

0.55 B<sub>5</sub>H<sub>9</sub>, 4.33 H<sub>2</sub>, 0.87 B<sub>2</sub>H<sub>6</sub>, 0.002 B<sub>4</sub>H<sub>10</sub>, 1.544 B<sub>6</sub>H<sub>x</sub>, and 0.7 TMA·BH<sub>3</sub>. The B<sub>6</sub>H<sub>x</sub> fraction included a very unstable component which could have been B<sub>6</sub>H<sub>12</sub>, the decomposition of which left 1.383 mmol of purified B<sub>6</sub>H<sub>10</sub>—representing 25.5% of the unrecovered B<sub>5</sub>H<sub>9</sub>. In a similar experiment, the possible 12% B<sub>6</sub>H<sub>12</sub> impurity was sought by low-temperature <sup>11</sup>B nmr but could not be recognized clearly. The actual presence of B<sub>6</sub>H<sub>12</sub> could have been far less than 12% if its decomposition included an attack upon the main component, B<sub>6</sub>H<sub>10</sub>. The decomposition products included 0.067 mmol of B<sub>2</sub>H<sub>6</sub>, 0.025 mmol each of B<sub>5</sub>H<sub>9</sub> and B<sub>5</sub>H<sub>11</sub>, and 7 mg of nonvolatile solids.

Two further experiments of similar scale and character showed a B<sub>6</sub>H<sub>10</sub> yield of only 9% when the B<sub>5</sub>H<sub>9</sub>·2TMA·2HCl was allowed to decompose in the presence of much diborane, or only 4% when HCl was present in large excess.

The sublimates from all such experiments consisted chiefly of TMA·BH<sub>2</sub>Cl and TMA·B<sub>3</sub>H<sub>7</sub>, whose <sup>11</sup>B nmr spectra (in toluene) indicated molar ratios approximating 6:1. The experiment with excess HCl showed also a moderate amount of TMA·BHCl<sub>2</sub>, as might be expected. The glassy yellow-brown residues proved to be toluene soluble, with <sup>11</sup>B nmr spectra showing only that some TMA·BH<sub>2</sub>Cl and TMA·B<sub>3</sub>H<sub>7</sub> had been held back from sublimation. In sum, these TMA complexes probably represented about half of the boron material not volatile at 25°.

**Discussion.** It is interesting that the yields of B<sub>6</sub>H<sub>10</sub> represent almost half of the B<sub>3</sub>H<sub>7</sub> units which would be available if the decomposition of B<sub>5</sub>H<sub>9</sub>·2TMA·2HCl occurred primarily by removal of 2 TMA·BH<sub>2</sub>Cl. Also, the conversion of 2 B<sub>3</sub>H<sub>7</sub> to B<sub>6</sub>H<sub>10</sub> and 2 H<sub>2</sub> would account for two-thirds of the observed H<sub>2</sub>. A major loss of B<sub>6</sub>H<sub>10</sub> yield might be ascribed to the very strong Lewis-acid character of B<sub>3</sub>H<sub>7</sub>, such that it would compete with BH<sub>2</sub>Cl for attachment to TMA. Quite probably, it is just that effect which is minimized by keeping the temperature as low as possible during the decomposition. Competitive also would be the formation of B<sub>6</sub>H<sub>12</sub>, which seems to decompose mostly to B<sub>2</sub>H<sub>6</sub>, B<sub>5</sub>H<sub>9</sub>, and B<sub>5</sub>H<sub>11</sub>. More speculative would be the idea that BH<sub>2</sub>Cl, liberated by action of B<sub>3</sub>H<sub>7</sub> to remove TMA, would attack the precursors of B<sub>6</sub>H<sub>10</sub>, just as B<sub>2</sub>H<sub>6</sub> or HCl probably do.

