

# Alkylcobalt Carbonyls. 10.<sup>1</sup> CO Activation and Phase-Transfer-Active Coordination Sites in Organocobalt Carbonyls. Mechanism of the Reaction of Benzyl Halides and Tetracarbonylcobaltate(-I)<sup>2</sup>

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(4'-Halomethyl-1',2'-benzo)-15-crown-5 (RX, 1; X = Cl (a), I (b)) compounds were reacted with Na[Co(CO)<sub>4</sub>] (2). The corresponding  $\eta^1$ -RC(O)Co(CO)<sub>4</sub> (5),  $\eta^1$ -RCO(CO)<sub>4</sub> (6), and  $\eta^3$ -RCO(CO)<sub>3</sub> (7) derivatives were obtained through intermediates [ $(\eta^5$ -RX)Na][Co(CO)<sub>4</sub>] (3) and [ $(\eta^5$ -Na<sup>+</sup>)RC(O)Co(CO)<sub>3</sub>(X<sup>-</sup>)] (4). The reactions leading to 7 from 1 were found to be reversible. Derivatives of 4 and 5 were prepared by monosubstitution with PPh<sub>3</sub>, giving 8 and 9, respectively. The reversibility of the reaction of PhCH<sub>2</sub>Cl with 2 was also demonstrated.

## Introduction

The combination of transition-metal and phase-transfer catalysis (TM-PTC) has been proven<sup>4</sup> to be a very useful preparative tool in the last decade. Examples of systems containing transition-metal and PTC-active moieties in the same molecule are, however, surprisingly rare.<sup>5</sup>

The primary goal of the present work was to prepare ( $\eta^3$ -R)Co(CO)<sub>3</sub>, ( $\eta^1$ -R)Co(CO)<sub>4</sub>, and ( $\eta^1$ -RC(O))Co(CO)<sub>4</sub> (R = (4'-methylene-1',2'-benzo)-15-crown-5) compounds and to learn about their reactivity. In the course of the preparative work it was discovered that these compounds and some of their intermediates and derivatives provide a new picture of the activation mechanism of benzyl halides by cobalt carbonyls, a reaction that attracted much preparative<sup>6</sup> and mechanistic<sup>7</sup> effort during the last decade. Moreover, TM-PTC type carbonylation of benzyl halides

Table I. Spectra of the New Compounds and 2

compd	spectra <sup>a</sup>	solvent
2	IR: 1889 s, sh, 1886 vs, 1858 m IR: 1882 vs, 1852 sh, m	Et <sub>2</sub> O THF
3	IR: 1884 IR: 1882	Et <sub>2</sub> O THF
4a	IR: 1973.4 vs, 1929.4 vs, 1640 br, w	THF
4b	IR: 2024.5 w, 1954.0 vs, 1930.5 vs, 1640 m	THF
5	IR: 2103.0 m, 2054.0 s, 2022.0 s, 2002.0 s, 1728 m IR: 2104.5 m, 2047.0 s, 2025.0 s, 2006.0 vs, 1730 m IR: 2046 s, 2024 vs, 2024 vs, 2004 vs, 1710 m, br NMR: 3.6 (br virt s, 16 H, crown CH <sub>2</sub> ), 3.95 (s, 2 H, $\alpha$ -CH <sub>2</sub> ), 6.55 (m, 3 H, ring CH)	Nujol <i>n</i> -hexane THF C <sub>6</sub> D <sub>6</sub>
6	IR: 2097 s, 2034 w, 2006 vs, br IR: 2095.0 ms, 2029.0 s, 2013.5 vs, 2009.0 vs NMR: 3.28 (s, 2 H, $\alpha$ -CH <sub>2</sub> ), 3.6 (br virt s, 16 H, crown CH <sub>2</sub> ) 7.15 (m, 3 H, ring CH)	THF <i>n</i> -hexane C <sub>6</sub> D <sub>6</sub>
7	IR: 2050 s, 1984 vs, 1963 vs IR: 2047.0 vs, 1983.0 m, 1968.0 m NMR: 2.1 and 3.5 (d, 2 H, <i>J</i> = 2 Hz, $\alpha$ -CH <sub>2</sub> ), 3.7 (br virt s, 16 H, crown CH <sub>2</sub> ), 5.55 and 6.0 (d, 2 H, <i>J</i> = 3 Hz, ring 6- and 5-CH), 6.15 (d, 1 H, <i>J</i> = 3 Hz, ring 2-CH)	THF <i>n</i> -hexane toluene- <i>d</i> <sub>8</sub>
8	IR: 2044.5 m, 1979.9 vs, 1956.5 vs, 1670.7 m IR: 2046.0 m, 1981.4 vs, 1955.0 vs, 1680-1860 m, br	Et <sub>2</sub> O toluene
9	IR: 2043 m, 1978 vs, 1959 vs, 1670 m, br IR: 1957.4 m, 1923.4 vs, 1584 m	MeOH toluene
10	IR: 2107 m, 2061 s, 2003 vs, 1700 m IR: 2107 s, 2061 m, 2026 s, 2002 vs, 1700 m	KBr pellet Nujol
12	IR: 1884 IR: 1882	Et <sub>2</sub> O THF
13Aa	IR: 1960 s, 1935 s, 1650 w	Et <sub>2</sub> O
13Ac	IR: 1954.4 vs, 1932.5 vs, 1648 w	THF
13Ba	IR: 1957.9 vs, 1935.3 vs, 1648 w	THF
13Bb	IR: 2045 vw, 1956.4 vs, 1935.4 vs, 1640 m, br	THF
13Bc	IR: 2025.2 m, 1954.3 vs 1932.5 vs, 1650 m, br	THF

<sup>a</sup> IR data are  $\nu$ (CO) values in cm<sup>-1</sup>; NMR data are  $\delta$  values in ppm (vs TMS).

(mostly with Co) has been proven to be a very advantageous variant.<sup>8</sup> In an attempt<sup>9a</sup> to show whether the

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(4) Some useful reviews: (a) Alper, H. *Adv. Organomet. Chem.* 1981, 19, 183. (b) Alper, H. *Fundam. Res. Homogeneous Catal.* 1984, 4, 79. (c) des Abbayes, H. *Isr. J. Chem.* 1985, 26, 249. (d) Galamb, V. *Kem. Kozl.* 1985, 63, 227.

(5) (a) Odell, K. J. *J. Organomet. Chem.* 1979, 168, 103. (b) McLain, S. J. *J. Am. Chem. Soc.* 1983, 105, 6355. (c) Okano, T.; Iwahari, M.; Suzuki, T.; Konishi, T.; Kiji, J. *Chem. Lett.* 1986, 9, 1467.

(6) We cite here only two excellent reviews: (a) El Chahawi, M.; Prange, U. *Chem.-Ztg.* 1978, 102, 1. (b) Cassar, L. *Ann. N.Y. Acad. Sci.* 1980, 333, 208.

(7) Leading references: (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1962, 84, 2499. (b) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1963, 85, 2779. (c) Nagy-Magos, Z.; Bor, G.; Markó, L. *J. Organomet. Chem.* 1968, 14, 205. (d) Braterman, P. S.; Walker, B. S.; Robertson, T. H. *J. Chem. Soc., Chem. Commun.* 1977, 651. (e) Francalanci, F.; Foà, M. *J. Organomet. Chem.* 1982, 243, 59. (f) des Abbayes, H.; Buloup, A.; Tanguy, G. *Organometallics* 1983, 2, 1730. (g) Francalanci, F.; Gardano, A.; Abis, L.; Fiorini, T.; Foà, M. *J. Organomet. Chem.* 1983, 243, 87. (h) Francalanci, F.; Gardano, A.; Foà, M. *J. Organomet. Chem.* 1985, 282, 277. (i) Foà, M.; Francalanci, F.; Bencini, E.; Gardano, A. *J. Organomet. Chem.* 1985, 285, 293.

mechanistic information gathered with the crown-condensed benzyl halides could be generalized to simpler molecules, we reinvestigated some aspects of the reaction<sup>10</sup> of benzyl chloride and  $[\text{Co}(\text{CO})_4]^-$ . The results of these studies will be reported here.

