(Alkoxycarbonyl)- and [(Aryloxy)carbonyl]cobalt Carbonyls[1]

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(Alkoxycarbonyl)cobalt tetracarbonyls (**1**) were synthesized from $Co_2(CO)_8$ in THF and from $ICo(CO)_4$ by the reaction with the corresponding alkali-metal alkoxides in saturated hydrocarbons using crown ethers as solid/liquid phase-transfer catalysts. Both **1** and, for the first time, [(aryloxy)carbonyl]cobalt tetracarbonyls (**2**) were obtained in a homogeneous system containing $ICo(CO)_4$ and alkali-metal alkoxides or phenoxides, respectively, in THF. Tertiary phosphine derivatives of **1** and **2** were also prepared. The formation of complexes **1** and **2** proceeds through the ionic intermediates $[ICo(COOR)(CO)_3]^-$ which were characterized by their infrared spectra. Analogous ionic species $[Co(COOR)_2(CO)_3]^-$ are formed from the reaction of complexes **1** and RO^-. [(Allyloxy)carbonyl]cobalt tetracarbonyl shows thermal decarboxylation at 20 °C yielding $(\eta^3\text{-}C_3H_5)Co(CO)_3$ and CO_2.

Introduction

(Alkoxycarbonyl)cobalt carbonyls ($ROC(O)Co(CO)_n$, n = 3, 4 (**1**)) are believed to be intermediates in important catalytic reactions.[2,3] Moreover, recently it has been recognized[4,5] that acylcobalt carbonyls $RC(O)Co(CO)_3L$ (L = CO or $PMePh_3$) can be transformed to the corresponding $RCH_2OC(O)Co(CO)_3L$ compounds. Another challenging aspect of this chemistry is the relation of $ROC(O)Co(CO)_4$ compounds to CO_2: these complexes can be regarded (at least formally) as products of "abnormal" CO_2 insertion into a Co–C(alkyl) bond.[6,7]

Some derivatives of this compound class, $ROC(O)Co(CO)_2L^1L^2$ (R = Me, $L^1 = L^2$ = CO,[3d] L^1 = CO, L^2 = PPh_3;[3d] R = Me, $L^1 = L^2 = PPh_3$;[8b] R = Et, L^1 = CO, L^2 = PPh_3,[8a] $L^2 = P(OPh)_3$,[8b] $L^1 = L^2 = PPh_3$;[8b] R = *t*-Bu, L^1 = CO, L^2 = PPh_3[8a]) were prepared by using fairly complicated[9] approaches. In all of these syntheses the cobalt carbonyl was introduced as an ionic species.

The analogous [(aryloxy)carbonyl]cobalt carbonyls have not yet been reported.

In an attempt to extend the preparative accessibility of complexes **1**, we developed our experimental strategy with regard to the following points: more general utility could be expected by reacting RO^- (R = alkyl, aryl) anions with *neutral* cobalt carbonyls; – cobalt carbonyls relevant to homologation and similar reactions[2,3] were chosen; conditions avoiding the base reaction[12] were used.

Thus possible neutral cobalt carbonyl reaction partners include $HCo(CO)_4$, alkylcobalt tetracarbonyls, acylcobalt tetracarbonyls, halocobalt tetracarbonyls,[13] and dicobalt octacarbonyl. The first three could be ruled out for various reasons.[14] The iodide $ICo(CO)_4$ has two important advantages; i.e., (a) it is the most stable $XCo(CO)_4$ derivative (X = Cl, Br, I)[13] and (b) it is closely related to iodine-promoted catalysis by cobalt carbonyls.[19] For these rea-

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[1] Preliminary reports: (a) "Proceedings of the 18th Colloquium on Coordination Chemistry", Kecskemêt, Hungary, May 1983. (b) "Abstracts of Papers", 11th International Conference on Organometallic Chemistry, Callaway Gardens, GA, Oct 1983, p 140.

[2] For reviews see (a) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. (b) Wender, I. *Catal. Rev.* **1976**, *14*, 97. (c) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; p 42. (d) Falbe, J. "New Syntheses with Carbon Monoxide"; Springer: Berlin, 1980; p 226. (e) Bahrmann, H.; Cornils, B. *Chem.-Ztg.* **1980**, *104*, 39. (f) Bahrmann, H.; Lipps, W.; Cornils, B. *Chem.-Ztg.* **1982**, *106*, 249. (g) Röper, M.; Loevenich, H., In "Catalysis in C_1 Chemistry"; Keim, W., Ed.; D. Riedel Publishing Co.: Dordrecht, 1983; p 105.

[3] For key original papers, see: (a) Markô, L. *Proc. Chem. Soc.* **1962**, 67. (b) Goetz, R. W.; Orchin, M. *J. Org. Chem.* **1962**, *27*, 3698. (c) Albanesi, G. *Chim. Ind. (Milan)* **1973**, *55*, 319. (d) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150. (e) Wood, C. D.; Garrou, P. E. *Organometallics* **1984**, *3*, 170.

[4] (a) Deduced from the presence of HCOOEt within the products of MeOH homologation: Martin, J. T.; Baird, M. C. *Organometallics* **1983**, *2*, 1073. (b) Preparatively supported: Galamb, V.; Pâlyi, G.; Ungvâry, F.; Markô, L.; Boese, R.; Schmid, G., submitted for publication in *J. Am. Chem. Soc.*

[5] For Mn a similar reaction was preparatively proved. $PhCH_2C(O)Mn(CO)_5 + CO + H_2 \rightarrow PhCH_2CH_2OC(O)Mn(CO)_5$: Freudenberger, J. H.; Orchin, M. *Organometallics* **1982**, *1*, 1408.

[6] For reviews see: (a) Volpin, M. E.; Kolominkov, I. S. *Organomet. React.* **1975**, *5*, 313. (b) Sneeden, R. P. A. *J. Mol. Catal.* **1982**, *17*, 349. (c) Walther, D.; Dinjus, E.; Sieler, J. *Z. Chem.* **1983**, *23*, 237. (d) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[7] Indications for relevant chemistry of (phosphine)cobalt hydride or alkyl complexes: (a) Misono, A.; Uchida, Y.; Hidai, M.; Kuse, T. *J. Chem. Soc., Chem. Communs.* **1968**, 981. (b) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 371. (d) Kolominkov, I. S.; Stepovska, G.; Tyrlik, S.; Volpin, M. E. *Zh. Obshch. Khim.* **1972**, *42*, 1652. (e) Kolominkov, I. S.; Stepovska, G.; Tyrlik, S.; Volpin, M. E. *Zh. Obshch. Khim.* **1973**, *44*, 1743. (f) Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 75.