It is interesting that HCl attacks the solid product of the B<sub>2</sub>H<sub>6</sub>-B<sub>5</sub>H<sub>9</sub>-TMED reaction, to form (per mole of B<sub>5</sub>H<sub>9</sub>) 1.05 H<sub>2</sub>, 0.03 B<sub>2</sub>H<sub>6</sub>, 0.115 B<sub>4</sub>H<sub>10</sub>, and 0.11 B<sub>6</sub>H<sub>10</sub>. Here the mechanism of formation of B<sub>6</sub>H<sub>10</sub> may be very different, possibly involving a B<sub>6</sub>H<sub>x</sub> anion formed from B<sub>2</sub>H<sub>6</sub> and a B<sub>4</sub>H<sub>y</sub> fragment.

The reasons for three different structures for the three base-B<sub>5</sub>H<sub>9</sub> adducts might be surmised. The TMED complex would gain stability from the chelation of one boron to make a five-atom ring. A 2,3 attachment would be less favorable, and 1,2 or 2,4 seems quite unlikely. The mono-N base TMA would be free to attach to those boron atoms which bond best to its lone-pair electrons. A 2,4 attachment would make the two TMA molecules least competitive. It is unfortunate that the <sup>11</sup>B nmr spectrum cannot decide between 2,3 and 2,4 attachment. In our spectra (done in dichloroethane) the two kinds of boron appeared only as a broad singlet at 16.8 ppm and an even broader singlet (N-quadrupole effect?) at 39 ppm, measured from methyl borate. The 1-B atom was shown by a poorly resolved doublet at 71.8 ppm.

The 1-B attachment of one TMP would be favored by the adjacent skeletal electrons, the π attitude of which would permit some interaction with the phosphorus π-acceptor orbitals. More important might be the width of the sp hybrid on 1-B favoring bonding to P more than to N.

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**Registry No.** B<sub>5</sub>H<sub>9</sub>·2TMA, 12115-95-6; B<sub>5</sub>H<sub>9</sub>·2TMP, 39661-74-0; B<sub>5</sub>H<sub>9</sub>·TMED, 53965-74-5; B<sub>2</sub>H<sub>6</sub>, 19287-45-7; BF<sub>3</sub>, 7637-07-2; HCl, 7647-01-0; CH<sub>3</sub>OH, 67-56-1; B<sub>5</sub>H<sub>9</sub>·2TMA·2HCl, 54036-71-4.

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## Reactivity of Halogenotetrakis(diethyl phenylphosphonite)cobalt(II) Complexes with Carbon Monoxide

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In a previous paper<sup>2</sup> we have reported the synthesis and characterization of some phosphine-carbon monoxide and phosphine-isocyanide mixed-ligand low-spin cobalt(I) complexes obtained *via* reduction of halogenotetrakis(diethyl phenylphosphonite)cobalt(II) derivatives with CO and isocyanides, respectively.

Although the reduction of cobalt(II) complexes by carbon monoxide has been observed previously,<sup>3</sup> the mechanism and the nature of intermediates still remain to be clarified.

We now report on a study of the reduction of complexes of the type [CoXL<sub>4</sub>]<sup>+</sup> (X = Cl, Br, or I; L = PPh(OEt)<sub>2</sub>) by carbon monoxide with regard to stoichiometry and the nature of carbonyl intermediates.

## Experimental Section

**Materials.** Reagent grade anhydrous cobalt(II) halides were obtained from Alfa and used without further purification. The solvents were purified by standard methods and distilled under a current of nitrogen. The diethyl phenylphosphonite, PhP(OEt)<sub>2</sub>, was prepared by a method reported previously.<sup>4</sup>

**Apparatus.** The volume of CO taken up at constant pressure was measured by the gas-buret apparatus and procedure described previously.<sup>5</sup> Conductivities of 10<sup>-3</sup> M solutions of complexes in nitrobenzene were measured at 25° with an LKB bridge. Infrared spectra of solids as KBr pellets and/or as dichloromethane solutions were recorded on a Perkin-Elmer 621 spectrophotometer. A Bruker HFX-10 instrument equipped with a variable-temperature probe and using TMS as internal reference was used for pmr measurements. Gas chromatographic results were carried out with an Aerograph A-700 instrument.

