(CO)_2L_3][Co(CO)_4]$. Presumably this compound results from the reaction of $Co(CO)_2L_2^+$ with L. However, it is possible that $Co_2(CO)_6L_2$, initially formed via (7), undergoes a secondary photoprocess with L resulting in $[Co(CO)_2L_3][Co(CO)_4]$

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[8] (a) The polargam of a methanol solution containing $Co(CO)_2L_3^+$ shows a half-wave potential of $E_{1/2} = -1180$ mV (vs. SCE), which is clearly separated from the step of the starting complex $Co(CO)_3L_2^+$ with $E_{1/2} = -1120$ mV (vs. SCE). The 60-mV higher reduction stability is expected for a similar but more substituted complex. See, for instance: Heyrowsky, J.; Kuta, J. "Grundlagen der Polargraphie"; Akademie Verlag: Berlin, 1965; (b) Upon prolonged irradiation small amounts of $Co(CO)_3L^-$ are formed due to photolysis of **1b** (see also ref 5b).

[9] Arabi, M. S.; Maisonnat, A.; Attali, S.; Poilblanc, R. *J. Organomet. Chem.* 1974, *67*, 109.

[10] The conductivity of a methanol solution is that of a typical salt. The IR maximum of $Co(CO)_4^-$ at 1905 cm^{-1} is typical for the solvated anion and different from that of a contact ion pair: Braterman, P. S.; Leslie, A. E. *J. Organomet. Chem.* 1981, *214*, C45.

(vide infra). In any case under our reaction conditions $[Co(CO)_2L_3][Co(CO)_4]$ is photostable suggesting, in particular, that $Co(CO)_2L_3^+$ is photo inert.

The photochemistry of $Co(CO)_3L_2^+$ in the presence of H_2 is complicated by a number of possible secondary reactions. Under 50 bar H_2 $Co(CO)_3L_2^+$ is converted into a 1:1 mixture of $HCo(CO)_3L$ and $HCo(CO)_2L_2$. The final product mixture is acidic indicating the formation of H^+. Since the predominate photochemical reaction of $Co(CO)_3L_2^+$ is CO dissociation, both hydrides may originate from the intermediate $Co(CO)_2L_2^+$ via eq 9–11. Equation

$$Co(CO)_3L_2^+ \xrightarrow{h\nu} Co(CO)_2L_2^+ + CO \tag{9}$$

$$Co(CO)_2L_2^+ + H_2 \rightarrow HCo(CO)_2L_2 + H^+ \tag{10}$$

$$HCo(CO)_2L_2 + CO \rightleftharpoons HCo(CO)_3L + L \tag{11}$$

11 is a known equilibrium.[11] A process analogous to eq 10 has been reported for $Fe(CO)_5$, which is isoelectronic with $Co(CO)_3L_2^+$.[12] $Fe(CO)_4$, the primary photoproduct of $Fe(CO)_5$, reacts with H_2 to give $HFe(CO)_4^-$ and H^+.

Alternatively, dissociation of L from $Co(CO)_3L_2^+$ can lead to $HCo(CO)_3L$ formation via eq 12. The back-reaction of eq 11 would generate $HCo(CO)_2L_2$. Interestingly,

$$Co(CO)_3L^+ + H_2 \rightarrow HCo(CO)_3L + H^+ \tag{12}$$

photolysis of $Co(CO)_3L_2^+$ in the presence of H_2 and CO (H_2:CO = 1:1) results in a 9:1 molar ratio of $HCo(CO)_3L$ to $HCo(CO)_2L_2$. Added CO can increase the $HCo(CO)_3L$ concentration by driving equilibrium 11 to the right or can suppress $Co(CO)_2L_2^+$ formation, thus allowing eq 12 to predominate.

Photochemistry of $Co_2(CO)_6L_2$. In the absence of additives $Co_2(CO)_6L_2$ is the major photolysis product of the ionic complex $[Co(CO)_3L_2][Co(CO)_4]$. To evaluate the possibility of secondary photolysis of $Co_2(CO)_6L_2$, we have studied its photochemistry. $Co_2(CO)_6L_2$ absorbs a significant amount of light within the irradiation band width utilized in these studies. This is due to an intense absorption centered at 365 nm (Figure 1c) that has been assigned to the $\sigma \rightarrow \sigma^*$ transition of the electrons in the metal–metal bond.[13]