### Experimental Section

All reactions were carried out under deoxygenated CO or Ar by using carefully dried solvents.<sup>11</sup> The IR spectra were run on a Specord 75 instrument (Carl Zeiss, Jena, GDR), using simultaneous DCl or benzene calibration.<sup>12</sup> The  $\epsilon$  values of the IR bands used for quantitative analysis are reliable to 7–11 relative %. Concentrations of compounds 5, 6, and 7 were determined with use of the  $\epsilon$  values of complexes 14, 15, and 16. <sup>1</sup>H NMR spectra were obtained on an 80-MHz BS-487 spectrometer (Tesla, Brno, Czechoslovakia) and mass spectra on a JMS-01-SG-2 (JEOL, Tokyo, Japan) instrument. IR and <sup>1</sup>H NMR spectra are collected in Table I. GC measurements were performed by using a Hewlett-Packard 5830/A (Avondale, PA) chromatograph and a 25-m glass capillary column<sup>13</sup> coated with SP 2340 medium. Starting compounds were of commercial origin with the exception of  $\text{Co}_2(\text{CO})_8$ <sup>14</sup> and (4'-chloromethyl-1',2'-benzo)-15-crown-5 (1a) or (4'-iodomethyl-1',2'-benzo)-15-crown-5 (1b),<sup>15</sup> which were prepared by published procedures.

**Reaction of (4'-Chloromethyl-1',2'-benzo)-15-crown-5 (1a) with  $\text{Na}[\text{Co}(\text{CO})_4]$  (2).** Dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$  (171 mg, 0.5 mmol), was dissolved in 20 mL of  $\text{Et}_2\text{O}$  and the solution treated with 20 g of 1.5% Na/Hg, at room temperature, under a CO atmosphere until it became colorless (20–60 min). This solution was left to stand for about 1 h and decanted into a Schlenk vessel, and then 1a (287 mg, 0.9 mmol) dissolved in 10 mL of  $\text{Et}_2\text{O}$  was added with stirring within a few minutes. After the addition of the first drops a red oil separated. The latter showed a sharp  $\nu(\text{CO})$  (at 1880  $\text{cm}^{-1}$ ) absorption when it was quickly dissolved in  $\text{Et}_2\text{O}$  and a somewhat broader single band centered at the same wavenumber when it was investigated as a thin film between two KBr plates.<sup>16</sup> This red oil was assigned to be 3a in analogy with the spectra and formation of  $[\text{Na}(15\text{-crown-5})][\text{Co}(\text{CO})_4]$  (12) isolated as described later. The red oil 3a proved to be very unstable against loss of NaCl, and attempts to isolate it and obtain NMR spectra failed because of its limited solubility. The red oil dissolved in the reaction medium within

a few minutes; this was accompanied by the formation of a white crystalline precipitate (NaCl). The reaction mixture was stirred for an additional 2–2.5 h and the progress of the reaction monitored by IR spectroscopy. The characteristic bands of 2 and 3a at 1890 and 1880  $\text{cm}^{-1}$  respectively disappeared gradually, while a band at  $\sim 1970 \text{ cm}^{-1}$  increased after 10–20 min, achieved its maximum intensity after  $\sim 30$ –40 min, and then gradually disappeared. This band system was attributed to the anionic cobalt tricarbonyl 4a on the basis of analogies from the literature<sup>17</sup> and its formation in the reaction of 5 and NaCl as described later. The reaction mixture then was filtered and the solvent evaporated at  $-10$  to  $0^\circ \text{C}$  at reduced pressure. The residue was extracted with 20 mL of *n*-hexane (or *n*-pentane), and the extract was filtered again (excess 1a is insoluble in these solvents). This solution was analyzed by IR spectroscopy, which showed the characteristic band systems<sup>10a,c,17c,g,18</sup> of alkyl- and acylcobalt tetracarbonyls and an ( $\eta^3$ -benzyl)cobalt tricarbonyl complex. Thus, these bands were attributed to 5, 6, and 7. From the beginning of the formation of the white precipitate a complex band system between 2100 and 1960  $\text{cm}^{-1}$  started to gain intensity gradually. This part of the spectrum was attributed to the mixture of 5, 6, and 7, causing an ill-resolved (due to the relatively polar solvent) band envelope. Treatment of this solution with a slow Ar stream caused enrichment of 7 (and 6), while continued stirring under a CO atmosphere (or a slow CO stream) for 30–60 min caused disappearance of the bands due to 7 and a strong decrease in the intensity of the bands due to 6. The chilling of this latter solution resulted in the formation of a yellow crystalline material, which proved to be pure 5. IR and <sup>1</sup>H NMR data are given in Table I. Anal. Calcd for  $\text{C}_{20}\text{CoH}_{21}\text{O}_{10}$ : Co, 12.27. Found: Co, 12.3. Yield: 111 mg (26%, with respect to 1a).

The displacement of the equilibrium between 5, 6, and 7 by treatment with CO or Ar was shown to be reversible in *n*-hexane; it could be repeated two to three times without considerable loss of the overall concentration, as monitored by the overall IR  $\nu(\text{CO})$  band intensity. This experiment was performed either under Ar or at reduced pressure for a few minutes, which caused the enrichment of 7 (and 6) so that an equilibrium was reached corresponding roughly to 5:6:7 = 2:5:10 (according to <sup>1</sup>H NMR spectra and overall IR intensities and values of compounds 14, 15, and 16). The solvent was evaporated at room temperature and reduced pressure; a light brown oil was obtained. This oil, when dissolved again, showed exclusively the bands of 7 in the IR  $\nu(\text{CO})$  spectrum. This substance could not be crystallized, and therefore, the product was analyzed by direct-inlet mass spectrometry, with use of the low-IP (15-eV) operation mode: *m/e* 424 (8), 396 (5) [M – CO], 368 (40) [M – 2CO], 340 (12) [M – 3CO], 281 (10) [M –  $\text{Co}(\text{CO})_3$ ], 268 (100) [M – {CHCo(CO)}<sub>3</sub>] (=benzo-crown)]. IR and <sup>1</sup>H NMR data are given in Table I. Yield: 115 mg (30% with respect to 1a).

The IR and <sup>1</sup>H NMR spectra of 6 were determined with use of solutions containing also different quantities of 5 and/or 7. The assignment was supported by variation of the concentration of these carbonylation/decarbonylation products by passing a CO or Ar stream into the solution. For IR and <sup>1</sup>H NMR data, see Table I.

In course of this experiment the intensity of the bands attributed to the more intense doublet of 4a did not exceed 0.1% of the overall  $\nu(\text{CO})$  absorption, while with THF (instead of  $\text{Et}_2\text{O}$ )

(8) (a) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* 1977, 134, C11. (b) Cassar, L.; Foá, M. *J. Organomet. Chem.* 1977, 134, C15. (c) des Abbayes, H.; Buloup, A. *J. Chem. Soc., Chem. Commun.* 1978, 1090. (d) Gambarotta, S.; Alper, H. *J. Organomet. Chem.* 1981, 212, C23. (e) Tanguy, F.; Weinberger, B.; des Abbayes, H. *Tetrahedron Lett.* 1983, 24, 4005. (f) Galamb, V.; Markó, L.; Palágyi, J.; Pályi, G.; Sámár-Szerencsés, E. Hung. Pat. Appl. 2105/1987.