**Syntheses of Complexes.** The preparation and characterization of the complexes [Co(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>3</sub>]BPh<sub>4</sub> and [CoI(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>2</sub>] have been reported elsewhere.<sup>2</sup>

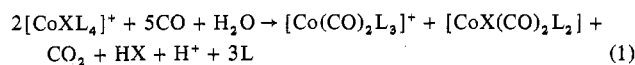
**Carbonyltetrakis(diethyl phenylphosphonite)cobalt(I) Iodide.** In a two-necked round-bottomed flask, equipped with magnetic stirrer and inlet and outlet tube, was placed anhydrous cobalt(II) iodide (3.12

g, 10 mmol), and the reaction flask was purged with nitrogen. Anhydrous acetone (80 ml) and diethyl phenylphosphonite (8 g, 40 mmol) were then added, and after replacing N<sub>2</sub> with CO, the reaction mixture was vigorously stirred at room temperature for 1 hr. Concurrent with a color change from deep green to yellow, there occurs a simultaneous appearance of a strong band at 1956 cm<sup>-1</sup> which may be followed by recording the ir spectrum of the solution. The final product was obtained by recrystallizing the oily product which remains after removal of the solvent under reduced pressure. The corresponding perchlorate and tetraphenylborate salts were precipitated by adding equimolar amounts of LiClO<sub>4</sub> or NaBPh<sub>4</sub>, respectively, to saturated anhydrous ethanol solutions of the complexes obtained by the method reported above.

**Bromodicarbonylbis(diethyl phenylphosphonite)cobalt(I).** This complex has been prepared together with the [Co(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>3</sub>]BPh<sub>4</sub> compound in accordance with reaction 1 following a procedure identical with that used for the corresponding iodo derivative, except that CoBr<sub>2</sub> was substituted for CoI<sub>2</sub>. Although ir experiments suggest that reaction 1 also occurs with anhydrous cobalt(II) chloride, the resulting [CoCl(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>2</sub>] complex appears to be quite unstable and all the attempts to isolate it as a pure crystalline material have been unsuccessful.

## Results and Discussion

The stoichiometry of the reaction



(X = Cl, Br, or I; L = PhP(OEt)<sub>2</sub>)

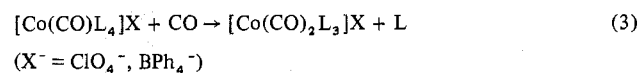
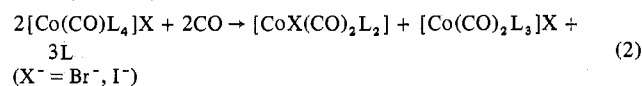
is substantiated by the following results: (a) the final average mole ratio of CO absorbed per starting cobalt(II) complex is 2.48; (b) the two final dicarbonyl diamagnetic complexes are formed in equivalent amounts and can be recovered in quantitative yields; (c) the ir spectrum of the final reaction mixture in the 2200–1800-cm<sup>-1</sup> region is identical with that of a 1:1 solution of [CoX(CO)<sub>2</sub>L<sub>2</sub>] and [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup> (X = Br or I; L = PhP(OEt)<sub>2</sub>); (d) the presence of CO<sub>2</sub> has been detected by gas chromatography both in the final solution and in the corresponding vapor phase. The source of water is apparently that small fraction of H<sub>2</sub>O which is present in the solvent used. These results thus appear to exclude a disproportionation of the starting cobalt(II) complexes and the possibility that the phosphine ligand is functioning as the reducing species. CO is thus implicated as the predominant reductant of cobalt(II) to more thermally stable cobalt(I) carbonyl derivatives.