Slight decomposition is observed in both hexane and methanol in the absence of L. The primarily formed $\cdot Co(CO)_3L$ recombines rapidly with a recombination rate constant equal to 9.1×10^7 M^{-1} s^{-1}.[14] Rather surprising is the solvent effect in the photochemistry of $Co_2(CO)_6L_2$ with excess L. In hexane $Co_2(CO)_5L_3$ and $Co_2(CO)_4L_4$ are the observed products. $Co_2(CO)_5L_3$ is initially formed, its concentration increasing and then gradually decreasing as the $Co_2(CO)_4L_4$ concentration increases. A photoequilibrium is achieved with a final $Co_2(CO)_6L_2$:$Co_2(CO)_4L_4$:$Co_2(CO)_5L_3$ ratio of approximately 0.5:3:1. A plausible mechanism that accounts for these results is given in eq 13–16.

$$Co_2(CO)_6L_2 \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} 2\cdot Co(CO)_3L \tag{13}$$

$$\cdot Co(CO)_3L + L \rightleftharpoons \cdot Co(CO)_2L_2 + CO \tag{14}$$

$$\cdot Co(CO)_2L_2 + \cdot Co(CO)_3L \underset{h\nu}{\overset{k_2}{\rightleftharpoons}} Co_2(CO)_5L_3 \tag{15}$$

$$2\cdot Co(CO)_2L_2 \underset{h\nu}{\overset{k_3}{\rightleftharpoons}} Co_2(CO)_4L_4 \tag{16}$$

$Co_2(CO)_5L_3$ and $Co_2(CO)_4L_4$ undoubtedly undergo photoinduced homolysis similar to $Co_2(CO)_6L_2$. Since the recombination constants k_1, k_2, and k_3 are presumably not equivalent,[14] a statistical distribution of the dinuclear metal carbonyl compounds is not expected.

When the photochemical reaction of $Co_2(CO)_6L_2$ and excess L is carried out in methanol, the ionic complexes $[Co(CO)_2L_3][Co(CO)_4]$ and $[Co(CO)_3L_2][Co(CO)_4]$ are the observed products. There is, however, no $HCo(CO)_3L$ or $HCo(CO)_2L_2$ formed when an excess of H_2 is present. The mechanism shown in Scheme I accounts for these observations.

Scheme I

$$Co_2(CO)_6L_2 \xrightarrow{h\nu} 2\cdot Co(CO)_3L \tag{17}$$

$$\cdot Co(CO)_3L + L \rightleftharpoons \cdot Co(CO)_3L_2 \tag{18}$$

$$\cdot Co(CO)_3L_2 + Co_2(CO)_6L_2 \rightarrow Co(CO)_3L_2^+ + Co_2(CO)_6L_2^{-\cdot} \tag{19}$$

$$Co_2(CO)_6L_2^{-\cdot} \rightarrow \cdot Co(CO)_2L_2 + Co(CO)_4^- \tag{20}$$

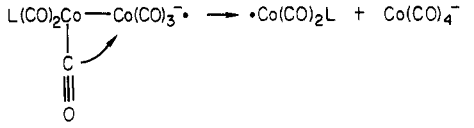
$$Co_2(CO)_6L_2^{-\cdot} \rightarrow \cdot Co(CO)_3L + Co(CO)_3L^- \tag{21}$$

$$\cdot Co(CO)_2L_2 + L \rightleftharpoons \cdot Co(CO)_2L_3 \tag{22}$$

$$\cdot Co(CO)_2L_3 + Co_2(CO)_6L_2 \rightarrow Co(CO)_2L_3^+ + Co_2(CO)_6L_2^{-\cdot} \tag{23}$$

Scheme I is similar to the one proposed by Brown et al. for the thermal reaction of $Co_2(CO)_8$ with tributylphosphine.[4b] The key step is the electron transfer from the 19-electron $\cdot Co(CO)_3L_2$ species to the neutral complex $Co_2(CO)_6L_2$ (eq 19). In $Co_2(CO)_6L_2^{-\cdot}$ the additional electron is mainly σ^* in character,[15] labilizing the Co–Co bond toward fragmentation.[16] Since $[Co(CO)_2L_3][Co(CO)_4]$ is the major product, we conclude that fragmentation of $Co_2(CO)_6L_2^{-\cdot}$ occurs mainly by eq 20. This may involve initial ligand loss followed by intramolecular transfer of CO (eq 24–26). Recent ESR work supports the plausibility of eq 24 in that the odd-electron density of $Co_2(CO)_6L_2^{-\cdot}$ is somewhat delocalized into the σ^* orbital of the Co–P bond.[15]

$$Co_2(CO)_6L_2^{-\cdot} \rightarrow Co_2(CO)_6L^{-\cdot} + L \tag{24}$$



$$L(CO)_2Co{-}Co(CO)_3^{-\cdot} \rightarrow \cdot Co(CO)_2L + Co(CO)_4^- \tag{25}$$

$$\cdot Co(CO)_2L + L \rightarrow \cdot Co(CO)_2L_2 \tag{26}$$

In the photochemistry of $Co_2(CO)_6L_2$ with excess L solvation of the ions by methanol undoubtedly contributes strongly to the driving force of the reaction. In the case of alkane solvents the electron-transfer steps would be severely inhibited and, hence, substitution occurs as shown in eq 14–17.