[8] (a) Heck, R. F. *J. Organomet. Chem.* **1964**, *2*, 195. (b) Hieber, W. Duchatsch, H. *Chem. Ber.* **1965**, *98*, 1744.

[9] The following approaches were used. (i) ROCl + $Na[Co(CO)_4]$:[8a] problem, difficult preparation[10] of alkyl hypochlorites which moreover can hardly be extended to phenols.[11] (ii) ROOCCl + $Na[Co(CO)_2L^1L^2]$:[8b] problem, cannot be used for $L^1 = L^2$ = CO because of low nucleophilicity of the carbonylcobaltate and preparation of the substituted carbonylcobaltate anions fairly laborious. (iii) $[Co(CO)_3(PPh_3)_2]^+ + RO^-$:[8b] problem, again cannot be used for $L^1 = L^2$ = CO. (iv) ROC(O)C(O)Cl + $Na(Tl)[Co(CO)_4]$;[3d] the reaction proceeds smoothly with good yields but the organic starting material can be prepared only with difficulty.

[10] "Houben-Weyl Methoden der Organischen Chemie"; Müller, E., Ed.; George Thieme: Stuttgart, 1962; Vol. 5/3 pp 764–765; 1963; Vol. 6/2, pp 490–502.

[11] (a) Denville, L.; Fort, R. *C. R. Hebd. Seances Acad. Sci.* **1952**, *235*, 1514, 1658; **1954**, *238*, 124. (b) Aubar, M.; Ginsburg, D. *Chem. Rev.* **1954**, *54*, 925.

[12] (a) Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952**, *74*, 1216. (b) Hieber, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953**, *86*, 700. (c) Attali, S.; Poilblanc, R. *Inorg. Chim. Acta* **1972**, *6*, 475.

[13] Pankowski, M.; Bigorgne, M. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264*, 1382.

[14] $HCo(CO)_4$, being a strong Brønsted acid,[15] can be expected to generate undissociated alcohols from the metal alkoxides introduced. Alkylcobalt tetracarbonyls are known[16] to react with alkoxides according to the reaction $RCo(CO)_4 + R'O^- \rightarrow [RCo(CO)_3(COOR')]^-$ which decomposes to organic products or the starting compounds but does not lead to **1**. Acylcobalt tetracarbonyls, $RC(O)Co(CO)_4$, contain a strongly electrophilic acyl carbon,[17] and thus they can be expected to yield esters with alkoxides.[18]

[15] Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717.

[16] $RCo(CO)_4 + R'O^- \rightarrow [RCo(COOR')(CO)_3]^-$ (R = $EtOOCCH_2$, NC; R' = Me): Francalanci, F.; Gardano, A.; Abis, L.; Foâ, M. *J. Organomet. Chem.* **1983**, *251*, C5.

[17] Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 2779.

[18] (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1220. (b) El-Chalawi, M.; Prange, U. *Chem.-Ztg.* **1978**, *102*, 1.

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sons $ICo(CO)_4$ and $Co_2(CO)_8$ were chosen as our cobalt carbonyl starting materials.

Thus we describe here our experiments regarding the reaction of alkoxide and aryl oxide ions with $Co_2(CO)_8$ and $ICo(CO)_4$.

Experimental Section

All reactions were carried out under deoxygenated CO or Ar using carefully dried (Na) solvents. The IR spectra were run on Specord 75 (Carl Zeiss, Jena, GDR) and the ^1H NMR spectra on 80 MHz BS-487 (Tesla, Brno, CSSR) instrument. The starting compounds were of commercial origin with the exception of $Co_2(CO)_8$ and $(\eta^6\text{-}C_6H_5CH_2OH)Cr(CO)_3$, which were prepared according to Markó et al.[20] and Galamb et al.,[4b] respectively.

Preparation of (Alkoxycarbonyl)cobalt Tetracarbonyls, $ROC(O)Co(CO)_4$ (1), from $Co_2(CO)_8$. $Co_2(CO)_8$ (85.5 mg, 0.25 mmol) was dissolved in 5 mL of THF, and the stirred solution was treated with 1 mmol of sodium or potassium alkoxide and 0.1 mmol of crown ether (15-crown-5 and 18-crown-6, respectively) at −78 °C. After 30 min 5 mL of *n*-heptane was added. The reaction mixture was then allowed to warm to 20–25 °C. The THF was removed under reduced pressure and the solution filtered. In this way the ionic products were removed and good quality IR ν(CO) spectra could be obtained from the resulting heptane solutions. The products could not be isolated in pure form, since after evaporation of the solvent reddish brown oils remained resisting attempts at crystallization. Yields of the crude products were ~40–50%. The products and PPh_3 derivatives were identified by IR spectra (Table I). This reaction could be performed to prepare the derivatives **Ia** (R = Me) and **1g** (R = c-Hex).

Preparation of $ICo(CO)_4$.[21] Dicobalt octacarbonyl, $Co_2(CO)_8$ (342 mg, 1 mmol), was dissolved in 5 mL of the solvent. This solution was treated with 508 mg (2 mmol) of I_2 in 40 mL of an apolar or 15 mL of a polar solvent. [Excess I_2 is necessary (compare ref 13, which uses a 1:1 ratio) to cover the iodine requirement of the byproduct CoI_2 (black form[24]).] The reaction should be carried out in the dark.[25] The reaction temperature depends on the solvent used: *n*-hexane (20–25 °C), benzene (20–25 °C), toluene (20–25 °C), THF (−78 °C). The product was identified by the ν(CO) spectrum: *n*-hexane, 2116.2 (s), 2047.9 (vs) cm^{-1};[27] THF, 2111.3 (s), 2037.5 (vs) cm^{-1} (obtained in a flow-through cell thermostated to −20 °C). $ICo(CO)_3PPh_3$ was formed upon addition of PPh_3. The latter was identified by comparison (analysis and IR) with an authentic sample.[29] The $ICo(CO)_4$ could not be isolated in pure form since it decomposes to CoI_2 and $Co_2(CO)_8$ during evaporation of the solvent and could not be crystallized.