The progress of the reaction can be followed most conveniently by recording ir spectra of the mixture and simultaneously measuring the CO uptake. When solutions of [CoXL<sub>4</sub>]<sup>+</sup> (or CoX<sub>2</sub> and L in 1:4 ratio, forming immediately [CoXL<sub>4</sub>]<sup>+</sup>; X = Cl, Br, or I) are treated with CO, a very fast absorption of 1 mol of CO/mol of cobalt(II) complex is observed, and a strong band in the region 2030–2028 cm<sup>-1</sup> (depending on X) appears in the ir spectrum. This band is tentatively attributed to a [CoX(CO)L<sub>3</sub>]<sup>+</sup> intermediate. Owing to its instability we have not been able to isolate this species in pure form, however. Rather, when the reaction is stopped at this point, an impure material is recovered whose spectrum exhibits other absorptions due to the subsequent reaction products in addition to the band at 2030–2028 cm<sup>-1</sup> (see below). This assignment seems reasonable, however, on the basis that, due to the higher oxidation state of the metal atom in the carbonyl cobalt(II) species and the positive charge of the complex, this band is observed as expected at higher energy than those of the cobalt(I) complexes. Furthermore, the deep green color of the reaction mixture, characteristic of these five-coordinate cobalt(II) species, does not show any appreciable change to this point. Cobalt(II) carbonyl complexes have been previously suggested as reaction interme-

diates.<sup>3a,6</sup> The very fast uptake of the first mole of CO is thus attributed to the addition reaction [CoXL<sub>3</sub>]<sup>+</sup> + CO → [CoX(CO)L<sub>3</sub>]<sup>+</sup>, where the tetracoordinate cobalt(II) species originates from the equilibrium [CoXL<sub>4</sub>]<sup>+</sup> ⇌ [CoXL<sub>3</sub>]<sup>+</sup> + L. When a large excess of free phosphine ligand (CoX<sub>2</sub>:L ≥ 1:20) is present in the initial reaction mixture, the [CoX(CO)L<sub>3</sub>]<sup>+</sup> intermediate is formed more slowly probably due to a decrease in the concentration of four-coordinate cobalt(II) species. The further absorption of CO (0.5 mol/mol of Co(II)) seems to be associated with the rate-determining step. Concurrent with this absorption, there occurs a color change from deep-green to yellow suggesting reduction of a five-coordinate cobalt(II) species to the [Co(CO)L<sub>4</sub>]<sup>+</sup> cation. The rate of this step depends on the nature of the halogen increasing in the order Cl < Br < I and indicating that this ligand is still coordinated in the reactive species. At the same time, the 2030–2028-cm<sup>-1</sup> band gradually disappears and a very strong absorption at 1956 cm<sup>-1</sup> together with a broad and very weak one at 2004 cm<sup>-1</sup>, attributable to the [Co(CO)L<sub>4</sub>]<sup>+</sup> complex, appears. By quenching the reaction at this point the carbonyltetrakis(diethyl phenylphosphonite)cobalt(II) intermediate can be isolated and characterized.

If the reaction is allowed to proceed, a further mole of CO is taken up by the solution which is accompanied by a disappearance of the 1956- and 2004-cm<sup>-1</sup> bands and appearance of four absorptions in the regions 1996–1994, 1935–1931 cm<sup>-1</sup> and 2021, 1972 cm<sup>-1</sup> due to the [CoX(CO)<sub>2</sub>L<sub>2</sub>] (X = Cl, Br, or I) and [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup> final products, respectively.

Our preliminary investigations on the reactivity of the complexes reported here show that the intermediate [Co(CO)L<sub>4</sub>]<sup>+</sup> reacts at room temperature with CO (1 atm) in accordance with the reactions



The monocarbonyl complex reacts also with isocyanides to give complexes of the type [Co(CNR)<sub>5-x</sub>L<sub>x</sub>]<sup>+</sup> (x = 2 or 3) (see Scheme I). While the [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup> complex is fairly inert (it does not react with CO or with very large excesses of L or halides), treatment of [CoX(CO)<sub>2</sub>L<sub>2</sub>] derivatives with excess diethyl phenylphosphonite affords [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup>, both the [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup> and [Co(CO)L<sub>4</sub>]<sup>+</sup> compounds, or only [Co(CO)L<sub>4</sub>]<sup>+</sup>, depending upon the [CoX(CO)<sub>2</sub>L<sub>2</sub>]:L ratios (1:20, 1:30, or 1:50, respectively). These results are summarized in the Scheme I.

