Alkylcobalt Carbonyls. 7.[1] (η^1-Benzyl)-, (η^3-Benzyl)-, and (η^1-Phenylacetyl)cobalt Carbonyls[2]

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Contribution from the Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém, Hungary, the Institute of Organic Chemistry, University of Veszprém, H-8200 Veszprém, Hungary, and the Institute of Inorganic Chemistry, University of Essen, D-4300 Essen 1, GFR. *Received October 16, 1984*

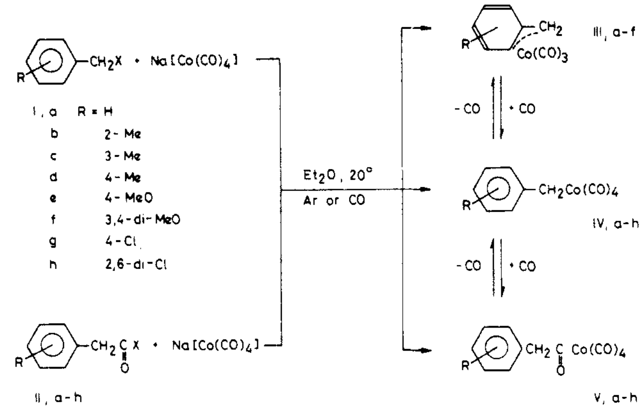
Abstract: Benzyl- or phenylacetyl halides react with $Na[Co(CO)_4]$ to yield an equilibrium mixture of (η^1-benzyl)-, (η^3-benzyl)-, and (η^1-phenylacetyl)cobalt carbonyls. The equilibria are reversible and can be shifted by bubbling Ar or CO through the reaction mixture, resulting in enrichment of the CO-deficient and -rich derivatives, respectively. The mono-PPh_3 derivatives of the η^1 complexes show similar behavior. Styrenes react with $HCo(CO)_4$ to α-methyl derivatives of the former compounds and (β-phenylpropionyl)cobalt tetracarbonyls. 2,6-$Cl_2C_6H_3CH_2COCo(CO)_3PPh_3$ (**VIIh**) and η^1-[η^6-(4-$MeC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$ (**XIb**) were characterized by X-ray crystallography as first examples of a nonfluorinated alkylcobalt tetracarbonyl and an acylcobalt carbonyl. Complex **VIIh** crystallizes in a triclinic cell of dimensions a = 8.866 (2) Å, b = 11.525 (4) Å, and c = 14.338 (3) Å, α = 74.74 (2)°, β = 83.42 (2)°, and γ = 80.84 (2)°, Z = 2, space group $P\bar{1}$, and R = 0.052. The molecule consists of a trigonal bipyramid with axial acyl and PPh_3 groups. Crystals of compound **XIb** show a monoclinic cell of dimensions a = 12.365 (2) Å, b = 7.031 (1) Å, c = 19.656 (3) Å, β = 97.68 (1)°, Z = 4, space group $P2_1/c$, and R = 0.077. The molecule shows a trigonal-bipyramidal geometry.

Alkylcobalt carbonyls[3] are proved or believed to play key roles as intermediates in some important catalytic reaction cycles (hydrogenations, hydroformylation, homologation of alcohols, etc.).

The special reactivity of the benzyl- and/or (phenylacetyl)cobalt tetracarbonyls was recognized already several years ago.[4-7] The preparation and reversible CO uptake of the triphenylphosphine derivative of benzylcobalt tetracarbonyl has been reported by one of us in 1968.[8]

Following the pioneering works of Alper[9] and Foa[10] on the two-phase carbonylation of benzyl halides, the interest in such systems revived again in the late 1970s.[11-17] Another motive of recent interest in this chemistry was provided by indications of radical pathways[18] in the reaction of styrene and its derivatives with $HCo(CO)_4$.[19-26]

Scheme I



These works, however, did not report the isolation and characterization of benzylcobalt tetracarbonyl and its derivatives. The lack of preparative data prompted us to perform the study which will be reported here as a continuation of our earlier works on alkylcobalt carbonyls (c.f., ref 1-3 and references cited therein).

Results and Discussion

Preparative Results. Benzyl (**I**) or phenylacetyl (**II**) halides react with $Na[Co(CO)_4]$ under 1 bar of CO or Ar to yield an equilibrium mixture of (η^3-benzyl)cobalt tricarbonyls (**III**) and (η^1-benzyl)-(**IV**) and (η^1-phenylacetyl)cobalt tetracarbonyls (**V**) (Scheme I).

The structure of compounds **III** and **V** was confirmed by analyses and spectra but that of complexes **IV** only by spectra since the two carbonylation/decarbonylation equilibria prevented the isolation of **IV** in pure form. This was rendered even more difficult by the fact that compounds **IV** and **V** are oils like most other alkyl- or acylcobalt carbonyls.[27-30]

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(2) Preliminary communications: (a) Galamb, V.; Pályi, G. *J. Chem. Soc., Chem. Commun.* **1982**, *487*. (b) Galamb, V.; Pályi, G. Boese, R.; Schmid, G. *Proc. Int. Conf. Coord. Chem., 20th, 1982* **1982** (*Aug 23-27*), *1* (*Abstr.*), 107.
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(8) Nagy-Magos, Z.; Bor, G.; Markó, L. *J .Organomet. Chem.* **1968**, *14*, 105.
(9) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* **1977**, *134*, C11.
(10) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1977**, *134*, C15.
(11) Bratermann, P. S.; Walker, B. S.; Robertson, T. H. *J. Chem. Soc., Chem. Commun.* **1977**, 651.
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(15) Francalanci, F.; Foa, M. *J. Organomet. Chem.* **1982**, *232*, 59.
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(21) Roth, J. A.; Wiseman, P. *J. Organomet. Chem.* **1981**, *217*, 231.
(22) Nalesnik, T. E.; Freundenberger, J. H.; Orchin, M. *J. Organomet. Chem.* **1981**, *221*, 193.
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(24) Ungváry, F.; Markó, L. *Organometallics* **1982**, *1*, 1120.
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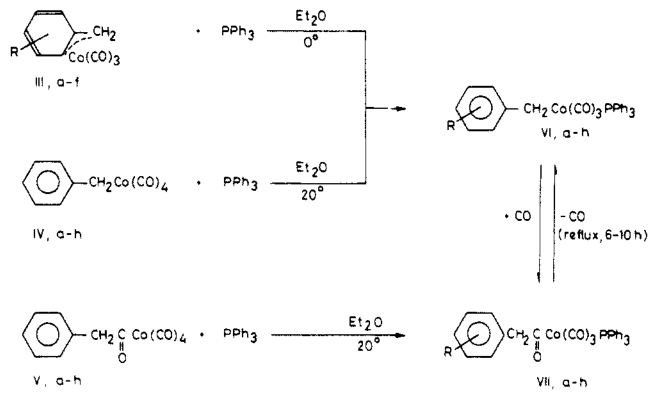
Scheme II



Compounds **III** are dark-red, air-sensitive oily substances with the exception of **IIIf** which is a black, microcrystalline solid. The compounds undergo in a few days a reaction even if stored at −70 to −80 °C. This transformation is characterized by a significant loss in solubility and the appearance of new peaks in the mass spectra which can be deduced from the dimer and higher oligomer(s).[31] This prevented X-ray structure determination. The mechanism of this oligomerization is unclear.

The equilibrium nature of the transformations **III** ⇌ **IV** and **IV** ⇌ **V** was proved chemically as follows:

(i) Both compounds **I** and **II** yielded practically the same reaction mixture (as detected by measuring the relative intensities of characteristic ν(C–O) bands) if the CO partial pressure was the same.