Preparation of (Alkoxycarbonyl)cobalt Tetracarbonyls, $ROC(O)Co(CO)_4$ (1), in Saturated Hydrocarbons. A solution of 0.1 mmol of $ICo(CO)_4$ in 20 mL of *n*-hexane was cooled to −78 °C. Then 0.25 mmol of the alkoxide (Na or K salt) and 0.025 mmol of the crown ether (15-crown-5 or 18-crown-6, respectively) as phase-transfer catalyst were added. The reaction mixture was stirred for 2 h at −78 °C and 1 h at 20–25 °C. The light brown solution was filtered and concentrated. The products were obtained as reddish brown oils after evaporation of the solvent. However, since they resisted attempts at crystallization (cf. also ref 3d), they could not be obtained in pure form. Yields of the crude products were ~25–35%.

The R = Me (**a**), Et (**b**), *i*-Pr (**c**), *t*-Bu (**d**), *n*-Pent (**e**), *n*-Dec (**f**), c-Hex (**g**), Bz (**h**), and 2-Me-2-PhEt (**j**) derivatives were obtained by this method. The products and PPh_3 derivatives (vide infra) were identified by IR ν(CO) spectra (Table I).

Preparation of Compounds 1 and [(Aryloxy)carbonyl]cobalt Tetracarbonyls (2) in THF. A solution of 0.1 mmol of $ICo(CO)_4$ was prepared in 10 mL of THF at −78 °C. While cold this solution was treated with 0.3 mmol of lithium, sodium, or potassium alkoxide or phenoxide and 0.03 mmol of the crown ether (12-crown-4, 15-crown-5, or 18-crown-6, respectively) during 3 h. The resulting reaction mixture was stirred for an additional 2 h. The color changed from brown to greenish brown. The solution was then allowed to warm to 20–25 °C in the case of the alkyl or to −10 °C in the case of the aryl derivatives. After addition of 5 mL of *n*-heptane, the solution was filtered to remove the ionic products. Removal of THF from the filtrate resulted in *n*-heptane solutions which gave good-quality IR spectra. Compounds 1 and 2 were obtained as reddish brown oils upon evaporation of the solvent. These oils could not be crystallized with the exception of **1i**.

This reaction was performed for $ROC(O)Co(CO)_4$: R = Me (**1a**), Et (**1b**), *i*-Pr (**1c**), *t*-Bu (**1d**), *n*-Pent (**1e**), *n*-Dec (**1f**), *c*-Hex (**1g**), Bz (**1h**), $Cr(CO)_3$ (η^6-Bz) (**1i**), 2-Me-2-PhEt (**1j**), allyl (**1k**); R = Ph (**2a**), 2-MePh (**2b**), 4-*t*-BuPh (**2c**), 4 MeOPh (**2d**), 4-BrPh (**2e**), 4-MeC(O)Ph (**2f**), α-naphth (**2g**), β-naphth (**2h**).

The yields of the crude products were in the range of 50–70% for the isolated **1i** (55%). For **1i** satisfactory elemental analyses were obtained. IR data are shown in Table I and ^1H NMR data in Table II.

Preparation of $ROC(O)Co(CO)_3PPh_3$ (3 and 4) Compounds. (a) From Complexes 1 or 2. A solution of $ROC(O)Co(CO)_4$ in *n*-heptane was treated with excess PPh_3 at 20–25 °C in the case of R = alkyl or at −10 °C in the case of R = aryl. The reaction mixture was stirred for 1 h and then allowed to warm to 20–25 °C, concentrated, filtered, and crystallized at −78 °C from Et_2O/pentane (1:1). An attempt at purification by column chromatography (15 × 500 mm, eluent *n*-hexane) was also successful for **3h** and **4h**.

The yields were almost quantitative (80–90%). The reaction was performed for the following derivatives: R = Me (**3a**), Et (**3b**), *i*-Pr (**3c**), *t*-Bu (**3d**), *n*-Pent (**3e**), *n*-Dec (**3f**), c-Hex (**3g**), Bz (**3h**), 2-Me2-PhEt (**3j**); R = Ph (**4a**), 4-*t*-BuPh (**4c**), 4-MeOPh (**4d**), 4-BrPh (**4e**), β-Naphth (**4h**).

The derivatives **3b,c,h,j** and **4c,d,h** were isolated in analytically pure form. The remaining derivatives were identified by IR (Table I) and ^1H NMR (Table II) spectra.

(b) From $ICo(CO)_3PPh_3$ and Alkoxides. The iodide $ICo(CO)_3PPh_3$ (53 mg, 0.1 mmol) was dissolved in 4 mL of THF under Ar. The metal alkoxide, 0.2 mmol of ROM (R = Me, Et, Bz, M = Na, K), and 0.02 mmol of the corresponding crown ether (15-crown-5 or 18-crown-6) were added. The reaction mixture was stirred at 20–25 °C for 1 h. The IR spectrum showed the disappearance of $ICo(CO)_3PPh_3$ and the presence of (3) and $M[Co(CO)_3PPh_3]$.

Then 4–6 mL of *n*-heptane was added, THF was evaporated at reduced pressure, the ionic products were filtered off, and the solvent (*n*-heptane) was evaporated from the filtrate under vacuum. The residue was recrystallized from Et_2O/*n*-pentane

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(19) A strange element in mechanistic speculations[2d–g] regarding reactions using iodine-promoted $Co_2(CO)_8$ should be noted. Several iodine-containing cobalt carbonyls (e.g., $HCoI(CO)_2$, $CH_3(H)CoI(OH)(CO)_2$, $(CH_3CO)(H)_2CoI(CO)_2$, etc., from ref 2g, p 123) were suggested as intermediates in these reactions, but not even counterarguments against the possible intermediacy of the only one iodine/cobalt/carbonyl ternary compound ($ICo(CO)_4$) were discussed—to the best of our knowledge. This paper is (in part) intended to investigate this aspect.