The new complexes reported here have been characterized

### Scheme I

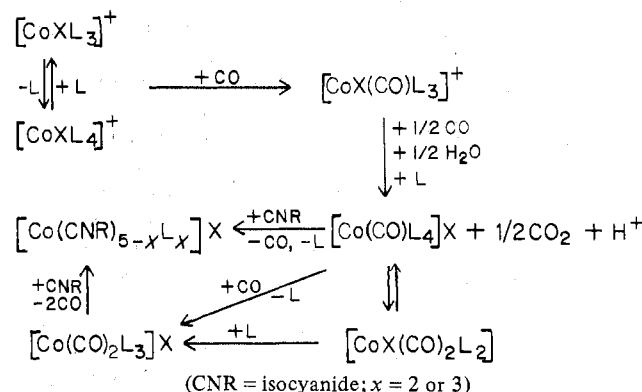


Table I. Properties of Some Cobalt(I) Complexes Reported in this Paper

| Compd  | Color      | Dec pt, <sup>a</sup> °C | $\Lambda^b$ | % C   |       | % H   |       | % Hal |       | % P   |       |
|--|------------|-------------------------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|
|  |            |                         |             | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]I                | Yellow     | 113                     | 24.9        | 48.92 | 48.8  | 6.01  | 5.97  | 12.61 | 12.6  | 12.32 | 11.9  |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]BPh <sub>4</sub> | Yellow     | 116                     | 15.7        | 65.12 | 65.0  | 6.73  | 6.59  |       |       | 10.33 | 10.8  |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]ClO <sub>4</sub> | Yellow     | 159                     | 15.2        | 50.29 | 50.5  | 6.18  | 6.17  | 3.62  | 3.6   | 12.66 | 12.4  |
| [CoBr(CO) <sub>2</sub> (PhP(OEt) <sub>2</sub> ) <sub>2</sub> ] | Red-orange | 98                      |             | 44.69 | 44.6  | 5.11  | 5.14  | 13.52 | 13.1  | 10.49 | 10.6  |

<sup>a</sup> The decomposition temperatures are uncorrected. <sup>b</sup> Equivalent conductivities at 25° (in cm<sup>2</sup> ohm<sup>-1</sup> M<sup>-1</sup>) of 10<sup>-3</sup> M solutions in nitrobenzene.

Table II. Ir and Pmr Data for the Complexes Discussed in this Paper

| Compd  | $\nu_{CO}$ in solution <sup>a</sup> and (solid), cm <sup>-1</sup> | $\nu_{C^{13}O}$ , cm <sup>-1</sup> | Chem shift ( $\tau$ ) <sup>b</sup> |                 |        |        |
|--|---|------------------------------------|------------------------------------|-----------------|--------|--------|
|  |   |                                    | Phenyl                             | Methylene       | Methyl |        |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]I                              | 2004 vw<br>(1998 vw)  | 1956 vs<br>(1946 vs)               | (1901.5)                           | 2.59 br         | 6.14 m | 8.94 t |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]BPh <sub>4</sub>               | 2005 vw<br>(1998 vw)  | 1956 vs<br>(1946 vs)               |                                    | 2.58 br 3.11 br | 5.88 m | 8.88 t |
| [Co(CO)(PhP(OEt) <sub>2</sub> ) <sub>4</sub> ]ClO <sub>4</sub>               | 2004 vw<br>(1995 vs)  | 1955 vs<br>(1944 vs)               | (1899)                             | 2.60 br         | 5.80 m | 8.87 t |
| [CoI(CO) <sub>2</sub> (PhP(OEt) <sub>2</sub> ) <sub>2</sub> ]                | 1996 s<br>(1989 s)  | 1935 vs<br>(1925 vs)               | (1901)                             | 2.18 br 2.59 br | 5.97 m | 8.71 t |
| [CoBr(CO) <sub>2</sub> (PhP(OEt) <sub>2</sub> ) <sub>2</sub> ]               | 1995 s<br>(1989 s)  | 1933 vs<br>(1922 vs)               | (1899)                             | 2.20 br 2.61 br | 6.00 m | 8.80 t |
| [Co(CO) <sub>2</sub> (PhP(OEt) <sub>2</sub> ) <sub>2</sub> ]BPh <sub>4</sub> | 2021 s<br>(2014 m) (1969 s)                                       | 1972 vs<br>(1960 s)                | (1937)                             | 2.56 br 3.15 br | 6.14 m | 8.80 t |