(ii) The composition of the reaction mixture depended on the nature of the atmosphere used: under CO, concentrations of **IV** and **V** were higher, while under Ar the formation of more **III** could be observed. Application of 2–7 bar of CO pressure resulted in an almost exclusive formation of **V**. These shifts in the composition of the solutions containing **III**, **IV**, and **V** could be repeated several times without significant decrease in the overall concentration. The equilibria are reached within $^1/_2$–4 h at atmospheric pressure and room temperature.

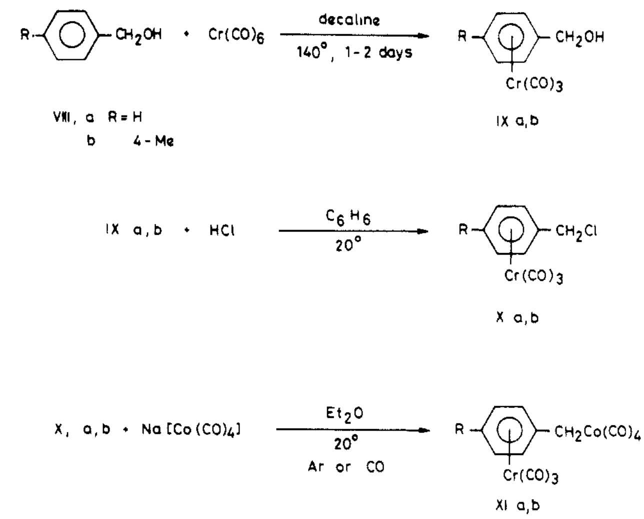
Substituent(s) on the phenyl ring influenced the equilibrium composition markedly. Electronegative substituents (4-Cl, 2,6-Cl_2) disfavored the formation of **III** and **V** complexes while electron-releasing ones 3- or 4-Me and -OMe resulted in relatively more **III** and **V**.

Equilibrium data could not be obtained yet due to experimental difficulties. In one case the equilibrium of an alkyl/acyl pair could be measured: $K \sim 1$ at 740 mmHg CO, 25 °C for the **IVa**/**Va** couple.

In an attempt to obtain more stable derivatives of type **III** and solid ones from compounds **IV** and **V**, we reacted the equilibrium mixtures of these compounds with PPh_3. The results are summarized in Scheme II.

The fact that compounds **III** yield the substituted alkyl derivatives **VI** instead of a PPh_3-substituted (η^3-benzyl)cobalt dicarbonyl shows very well that the most loosely coordinated "ligand" in **III** is the aromatic ring. This is in good agreement with the asymmetric coordination of the benzyl group to the metal in similar complexes[33,34] and can be visualized by attributing some reality even to the σ,π-type form **IIIB**. This behavior is markedly different

Scheme III



from that of (η^3-allyl)cobalt tricarbonyl,[35] where the organic ligand is much more symmetric and more tightly bound to the metal.[39]

IIIA IIIB

The substituted derivatives of **VI** and **VII** showed a similar carbonylation–decarbonylation behavior as the corresponding tetracarbonyls, in agreement with observations on the **VIa** ⇌ **VIIa** couple.[8]

Compounds **VI** and **VII** are solids, and thus crystals suitable for X-ray structure determination could be grown for one representative of the η^1-acyl-type complexes: **VIIh**. In spite of the large importance of acylcobalt carbonyls as intermediates of the hydroformylation reaction (c.f., e.g., ref 3 and 40–42), to the best of our knowledge no x-ray diffraction structural study[43] has been reported earlier on this class of compounds. The structure will be discussed later in the paper.

A representative of compounds **IV** could be isolated by coordinating the aromatic ring as an η^6-ligand to a transition metal. We prepared[44] $Cr(CO)_3$-substituted benzyl chlorides and reacted these with $Na[Co(CO)_4]$ as shown in Scheme III. The η^6-coordinated aromatic ring has apparently lost its capacity to replace one of the CO ligands due to the strong electronic effect of the coordinated $Cr(CO)_3$ group[45] and also prevented the formation of the η^1-acyl derivative.[47]

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

(31) η^3-Benzyl Pd complexes were found to show a similar "annoying feature"[32] which hampered the determination of the molecular structure by X-ray diffraction. The size of the unit cell, however, could be determined in this case, and it showed a marked increase accompanying the "aging" of the sample. This hints again at a solid-state oligomerization process.

(32) Roberts, J. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 2509.

(33) η^3-$(C_6H_5CH_2)Co[P(OMe)_3]_3$: (a) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920. (b) Bleeke, J. R.; Burch, R. R.; Caulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316.

(34) (a) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339. (b) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709.

(35) (η^3-Allyl)cobalt tricarbonyls yield CO-substitution products with tertiary phosphines,[36] but if the tertiary phosphine is present already during the reaction of $Na[Co(CO)_4]$ with the allyl halogenide, the substituted (η^1-allyl)cobalt compound is formed.[37] However, the reaction of (η^3-allyl)cobalt with CO was shown recently to yield the (η^1-allyl)cobalt tetracarbonyl[38] (although photochemically in the CO matrix).

(36) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097.

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(41) (a) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer: Berlin, 1970. (b) *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer: Berlin, 1980.

(42) Pino, P.; Piacenti, F.; Bianchi, M. *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 43.

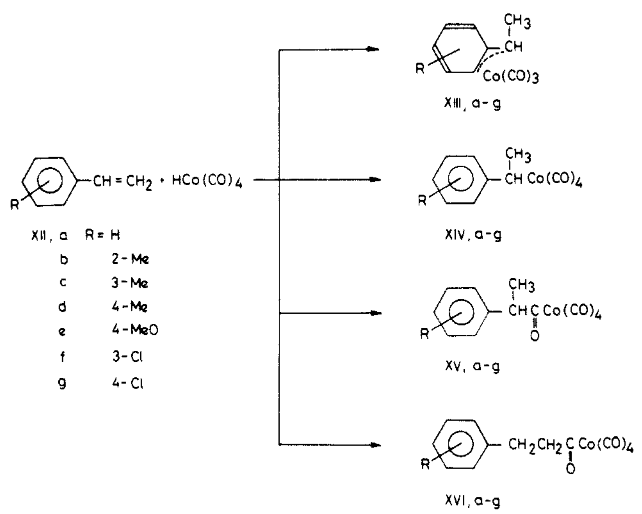
(43) It should be noted that the structure of a compound containing the acyl group of an inorganic (carbonic) acid has been reported recently. $MeOC(O)Co(CO)_3PPh_3$: Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(44) The reactions leading to the $Cr(CO)_3$-substituted benzyl chlorides were described for R = H (Holmes, J. D.; Jones, D. A. K.; Pettit, R. *J. Organomet. Chem.* **1965**, *4*, 324). R = Me was prepared analogously.

(45) Approximately equal to that of a p-NO_2 group.[46]

(46) Nichols, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

Scheme IV



In fact the $Cr(CO)_3$-substituted benzylcobalt tetracarbonyls **XI** were crystalline, relatively stable substances which could be isolated in pure form, and the molecular structure of **XIb** could be determined by X-ray diffraction. To the best of our knowledge, this is the first X-ray structure of a nonfluorinated alkylcobalt tetracarbonyl.[23,48] The details of the structure will be discussed later.

Compounds **XI** were reacted with 40 bar of CO. Samples were taken from the autoclave and analyzed by IR spectroscopy. The ν(C–O) spectrum indicated low concentrations of the corresponding acylcobalt compounds, and a yellow precipitate was formed. In an attempt to obtain the IR spectrum of this material by dissolving it in *n*-hexane (at atmospheric CO pressure), an orange solution was obtained which showed only the bands of the starting compound **XI**.