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

(21) Two papers report the preparation[13,22] of $ICo(CO)_4$ without giving much experimental details. Thus it seems worthwhile to describe the procedure used by us to obtain this compound which could provide a useful entry to cobalt carbonyl chemistry.[23]

(22) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1437.

(23) We are currently investigating refinement of preparative methods for $ICo(CO)_4$ and syntheses starting from this compound.

(24) Identified by elemental analysis, cf. also: "Gmelins Handbuch der Anorganischen Chemie", Verlag Chemie: Weinheim, Germany, 1961; Vol. 58/A, p 595.

(25) Irradiated (λ 220–400 nm) *reaction mixture* (*n*-hexane, 21.0 °C) yielded 100% yield of CoI_2 and 8 mol of CO/mol of $Co_2(CO)_8$ (which was measured volumetrically). However *ready solutions* of $ICo(CO)_4$ did not show strong photosensitivity. These could be handled in daylight or artificial light for shorter periods.

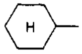
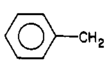
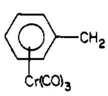
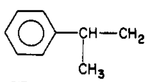
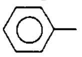
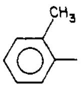
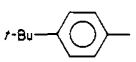
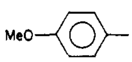
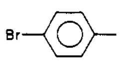
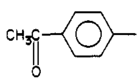
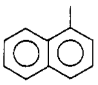
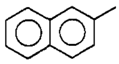
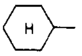
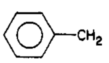
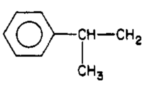
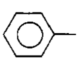
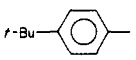
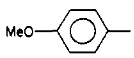
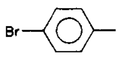
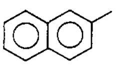
(26) In the course of this work a paper reporting the analogous procedure in THF appeared, cf. ref 22, however, without reporting details of the identification of $ICo(CO)_4$.

(27) The number of bands observed by us is less than those described by ref 13. We believe the sample investigated by these authors contained some $Co_2(CO)_8$. The difference between the observed (A_1 + E) spectrum of $ICo(CO)_4$ and that which could be expected for a C_{3v} $XCo(CO)_4$ species ($2A_1$ + E)[13,28a] may be due to a vibrational coupling between the electrons of the carbonyl groups and those of the iodine atom.[28b]

(28) (a) Bor, G. *Inorg. Chim. Acta* **1967**, *1*, 82. (b) Bor, G., personal communication, 1983.

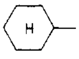
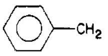
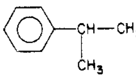
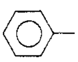
(29) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2530.

Table I. Infrared ν(CO) Spectra of [(Alkyloxy)carbonyl]- (1) and [(Aryloxy)carbonyl]cobalt Tetracarbonyls (2), $ROC(O)Co(CO)_4$, and the Corresponding Triphenylphosphine-Substituted Derivatives 3 and 4, $ROC(O)Co(CO)_3PPh_3$

		absorptn maxima,[a] cm^{-1}					
R		A_1	A_1	E		$\nu(CO)_{acyl}$	others
CH_3	(1a)	2118.5 (m)[b]	2054.7 (s)[b]	2043.3 (vs)[b]	2032.8 (vs)[b]	1690.8 (m)[b]	
CH_3CH_2	(1b)	2118.4	2054.6	2043.6	2030.6	1691.0	
$(CH_3)_2CH$	(1c)	2116.6	2052.9	2041.6	2028.6	1688.8	
$(CH_3)_3C$	(1d)	2114.4	2050.4	2038.9	2024.9	1690.2	
$CH_3(CH_2)_3CH_2$	(1e)	2118.1	2053.6	2042.1	2029.6	1691.3	
$CH_3(CH_2)_8CH_2$	(1f)	2117.5	2054.1	2042.7	2030.0	1691.3	
	(1g)	2115.6	2052.2	2041.1	2027.7	1689.1	
	(1h)	2117.4	2053.9	2042.8	2029.9	1691.6	
	(1i)	2119.3	2054.4	2042.9	2032.9	1687.3	1974.3 (s, br), 1903.3 (s) ($Cr(CO)_3$ part)
	(1j)	2117.4	2053.9	2042.8	2029.9	1694.3	
$CH_2{=}CHCH_2$	(1k)	2119.1	2054.9	2042.3	2031.2	1689.1	
	(2a)	2121.2 (m)[b]	2059.9 (s)[b]	2047.1 (vs)[b]	2034.2 (vs)[b]	1696.3 (m)[b]	
	(2b)	2119.6	2056.5	2033.4	2024.6	1679.3	
	(2c)	2117.2	2054.1	2041.6	2028.3	1702.5	
	(2d)	2121.3	2058.5	2045.2	2031.9	1688.5	
	(2e)	2119.6	2054.9	2043.1	2033.2	1687.3	
	(2f)	2119.7	2054.3	2041.6	2031.9	1686.7	1714.2 (ketonic)
	(2g)	2121.2	2058.6	2045.9	2032.4	1687.4	
	(2h)	2119.3	2053.6	2041.7	2030.6	1678.3	
CH_3	(3a)	2060.7 (w)[b]		1996.4 (vs)[b]	1984.5 (vs)[b]	1669.1 (m)[b]	
CH_3CH_2	(3b)	2060.5		1994.8	1983.4	1669.6	
$(CH_3)_2CH$	(3c)	2060.2		1994.4	1981.5	1666.3	
$(CH_3)_3C$	(3d)	2059.2		1992.6	1979.4	1667.9	
$CH_3(CH_2)_3CH_2$	(3e)	2059.9		1994.5	1982.4	1666.8	
$CH_3(CH_2)_8CH_2$	(3f)	2060.4		1994.7	1981.9	1667.3	
	(3g)	2059.7		1993.8	1982.2	1665.5	
	(3h)	2061.4		1996.4	1984.4	1671.3	
	(3j)	2059.9		1995.6	1982.7	1664.1	
	(4a)	2064.0 (w)[b]		1999.8 (vs)[b]	1987.1 (vs)[b]	1684.3 (m)[b]	
	(4c)	2062.9		1997.4	1985.5	1683.6	
	(4d)	2062.9		1996.8	1984.5	1688.1	
	(4e)	2061.1		1992.8	1983.2	1665.1	
	(4h)	2061.4		1993.2	1983.3	1665.6	

[a] Assignments according to idealized C_{3v} symmetry.[28a] [b] Intensity patterns of the spectra were similar. Therefore we indicated the intensities only at the first representative of a type.