(9) (a) This was suggested by a reviewer of a preliminary communication of this paper. (b) This was suggested by a reviewer of the full paper. These suggestions are gratefully acknowledged.

(10) Data on the preparation, structure, and interconversions of benzylcobalt carbonyls were reported recently: (a) Galamb, V.; Pályi, G. *J. Chem. Soc., Chem. Commun.* 1982, 487. (b) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* 1984, 59, 203. (c) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* 1986, 108, 3344.

(11) (a) Herzog, S.; Dehnert, J. *Z. Chem.* 1964, 4, 1. (b) Shriver, D. *F. Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969. The solvents were dried as follows: *n*-pentane and *n*-hexane, Na wire/benzophenone;  $\text{Et}_2\text{O}$ , THF, and toluene, Na wire/benzophenone or Na/K; DMSO, molecular sieves (3A); MeOH and EtOH, Mg grain; crown ether, molecular sieves (3A).

(12) Bor, G. *Acta Chim. Acad. Sci. Hung.* 1962, 34, 315.

(13) HCl gas treated inner surface: (a) Simon, A.; Ötvös, I.; Pályi, G. *Kem. Kozl.* 1972, 37, 81. (b) Alexander, G.; Garzó, G.; Pályi, G. *J. Chromatogr.* 1974, 91, 25.

(14) Szabó, P.; Markó, L.; Bor, G. *Chem. Tech. (Leipzig)* 1961, 13, 549.

(15) (a) Pedersen, C. J. *J. Am. Chem. Soc.* 1967, 89, 7033. (b) Empsall, H. D.; Hyde, E. N.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* 1975, 1690. (c) Ungaro, R.; Smid, J. *J. Am. Chem. Soc.* 1976, 115, 5198. The purity of the intermediates and the end products was checked by <sup>1</sup>H NMR spectroscopy melting and  $n_D$  values.

(16) This is a marked difference from the  $T_g$  absorption of uncoordinated  $\text{Na}[\text{Co}(\text{CO})_4]$  in  $\text{Et}_2\text{O}$  at 1886  $\text{cm}^{-1}$  according to our measurement. Compare also: (a) Edgell, W. F.; Yong, M. T.; Koizumi, N. *J. Am. Chem. Soc.* 1965, 87, 2563. (b) Calderazzo, F.; L'Epplattenier, P. *Inorg. Chem.* 1967, 6, 1220. (c) Edgell, W. F.; Lyford, J. *J. Chem. Phys.* 1970, 52, 4329.

(17) (a) Francalanci, F.; Gardano, A.; Abis, L.; Foá, M. *J. Organomet. Chem.* 1983, 251, C5. (b) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* 1984, 106, 995. (c) Tasi, M.; Pályi, G. *Organometallics* 1985, 4, 1523. (d) Vlačić, G.; Bart, J. C. J.; Foá, M.; Francalanci, F.; Clement, R. *J. Organomet. Chem.* 1985, 287, 369. (e) Tasi, M.; Pályi, G. *Kem. Kozl.* 1986, 65, 160. (f) Röper, M.; Schieren, M.; Heaton, B. T. *J. Organomet. Chem.* 1986, 299, 131. (g) Galamb, V.; Pályi, G.; Boese, R.; Schmid, G. *Organometallics* 1987, 6, 861. (h) Röper, M.; Krüger, C. *J. Organomet. Chem.* 1988, 339, 159. (i) Tasi, M.; Posztor, Z.; Pályi, G. To be submitted for publication. Group IVA metal analogues: (j) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* 1977, 686.

(18) (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1962, 84, 2499. (b) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* 1963, 44, 184. (c) Bor, G. *Inorg. Chim. Acta* 1967, 1, 81. (d) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* 1981, 209, 183. (e) Pályi, G.; Galamb, V.; Röder, A. *Atti Accad. Sci. Ist. Bologna, Cl. Sci. Fis., Rend.* 1981, 269(13/B), 67. (f) Ungváry, F. *J. Chem. Soc., Chem. Commun.* 1984, 824; *J. Organomet. Chem.* 1986, 303, 251.

as solvent these bands became much more pronounced, reaching 17% of the overall intensity in the CO stretching range.

**Reaction of Complex 5 (or a Mixture of 5, 6, and 7) with NaI (Eq vi).** (4'-Chloromethyl-1',2'-benzo)-15-crown-5 (129 mg, 0.45 mmol) and sodium tetracarbonylcobaltate,  $\text{Na}[\text{Co}(\text{CO})_4]$  (0.5 mmol, prepared from  $\text{Co}_2(\text{CO})_8$ , 86 mg), were allowed to react in  $\text{Et}_2\text{O}$  (20 mL) under CO as described above. At the end of the reaction the solvent was evaporated at 0 °C and reduced pressure. The residual yellow oil was dissolved in 10 mL of toluene under CO. The IR spectrum of this solution showed prominently the presence of 5. Then, sodium iodide was added to this solution with stirring in 15-mg (0.1-mmol) portions (suspended in 2 mL of toluene) until the IR  $\nu(\text{CO})$  spectrum of the reaction mixture showed that the band system of the mixture of 5, 6, and 7 was reduced to about 25% of its original intensity. This generally required the addition of 45 mg (0.3 mmol) of NaI. During this operation a brown precipitate was formed, which then was filtered, washed with toluene (5 mL) under a CO atmosphere, and dried in a CO stream.

The reaction can also be carried out by starting with an equilibrium mixture of 5, 6, and 7 obtained under Ar as described above and adding the sodium iodide (45 mg, 0.3 mmol) in one portion.

In both cases a yellow solid is obtained, which was identified as 4b on the basis of its IR spectra (Table I) and analyses. Anal. Calcd (found) for  $\text{C}_{19}\text{CoH}_{20}\text{I}\text{NaO}_5$ : C, 37.96 (37.9); Co, 9.79 (9.5); H, 3.35 (3.8); I, 21.07 (20.6). Calcd for Co/I (measured independently): 1.00; found: 1.06. Dec pt: 95–98 °C. Yield: 145–160 mg (80–90% with respect to NaI).

Complex 4a was prepared analogously from 5 and NaCl in THF. This substance could not be isolated, but its IR spectrum (Table I) was obtained.

**Decomposition of 4a under CO (Eqs iv and ii). Method A.** A solution of complex 4a (60 mg, 0.1 mmol) in 10 mL of THF, prepared as described above at room temperature under CO, was stirred and analyzed by the IR spectra from time to time. Already after 10 min the sharp absorption band of 3a at  $1880\text{ cm}^{-1}$  appeared and the bands of 4a started to lose intensity. After 30–50 min the band of 3a became predominant and the bands of 4a almost disappeared. Then the solvent was evaporated at room temperature and reduced pressure and the residue was analyzed by mass spectrometry. (4'-Chloromethyl-1',2'-benzo)-15-crown-5 was the only organic material identified.<sup>19</sup> A separate demonstration of reaction ii could not be achieved.

**Method B.** Complex 4b (21.7 mg, 0.036 mmol) was dissolved at room temperature in 1.6 mL of DMSO, under CO, to yield a reddish brown solution, which turned light yellow and then almost colorless pink within a few minutes. The only cobalt carbonyl detected after 10 min was  $[\text{Co}(\text{CO})_4]^-$ . Then the product was analyzed for benzyl halide<sup>20a</sup> and  $\text{Na}[\text{Co}(\text{CO})_4]$  (2).<sup>20b</sup> Yield of 1b: calcd, 0.036 mmol; found, 0.036 mmol (100.0% with respect to 4b). Yield of 2: calcd, 0.036 mmol; found, 0.026 mmol (72.0% with respect to 4b).