Reaction of compounds **XI** with triphenylphosphine led to the monosubstituted acylcobalt compounds which could be decarbonylated to the corresponding alkylcobalt derivatives. The substitution occurred exclusively on the Co atom. This could be expected on the basis of the relative positions of the ν(C–O) bands corresponding to the $Co(CO)_4$ and $Cr(CO)_3$ fragments in **XI** which indicate that the carbonyl ligands on Co are the more reactive ones.[49]

We also intended to prepare α-alkyl-substituted analogues of compounds **III**, **IV**, and **V**. The reaction of styrene and its ring-substituted derivatives **XII** with $HCo(CO)_4$ were chosen for this purpose. In fact styrenes **XII** reacted smoothly with $HCo(CO)_4$ according to Scheme IV. Compounds **XIII–XVI** were not isolated in pure form but detected by (mostly IR) spectroscopy, using the analogy of the spectra to those of the corresponding complexes **III–V**.

The following observations should be mentioned:

(i) The (η^3-benzyl)cobalt complexes were formed in these systems even if the aromatic ring carried electronegative substituents (**XIIIf,g**). This shows the greater tendency of formation of α-alkyl-substituted η^3-benzyl complexes. Accordingly the formation of intermediates of type **XIII** should be considered in atmospheric (stoichiometric) carbonylations of structures related to styrene.

(ii) It has been tested whether the results of the reaction between 2-phenylethyl bromide and $Na[Co(CO)_4]$ are comparable to those of the styrene + $HCo(CO)_4$ reaction. We have found practically identical product compositions (as analyzed by IR spectroscopy) in the two cases, proving that earlier attempts to model the problems of carbonylations using the alkyl halide + $Na[Co(CO)_4]$ route have provided reliable results.[1,2,8,30] (Kinetic and CIDNP results of the $HCo(CO)_4$ + styrene reaction were published elsewhere.[24,25,50])

(iii) When the reaction mixtures in *n*-octane solution were left to stand for 1–3 days, compounds **XIII–XV** slowly decomposed and a new type of cobaltoorganic species formed which seemed to be the most stable against decomposition. This turned out to be $RC_6H_4CH(CH_3)CH_2OC(O)Co(CO)_4$,[51a] i.e., the (alkoxycarbonyl)cobalt tetracarbonyl derived from the alcohol formed by the reduction of α-formylated styrene. This observation can be interpreted as an independent preparative support of the recent work of Martin and Baird,[51b] suggesting that acylcobalt carbonyls derived from carboxylic acids ($RC(O)Co(CO)_3L$, L = *tert*-(phosphine) may be transformed to the corresponding "homologous" (alkoxycarbonyl)cobalt carbonyls ($RCH_2OC(O)Co(CO)_3L$, derived from half esters of carbonic acid). It should be mentioned that an analogous reaction of acylmanganese carbonyls has been characterized by Freudenberger and Orchin.[51d] We are currently investigating this interesting reaction which might be of primary importance in all cases where $RC(O)Co(CO)_nL_{4-n}$-type acylcobalt carbonyls occur (hydroformylation, homologation, and other carbonylations catalyzed or assisted by Co).

Spectra and Structures

The IR ν(C–O) data are collected in Table I and the ^{1}H NMR spectra in Table II.

The structure of compounds **III** is based on analogies of the spectra. The IR spectra show a distorted, C_{3v} (A_1 + E)[52a,b] band pattern, showing a more rigid asymmetric organic ligand than that of the (η^3-allyl)cobalt tricarbonyl.[52c] Even the separation of the higher (A_1) band of the lower E (or split E) system is similar, 66.5 cm^{-1} at $[\eta^3\text{-}(C_3H_5)]Co(CO)_3$ and, e.g., 72.0 cm^{-1} for **IIIf**. The most characteristic features of the ^{1}H NMR spectra are the diastereotopic separation of the signals of the benzylic CH_2 protons and the high-field shift of the signals corresponding to the ring protons with respect to the values of aromatic systems. This behavior is similar to the low-temperature proton resonance pattern of some (η^3-benzyl)molybdenum and -tungsten complexes[34] (as shown with an example in Table II). These data show that complexes **III** are nonfluxional at room temperature which is a rare phenomenon within (η^3-benzyl)metal complexes.[53] Eventual fluxionality at higher temperatures was tested with **IIIf** but the ^{1}H NMR spectrum did not change when the sample was heated to +60 °C.

It seems reasonable to suppose that the small difference between the δ values corresponding to the methoxy groups in **IIIf** indicates that the 3-methoxy group and the Co atom are situated on the opposite edges of the ring. Since this can be attributed to steric factors, a similar geometry can be expected for **IIIc** and especially for **IIIb**.

Because of the equilibria with alkyl and acyl derivatives, it was not possible to obtain good quality ^{1}H NMR spectra for compounds **XIII**. Their overall structure can be deduced therefore only from analogies between their IR spectra with those of compounds **III**.

The structures suggested for compounds **IV**, **V**, and **XI** are based on their IR spectra,[3,27,30] the IR spectra of the phosphine-substituted derivatives (vide infra), the thorough normal coordinate analysis of the ν(C–O) vibrations of $RM(CO)_4$ molecules,[54] and the structures of compounds **XIb** and **VIIh**. It is of interest to note that there is no detectable vibrational coupling between the cobalt and chromium carbonyl parts in compounds **XI** and their

(47) Decreased electron density on the α-C(alkyl) atom in $RCo(CO)_4$ compounds was found to correlate with decreased activity in the CO insertion reaction.[3]

(48) Structures of phosphine-substituted derivatives are known.[3]

(49) Bigorgne, M. *Bull. Soc. Chim. Fr.* **1960**, 1986.

(50) Bockman, M. T.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F. *J. Organomet. Chem.* **1985**, *279*, 165.

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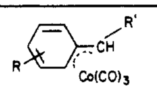
(52) (a) Brown, D. A. *J. Chem. Soc.* **1962**, 3849. (b) Fischer, R. D. *Chem. Ber.* **1960**, *63*, 165. (c) Bor, G. *Collect. Pap. Symp. Coord. Chem., Tihany (Hungary)* **1964** (*Sept*), *I*, 397.

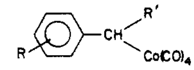
(53) Only some η^3-(2- and 3-thenyl) complexes show similar behavior: King, R. B.; Kapoor, R. N. *Inorg. Chem.* **1969**, *8*, 2535.

(54) Bor, G. *Inorg. Chim. Acta* **1967**, *1*, 81.

Table I. Infrared ν(C–O) Data of the New Cobalt Carbonyls (n-Hexane, DCl Calibrated, ±0.5 cm^{-1})

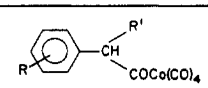


R′ = H, **III** (R′ = Me), **XIII**

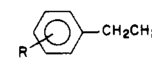


R′ = H, **IV** (R′ = Me), **XIV**

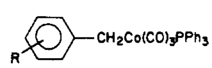
type	III / XIII		IV / XIV		
assignment[a]	A_1	E	A_1	A_1	E
substitutents R, R′ = H (R′ = Me)					
H, **a**	2055.5 s	1994.5 s (1990) 1978.5 s (1973)	2099 m (2094)	2033 m	2015 vs
2-Me, **b**	2054 s	1992.5 s (1990) 1974 s (1971)	2097 m (2093)	2032.5 m	2014 vs
3-Me, **c**	2054 s	1991.5 s (1987) 1975 s (1972)	2098 m (2093)	2032 m	2014 vs
4-Me, **d**	2054 s	1990.5 s (1885) 1973 s (1968)	2097 m (2093)	2032 m	2013 vs
4-MeO, **e**	2049 s	1989 s (1983) 1969.5 s (1967)	2096 m (2091)	2029 m	2011 vs
3,4-$(MeO)_2$, **f**	2047.5 s	1983.5 s 1967.5 s	2095 m	2029 m	2008 vs
4-Cl, **g**	2056 s	1997 s (1996) 1979 s (1977)	2099 m (2095)	2034 m	2015 vs
2,6-Cl_2, **h**		1983.5 s 1967.5 s	2101.5 m	2035.5 m	2021.5 vs