Table II. ^1H NMR Data of Complexes 3 and 4, $ROC(O)Co(CO)_3PPh_3$

R		δ (Me_4Si, $CDCl_3$)
CH_3	(**3a**)	3.45 (s, 1 H, CH_3), 7.26 (br s, 15 H, $P(C_6H_5)_3$)
CH_3CH_2	(**3b**)	1.18 (t, J = 6 Hz, 3 H, CH_3), 4.08 (q, J = 8 Hz, 2 H, CH_2), 7.24 (br s, 15 H, $P(C_6H_5)_3$)
$(CH_3)_2CH$	(**3c**)	1.15 (d, J = 6 Hz, 6 H, CH_3), 2.13 (m, 1 H, CH), 7.25 (br s, 15 H, $P(C_6H_5)_3$)
$CH_3(CH_2)_3CH_2$	(**3e**)	0.85 (t, J = 6 Hz, 3 H, CH_3), 1.24 (m, 6 H, 2,3,4-CH_2), 3.60 (t, J = 8 Hz, 2 H, 1-CH_2), 7.28 (br s, 15 H, $P(C_6H_5)_3$)
$CH_3(CH_2)_8CH_2$	(**3f**)	0.83 (t, J = 6 Hz, 3 H, CH_3), 1.20 (m, 16 H, 2–9-CH_2), 3.51 (t, J = 6 Hz, 2 H, 1-CH_2), 7.18 (br s, 15 H, $P(C_6H_5)_3$)
	(**3g**)	1.3–1.8 (m, 10 H, 2–6-CH_2), 3.59 (m, 1 H, 1-CH), 7.26 (br s, 15 H, $P(C_6H_5)_3$)
	(**3h**)	4.57 (s, 2 H, CH_2), 7.2 (br s, 5 H, C_6H_5), 7.3 (br s, 15 H, $P(C_6H_5)_3$)
	(**3j**)	1.17 (d, J = 6 Hz, 3 H, CH_3), 2.85 (m, 1 H, CH), 3.29 (d, J = 6 Hz, CH_2), 7.3 (br s, 20 H, C_6H_5)
	(**4a**)	6.73 (m, 5 H, OC_6H_5), 7.2 (br s, 15 H, $P(C_6H_5)_3$)[a]

[a] Solvent CCl_4.

Table III. Analytical Data for $ROC(O)Co(CO)_3PPh_3$[a]

				Co		P	
R	no.	mp, °C	formula	found	calcd	found	calcd
Et	**3b**	57	$C_{24}H_{20}O_5CoP$	12.17	12.32	6.7	6.47
i-Pr	**3c**	57–58	$C_{25}H_{22}O_5CoP$	11.92	11.97	6.3	6.29
$PhCH_2$	**3h**	56	$C_{29}H_{22}O_5CoP$	10.79	10.91	5.8	5.73
$PhCH(CH_3)CH_2$	**3j**	62 dec	$C_{31}H_{26}O_5CoP$	10.30	10.37	5.5	5.45
p-*t*-BuC_6H_4	**4c**	52	$C_{32}H_{28}O_5CoP$	10.41	10.12	5.3	5.32
p-$MeOC_6H_4$	**4d**	54	$C_{29}H_{22}O_6CoP$	10.31	10.59	5.7	5.57
β-naphth	**4h**	72	$C_{32}H_{22}O_5CoP$	9.99	10.22	5.3	5.37

[a] η^1-$[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2)]OC(O)Co(CO)_4$ (**1i**): decomposition starts at ~60 °C. Anal. Calcd for $C_{15}H_7O_9CoCr$: Co, 13.33; Cr, 11.76. Found: Co, 13.30; Cr, 11.71.

(1:1) at −78 °C. The isolated yields of the pure products were 30–40%.

Attempts at Identification and Isolation of the Ionic Derivatives $[XCo(COOR)(CO)_3]^-$ [X = I (5) and COOR (6)]. Observation of Complexes 5. The reaction of $ICo(CO)_4$ and RONa(crown) in THF was initiated at −78 ° as described above. Samples were taken periodically. After a few minutes the $ICo(CO)_4$ bands already diminished and a new band system consisting of two terminal (low-lying) and an acyl-type absorption appeared near the bands of compounds **1** or **2**. The low-lying band system was assigned (cf. Discussion) to $[ICo(COOR)(CO)_3]^-$ (**5**). After about 30 min the bands of **5** were dominant in the ν(CO) region.

Then the solution was left to warm to 20–25 °C. The bands of complexes **1** or **2** gradually started to develop concurrently with diminution of the bands of **5**.

In the following cases the complexes **5** could be obtained in high enough concentrations for good-quality IR spectra [ν(CO) (THF, cm^{-1})]: R = CH_3, 1963.9 (s, sh), 1951.7 (vs), 1643.0 (m); R = Bz, 1962.7 (s, sh), 1951.4 (vs), 1641.2 (m); R = Ph, 1960.4 (s, sh), 1950.7 (vs), 1642.4 (m); R = 2-MeC_6H_4, 1962.2 (s, sh), 1951.7 (vs), 1641.6 (m); R = 4-BrC_6H_4, 1966.3 (s, sh), 1951.1 (vs), 1641.6 (m). For comparison IR ν(CO) (THF, cm^{-1}) of $[N{\equiv}CCH_2Co(COOMe)(CO)_3]^-$: 1948 (vs) and 1635 (s) from ref 16.

Complexes 5 from 1 and Alkali Iodides. Complex **1** (0.5 mmol) was dissolved in 2 mL of *n*-heptane plus 5 mL of THF under Ar. After the solution was thermostated to −10 °C, 12 mg (0.5 mmol) of 15-crown-5 in one portion and then small portions of 75 mg (0.5 mmol) of NaI over 1 h were added. After addition of all the NaI, the IR spectrum of **5** gradually developed accompanied by decrease in the intensity of the bands of **1**. An equilibrium state was achieved containing ca. 60% **5** and 40% **1**. **5** could not be isolated in pure form. Addition of large (5–10-fold) excess of Na(cr)I, addition of equimolar NaI at once, or working at 20–25 °C caused decomposition where $Na[Co(CO)_4]$ was the only organometallic product which could be identified.