**Method C.** Complex 4b (30 mg, 0.05 mmol) was dissolved at room temperature in 1.8 mL of methanol, under CO. The infrared  $\nu(\text{CO})$  spectrum was monitored at various times. After ~1 min the spectrum showed that 4b had already decomposed and the band systems of 2, 5, and 6 were observed (~1.5:10:2, as determined from  $\epsilon_{1880}$ ,  $\epsilon_{2104.5}$ , and  $\epsilon_{2095}$  values for these compounds). Additional stirring for 1 h caused only a change of this ratio in favor of 2, i.e., 10:5:1.

**Reaction of Compound 5 with  $\text{NaBF}_4$ .** A solution of complexes 5, 6, and 7 (~1 mmol of Co) in 10 mL of toluene was prepared as described above and treated with CO, to obtain a solution that contained predominantly 5 (~80%). To this solution were added 56.9-mg (0.5-mmol) portions of sodium tetrafluoroborate. The suspension was stirred under CO at room temperature, and the progress of the reaction was monitored by the IR spectra. The bands of 5 decreased, and a precipitate was formed.

It was necessary, however, to add a total of 2 mmol of  $\text{NaBF}_4$  to achieve a relatively good conversion (~90%). Then, the product was mixed with an excess of  $\text{NaBF}_4$ . It decomposed upon attempted recrystallization. The IR spectrum of the precipitate (contaminated by  $\text{NaBF}_4$ ) showed only one  $\nu(\text{CO})$  (Table I) band system.

**Reaction of Compound 5 (and 6) with  $\text{PPh}_3$ .** A solution of complexes 5 and 6 (~10:1, practically free of 7; ~0.5 mmol of Co) in 20 mL of  $\text{Et}_2\text{O}$  was prepared as described before (enrichment in 5 by CO). To this solution, while it was stirred under CO at room temperature, was added triphenylphosphine (145 mg, 0.55 mmol), and the mixture was stirred for an additional 20 min. Then to this solution was added 20 mL of *n*-pentane and the solution was shaken for 1–3 min. This caused the separation of a dense yellow oil. Alternatively, without addition of *n*-pentane, the ethereal solution was chilled to -40 °C for 2–3 h. This caused the precipitation of a yellow solid, which was characterized as being complex 8 on the basis of its IR spectra (Table I) and analyses. Anal. Calcd for  $\text{C}_{37}\text{CoH}_{35}\text{O}_5\text{P}$ : Co/P, 1.00. Found: Co/P, 0.95. Yield: 320–328 mg (90–92% with respect to starting Co, for both the oily and solid products).

**Preparation of Complex 9. Method A.** A solution of complex 8 (365 mg, 0.5 mmol) in 20 mL of toluene was prepared as described before. To this solution, while it was stirred at room temperature under CO, were added 15-mg (0.1-mmol) portions of NaI (suspended in 3 mL of toluene). The progress of the reaction was monitored by IR spectra recorded after each portion of NaI. After addition of the fifth portion no further change was observed. This resulted in diminution of the  $\nu(\text{CO})$  bands due to 8 while a new band system emerged gradually, which was attributed to 9 (Table I). Attempts to obtain good-quality NMR spectra or purified samples of 9 failed because of its limited solubility in nonpolar solvents and decomposition in more polar solvents.

**Method B.** Complex 4b (300 mg, 0.5 mmol) was suspended (partly dissolved) in 10 mL of toluene at room temperature under CO. To this solution, while it was stirred, was added  $\text{PPh}_3$  (130 mg, 0.5 mmol). The stirring was continued for an additional 1 h, and IR spectra were recorded. After this period the spectra showed the presence of complexes 8 and 9 (~2:10). Then the solution was evaporated to dryness (at room temperature) and the residue dissolved in 3 mL of methanol. This solution was stirred under CO for 15–20 min, and then the IR spectrum was registered. This showed 8 as the only organocobalt product in the solution. The overall intensity of the spectrum indicated that the conversion was approximately quantitative.

**Attempted Reaction of 1a with  $[\text{PPN}][\text{Co}(\text{CO})_4]$ .** Benzyl halide 1a (287 mg, 0.9 mmol) was dissolved in 10 mL of THF. To this solution, while it was stirred at room temperature under CO, was added  $[\text{PPN}][\text{Co}(\text{CO})_4]$ <sup>21</sup> (689 mg, 1 mmol). The reaction mixture was then stirred for an additional 5 h, and IR spectra were recorded every 30–40 min. Even after 5 h no change was observed with respect to the solution of  $[\text{PPN}][\text{Co}(\text{CO})_4]$  in THF.

**Preparation of the Equilibrium Mixture of  $(\eta^1\text{-PhCH}_2\text{C}(\text{O}))\text{Co}(\text{CO})_4$  (14),  $(\eta^1\text{-PhCH}_2)\text{Co}(\text{CO})_4$  (15), and  $(\eta^3\text{-PhCH}_2)\text{Co}(\text{CO})_3$  (16). A. Preparative Variant.** A solution of dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$  (171 mg, 0.5 mmol), in 20 mL of  $\text{Et}_2\text{O}$  was treated with 1.5% Na/Hg (20 g) until it became colorless. The resulting solution of  $\text{Na}[\text{Co}(\text{CO})_4]$  (2) in  $\text{Et}_2\text{O}$  was filtered and treated with benzyl chloride (11a; 126 mg, 115  $\mu\text{L}$ , 1 mmol), as described in ref 10c. The progress of the reaction was followed by IR spectroscopy (as usual) and (additionally) by gas chromatography to assure that the product contained solely 14, 15, and 16 as cobalt carbonyls and that it was free of 11a. This latter requirement was met only after a prolonged reaction time of 10–12 h. Then  $\text{Et}_2\text{O}$  was evaporated, the residue was extracted with 20 mL of *n*-hexane, and the extract was filtered and stored under CO at -78 °C until used for further experiments.

A weighed part of the residue after the evaporation of  $\text{Et}_2\text{O}$  was dissolved in THF. This solution was treated with an Ar or CO stream at room temperature and thus enriched in 14 and 16. These experiments, combined with Co concentration measurements, enabled the determination of the  $\epsilon$  values of one band each

(19) (a) *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. 1, p 531. (b) Hvistendahl, G.; Undheim, K.; Györfösi, P. *Org. Mass. Spectrom.* 1973, 7, 903.

(20) (a) Potentiometric I<sup>-</sup> determination by  $\text{AgNO}_3$ . (b) Determined by using  $\epsilon^{1889} = 4680\text{ cm}^2\text{ mmol}^{-1}$  for  $\text{Na}[\text{Co}(\text{CO})_4]$ .

(21) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* 1974, 15, 84.

of 14, 15, and 16. These are as follows: 14,  $\epsilon_{2106} = 415 \text{ cm}^2 \text{ mmol}^{-1}$ ; 15,  $\epsilon_{2097} = 410 \text{ cm}^2 \text{ mmol}^{-1}$ ; 16,  $\epsilon_{1963} = 3750 \text{ cm}^2 \text{ mmol}^{-1}$ .

The IR  $\nu(\text{CO})$  spectral data for these compounds in THF are shown in Table I.