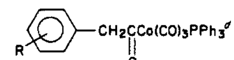
R = H, **V** (R = Me), **XV**



type	V / XV				$ArCH_2CH_2$
assignment[a]	A_1	A_1	E	acyl	acyl
substituents R, R′ = H (R′ = Me)					
H, **a**	2106.5 m (2105)	2048.5 m (2046)	2026 vs (2025) 2006.5 vs (2005)	*b* (1699)	1715
2-Me, **b**	2105.5 m (2104)	2048 m (2044)	2025 vs (2024) 2004 vs (2003)	*b* (1708)	1719
3-Me, **c**	2105.5 m (2104)	2044 m (2045)	2024 vs (2025) 2005 vs (2004)	*b* (1719)	1720
4-Me, **d**	2105.5 m (2104)	2047 m (2045)	2025 vs (2025) 2005 vs (2004)	*b* (1705)	1720
4-MeO, **e**	2105 m (2103)	2047 m (2044)	2025 vs (2023) 2005 vs (2003)	*b* (1707)	1718
3,4-MeO_2, **f**	2105 m	2047 m	2024 vs 2004 vs	*b*	
4-Cl, **g**	2106.5 m (2106)	2050 m (2048)	2027 vs (2027) 2006 vs (2006)	(1707)	1715
2,6-Cl_2, **h**	2107.5 m	2049.5 m	2029 vs 2009 vs	*b*	

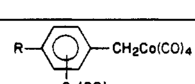


(VI)

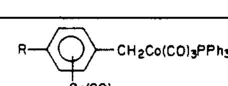


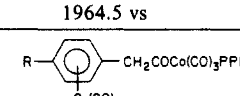
(VII)

type	(VI)		(VII)	
assignment[a]	A_1	E	A_1	E
substituent R				
H, **a**	2037 w	1965 vs	2051.5 m	1985 vs 1961 vs
2-Me, **b**	2032 vw	1967 vs 1960 vs	2048.5 w	1982.5 vs 1957.5 vs
3-Me, **c**	2033 vw	1963.5 vs	2049 w	1984.5 vs 1961 vs
4-Me, **d**	2033 vw	1962 vs	2047.5 w	1981 vs 1957 vs
4-MeO, **e**	2033 vw	1963.5 vs	2048 w	1981.5 vs 1957 vs
3,4-$(MeO)_2$, **f**	2031.5 vw	1959.5 vs	2048 w	1981.5 vs 1956.5 vs
2,6-Cl_2, **h**	2036 vw[c]	1964.5 vs[c]	2052.5 w	1987.5 vs 1964.5 vs



(XI)

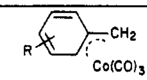


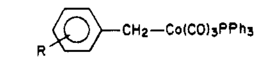
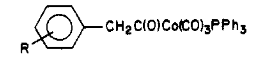


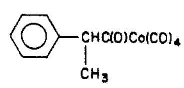
type	(XI)						
assignment[a]	A_1(Co)	A_1(Co)	E(Co)	A_1(Cr)	E(Cr)		
substituent R							
H, **a**	2103 m	2040 m	2023 s	2015 s	1977 vs 1913.5 vs		
Me, **b**	2102 m	2039 m	2022 s	2013.5 s	1972.5 vs 1909.5 s	2037.5 w, 1970.5 s 1960.5 vs, 1892.5 m	2053.5 vw, 1989 s, 1971 vs 1962 sh, 1897.5 s

[a] Assignments were made supposing idealized, higher symmetry point groups following ref 27, 30, 55. [b] $\nu(C-O)_{acyl}$ 1750–1730 cm^{-1}, br, low intensity band. [c] Solvent: Et_2O. [d] Solvent: CCl_4; $\nu(C-O)_{acyl}$ 1690–1670 cm^{-1}, br, low intensity band.

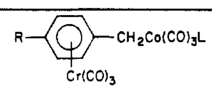
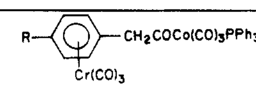
Table II. η^1 H NMR Spectra of (η^3-Benzyl)cobalt Tricarbonyls and of Triphenylphosphine-Substituted Alkyl- and Acylcobalt Carbonyls (C_6D_6, δ Values Relative to δ_{TMS} O)

substituent(s)	
2-Me, **IIIb**	1.58 and 2.86 (d, 1 H, J = 3 Hz, CH_2), 1.80 (s, 3 H, CH_3), 5.15 (d, 1 H, J = 6 Hz, ring-6-CH), 6.47 (d, 1 H, J = 6 Hz, ring-3-CH), 6.6–6.9 (m, 2 H, ring-4 and 5-CH)
3,4-MeO, **IIIf**	2.04 and 3.01 (d, 1 H, J = 3 Hz, CH_2), 3.16 and 3.21 (s, 3 H, OCH_3), 5.41 and 5.90 (d, 1 H, J = 6.2 Hz, ring-5 and 6-CH), 6.08 (d, 1 H, J2 Hz, ring-2-CH)
η^3-($C_6H_5CH_2$)Mo(CO)$_2$[η^5-(C_5H_5)][34b] (for comparison) (CCl_3F, −30 °C)	1.81 and 2.82 (d, 1 H, J = 3 Hz, CH_2), 5.20, 6.31, 6.88, 7.03, 7.09 (ring-CH)

	 (III)		 (IV)	
substituent(s)	−CH_2	substituent H	−CH_2	substituent H
H, **a**	3.34 s[a]		3.97 s[b]	
2-Me, **b**	3.55 d (J = 3.5 Hz)	2.4 s	4.5 s	2.2 s
3-Me, **c**	3.45 d (J = 1.5 Hz)	2.2 s	4.25 s	1.95 s
4-Me, **d**	3.50 d (J1 Hz)	1.80 s	4.25 s	1.9 s
4-MeO, **e**	3.55 s, br	3.10 s	4.20 s	3.10 s
3,4-(MeO)$_2$, **f**	3.70 d (J = 2 Hz)	3.30 s 3.50 s	4.30 s	3.25 s 3.40
2,6-Cl_2, **h**	3.55 d (J = 2 Hz)		5.0 s	



XVa

	
R = H, 2.25 (s, α-CH_2), 4.50 (s, ring H-s) L = CO	
R = 4-Me, L = CO 1.50 (s, 4-CH_3), 2.20 (s, α-CH_2), 4.35 (ring AB system, J_1 = 25, J_2 = 7 Hz)	1.50 ns, 4-CH_3), 4.10 (s, α-CH_2), 4.60 (ring AB system, J_1 = 30, J_2 = 27 Hz)
R = 4-Me, L = PPh_3 1.40 (s, 4-CH_3), 2.80 (s, br, α-CH_2), 4.80 (ring AB system, J_1 = 58, J_2 = 7 Hz)	

[a] In CD_3OD: 3.54. [b] In CD_3OD: 4.34 s.

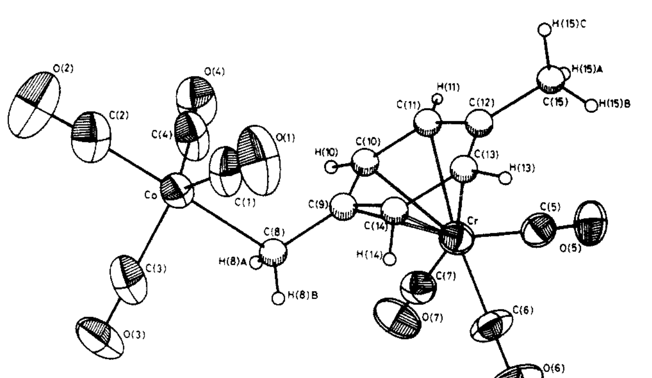


Figure 1. Structure of **XIb**.

acyl- and phosphine-substituted derivatives.