Conclusion

The major photochemical reactions of $[Co(CO)_3L_2][Co(CO)_4]$ are initiated by the photolysis of the cation,

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[11] Van Boven, M.; Alemdaroglu, N.; Penninger, J. M. L. *J. Organomet. Chem.* **1975**, *84*, 65.

[12] Krusic, P. *J. Am. Chem. Soc.* **1981**, *103*, 2131.

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[14] Wegman, R. W.; Brown, T. L. *Inorg. Chem.* **1983**, *22*, 183.

[15] Hayashida, S.; Kawamura, T.; Yonezawa, T. *Chem. Lett.* **1982**, *21*, 2235.

[16] Watlz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

resulting in dissociation of either CO or L. The formed coordinatively unsaturated species react with any potential ligand to give a new cation or after electron transfer a neutral molecule.

The neutral complex $Co_2(CO)_6L_2$ is photostable in the absence of phosphine. With an excess of phosphine it undergoes either photosubstitution, via a radical pathway, or photodisproportionation to ionic products, depending on the nature of the solvent (hexane or methanol, respectively).

Experimental Section

Hydrogen (99.9%), carbon monoxide (99% + 0.5% H_2), Messer-Griesheim, tributylphosphine (EGA), cobalt acetate (Merck), and solvents were commercial products, which were used without further treatment. Predrying the methanol did not influence the results. All procedures were carried out in an inert-gas atmosphere (N_2 or Ar). For irradiations a low-pressure mercury lamp (TNN 15/32, Hanau, quartz filter) or a 1000-W Hg–Xe lamp (Hanovia) were used. Monochromatic light was produced with a 1000-W Hg–Xe lamp and a grating monochromator (Kratos-Schoeffel). Quantum yields were determined with the dye actinometer introduced by Heller et al.[17] For the reactions studied the quantum yields typically ranged from 0.1 to 0.2. However, due to the internal filter effect of the products the absolute quantum yields are accurate only within 50%.

Samples at normal pressure were irradiated in standard 1-cm quartz cells (HELLMA), equipped with a rubber cap and a stopcock for argon flushing. For high-pressure photochemical experiments a 1-mL micro-UV-autoclave[5b] was used.

IR spectra were measured in a cell of defined path length (determined by interference measurements) with CaF_2 windows in a Perkin-Elmer 283B or a Zeiss IRM 25 spectrometer. For polarography a Metrohm E 505 instrument was used, and for UV spectra a Cary 118 instrument was used.

Preparation of $[Co(CO)_3L_2][Co(CO)_4]$. A 5-mmol sample of tributylphosphine was added to 0.8 g (2.3 mmol) $Co_2(CO)_8$ in 150 mL of hexane. After 30 min of stirring at 25 °C, the yellow crystals of $[Co(CO)_3L_2][Co(CO)_4]$ were filtered and washed with hexane (90% yield, 99% purity). For IR data see Table I.[6b]

Preparation of $Co_2(CO)_7L$. A 110-mg (0.32-mmol) sample of $Co_2(CO)_8$ and 250 mg (0.36 mmol) of $Co_2(CO)_6L_2$ in 40 mL of CO-saturated hexane were irradiated for 2 min with 1000-W lamp through Pyrex. Methanol (40 mL) was added to disproportionate unreacted $Co_2(CO)_8$. The hexane layer contained 40% $Co_2(CO)_7L$ and 60% unreacted $Co_2(CO)_6L_2$. Spectroscopic identification of $Co_2(CO)_7L$ was possible without further separation. Two hours of additional photolysis did not change the product distribution, indicating that a photoequilibrium was reached.[14]

Preparation of $[Co(CO)_3L_2](OAc)$. A 125-mg (0.5-mmol) sample of $Co(OAc)_2 \cdot 4H_2O$ and 0.2 mL (1 mmol) of tributylphosphine in 40 mL of methanol were stirred for 2 h under 80 bar of CO and H_2 ($CO:H_2 = 1$) at 225 °C. The solution contained 80% of the cobalt as $[Co(CO)_3L_2](OAc)$ and 20% as $Co(OAc)_2$. Twenty percent of the phosphine remained uncomplexed. The solution was used for photolysis experiments without further treatment.