**B. Mechanistic Variant without Crown Ether.** The reaction mixture used for the preparative variant of this experiment was analyzed by IR spectroscopy from time to time. After 10–15 min of reaction time a low- to medium-intensity doublet at 1935 and 1960  $\text{cm}^{-1}$  emerged but never became the main band system of the spectrum (maximum 10–20% of the overall intensity). This doublet was attributed to **13Aa** on the basis of analogies. After prolonged (30–60 min) stirring this doublet disappeared and the bands of 14, 15, and (some) 16 became dominant.

**C. Mechanistic Variant with Crown Ether.** The reaction mixture used to obtain 14 + 15 + 16 was prepared as described before, but as soon as the colorless solution of **2** was obtained, 15-crown-5 (220 mg, 1 mmol) was added. This was followed by the addition of **11a** (126 mg, 1 mmol) at once. Then the infrared spectrum of the solution was monitored from time to time. A band system, attributed to **13Ba**, at 2075 vw, 1985 vs, 1935 vs, and 1650 w  $\text{cm}^{-1}$  emerged. It became much more intense (up to 50%) than in the case without added crown ether. After prolonged stirring for an additional 1–1.5 h, 14, 15, and 16 remained as the only organocobalt products.

**Reaction of the Equilibrium Mixture of Complexes 14, 15, and 16 with NaI. Method A.** A 5-mL portion of the stock solution of compounds 14, 15, and 16 (containing 0.25 mmol of Co) was poured into a reaction vessel at room temperature and under CO. Then the solvent (*n*-hexane) was evaporated at reduced pressure and the oily residue dissolved in 5 mL of THF under CO. A control IR spectrum showed the presence of only 14, 15, and 16 (~10:2:0.5) as cobalt carbonyls, and a repeated GLC control demonstrated that the solution was free of **11c**. To this solution, while it was stirred under CO, was added sodium iodide in 15-mg (0.1-mmol) portions until a total of 0.5 mmol was reached. The progress of the reaction was monitored by IR spectroscopy. The changes in the spectra were characterized by the emergence of a strong doublet at 1954.4 and 1932.5  $\text{cm}^{-1}$  (attributed to **13Ac**) and (later) by the strong band of **2** at 1882 vs, 1852 sh, m  $\text{cm}^{-1}$ . The reaction mixture after 1.5 h was analyzed by GC/MS, and **11c** (60%), accompanied by some PhCH<sub>2</sub>OH (40%), was identified (on the basis of a comparison of the retention times and mass spectra with those of authentic samples).

**Method B.** If the reaction described under method A was performed in the presence of 15-crown-5 (110 mg, 0.5 mmol) added at once, together with the NaI (0.5 mmol) added in one portion, the formation of complexes **12** (1880  $\text{cm}^{-1}$ ) and **13Bc** (2025.2 m, 1954.3 vs, 1932.5 vs, 1650 br, m  $\text{cm}^{-1}$ ; cf. Table I) resulted, while additional stirring for 1 h under CO caused the decomposition of **13**, leaving only **12** as the cobalt carbonyl species and providing **11c** (66%) and PhCH<sub>2</sub>OH (34%) as identified and determined by GC/MS. The identification was based on a comparison of the retention times and mass spectra with those of authentic samples.

**Method C.** When the reaction was performed as in method A, under identical conditions but with 5 mL of toluene as solvent, no change was observed in the IR and GC/MS spectra even upon the addition of 5 mmol of NaI (10-fold of the former) at the end of stirring for 1.5 h. Then 15-crown-5 (220 mg, 1 mmol) was added and the IR spectrum obtained again. This showed the presence of a small amount (~10%) of complex **13Ac**.

Complexes **13** could not be obtained in pure form. The IR spectra recorded in THF solvent show a close analogy with the spectrum of complex **4b**, as well as with the spectra of several [XYCo(CO)<sub>3</sub>]<sup>-</sup> anionic complexes.<sup>17</sup>

**Reaction of the Equilibrium Mixture of Complexes 14, 15, and 16 with NaCl.** Complexes 14, 15, and 16 from a 5-mL portion of the *n*-hexane stock solution of these complexes were evaporated to dryness and then dissolved in 5 mL of THF (~0.25 mmol of Co). Then carefully dried sodium chloride (116 mg, 2 mmol) was added and the reaction mixture was stirred for 1.5 h under CO at room temperature. After this period the IR spectrum did not show any difference with respect to a control solution prepared identically but without NaCl. Then 15-crown-5 (220 mg, 1 mmol) was added at once, and while the stirring was continued, the IR spectra were recorded from time to time. A new band system emerged, characterized by a strong doublet at 1957.9 and 1935.3

$\text{cm}^{-1}$  and weak absorptions at 2075 and 1648  $\text{cm}^{-1}$  (attributed to **13Ba**), and the strong, sharp band of complex **12** at 1880  $\text{cm}^{-1}$  increased. After 10–20 min only the band of complex **12** increased; the others diminished quickly. Then stirring was continued for an additional 30–60 min and the solution was analyzed by GC/MS: **11a** (~60%) and PhCH<sub>2</sub>OH (~40%) could be detected and their amounts determined.

No reaction could be observed with toluene as solvent either in the absence or in the presence of the crown ether.

In THF solvent, on addition of a 1–2 mol excess of NaBr in the presence of 15-crown-5, the IR spectrum of the supposed **13Bb** could be observed: IR data are given in Table I.

**Preparation of [Na(15-crown-5)][Co(CO)<sub>4</sub>] (**12**).** A colorless solution of sodium tetracarbonylcobaltate(-I), Na[Co(CO)<sub>4</sub>] (194 mg, 1 mmol), was prepared from Co<sub>2</sub>(CO)<sub>8</sub> (171 mg, 0.5 mmol) by reaction with 1.5% Na/Hg (20 g) in 20 mL of Et<sub>2</sub>O according to the known method,<sup>22</sup> also described briefly earlier in this paper. To this solution, while it was stirred at room temperature under CO, was added 15-crown-5 (220 mg, 1 mmol) in two to three portions and the changes in the IR  $\nu(\text{CO})$  spectrum were followed. The strong, broad band system of Na[Co(CO)<sub>4</sub>] at 1889 s, sh, 1886 vs, 1858 m  $\text{cm}^{-1}$  gradually disappeared and a strong, much sharper band at 1884  $\text{cm}^{-1}$  emerged, while a dense yellow oil deposited. Then two-thirds of the solvent was evaporated and the rest of the reaction mixture was decanted from the orange-red oil. This was dissolved again in Et<sub>2</sub>O and in THF, which gave a yellow solution. The IR  $\nu(\text{CO})$  spectrum consisted of one sharp strong band at (Et<sub>2</sub>O) 1884 or (THF) 1882  $\text{cm}^{-1}$ . This was attributed to [Na(15-crown-5)][Co(CO)<sub>4</sub>]. The sharpening and lower wavenumber shift of the [Co(CO)<sub>4</sub>]<sup>-</sup> band are in good agreement with an increased Na<sup>+</sup>/[Co(CO)<sub>4</sub>]<sup>-</sup> separation.<sup>23–25</sup> Yield: 257 mg (62%). Anal. Calcd (found) for C<sub>14</sub>CoH<sub>20</sub>NaO<sub>9</sub>: Co, 14.23 (13.9); C, 40.59 (40.8); H, 4.87 (5.1).

## Results and Discussion

**Preparative Results.** The preparative results of the present work are summarized in Schemes I and II.

The benzyl chloride derivative **1a** reacts with **2** (Et<sub>2</sub>O, CO, 20 °C) smoothly to give a mixture of **5**, **6**, and **7**, which are easily interconvertible by equilibria viii–x as expected.<sup>7c,10</sup> However, the crown ether part of the organic ligand enables the detection of intermediates **3** and **4** and the observation of equilibria i/ii (i, Et<sub>2</sub>O or THF, CO, 20 °C; ii, THF, CO, 20 °C), iii/iv (iii, Et<sub>2</sub>O, CO, 20 °C; iv, THF, CO, 20 °C), and v/vi (v, Et<sub>2</sub>O, MeOH, or EtOH, CO, 20 °C; vi, toluene or THF, CO, 20 °C) utilizing solvent effects.