The phosphine-substituted derivatives show ν(C–O) spectra corresponding to a more or less distorted C_{3v} geometry, which corresponds to a trigonal-bipyramidal geometry with axial alkyl (acyl) and phosphine groups. This array is confirmed by the P, H coupling between the PPh_3 ligand and the α-CH_2 group.[30,55] However, the final proof for the structure of these compounds is again based on X-ray diffraction results: on those of $HCF_2CF_2Co(CO)_3PPh_3$[56] and $PhCH_2OC(O)CH_2Co(CO)_3PPh_3$[30] for the alkyl derivatives and on that of **VIIh** for the acyl derivatives.

Thus it can be stated that the most important source of information from the IR spectra is the similarity within each type, which proves that the X-ray structures can be generalized.

(55) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944.
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Table III. Bond Lengths and Angles of **XIb** with Standard Deviations in Parentheses[a]

distances, Å		angles, deg	
Co–C(1)	1.791 (6)	C(1)–Co–C(2)	91.5 (3)
Co–C(2)	1.806 (8)	C(4)–Co–C(2)	94.6 (3)
Co–C(3)	1.788 (8)	C(3)–Co–C(2)	94.6 (4)
Co–C(4)	1.848 (6)	C(8)–Co–C(2)	179.2 (3)
Co–C(8)	2.126 (7)	C(1)–Co–C(4)	122.5 (3)
C(1)–O(1)	1.141 (8)	C(1)–Co–C(3)	116.9 (3)
C(2)–O(2)	1.132 (10)	C(4)–Co–C(3)	119.4 (3)
C(3)–O(3)	1.138 (10)	Co–C(8)–C(9)	112.3 (4)
C(4)–O(4)	1.085 (8)	C(8)–C(9)–C(14)	121.0 (6)
C(8)–C(9)	1.498 (9)	C(8)–C(9)–C(10)	122.0 (5)
C(9)–C(10)	1.416 (9)	C(14)–C(9)–C(10)	116.9 (6)
C(9)–C(14)	1.404 (8)	C(9)–C(10)–C(11)	122.2 (5)
C(10)–C(11)	1.388 (9)	C(9)–C(14)–C(13)	121.0 (6)
C(11)–C(12)	1.421 (8)	C(10)–C(11)–C(12)	120.2 (6)
C(12)–C(13)	1.386 (9)	C(14)–C(13)–C(12)	121.7 (6)
C(13)–C(14)	1.408 (9)	C(13)–C(12)–C(15)	122.0 (5)
C(12)–C(15)	1.506 (9)	C(11)–C(12)–C(15)	120.0 (6)
Cr–C(5)	1.826 (6)	C(5)–Cr–C(6)	89.0 (3)
Cr–C(6)	1.850 (7)	C(5)–Cr–C(7)	89.3 (3)
Cr–C(7)	1.829 (7)	C(6)–Cr–C(7)	89.6 (3)
Cr–C(9)	2.261 (6)		
Cr–C(10)	2.204 (6)		
Cr–C(11)	2.221 (6)		
Cr–C(12)	2.246 (7)		
Cr–C(13)	2.212 (7)		
Cr–C(14)	2.228 (7)		
C(5)–O(5)	1.162 (8)		
C(6)–O(6)	1.147 (9)		
C(7)–O(7)	1.163 (8)		

[a] Distance Cr to best plane of [C(9)–C(14)] = 1.731 Å.

The structure of **XIb** is shown in Figure 1, and Table III provides some characteristic geometric information. This structure

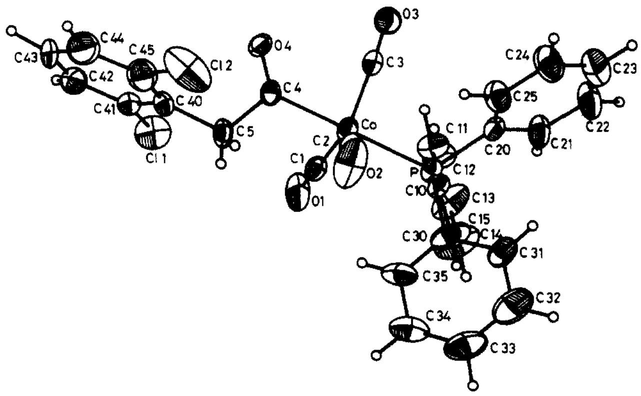

Figure 2. Structure of **VIIh**.

Table IV. Bond Lengths and Bond Angles in the Molecule **VIIh** with Standard Deviations in Parentheses

lengths, Å		angles, deg	
Co–C(1)	1.778 (5)	C(4)–Co–C(1)	87.2 (2)
Co–C(2)	1.777 (4)	C(4)–Co–C(2)	88.7 (2)
Co–C(3)	1.798 (6)	C(4)–Co–C(3)	88.1 (2)
Co–C(4)	1.996 (4)	C(4)–Co–P	178.9 (1)
Co–P	2.259 (1)	C(5)–C(4)–Co	116.1 (3)
		C(5)–C(4)–O(4)	119.9 (4)
C(1)–O(1)	1.143 (6)		
C(2)–O(2)	1.139 (5)	Co–C(4)–O(4)	124.0 (4)
C(3)–O(3)	1.132 (7)	C(4)–C(5)–C(40)	114.5 (4)
C(4)–O(4)	1.193 (5)	Co–P–C(10)	113.6 (1)
C(4)–C(5)	1.537 (7)	Co–P–C(20)	115.2 (1)
C(5)–C(40)	1.509 (6)	Co–P–C(30)	114.5 (1)
P–C(10)	1.810 (3)		
P–C(20)	1.823 (4)		
P–C(30)	1.823 (4)		

is the first direct experimental evidence for the trigonal-bipyramidal geometry (with axial alkyl group) of alkylcobalt tetracarbonyls.

The equatorial carbonyl groups are slightly bent toward the (very bulky) alkyl group, confirming the prediction of Bor[54] based on approximate force-field analysis of ν(C–O) spectra of RM(CO)$_4$ systems. This result shows that even approximate normal coordinate analysis may furnish fine structural details if applied in a sophisticated manner.

The length of the α-C(alkyl)–Co bond is definitely longer (212.6 (7) pm) than the sum of the covalent radii (202 pm).[57] This feature has also been observed in the case of $PhCH_2OC(O)CH_2Co(CO)_3PPh_3$ (210.9 (8) pm),[30] which, however, is a phosphine derivative. The present observation demonstrates this is an apparently general feature of alkylcobalt carbonyls containing an sp^2 carbon atom in the β-position and is therefore not the consequence of a trans influence[58] of the phosphine ligand. According to approximate (Extended Hückel/Wolfsberg–Helmholz) MO calculations,[59] it can be explained by relatively high electron densities accumulated on the C(alkyl)–Co antibonding orbitals.