$Co_2(CO)_6L_2$ and $Co_2(CO)_8$ were prepared according to literature procedures.[6b,18]

Irradiation of $[Co(CO)_3L_2][Co(CO)_4]$ (Eq 1). A 4-mL sample of a 0.013 M solution of $[Co(CO)_3L_2][Co(CO)_4]$ in methanol was irradiated for 10 min with a low-pressure Hg lamp through quartz. To separate the products, the methanol was removed at reduced pressure and the residue treated with hexane. The hexane contained $Co_2(CO)_6L_2$ and $Co_2(CO)_7L$ in a 70:30 ratio. Unreacted $[Co(CO)_3L_2][Co(CO)_4]$ (50%) was insoluble in hexane.

Irradiation of $[Co(CO)_3L_2][Co(CO)_4]$ or $[Co(CO)_3L_2](OAc)$ under CO or H_2. A 1-mL sample of 0.012 M solution in methanol was transferred to a micro-UV-autoclave, twice flushed with 20 bar of CO (or H_2), and then irradiated for 15 min with a low-pressure Hg lamp. The solution was analyzed by IR spectroscopy (see Table I).

Irradiation of $[Co(CO)_3L_2][Co(CO)_4]$ or $[Co(CO)_3L_2](OAc)$ in the Presence of Phosphine. To 3 mL of a methanol solution of $[Co(CO)_3L_2][Co(CO)_4]$ (12 mmol) or $[Co(CO)_3L_2](OAc)$ (10 mmol) in a quartz cell was added tributylphosphine through a rubber cap. The solution was irradiated with a low-pressure mercury lamp. At regular time intervals 100-μL samples were removed and analyzed by IR spectroscopy (see Table I).

Irradiation of $[Co(CO)_3L_2](OAc)$ (Eq 3). An appropriate aliquot of a methanol solution of the compound was irradiated in a quartz cell with a Hg–Xe lamp for 1 min. The IR spectrum contained a new band at 1915 cm^{-1}, which was tentatively assigned to $AcO–Co(CO)_2L_2$. Treating this reaction mixture with 40 bar of CO or a 10-fold excess of phosphine yielded $Co(CO)_3L_2^+$ and $Co(CO)_2L_3^+$, respectively.

Irradiation of $Co_2(CO)_6L_2$. A 4.8-mmol solution of $Co_2(CO)_6L_2$ in methanol or hexane was irradiated for 7 min with a low-pressure Hg lamp. This resulted in a 5% loss of starting material. The decomposition products could not be detected in the CO stretching region of the IR spectrum. After 30-min photolysis 20% of $Co_2(CO)_6L_2$ was converted with formation of trace amounts of $Co_2(CO)_7L$.

Irradiation of $Co_2(CO)_6L_2$ and H_2. A 1-mL sample of a 4.8-mmol methanol solution of $Co_2(CO)_6L_2$ under 50 bar of H_2 was irradiated for 15 min with a low-pressure Hg lamp. Twenty percent of the starting material was converted, but no products could be identified from the IR spectrum.

Irradiation of $Co_2(CO)_6L_2$ with Tributylphosphine (L) in Methanol. A 2-mL sample of a 4.6-mmol methanol solution of $Co_2(CO)_6L_2$ was irradiated with 254- or 366-nm light in the presence of a 10-fold excess of L. The solution was analyzed by IR spectroscopy (Table I).

Irradiation of $Co_2(CO)_6L_2$ with Tributylphosphine in Hexane. A 5-mL sample of a hexane solution containing 5.0 mmol of $Co_2(CO)_6L_2$ and 50 mmol of tributylphosphine was irradiated with 366-nm light for 1.0 h. Samples were periodically withdrawn for IR analysis.

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Registry No. $[Co(CO)_3L_2][Co(CO)_4]$, 15157-80-9; $Co_2(CO)_8$, 10210-68-1; Co2(CO)$_7$L, 19298-62-5; $Co_2(CO)_6L_2$, 14911-28-5; $[Co(CO)_3L_2](OAc)$, 89556-53-6; $AcO–Co(CO)_2L_2$, 89556-54-7; $[Co(CO)_2L_3][Co(CO)_4]$, 89556-56-9; $HCo(CO)_3L$, 20161-43-7; $HCo(CO)_2L_2$, 22392-50-3; $Co_2(CO)_4L_4$, 89556-57-0; $Co_2(CO)_5L_3$, 89556-58-1; Co, 7440-48-4.

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