The equilibrium mixture of **5**, **6**, and **7** reacts with PPh<sub>3</sub> (Et<sub>2</sub>O, CO, 20 °C) selectively to form **8**, which reacts with NaI (toluene, CO, 20 °C) in an addition-like reaction (xii) to give **9b**. Again a solvent effect enabled regeneration of **8** (xiii, MeOH, CO, 20 °C).

While soft anionic Lewis bases such as Cl<sup>-</sup> and I<sup>-</sup> coordinate easily to Co as indicated by **4a,b**, the hard anion in Na[BF<sub>4</sub>] does not interact with the metal in **10**. The problem of whether the coordinated Na<sup>+</sup> (hard Lewis acid) does or does not interact with the acyl-carbonyl group<sup>26</sup> will be discussed later.

We regard as one of the most interesting observations of this study that the activation of the alkyl halides by **2** could be reversed, either from complex **4** (DMSO, CO, 20

(22) Hieber, W.; Vohler, O.; Braun, G. *Z. Naturforsch.* **1958**, *13B*, 192.

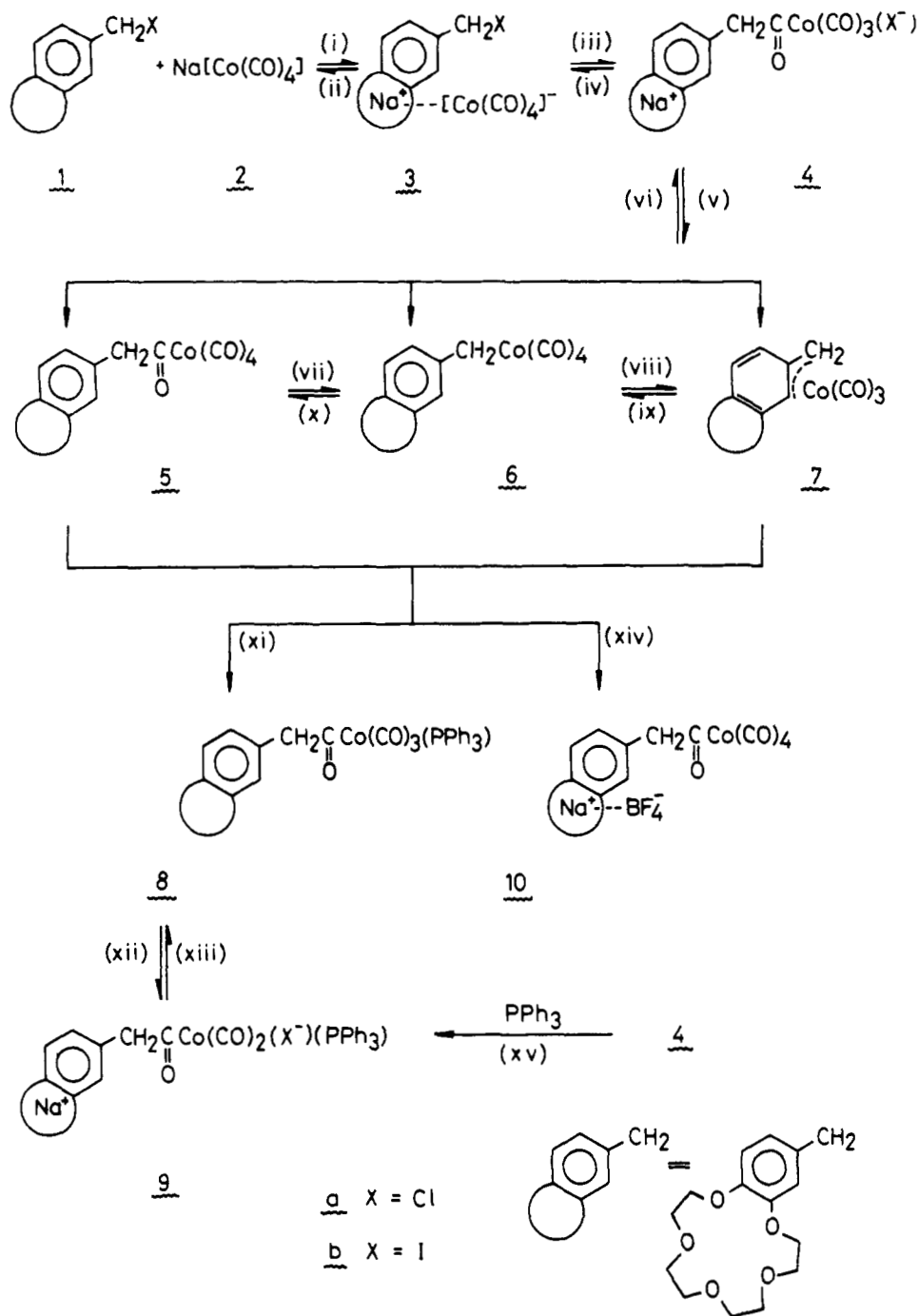
(23) Ellis, J. *J. Organomet. Chem.* **1975**, *86*, 1.

(24) (a) Braterman, P.; Walker, B.; Robertson, T. *J. Chem. Soc., Chem. Commun.* **1977**, 651. (b) Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 147. (c) Chen, C. K.; Cheng, C. H. *Inorg. Chem.* **1983**, *22*, 3378.

(25) (a) Fachinetti, G.; Del Cima, F.; Braca, G.; Funaioli, T. *J. Organomet. Chem.* **1984**, *275*, C25. (b) Fachinetti, G.; Del Cima, F.; Sbrana, G.; Funaioli, T. *J. Organomet. Chem.* **1985**, *287*, C23. (c) Fachinetti, G.; Fochi, G.; Funaioli, T. *J. Organomet. Chem.* **1986**, *301*, 91.

(26) This could be expected on the basis of the observations of S. J. McLain: ref 5b and personal communication, 1983.

Scheme I



$^{\circ}\text{C}$ ) or from **5** + **6** + **7** (toluene or THF, CO, 20  $^{\circ}\text{C}$ , via **4**), leading to regeneration of the starting organic compound **1**. A crossover experiment, that is, starting from **1a** and generating **1b** and **2** quantitatively via isolated **5** and **4b** provides additional support of this picture.

Since the preparative results with the crown ether condensed benzyl halides **1** seemed to shed new light upon the activation of benzyl halides **1** by  $[\text{Co}(\text{CO})_4]^-$ , we supplemented<sup>3a</sup> our preparative work by a reinvestigation of some aspects of the reaction of (unsubstituted) benzyl chloride with  $\text{Na}[\text{Co}(\text{CO})_4]$ .

In the course of these experiments we observed that tricarbonylcobalt anions **13** can be detected in this reaction as intermediates of the formation of the acyl-/alkyl-/ ( $\eta^3$ -benzyl)-cobalt equilibrium product mixture (well-known from earlier studies<sup>10,20</sup>).