In terms of reactivity, this means that the relative kinetic stability of these compounds against CO insertion may be due to the lower nucleophilicity of the α-carbon atom because of a significant decrease of its electron density.[60]

The molecular structure of **VIIh** is displayed in Figure 2, and characteristic bond data are summarized in Table IV. It can be seen that the overall geometry represents a trigonal-bipyramidal array with axial acyl and PPh_3 as supposed already on the basis of infrared data. Since CO "insertion"[61] is a 1,2-alkyl migration and the alkyl complex **XIb** has an axial alkyl type structure, an axial phosphine, equatorial acyl type product would not be surprising either. Obviously a rearrangement takes place either in the intermediate (most probably an acylcobalt tricarbonyl) or immediately after the product has been formed.[62]

The C(acyl)–Co bond distance is remarkably shorter (199.6 (4) pm) than the α-C(alkyl)–Co distance in $PhCH_2OC(O)CH_2Co(CO)_3PPh_3$[30] or in **XIb** but near to that of $HCF_2CF_2Co(CO)_3PPh_3$ (195 (3) pm).[56] Since it is obvious to suppose some pπ–dπ interaction between the acyl group and the Co atom in an acylcobalt carbonyl, the back-bonding-type stabilization mechanism suggested to explain the stability of fluorinated alkylcobalt carbonyls[63] is supported by this comparison.

Experimental Section

Starting compounds were of commercial origin except $Co_2(CO)_8$ which was prepared by a known high-pressure method.[64] A conventional inert experimental technique was used, employing dried (P_2O_5, silica), CO_2- and O_2-free (KOH, DEOXO) gases (CO, Ar) as well as peroxide- and O_2-free, dry solvent (alumina, sodium wire, distillation under Ar).

The spectra were recorded with the following instruments: IR (n-hexane, DCl calibrated), IR-75 (Carl Zeiss, Jena, GDR); ^{1}H NMR (80 MHz, TMS), BS-487 (Tesla, Brno, CSSR); MS JMS 01-SG-2 (Jeol, Japan).

X-ray Diffraction Study of VIIh and XIb. A pale-yellow crystal of **VIIh** and a plate-shaped orange crystal of **XIb** were sealed under nitrogen in glass capillaries and measured with 2θ–ω scan techniques on a R3 Syntex four-circle diffractometer. The intensity of three check reflections, measured every 100 reflections in the data collection of **XIb**, decreased by 20% due to decomposition of the crystal, becoming brown. All data were corrected by a decomposition curve, evaluated from the check reflections. The structure solutions obtained by direct methods and structure refinements with block cascades and display were performed with SHELXTL software[65] on a NOVA 3/12 computer (Data General). Neutral scattering factors were applied as incorporated in SHELXTL.[65]

For **VIIh** the phosphorus-bonded phenyl groups including hydrogen atoms were refined as rigid groups (C–C distance 139.5 pm, C–H distance 96.0 pm). The positions of the two hydrogen atoms bonded to C(5) were calculated and included to structure refinement. A difference Fourier revealed the positions of the hydrogen atoms bonded to C(42), C(43), and C(44). Their positional parameters were refined with a unique temperature factor (U = 0.16 (1)).

The positions of the hydrogen atoms of **XIb**, bonded to C(15) and C(8), were calculated and refined as rigid groups (unique temperature factor U = 0.078 (9)); those bonded to C(10), C(11), C(13), and C(14) were taken from a difference Fourier and refined with a unique temperature factor (U = 0.049 (8)).

Crystal dimensions and supplement data are summarized in Table V. Tables VI and VII contain the atomic coordinates and Tables 8 and 9 (supplementary material) the anisotropic temperature parameters of **XIb** and **VIIh**, respectively.

Reaction of Benzyl of Phenylacetyl Chlorides with Na[Co(CO)$_4$]. A Na[Co(CO)$_4$] solution in 30 cm^3 of Et_2O was prepared from 0.34 g (1 mmol) of $Co_2(CO)_8$ and excess 1.5% Na/Hg. The colorless liquid was decanted into a Schlenk vessel under CO or Ar, and 1.9 mmol of substituted benzyl chloride was added at room temperature. If the reaction was performed under CO, some CO absorption was observed. After the solution was stirred for 1–8 h, the precipitation of NaCl was complete and the 1890-cm^{-1} band of $[Co(CO)_4]^-$ had disappeared from the IR spectrum. The resulting orange solution was filtered and the solvent evaporated at 0 °C, leaving a dark-red oil. This product was according to IR spectra (n-hexane) a mixture of compounds **III**, **IV**, and **V**.

The use of the corresponding phenylacetyl chlorides instead of benzyl chlorides led to the same product with practically the same ratio of compounds **III**, **IV**, and **V**. The reaction time, however, was shorter (~20 min at room temperature), and some evolution of CO was observed independently of the atmosphere used.

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(59) (a) Cser, F.; Galamb, V.; Pályi, G. *Inorg. Chim. Acta* **1979**, *37*, L517. (b) Cser, F.; Galamb, V.; Pályi, G. *Hungarian Colloq. Coord. Chem., 15th* **1980** (*May 19–21*), 1.
(60) Taking into account the presently accepted mechanism of the CO "insertion" reaction.[61]
(61) (a) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 3055. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.
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Table V. Crystal Dimensions and Supplement Data of **VIIb** and **XIb**

	VIIb	XIb
formula	$C_{29}H_{20}Cl_2CoO_4P$	$C_{15}H_9CoCrO_7$
fw	595.26	412.14
cryst dimensions, mm	0.18 × 0.02 × 0.01	0.20 × 0.30 × 0.05
a, Å	8.866 (2)	12.365 (2)
b, Å	11.525 (4)	7.031 (1)
c, Å	14.338 (3)	19.656 (3)
α, deg	74.74 (2)	90
β, deg	83.42 (2)	97.68 (1)
γ, deg	80.84 (2)	90
cell vol, $Å^3$	1391.4 (6)	1693.4 (4)
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
Z	2	4
density calcd, g/cm^{-3}	1.42	1.61
μ (Mo Kα), cm^{-1}	8.96	16.23
λ (Mo Kα) graphite monochromator, Å	0.71073	0.71073
max 2θ, deg	50	55
scan speed variable, deg/min (min at $I <$ 150 counts/s, max at $I >$ 2500 counts/s)	1.5–10	1.5–15
scan to background time ratio	1:1	1:1
no. of independent reflections	4800	3020
no. of obsd reflections	3187	1988
observation limit	$F_o \geq 3.5\sigma(F)$	$F_o \geq 2.5\sigma(F)$
internal merging *R* factor before empirical absorption correction	1.6%	5.46%
after correction	1.3%	2.69%
R value	5.2%	7.7%
R_w value, $w^{-1} = \sigma^2(F_o) + AF_o^2$	4.6%	5.9%
A	2.2×10^{-4}	1×10^{-4}
max rest electron density, e $Å^{-3}$	0.38	0.67