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>. The  $\nu_{CO}$  for the complexes of type [CoX(CO)L<sub>3</sub>]<sup>+</sup> are 2030, 2029, and 2028 cm<sup>-1</sup> for X = I, Br, and Cl, respectively. <sup>b</sup> In (CD<sub>3</sub>)<sub>2</sub>CO.

by their chemical and physical properties (Tables I and II). The ir spectrum of the [Co(CO)L<sub>4</sub>]I complex in the solid state at room temperature and at -180° shows a weak band at 1901.5 cm<sup>-1</sup>, a very strong absorption at 1946 cm<sup>-1</sup>, and a broad and very weak one at 1998 cm<sup>-1</sup>. The frequency ratio between the first two bands is 0.9771, which allows the assignment of the 1901.5-cm<sup>-1</sup> band to the carbon-13 satellite, in agreement with similar results reported for [CoCl<sub>2</sub>(CO)(PR<sub>3</sub>)<sub>2</sub>] complexes.<sup>8</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution the ir spectrum remains the same except for the disappearance of the 1901.5-cm<sup>-1</sup> band and a shift of the other two bands to 1956 and 2004 cm<sup>-1</sup>. The two absorptions, at 2024 and 2057 cm<sup>-1</sup>, present in the ir spectrum of the complex [Co(CO)(P(OCH<sub>2</sub>)<sub>3</sub>CC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]BPh<sub>4</sub> have been explained in terms of two isomers with the carbonyl group in an equatorial or apical position, respectively.<sup>9</sup> This does not seem to be the case with the [Co(CO)L<sub>4</sub>]<sup>+</sup> cation because of the constant intensity ratio between the 2004- and 1956-cm<sup>-1</sup> bands by changing physical state, temperature, solvent, and counterion (I<sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>). Moreover the difference between the two bands of the complex [Co(CO)(P(OCH<sub>2</sub>)<sub>3</sub>CC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sup>+</sup> (33 cm<sup>-1</sup>) is much lower than that of the compound [Co(CO)L<sub>4</sub>]<sup>+</sup> (48 cm<sup>-1</sup>). For these reasons the 2004-cm<sup>-1</sup> absorption is tentatively attributed to a combination band.<sup>8</sup>

The pmr spectra of the [Co(CO)L<sub>4</sub>]Y compounds at room temperature show a sharp triplet centered at  $\tau$  8.94-8.87 ( $J_{HH} = 7$  Hz) due to the phosphine methyl protons indicating that these four ligands are equivalent. These signals and indeed the entire spectrum remain unchanged on cooling to -100°. This spectrum therefore is incompatible with the trigonal-bipyramidal structure usually found for five-coordinated cobalt(I) complexes both in solid state<sup>10</sup> and in solution.<sup>2</sup> At room temperature the pmr spectrum of [Co(CO)L<sub>4</sub>]<sup>+</sup> is quite similar to that for [Co(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup>, which is less sterically hindered. However, at -60° two equivalent phosphines different from a third are clearly detected in the pmr spectrum of the dicarbonyl compound, and while a nonrigid structure may be assumed to explain the pmr data for this complex, an analogous situation can probably be excluded for the monocarbonyl one (as shown by the fact that its pmr spectrum does not change in the range +25 to -100°). Therefore, we

suggest that the steric crowding of the four phosphines in the [Co(CO)L<sub>4</sub>]<sup>+</sup> complex brings about a distorted geometry in which such ligands are equivalent. A similar situation has been found for HCoL<sub>4</sub>.<sup>11</sup>

All these reactions can be conveniently followed with spectrophotometric techniques. These systems are of considerable interest in connection with the kinetic behavior of five-coordinated transition metal complexes. Further studies of the details of the carbon monoxide reduction step are in progress.