Observation of Complexes 6. 1a or **1h** (0.1 mmol) was dissolved in 2 mL of *n*-heptane under an Ar atmosphere at 20–25 °C. This solution was treated successively with 5 mL of THF, 0.5 mmol of the (corresponding) RONa, and 0.5 mmol of 15-crown-5. The solution was then stirred for 20 min, and IR spectra were taken. The bands of complex **1** completely disappeared, and a new band system developed which was assigned (cf. Discussion) to $[Co(COOR)_2(CO)_3]^-$. This was the only observable Co carbonyl.

The following IR ν(CO) (THF, cm^{-1}) spectra were observed: R = CH_3, 2038.0 (s), 1957.4 (vs), 1943.1 (sh), 1629.1 (m), 1591.4 (m); R = Bz, 2039.0 (vs), 1959.5 (vs), 1944.2 (sh), 1654.0 (m), 1592.4 (m).

Attempts at Isolation of Complexes 5 and 6. 5. The reaction of $ICo(CO)_4$ with RONa(cr) was performed as described above. While the reaction mixture was still cold, a fivefold volume of cold (−70 to −78 °C) *n*-heptane was added. The precipitate was filtered off. A KBr pellet of this precipitate showed only $[Co(CO)_4]^-$ in its IR spectrum. A part of the precipitate was dissolved again in THF. The IR spectra of this solution showed $[Co(CO)_4]^-$ and $ROC(O)Co(CO)_4$ (**1**) ν(CO) bands.

5 and 6. A THF solution of **5** or **6** was prepared as described above. To this solution (at −78 °C in the former and at 20–25 °C in the latter case) was added approximately an equimolar amount of a CH_2Cl_2 solution of bis(triphenylphosphine)nitrogen chloride [$(PPN)^+Cl^-$]. The precipitate was filtered off. KBr pellet of the precipitate showed only the $[Co(CO)_4]^-$ spectrum. The remaining solution was concentrated (a part of the solvent drawn off), and the IR spectra were taken; only bands of complexes **1** or **2** could be observed for **5** and complex **6** decomposed.

Decarboxylation of [(Allyloxy)carbonyl]cobalt Tetracarbonyl (1k). The reaction of sodium allyl oxide with $ICo(CO)_4$ in THF was used to prepare **1k** as described above. As soon as the IR analysis showed that the reaction was complete at −78 °C, the reaction mixture was warmed to −5 to −10 °C and an equal volume of cold *n*-heptane was added. Subsequently the THF was removed at reduced pressure while cautiously the low temperature was maintained. Then the solution was filtered and poured (under Ar) into a Schlenk tube which was connected with a gas washing flask that containing saturated $Ba(OH)_2$ in distilled boiled (to remove traces of CO_2) water, saturated with Ar. Then this system was connected to a pump through the head space of the aqueous solution, and the heptane solution was left to warm to 20–25 °C. Thus the gas evolved upon warming passed through a sintered glass filter into the $Ba(OH)_2$ solution. Already at the very beginning of this operation a white precipitate was formed which continued until the gas passed through. Analysis indicated the precipitate to be $BaCO_3$. Then the heptane solution was adjusted to atmospheric pressure, and a sample was analyzed again by IR spectroscopy: the only cobalt carbonyl which could be detected was $(\eta^3\text{-}C_3H_5)Co(CO)_3$. This was identified on the basis of its literature spectrum[30b] and compared with the spectrum of an authentic sample.[30a] **1k** could be identified only in solution through its ν(CO) spectrum, since the phosphine substitution could not be observed below 0 °C and, on the other hand, **1k** is rapidly transformed to $(\eta^3\text{-}C_3H_5)Co(CO)_3$ above this temperature.

Results and Discussion

Preparative Results. Octacarbonyldicobalt did not react with sodium (or potassium) alkoxide in saturated hydrocarbons even in the presence of crown ether as a solid/liquid phase-transfer catalyst in the temperature range of −78 to +25 °C. Using, however, Et_2O or THF as solvent and starting the reaction at dry ice temperature (−78 °C) (alkoxycarbonyl)cobalt tetracarbonyls (**1**) could be prepared according to reaction 1. A similar reaction of phenoxides was not observed.

$$RO[Na(cr)] + Co_2(CO)_8 \xrightarrow{CO} \underset{\mathbf{1}}{ROC(O)Co(CO)_4} + [Na(cr)][Co(CO)_4] \quad (1)$$

$$R = Me,\ c\text{-}Hex$$

This observation demonstrates that complexes **1** may form even in catalytic carbonylations of alcohols without promoters. Furthermore reaction 1 has some implications regarding the mechanism of the reaction of $Co_2(CO)_8$ with hard Lewis bases. It has been suspected[12a] for a long time that the disproportionation of the starting Co^0 complex proceeds in two steps (reactions 2–4). However, the intermediate Co^+ species (most probably[31] $[Co(CO)_4L]^+$, where L = CO or the hard Lewis base) was suggested only by indirect, nonpreparative methods.[32] Our observation can be interpreted as a preparative piece of evidence in favor of this hypothesis.

$$6Co^0 \rightarrow 3Co^+ + 3Co^- \quad (2)$$

$$3Co^+ \rightarrow 2Co^{2+} + 1Co^- \quad (3)$$

$$6Co^0 \rightarrow 2Co^{2+} + 4Co^- \quad (4)$$

The cobalt(I) carbonyl iodide, $ICo(CO)_4$, reacted with alkali-metal alkoxides (Li, Na, K) in saturated hydrocarbons and with both alkoxides and phenoxides in the presence of 10 mol % suitable crown ether in THF (eq 5).

$$ROM(cr) + ICo(CO)_4 \xrightarrow{CO} ROC(O)Co(CO)_4 + M(cr)I \quad (5)$$

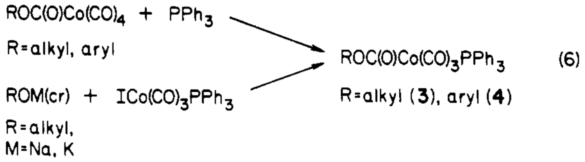
$$M = Li,\ Na,\ K$$

R =
Me (**1a**), Et (**1b**), *i*-Pr (**1c**), *t*-Bu (**1d**), *n*-Pent (**1e**), *n*-Dec (**1f**), c-Hex (**1g**), Bz (**1h**), $Cr(CO)_3$ (η^6-Bz) (**1i**), 2-Me-2PhEt (**1j**), allyl (**1k**); Ph (**2a**), 2-MePh (**2b**), 4-*t*-BuPh (**2c**), 4-MeOPh (**2d**), 4-Br (**2e**), 4-AcPh (**2f**), α-naphth (**2g**), β-naphth (**2h**)

The formation of 10–40% tetracarbonylcobaltate was always observed. The poorly reproducible reaction in apolar media proceeds with low to moderate yields, while in THF good, reproducible yields were observed.