The analogy of the behavior of **11a** with that of **1a** was found to be quite general; the key intermediate **13** could

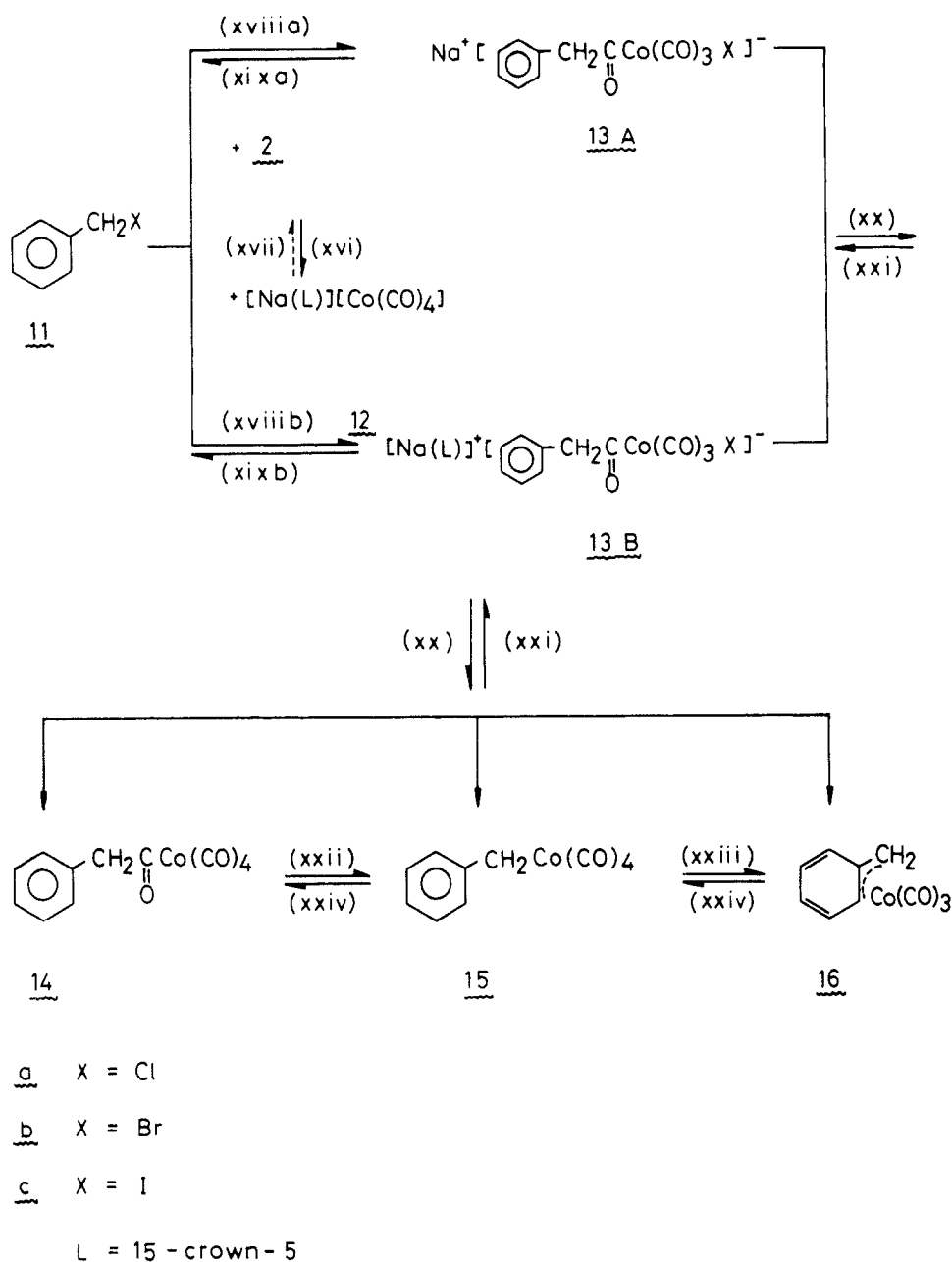
be obtained from the equilibrium mixture **14** + **15** + **16** under the influence of sodium halides, and decomposition of **13** to benzyl halides **11** could be demonstrated.

The origin of benzyl alcohol in the reaction products of these "reverse" reactions still is not clear. This product can be (in part) the result of the presence of moisture (5–10  $\mu\text{mol/mL}$ ) in the solvents that was left after the drying procedure.<sup>3b</sup> Another point that needs further exploration is the absence of alkyl analogues of acyl complexes **4**, **9**, **10**, and **13**, as well as the absence of the phenylacetyl halides (corresponding to **1** and **11**) in these reactions.

The fact that intermediate **13** can be observed much more readily in the presence of crown ether indicates that such  $[\text{XYCo}(\text{CO})_3]^-$  type anions are kinetically favored or stabilized by charge separation effects.<sup>23–25,27–29</sup>

(27) In accordance with the relatively outstanding stability of Röper's  $[\text{PPN}][\text{AcCo}(\text{CO})_3]$ .<sup>17f,h</sup>

Scheme II



**Spectra and Structures.** Compounds 4, 5, 8, and 12 could be isolated in analytically pure form. Complexes 14, 15, and 16 were known from an earlier study.<sup>10c</sup>

The structure of intermediate 3 is based on an analogy with the isolated 12. Similarly, the structure of complex 13 is based on a comparison with the isolated 4.

The structures of alkyl- and acylcobalt tetracarbonyls 5, 6, 10, 14, and 15 are based on a vast choice of analogies<sup>10,17g,18</sup> of the IR  $\nu(\text{CO})$  spectra, supported by X-ray structure determinations.<sup>10c,17g,18d,30</sup>

The ( $\eta^3$ -benzyl)cobalt complexes 7 and 16 (the latter has been reported<sup>10c</sup>) were identified as analogues of a number

of known (isolated) derivatives.<sup>10c,31,32</sup>

Key intermediates 4 and 13 were identified by (beyond satisfactory analyses for 4b) IR spectra, showing close analogy with the spectra of reported  $[\text{XYCo}(\text{CO})_3]^-$  complexes.<sup>17</sup> This argument gains additional support from an earlier solution X-ray study<sup>17d</sup> of  $[\text{NCCH}_2\text{Co}(\text{COOMe})(\text{CO})_3]^-$  and by a recent single-crystal X-ray structure determination<sup>17h</sup> of  $[\text{PPN}]^+[\text{MeC}(\text{O})\text{Co}(\text{CO})_3\text{I}]^-$  (reported while this paper was in revision).

Compound 9 could not be obtained in pure form. Its structure is based only on the analogy of its formation to that of 4 as well as the analogy of its IR spectrum to those of  $\text{RCo}(\text{CO})_2\text{L}_2$  derivatives.<sup>10b</sup>

One of the most challenging problems of this work is the question of the eventual interaction of the crown-coordi-

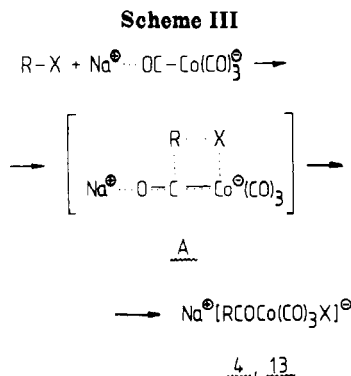
(28) A phase-transfer catalyst is able not only to carry a species from one phase to another but also to activate it as well; see e.g.: (a) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis*; Academic Press: New York, 1978. (b) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, FRG, 1980. (c) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147.

(29) The increased charge separation achieved by crown ether coordination in the present system is demonstrated by the relatively high stability of 4 and by comparison of the  $\nu(\text{CO})$  spectra of 2 and 12 (Experimental Section).

(30) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(31) ( $\eta^3$ -Allyl)cobalt analogues: (a) Fischer, R. D. *Chem. Ber.* **1960**, *93*, 165. (b) Brown, D. A. *J. Chem. Soc.* **1962**, 3849. (c) Bor, G. *Collect. Pap. Symp. Coord. Chem., Tihany (Hungary)* **1964**, *1*, 397.