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**Registry No.** [Co(CO)(PhP(OEt)<sub>2</sub>)<sub>4</sub>]I, 54036-81-6; [Co(CO)(PhP(OEt)<sub>2</sub>)<sub>4</sub>]BPh<sub>4</sub>, 54036-84-9; [Co(CO)(PhP(OEt)<sub>2</sub>)<sub>4</sub>]ClO<sub>4</sub>, 54036-83-8; [CoI(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>2</sub>], 54082-40-5; [CoBr(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>2</sub>], 54036-85-0; [Co(CO)<sub>2</sub>(PhP(OEt)<sub>2</sub>)<sub>2</sub>]BPh<sub>4</sub>, 54141-85-4.

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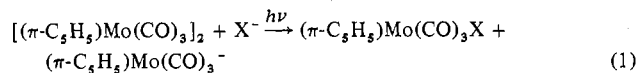
### Photochromism in the $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2 + \text{Br}^-$ System

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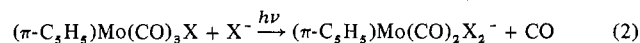
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In an earlier paper<sup>1</sup> we reported on the light-induced reactions between  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  and  $\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I},$  or  $\text{NCS}$ ). In these reactions the metal-metal bond is cleaved in a net disproportionation reaction  $[\text{MoI}_2 \rightarrow \text{Mo}^{\text{II}} + \text{Mo}^0]$



The initial reaction is followed by a second light-catalyzed step in which CO is displaced from  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}^2$



The thermal reverse of eq 1, in which a halide ion is displaced by an organometallic anion, e.g.



has proven to be a useful general reaction for the preparation of metal-metal bonds. In some cases, although the metal-metal bond appears to be favored thermodynamically, the reactions are slow. However, the metal-metal bonds can be prepared by using long reaction times or, in some cases, elevated temperatures.

The known examples provided by reactions 1 and 3 suggested to us that it might be possible to design a photochromic system in which the photochromism was based upon the net formation and cleavage, by disproportionation, of a metal-metal bond. We report here the results of our studies on the  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2 + \text{Br}^-$  system.

### Experimental Section

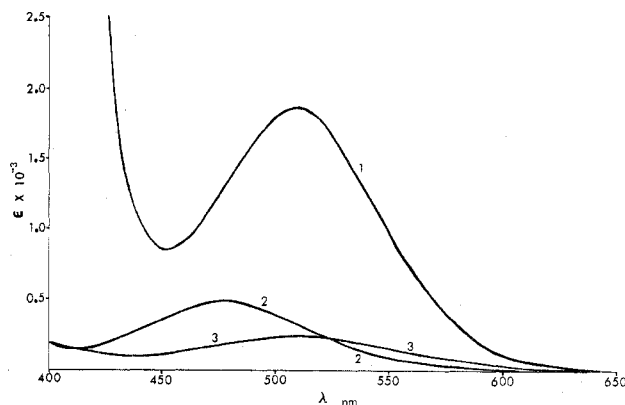
**Solvents.** Reagent grade solvents were predried with Drierite ( $\text{CaSO}_4$ ) and fractionally distilled. Tetrahydrofuran was freshly distilled from lithium aluminum hydride and kept under a nitrogen atmosphere.

**Chemicals.** Both  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  (Alfa Inorganics) and  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}^-$  were recrystallized by slowly adding hexane to a prefiltered, saturated methylene chloride solution. The solutions were manipulated under nitrogen and without excess light.  $[(n\text{-C}_4\text{H}_9)_4\text{NBr}]$  (Eastman Organics) was predried in a vacuum oven ( $80^\circ$  (2 mm)) for 2 hr. The dried salt was dissolved in benzene (5 ml/g) and heptane was added (1 ml/g). The solution was warmed until clear and then frozen to effect crystallization. The crystals were washed with heptane and dried in a vacuum oven ( $80^\circ$  (2 mm)) for 20 hr. The crystalline solid was stored in a vacuum desiccator in pretared 10-ml volumetric flasks.

**Spectral Measurements.** Uv-visible spectra were recorded on a Cary Model 14 spectrophotometer. The progress of the photochemical and thermal reactions was monitored on Cary 14 or Gilford Model 240 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrophotometer and were calibrated against polystyrene.