Table VI. Atomic Coordinates for **XIb**, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Co	0.69718 (7)	1.03419 (14)	0.20187 (4)
Cr	0.77775 (8)	1.42351 (16)	−0.01447 (5)
C(1)	0.6212 (5)	0.9149 (11)	0.1306 (3)
C(2)	0.6896 (6)	0.8293 (12)	0.2563 (4)
C(3)	0.6229 (6)	1.1857 (12)	0.2518 (3)
C(4)	0.8472 (5)	1.0433 (12)	0.2144 (3)
C(5)	0.8474 (5)	1.5338 (10)	−0.0804 (3)
C(6)	0.6529 (6)	1.5537 (11)	−0.0489 (4)
C(7)	0.8186 (5)	1.6236 (10)	0.0425 (3)
C(8)	0.7036 (6)	1.2752 (9)	0.1374 (3)
C(9)	0.7473 (5)	1.2278 (9)	0.0721 (3)
C(10)	0.8597 (5)	1.2373 (9)	0.0665 (3)
C(11)	0.9005 (5)	1.1941 (9)	0.0060 (3)
C(12)	0.8289 (5)	1.1424 (9)	−0.0536 (3)
C(13)	0.7184 (5)	1.1390 (10)	−0.0492 (3)
C(14)	0.6775 (5)	1.1794 (10)	0.0126 (3)
C(15)	0.8734 (6)	1.0993 (11)	−0.1195 (3)
O(1)	0.5706 (4)	0.8371 (9)	0.0865 (2)
O(2)	0.6816 (6)	0.7017 (9)	0.2902 (3)
O(3)	0.5736 (5)	1.2838 (9)	0.2817 (3)
O(4)	0.9353 (4)	1.0442 (10)	0.2237 (3)
O(5)	0.8926 (4)	1.5978 (7)	−0.1232 (2)
O(6)	0.5761 (4)	1.6350 (10)	−0.0709 (3)
O(7)	0.8439 (5)	1.7520 (8)	0.0783 (3)
H(8)A	0.7492 (6)	1.3615 (9)	0.1660 (3)
H(8)B	0.6315 (6)	1.3266 (9)	0.1284 (3)
H(15)A	0.9402 (6)	1.1662 (11)	−0.1216 (3)
H(15)B	0.8209 (6)	1.1371 (11)	−0.1573 (3)
H(15)C	0.8860 (6)	0.9651 (11)	−0.1219 (3)
H(10)	0.9019 (36)	1.2850 (70)	0.1086 (15)
H(11)	0.9784 (11)	1.2170 (76)	0.0064 (25)
H(13)	0.6684 (32)	1.1236 (73)	−0.0917 (14)
H(14)	0.6025 (16)	1.2228 (70)	0.0128 (23)

Table VII. Atomic Coordinates for **VIIh** with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Co	−0.05319 (7)	0.23476 (5)	0.74397 (4)
P	−0.24243 (12)	0.32359 (10)	0.83203 (8)
Cl(1)	0.1255 (2)	−0.1498 (2)	0.6430 (1)
Cl(2)	0.2440 (3)	0.2818 (2)	0.4152 (1)
C(1)	−0.1332 (5)	0.0963 (4)	0.7774 (3)
C(2)	−0.0935 (5)	0.3504 (4)	0.6370 (3)
C(3)	0.0918 (5)	0.2485 (4)	0.8169 (4)
C(4)	0.1115 (5)	0.1538 (4)	0.6663 (3)
C(5)	0.0615 (5)	0.1226 (5)	0.5776 (3)
C(10)	−0.3098 (3)	0.2205 (3)	0.9419 (2)
C(11)	−0.2017 (3)	0.1564 (3)	1.0067 (2)
C(12)	−0.2478 (3)	0.0775 (3)	1.0934 (2)
C(13)	−0.4021 (3)	0.0628 (3)	1.1154 (2)
C(14)	−0.5102 (3)	0.1270 (3)	1.0506 (2)
C(15)	−0.4641 (3)	0.2058 (3)	0.9638 (2)
C(20)	−0.1919 (4)	0.4471 (3)	0.8747 (2)
C(21)	−0.2476 (4)	0.4655 (3)	0.9655 (2)
C(22)	−0.2154 (4)	0.5659 (3)	0.9929 (2)
C(23)	−0.1275 (4)	0.6479 (3)	0.9295 (2)
C(24)	−0.0718 (4)	0.6295 (3)	0.8388 (2)
C(25)	−0.1040 (4)	0.5291 (3)	0.8114 (2)
C(30)	−0.4131 (4)	0.3926 (3)	0.7678 (2)
C(31)	−0.4938 (4)	0.5025 (3)	0.7800 (2)
C(32)	−0.6213 (4)	0.5556 (3)	0.7278 (2)
C(33)	−0.6683 (4)	0.4988 (3)	0.6635 (2)
C(34)	−0.5877 (4)	0.3889 (3)	0.6513 (2)
C(35)	−0.4601 (4)	0.3358 (3)	0.7034 (2)
C(40)	0.1890 (4)	0.0608 (3)	0.5211 (2)
C(41)	0.2194 (4)	−0.0656 (3)	0.5459 (2)
C(42)	0.3317 (4)	−0.1246 (3)	0.4916 (2)
C(43)	0.4136 (4)	−0.0571 (3)	0.4124 (2)
C(44)	0.3832 (4)	0.0693 (3)	0.3876 (2)
C(45)	0.2709 (4)	0.1283 (3)	0.4420 (2)
O(1)	−0.1815 (5)	0.0059 (3)	0.8006 (3)
O(2)	−0.1222 (5)	0.4248 (3)	0.5690 (3)
O(3)	0.1840 (4)	0.2546 (4)	0.8632 (3)
O(4)	0.2417 (3)	0.1276 (3)	0.6859 (2)
H(42)	0.358 (7)	−0.211 (1)	0.514 (4)
H(43)	0.489 (5)	−0.104 (5)	0.379 (4)
H(44)	0.455 (6)	0.104 (5)	0.337 (3)

The red oil obtained as described above was worked up as described in the following sections.

Reaction with CO and Decarbonylation. Et_2O or *n*-hexane solutions of the red oil obtained in the preceding experiment were purged by CO or Ar at room temperature. The former caused enrichment of the acyl derivative V, while the latter enhanced the formation of the derivatives III and IV. This easy transformation was used to assign IR ν(CO) spectra of those products which could not be isolated in analytically pure form.

Preparation of (η^3-Benzyltricarbonyl)cobalt III Compounds. $Co_2(CO)_8$ (0.68 g, 2 mmol) was transformed into $Na[Co(CO)_4]$ in 60 cm^3 of Et_2O. Benzyl chloride (substituted) (3.8 mmol) was added to the filtered solution under Ar atmosphere. The reaction mixture was stirred for 8 h at room temperature and then the solution was cooled to 0 °C and an Ar stream (40–80 cm^3/min) was bubbled through it for 6–10 h until the solvent was completely evaporated. The remaining dark oily product was extracted by 20 cm^3 of *n*-hexane; the solution was filtered and analyzed by IR spectroscopy. Only **III** and **IV** were present, the latter amounting to 5–15%.

When the *n*-hexane solution obtained with 3,4-dimethoxybenzyl chloride was chilled to −78 °C, a black microcrystalline substance was isolated in analytically pure form as **IIIf**, yield 100 mg (0.34 mmol), 9%.

If the compounds **III** were stored for a few days at −78 °C under Ar, they lost their solubility in hexane, and also their solubility in benzene diminished. This was accompanied by a gradual change in the mass spectra marked by the increase of fragments higher than the original *m/e* (294). Freshly prepared **IIIf**: mass spectrum, *m/e* (rel intensity) 294 (*m/e*, 9), 266 (30), 238 (40), 210 (100), 180 (54), 151 (60), 59 (18), 28 (40), (additional peaks after 2 weeks) 488 (1), 476 (5), 460 (13), 448 (59), 432 (16), 420 (89), 404 (5), 376 (8), 348 (9), 320 (11), 302 (80).

Preparation of (Phenylacetyl)cobalt Tricarbonyl Triphenylphosphine (VII) Compounds. $Na[Co(CO)_4]$ (4 mmol) was prepared in 60 cm^3 of Et_2O, and 3.8 mmol of a benzyl or phenylacetyl chloride was added under CO at room temperature. After 1–8 h of stirring, 0.52 g (2 mmol) of PPh_3 was added. Vigorous CO evolution was observed which ceased after

20–30 min. The resulting yellow solution was then filtered and chilled to −78 °C and an equal volume of cold *n*-pentane was added. A yellow powder precipitated, which was purified by repeated recrystallization(s) from Et_2O/*n*-pentane. Yields ranged between 35% and 50% (with respect to the benzyl chloride).