(32) X-ray structure of phosphite-substituted derivative: (a) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920. (b) Blecke, J. R.; Burch, R. R.; Caulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316.



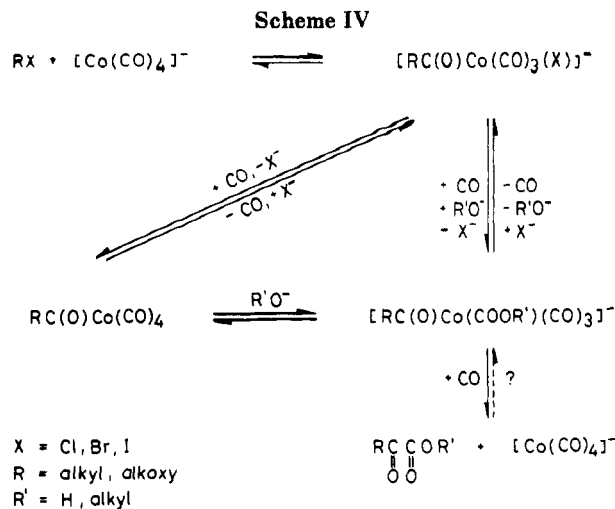
nated  $Na^+$  and the acyl oxygen.<sup>26</sup> Since the acyl  $\nu(CO)$  frequencies are shifted (toward lower wavenumbers) in the order  $5 \rightarrow 8 \rightarrow 9$ ,  $5 \rightarrow 10$ , or  $5 \rightarrow 4$ , it can be supposed that negative charge was accumulated on the cobalt carbonyl framework. This seems to be due to CO substitution by  $PR_3$ , to a negatively charged ligand, or, in the case of  $5 \rightarrow 10$ , to the increased electron-acceptor character of the organic group. This problem, however, cannot be settled until suitable crystals of one of these compounds (or of a derivative) can be grown.

**Mechanistic Considerations.** The preparative results of the present work provide a new contribution to the mechanistic picture of the reaction of benzyl (probably generally alkyl<sup>17e</sup>) halides and the tetracarbonylcobaltate ion. The most striking features of this mechanism are (i) the intermediacy of  $[XYCo(CO)_3]^-$  type (X, Y = one-electron or charged two-electron ligands) complexes and (ii) the reversibility of the activation of the carbon-halogen bond.

Both aspects merit some comment.

The presence of  $[XYCo(CO)_3]^-$  type complexes in reaction mixtures of carbonylations of organic halides was indicated by spectroscopic and other (indirect) evidence by Foá's group.<sup>7e,g-i,17a</sup> Since the formation of complexes such as 4 and 13 can be regarded (formally) as a kind of addition of the alkyl halide to the ionic reactant,  $Na[Co(CO)_4]$ , this reaction sheds new light upon the most interesting result of Foá et al.<sup>33</sup> stating that the reaction of  $RX$  with  $Na[Co(CO)_4]$  proceeds through an  $S_N2$  path with an intermediate containing both reactants. Complexes 4 and 13 could be regarded as such intermediates. The transition state leading to the formation of these complexes can be assumed as A in Scheme III.

The reversibility of the reaction of a carbon-halogen bond with a transition-metal center is well documented for other metals,<sup>34</sup> but it had no precedent in cobalt carbonyl chemistry, which involves the metal that is most important in alkyl halide carbonylation.<sup>4,6-8</sup> These two concepts together open several new possibilities of interpreting relevant reaction pathways. The most striking of these is the explanation of the cobalt-catalyzed so-called double carbonylation.<sup>4,6b,7e,g,8a,c,35</sup> As we pointed out ear-



lier,<sup>17c,e</sup> the reaction course in Scheme IV should be considered. This would mean that "double carbonylations" (at least a large part) with cobalt proceed through  $[Co(CO)_3XY]^-$  type intermediates and that the formation of the actual product involves the elimination of  $XY$  (e.g.  $X = RC(O)$ ,  $Y = C(O)OR'$ ), leaving the unsaturated  $[Co(CO)_3]^-$  anion, which could easily re-form the actual starting  $[Co(CO)_4]^-$  species.

A closely related picture has been proposed for the Pd-catalyzed double carbonylation.<sup>36</sup>

Both the anionic mechanism described here and Foá's proposal<sup>17a</sup> about the intermediacy of the alkylation products of these anions, that is,  $RCo(X)(Y)(CO)_3$  complexes, require further studies, which are in progress in our laboratories.

**Acknowledgment.** We are indebted to Prof. L. Markó (Veszprém, Hungary) and Dr. S. J. McLain (Wilmington, DE) for discussions. Research Grants OTKA 133/1987-89 (F.H. and V.G.) and OTKA 1749/1987-89 (G.P.) from the Hungarian Academy of Sciences are acknowledged. Help in obtaining the analyses was given by Drs. I. Ötvös and E. Halmos-Galampos (Veszprém, Hungary).

**Registry No.** 1a, 69543-01-7; 2, 14878-28-5; 3a, 129174-81-8; 4a, 129174-82-9; 4b, 129174-97-6; 5, 129193-62-0; 6, 129174-83-0; 7, 129174-84-1; 8, 129174-85-2; 9b, 129193-63-1; 10, 129174-87-4; 11a, 100-44-7; 11c, 620-05-3; 12, 129174-88-5; 13Aa, 129174-89-6; 18Ac, 129174-90-9; 13Ba, 129174-92-1; 13Bb, 129174-94-3; 13Bc, 129174-96-5; 14, 65876-86-0; 15, 65876-85-9; 16, 83267-99-6;  $[PP-N][Co(CO)_4]$ , 53433-12-8.

(36) (a) Chen, J.; Sen, A. *J. Am. Chem. Soc.* 1984, 106, 1506. (b) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1984, 3, 692. (c) Ozawa, F.; Sugimoto, T.; Ynasa, Y.; Santara, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1984, 3, 683. (d) Ozawa, F.; Soyama, H.; Yanagihara, H.; Ayoma, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* 1985, 107, 3235. (e) Tanaka, M.; Kobayashi, T.; Sakakura, T. *J. Chem. Soc., Chem. Commun.* 1985, 537. (f) Tanaka, M.; Kobayashi, T.; Sakakura, T.; Itatani, H.; Danno, K.; Zushi, K. *J. Mol. Catal.* 1985, 32, 115. (g) Ozawa, F.; Kawasaki, N.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* 1985, 567. (h) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1985, 4, 1130. (i) Sen, A.; Chen, J.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* 1987, 109, 148. (j) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1987, 6, 1640.

(33) Moro, A.; Foá, M.; Cassar, L. *J. Organomet. Chem.* 1980, 185, 79.

(34) See e.g.: (a) Vaska, L. *Acc. Chem. Res.* 1968, 1, 335. (b) Collman, J. P. *Acc. Chem. Res.* 1968, 1, 136.

(35) (a) Perron, R. (Rhône-Poulenc) Ger. Pat. 2,600,541, 1976. (b) Foá, M.; Moro, A.; Gardano, A.; Cassar, L. (Montedison) U.S. Pat. 4,531,952, 1982. (c) Francalanci, F.; Foá, M.; Gardano, A. (Montedison) Eur. Pat. Appl. 0,076,721, 1983. (d) Fell, B.; Chrobaczek, H. *Chem.-Ztg.* 1984, 108, 291. (e) El Chahawi, M. (Dynamit Nobel) Ger. Pat. DE 2,828,041, 1984. (f) Alper, H.; Arzoumanian, H.; Petrignani, J. F.; Sandana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* 1985, 340.