**General Procedures.** All solutions were manipulated in subdued lighting and were transferred with syringes which had been previously deaerated with nitrogen. Infrared solution cells were fitted with serum caps and were preflushed with nitrogen. The solutions were also shielded from ambient light prior to measurements. The serum caps were preextracted with warm tetrahydrofuran.

For the photochromism experiments, a tetrahydrofuran solution of  $[(n\text{-C}_4\text{H}_9)_4\text{NBr}]$  of the appropriate concentration was transferred via syringe to a light-shielded volumetric flask containing a preweighed amount of  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ . Aliquots of 4.0 ml were subjected



**Figure 1.** Visible spectra of (1)  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  ( $\lambda_{\text{max}}$  507 nm,  $\epsilon$  1870), (2)  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}$  ( $\lambda_{\text{max}}$  476 nm,  $\epsilon$  490), and (3)  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{Br}_2^-$  ( $\lambda_{\text{max}}$  512 nm,  $\epsilon$  250  $\pm$  10%) in tetrahydrofuran.

to three freeze-pump-thaw cycles on a high vacuum line and sealed at  $2 \times 10^{-6}$  mm.

Samples were irradiated on a merry-go-round apparatus equipped with a Hanovia 450-W medium-pressure mercury lamp (Model 679A36) in a water-jacketed Pyrex immersion well. A Corning 3-70 (No. 3384) filter was used to transmit radiation of wavelengths longer than 490 nm. Irradiation was continued until the absorbances (Gilford) reached a minimum value ( $\sim 10$ –25 min). The samples were then heated ( $60 \pm 2^\circ$ ) in the dark, and the absorbance changes at 526, 507, 476, and 387 nm (whenever possible) were monitored.

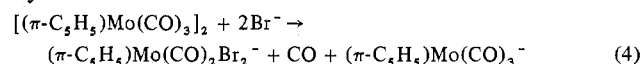
For each run two sealed sample tubes were prepared. One sample tube had a 1 mm cylindrical fused quartz cell attached for uv-visible monitoring. The extra sample tube was included in order to correlate infrared spectra with the observed absorbance changes due to irradiation. Blank runs were made for tetrahydrofuran with and without  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ .

### Results and Discussion

The visible spectra of the complexes  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ ,  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}$ , and  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{Br}_2^-$  in tetrahydrofuran (THF) are shown in Figure 1. The molybdenum dimer,  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ , also has an intense absorption band at 387 nm ( $\epsilon$  21,000). The band at 387 nm, which is apparently the  $\sigma \rightarrow \sigma^*$  transition of the metal-metal bond, is useful for monitoring  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  since the other compounds are essentially transparent in this region. The anion  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  does not absorb appreciably above 335 nm.

Each of the complexes has characteristic  $\nu(\text{CO})$  bands in the infrared, making infrared spectra a useful means for following net reactions. In THF the  $\nu(\text{CO})$  bands appear at 2011 (w), 1961 (s) and 1917 (s)  $\text{cm}^{-1}$  for  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ ; 2049 (m) and 1964 (s)  $\text{cm}^{-1}$  for  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}$ ; 1900 (s), 1781 (s) and 1765 (s)  $\text{cm}^{-1}$  for  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$ ; and at 1943 (s) and 1842 (s)  $\text{cm}^{-1}$  for  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{Br}_2^-$ .

Visible photolysis of solutions of  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  and  $\text{Br}^-$  in THF results in two stepwise photochemical reactions (eq 1 and 2). The first reaction, in which  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}$  and  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  are the products, is photochemically more efficient than the second reaction under the conditions used for the photolyses. As a consequence, by using limited photolysis times or a less than stoichiometric amount of  $\text{Br}^-$ , the dominant net reaction is eq 1. With a stoichiometric excess of  $\text{Br}^-$ , the first step is followed by the light-catalyzed displacement of CO from  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Br}$  by  $\text{Br}^-$  and the net reaction becomes



By controlling photolysis times and conditions it is, therefore,