Compounds **1** and **2** are oily substances which resist crystallization. Even large rigid organic residues as in **2c,f,g,h** did not give crystallizable derivatives. However, a useful trick for obtaining crystalline alkylcobalt carbonyls[4b] was also used in this chemistry: thus introducing the benzylalcoholate into reaction 5 in an η^6-complexed form to a $Cr(CO)_3$ group yielded a crystalline (**1**) derivative (**1i**) which could be isolated in analytically pure form. However, the crystals of **1i** were not of suitable quality for X-ray structure determination.

Both compounds **1** and **2** readily reacted with triphenylphosphine to yield the mono PPh_3 derivatives $ROC(O)Co(CO)_3PPh_3$ [R = alkyl (**3**) and aryl (**4**)]. Compounds **3** could be synthesized independently also from $ICo(CO)_3PPh_3$ and alkali-metal alkoxides (eq 6). Compounds **3** and **4** are solid substances, and thus they could be purified by recrystallization or even by column chromatography on silica gel.



(6)

Spectra and Structures. The structures of compounds **1** and **2** are mostly based on their IR spectra. The IR spectra show an $LM(CO)_4$ pattern resembling that of analogous compounds where the asymmetry of L reduces the original C_{3v} symmetry but the original shape of the ($2A_1$ + E) pattern is still recognizable: $CH_3C(O)Co(CO)_4$,[3] $ROOCCH_2Co(CO)_4$,[34] $PhCH_2Co(CO)_4$,[4b,35] or $[Cr(CO)_3(\eta^6\text{-}PhCH_2)]Co(CO)_4$.[4b,35] The X-ray structure of the last compound shows a trigonal-bipyramidal array having an axial alkyl group. A similar geometry can be assumed for all compounds **1** and **2** in the absence of a derivative forming crystals of suitable quality for X-ray analysis.

The structures of compounds **3** and **4** have an even more solid basis. The structure of a representative of these compounds (**3a**) has been determined by X-ray diffraction,[3d] and some further analogous structures are also known: $2,6\text{-}Cl_2C_6H_3CH_2C(O)Co(CO)_3PPh_3$,[4b] $C_2HF_4Co(CO)_3PPh_3$,[36] and $PhCH_2OOCCH_2Co(CO)_3PPh_3$.[34] All these have trigonal-bipyramidal geometry with the organic and the phosphorus ligands in axial (trans) positions. Here again the similarity of the spectra to those of compounds of known structure supports the proposed structures.

Mechanistic Studies. An inspection of the spectra during the formation of compounds **1** and **2** in reaction 5 showed that the disappearance of the spectrum of $ICo(CO)_4$ was accompanied by the appearance of two new band systems neither of which belonged to the final products **1** or **2**. One of these belongs to $[Co(CO)_4]^-$ and the other to an unknown ionic substance which we believe to be formed from the addition of the alkoxide or phenoxide ion to the neutral compound $ICo(CO)_4$: $[ICo(COOR)(CO)_3]^-$, R = alkyl or aryl (**5**). These substances, which could not be isolated, can be regarded as precursors of complexes **1** or **2** since the disappearance of **5** from the reaction mixture

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(30) (a) Preparation: Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 750. (b) IR: Bor, G. *Proc. Symp. Coord. Chem., 1964* **1965**, 361.

(31) For soft Lewis bases the formation of Co^+ complexes is well documented: (a) Reppe, W.; Schweckendiek, W. J. *Justus Leibigs Ann. Chem.* **1948**, *560*, 104. (b) Sacco, A. *Ann. Chim.* (*Rome*) **1953**, *43*, 495. (c) Sacco, A.; Freni, M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 566. (d) Hieber, W.; Freyer, W. *Chem. Ber.* **1958**, *91*, 1230.

(32) Tucci, E. R.; Gwynn, B. H. *J. Am. Chem. Soc.* **1964**, *86*, 4838.

(33) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184.

(34) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(35) Galamb, V.; Pályi, G. *J. Chem. Soc., Chem. Commun.* **1982**, 487.

(36) Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1967**, 2092.

(37) $CH_3Mn(CO)_5$ (or $CH_3COMn(CO)_5$) + LiI → $Li[IMn(CH_3CO)(CO)_3]$: Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1965**, *4*, 250.

parallels the formation of **1** or **2**, respectively, as monitored by IR spectroscopy.

Compounds **5** could be obtained independently from the corresponding complexes **1** and alkali iodides in the presence of stoichiometric amounts of crown ethers.

The structures of complexes **5** are based on the two independent routes of their formation and on the IR ν(CO) spectra (indicating asymmetrically substituted cobalt tricarbonyl containing an alkoxycarbonyl group) as well as the analogies in the formation and spectra of some Co[16,38,39] and Mn[37,40] complexes.

We observed also the formation of an anionic product formulated as $[Co(COOR)_2(CO)_3]^-$ (**6**, R = Me, $PhCH_2$) from the reactions of compounds **1** with the corresponding alkoxides. These products are also too unstable for isolation. However, their structures can be inferred from their IR spectra. The observation regarding complexes **5** and **6** complement each other well.

The ionic intermediates **5** suggest how iodine may be involved in the carbonylation mechanisms discussed extensively in ref 3d–g, that is, through the formation of *anionic* complexes from the neutral molecules involved in the catalytic cycles. Thus we believe the iodine-containing intermediates listed in our note[19] should instead be formulated as anionic species.