Preparation of Benzylcobalt Tricarbonyl Triphenylphosphine (VI) Compounds. (a) Decarbonylation of Compounds VII. (Phenylacetyl)-cobalt tricarbonyl triphenylphosphine (**VII**) compounds were prepared as described above. After the first precipitation with *n*-pentane, the precipitate was dissolved in 30–50 cm^3 of benzene and refluxed for 1–4 h until the IR spectra showed that the transformation had been completed. Then the benzene was evaporated at room temperature at reduced pressure. The yellow product was extracted with *n*-hexane, and chilling of the hexane solution resulted in pale-yellow crystals which were repeatedly recrystallized from *n*-hexane. Yields were 10–30% (with respect to the benzyl chloride).

(b) Substitution of Compounds III. Freshly prepared (η^3-benzyl)cobalt tricarbonyl **III** (0.2 mmol) was dissolved in 10 cm^3 of Et_2O, and 52 mg (0.2 mmol) of PPh_3 was added. The orange color of the solution turned quickly to yellow, and no gas evolution was observed. The Et_2O was drawn off and the resulting yellow product recrystallized as described above. Yields were not measured.

Preparation of η^1-[η^6-($RC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$ (XI) and (1,6-η-$RC_6H_4CH_2OH$)$Cr(CO)_3$ (IX) Compounds. $Cr(CO)_6$ (2.2 g, 10 mmol) and 15 mmol of benzyl or 4-methylbenzyl alcohol were dissolved in 30 cm^3 of decaline. The reaction mixture was refluxed under Ar and the $Cr(CO)_6$ which sublimed into the reflux condenser was mechanically returned from time-to-time into the reaction vessel. The reaction was complete if no $Cr(CO)_6$ sublimed anymore into the condenser (10–18 h). The reaction resulted in a yellow solution containing some green precipitate which was removed by filtration. Then the solvent and the small amount of unreacted $Cr(CO)_6$ was removed at reduced pressure (13 mbar/40 °C) and the residue dissolved in 100 cm^3 of *n*-hexane. When the hexane solution was chilled to −78 °C, oily or crystalline substances were obtained which were purified by repeated recrystallizations from *n*-hexane and characterized by their IR ν(C–O) spectra: (R = H, **IXa**) 1979 s, 1912 s, br (*n*-hexane); (R = 4-Me, **IXb**) 1975 s, 1908 s (*n*-hexane)

(1,6-η-RC_6H_4Cl)$Cr(CO)_3$ (X) Compounds. The benzyl alcohol complexes obtained as described above were dissolved in 30 cm^3 of benzene. This solution was intensively shaken with an equal volume of concentrated aqueous HCl for 10 min in a separatory funnel. After the separation of phases, the organic layer was quickly washed to neutral with cold water and dried over Na_2SO_4. The solvent was drawn off and the residue recrystallized from *n*-hexane. The products were yellow crystalline substances which were moderately sensitive to air. The purity (especially after longer periods of storage) can be best controlled by Cl analysis: yields (based on $Cr(CO)_6$) (R = H, **Xa**) 0.8 g (30.5%); (R = 4-Me, **Xb**) 1.5 g (38%). The compounds were identified by elemental analyses and IR ν(C–O) spectra: (R = H, **Xa**) 1984.5 s, 1922 s, 1915 s (*n*-hexane); (R = 4-Me, **Xb**) 1980 s, 1914 s (*n*-hexane).

Reaction of (1,6-η-$RC_6H_4CH_2Cl$)$Cr(CO)_3$ Compounds with Na[$Co(CO)_4$]. $Co_2(CO)_8$ (0.17 g, 0.5 mmol) was transformed into Na[$Co(CO)_4$] in 20 cm^3 of Et_2O. This solution was decanted into a Schlenk tube under Ar and 0.95 mmol of (1,6-η-$RC_6H_4CH_2Cl$)$Cr(CO)_3$ complex was added. The reaction mixture was stirred at room temperature for 3–4 h until no more precipitate (NaCl) was formed. During this time, the yellow color of the solution turned to orange. After filtration the solvent was evaporated at −10 °C and the residue dissolved in 10 (R = H) or 20 (R = 4-Me) cm^3 of *n*-hexane. This solution was chilled to −78 °C which resulted in orange–red needlelike crystals of compounds **XI** which were moderately light- and air-sensitive. The crystals of **XIa** were too thin for X-ray diffraction, while those of **XIb** were suitable: yields, (R = H **XIa**) 205 mg (56%), (R = 4-Me, **XIb**) 240 mg (61%).

Reaction of η^1-[η^6-($RC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$ (XI) Compounds with PPh_3. (a) Compound **XIa** was reacted with PPh_3 in Et_2O at room temperature. Vigorous gas evolution was observed, and no stable metal carbonyl could be isolated.

(b) **XIb** (200 mg, 0.49 mmol) was dissolved in 30 cm^3 of *n*-hexane under Ar, 131 mg (0.50 mmol) PPh_3 was added, and the reaction mixture was stirred for 20–30 min at room temperature. A yellow fluffy substance precipitated which was characterized as η^1-[η^6-(4-$MeC_6H_4CH_2CO$)$Cr(CO)_3$]$Co(CO)_3PPh_3$. The yield was not measured.

This compound (100 mg, 0.15 mmol) was suspended in 20 cm^3 of *n*-hexane and refluxed under Ar for 3–4 h. Decomposition products were removed by filtration. The filtrate was chilled to −78 °C and a yellow microcrystalline substance was obtained which was purified by repeated recrystallization from *n*-hexane. The product was characterized as η^1-[η^6-(4-$MeC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_3PPh_3$, yield 38–68 mg (40–70%).

Reaction of Styrenes with $HCo(CO)_4$. The reaction of (substituted) styrenes with $HCo(CO)_4$ was performed at 15 °C in a thermostated reaction flask connected to a gas buret for measuring the amount of absorbed CO after adding 2.0 mmol of $HCo(CO)_4$ in 10 cm^3 of *n*-octane. In about 30 min, the CO uptake ceased at about 0.4 mol/mol of $HCo(CO)_4$. The $Co_2(CO)_8$ formed in the reaction was removed by crystallization on dry ice, and infrared spectra were taken immediately after melting of the frozen yellow solutions. IR spectra showed ν(C–O) bands characteristic for acylcobalt carbonyls and some weak bands characteristic for η^1- and η^3-type benzyl complexes. The same solutions after storing for 24 h at 25 °C under CO showed new ν(C–O) bands resembling the spectrum of acylcobalt carbonyls. These new bands can be assigned to the corresponding $RC_6H_4CH(CH_3)CH_2OC(O)Co(CO)_4$ complexes as proved by an independent synthesis starting from the alcohol $RC_6H_4CH(CH_3)CH_2OH$ and $ICo(CO)_4$.[51a,c] $PhCH(CH_3)CH_2OC(O)Co(CO)_4$: IR ν(C–O) (*n*-hexane) 2117.4 w, 2054.9 m, 2042.3 vs, 2031.2 vs, $\nu(C–O)_{org}$ 1694.3 mw. $PhCH(CH_3)CH_2OC(O)Co(CO)_3PPh_3$: IR ν(C–O) (*n*-hexane) 2059.9 m, 1995.6 vs, 1982.7 vs, $\nu(C–O)_{org}$ 1664.1 m. ^1H NMR (δ, TMS, $CDCl_3$, 80 MHz): 1.17 (d, J = 6 Hz, 3 H, CH_3), 2.85 (m, 1 H, CH), 3.29 (d, J = 6 Hz, 2 H, CH_2), ~7.3 (br s, 20 H, *Ph* groups).

Correct elemental analyses were obtained for the latter. Details of preparation of the reference complexes are described in ref 51c.

Supplementary Material Available: Anisotropic temperature parameters for **XIb** (Table 8) and **VIIh** (Table 9) (3 pages). Ordering information is given on any current masthead page.