The existence of anionic complexes like our complexes **5** and **6** and those described in ref 16, 37, and 39 seems to indicate generally the possibility of the formation of anionic Co(I) complexes of the general formula $[XYCo(CO)_3]^-$ where X and Y may be equal or not and may represent halogen, acyl, alkyl, or COOR groups. Most probably they are formed in equilibrium reactions (as proved for eq 5 or for $[IMn(C(O)Me)(CO)_4]^-$ [37]) and may be in ligand (especially X and Y) exchange equilibria between each other. This possibility offers unexpected side or even main reaction routes. The so-called double carbonylation[41] may belong to the latter category, and it can be suggested that it might proceed through $[Co(C(O)R)(COOR')(CO)_3]^-$ intermediates by subsequent coupling of the C(O)R and COOR′ fragments yielding pyruvate esters. This would be in excellent accord with the mechanism established recently for Pd-promoted "double CO insertion"[42] or oxalate formation.[43]

Decarboxylation. Complexes **1**–**4** may be formally regarded as derivatives of CO_2 insertion into a cobalt–alkyl bond. Treatment of some reactive Co hydrides or alkyls (tertiary phosphine complexes) with CO_2 showed results which were compatible with this, and, even more, the orientation of the inserted CO_2 was found to be the same, R–O–C(O)–Co.[7] Thus we inspected this problem from the other direction, namely, decarboxylation. We have chosen decarboxylation reactions leading to products having high thermodynamic stability. Thermal decarboxylation of **1h** was unsuccessful. However, we could achieve quantitative decarboxylation of **1k** where (η^3-allyl)cobalt tricarbonyl was the final organometallic product and the CO_2 evolved was trapped as $BaCO_3$. Attempts at the inverse reaction $[(\eta^3\text{-}C_3H_5)Co(CO)_3 + 1\ \text{bar}\ CO_2]$ were unsuccessful yet.[44] Similar decarboxylation reactions could account for the fission of the C–O bond in the homologation of alcohols. If so, compounds **1** should be considered in the main reaction. We are currently investigating this possibility.

Conclusions

The preparative work described in this paper indicates the following.

(a) The direct reaction of alkoxide ions (or perhaps even undissociated alcohols) and $Co_2(CO)_8$ should be considered in studies of the mechanism of alcohol homologation.

(b) There are strong reasons to believe that $ICo(CO)_4$ and/or *anionic* iodine-containing complexes (instead of the generally supposed neutral ones) may play a certain role in homologation and related reactions.

(c) Important organic ligand (ex)change reactions may occur in carbonylation reactions in polar media through anionic Co(I) complexes of the type $[XYCo(CO)_3]^-$ where X and Y may be equal or not and may represent groups as alkyl, silyl, acyl, halogen, COOR, or even perhaps COOH.

(d) [(Aryloxy)carbonyl]cobalt carbonyls can be prepared.

(e) The chemistry of the alkoxycarbonylcobalt carbonyls can be linked, not only formally, to the organometallic CO_2 chemistry.

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Registry No. **1a**, 83269-56-1; **1b**, 86970-72-1; **1c**, 97170-43-9; **1d**, 94007-05-3; **1e**, 97170-44-0; **1f**, 97170-45-1; **1g**, 97170-46-2; **1h**, 97170-47-3; **1i**, 97170-48-4; **1j**, 97170-49-5; **1k**, 97170-50-8; **2a**, 97170-51-9; **2b**, 97170-52-0; **2c**, 97170-53-1; **2d**, 97190-23-3; **2e**, 97170-54-2; **2f**, 97170-55-3; **2g**, 97170-56-4; **2h**, 97170-57-5; **3a**, 83269-57-2; **3b**, 15244-99-2; **3c**, 97170-58-6; **3d**, 97170-59-7; **3e**, 97170-60-0; **3f**, 97170-61-1; **3g**, 97170-62-2; **3h**, 97170-63-3; **3j**, 97190-24-4; **4a**, 97170-64-4; **4c**, 97170-65-5; **4d**, 97170-66-6; **4e**, 97170-67-7; **4h**, 97170-68-8; **5** (R = CH_3), 97170-69-9; **5** (R = Bz), 97170-70-2; **5** (R = Ph), 97170-71-3; **5** (R = 2-MeC_6H_4), 97170-72-4; **5** (R = 4-BrC_6H_4), 97170-73-5; **6** (R = CH_3), 97170-74-6; **6** (R = Bz), 97170-75-7; $Co_2(CO)_8$, 10210-68-1; $ICo(CO)_3PPh_3$, 14376-37-5; $ICo(CO)_4$, 15976-97-3; CoI_2, 15238-00-3; $(\eta\text{-}C_3H_5)Co(CO)_3$, 12144-85-3; $Na[Co(CO)_4]$, 14878-28-5; $[Co(CO)_3PPh_3]^-$, 53513-20-5; 15-crown-5, 33100-27-5; 18-crown-6, 17455-13-9; 12-crown-4, 294-93-9; MeO^-, 3315-60-4; EtO^-, 16331-64-9; *i*-PrO^-, 15520-32-8; *t*-BuO^-, 16331-65-0; *n*-$PentO^-$, 26675-02-5; *n*-$DecO^-$, 97170-77-9; *c*-$HexO^-$, 80754-03-6; BzO^-, 45581-66-6; 2-Me-2-$PhEtO^-$, 124-41-4; $Cr(CO)_3(\eta^6\text{-}Bz)O^-$, 97170-76-8; PhO^-, 3229-70-7; 2-$MePhO^-$, 20217-30-5; 4-*t*-$BuPhO^-$, 28528-33-8; 4-$MeOPhO^-$, 29368-59-0; 4-$BrPhO^-$, 2042-41-3; 4-$MeC(O)Ph^-$, 18983-84-1; α-$naphthO^-$, 17545-30-1; β-$naphthO^-$, 15147-55-4; MeONa, 124-41-4; BzONa, 20194-18-7; PhONa, 139-02-6; 2-MePhONa, 4549-72-8; 4-BrPhONa, 7003-65-8; *c*-HexONa, 22096-22-6; sodium allyl oxide, 20907-32-8.

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