Organometallics 1987, *6*, 861-867

Alkylcobalt Carbonyls. 8.[1] (Chloromethyl)- and (Chloroacetyl)cobalt Carbonyls[2]

Vilmos Galamb and Gyula Pályi*

Research Group for Petrochemistry of the Hungarian Academy of Sciences,
H-8200 Veszprêm, Schönherz Z.u.8., Hungary

Roland Boese and Günter Schmid

Institute of Inorganic Chemistry, University of Essen, D-4300 Essen-1, FRG

Received May 30, 1986

(Chloroacetyl)cobalt tetracarbonyl, $ClCH_2C(O)Co(CO)_4$ (**1**), was prepared by the reaction of $ClCH_2C(O)Cl$ with $Na[Co(CO)_4]$. **1** readily decarbonylates to (chloromethyl)cobalt tetracarbonyl (**2**). **1** is formed from **2** at ~5 bar of CO pressure and room temperature or at 1 bar of CO by cooling to ~-10 °C in a reversible reaction. **2** gives with PPh_3 the CO-substituted acyl derivative $ClCH_2C(O)Co(CO)_3PPh_3$ (**3**) that can be decarbonylated at 50 °C to the corresponding alkyl complex $ClCH_2Co(CO)_3PPh_3$ (**4**). **4** takes up CO even under 1 bar of pressure at room temperature. The **3** ⇌ **4** equilibrium is reversible. **1** was characterized by IR spectra, **2**–**4** could be isolated, and the structures of **3** and **4** were determined by X-ray diffraction. **2** reacts with the methoxide ion to yield $CH_2(COOMe)_2$. These results represent the first examples of (a) the carbonylation/decarbonylation reaction couple of an XCH_2M vs. $XCH_2C(O)M$ (X = Cl, Br, I; M = transition metal) pair, (b) a ligand substitution reaction of a chloromethyl complex with a tertiary phosphine, and (c) the structure determination of a chloromethyl complex as well as (d) the structural study of an alkyl-/acylcobalt carbonyl pair with the same organic group. **3** crystallizes with monoclinic symmetry in the space group $P2_1/c$ with $Z = 4$ and cell dimensions of $a = 1212.3$ (2) pm, $b = 928.9$ (3) pm, $c = 2029.9$ (4) pm, and $\beta = 104.15$ (2)°. Structure solution by Patterson methods and refinement with 3305 unique observed reflections led to a final R value of 0.057. The crystals of **4** are tetragonal of space group $P4_3$, with $Z = 4$ in a unit cell of dimensions $a = b = 1086.3$ (1) pm and $c = 1815.5$ (4) pm. The structure was determined by direct methods and refined with 4358 unique observed reflections to a final R value of 0.033.

(Chloromethyl)- and (chloroacetyl)cobalt carbonyls are at the crossroads of three main currents of transition organometallic chemistry. Alkyl- and acylcobalt carbonyls are believed to be intermediates in various important catalytic reactions.[3,4] However, well-characterized examples of non-fluorinated alkylcobalt carbonyls are surprisingly few.[5] Since polar, electronegative substituents in the α-position of the alkyl group were shown to increase the stability[6] of these compounds, (chloromethyl)cobalt carbonyls can be expected to show interesting behavior. On the other hand, most of the very few examples[7] of the preparation of geminal bis carboxylic acids or esters from geminal dihalides are catalyzed by cobalt carbonyls and (chloromethyl)cobalt carbonyl species may be postulated as reasonable intermediates.

While, however, 29 chloromethyl derivatives of 10 transition metals (Mo (1), W (1), Mn (2), Re (1), Fe (1), Ru (1), Os (1), Co (4),[16] Rh (7), Ir (3), and Pt (7)) are known, a report on the preparation of such a cobalt carbonyl derivative is still lacking. The known derivatives were prepared (Scheme I) by electrophilic (a) and nucleophilic (b–e) substitution or by oxidative addition (f). In spite of efforts (involving all transition metals in Scheme I except for Co and Os) by Dilgassa and Curtis,[17b] none of the chloromethyl complexes could be prepared via decarbonylation of the corresponding chloroacetyl derivatives.[17,18] The only report[5d] of the preparation of a (chloroacetyl)cobalt carbonyl is lacking in experimental details.[19] Decarbonylation experiments were not reported. Carbonylation of chloro-, bromo-, or iodomethyl transition-metal complexes to the corresponding acyl derivatives has not been reported either.[20]

We report here the synthesis, interconversion, and structural characterization of (chloromethyl)- and (chlo-

---

* To whom correspondence should be addressed at the Institute of General and Inorganic Chemistry, L. Eötvös University, H-1088 Budapest, Hungary.

(1) Part 7: (a) Galamb, V.; Pályi, G. *J. Chem. Soc., Chem. Commun.* 1982, 487. (b) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* 1986, *108*, 3344.

(2) Preliminary communications: (a) Galamb, V.; Pályi, G. XIXth [Hungarian] Colloquium Coordination Chemistry, Visegrád, Hungary, May 1984. (b) Galamb, V.; Pályi, G.; Boese, R.; Schmid, G. XIIth International Conference Organometallic Chemistry, Wien, Austria, Sept 1985, Abstracts, 469.

(3) Recent reviews: (a) Orchin, M. *Acc. Chem. Res.* 1981, *14*, 59. (b) Alper, H. *Adv. Organomet. Chem.* 1981, *19*, 183. (c) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* 1984, *59*, 203. (d) Alper, H. *Fundam. Res. Homogeneous Catal.* 1984, *4*, 1.

(4) Some (recent) key original literature: (a) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* 1977, *134*, C11. (b) Braterman, P. S.; Walker, B. S.; Robinson, T. H. *J. Chem. Soc., Chem. Commun.* 1977, 651. (c) Foá, M.; Francalanci, F.; Gardano, A.; Cianelli, G.; Umani-Ronchi, A. *J. Organomet. Chem.* 1983, *248*, 225. (d) des Abbayes, H.; Buloup, A.; Taguy, G. *Organometallics* 1983, *2*, 1730. (e) Alper, H.; Arzoumanian, H.; Petrignani, J.-F.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* 1985, 340. (f) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* 1985, *107*, 666. (g) Foá, M.; Francalanci, F.; Bencini, E.; Gardano, A. *J. Organomet. Chem.* 1985, *285*, 293.

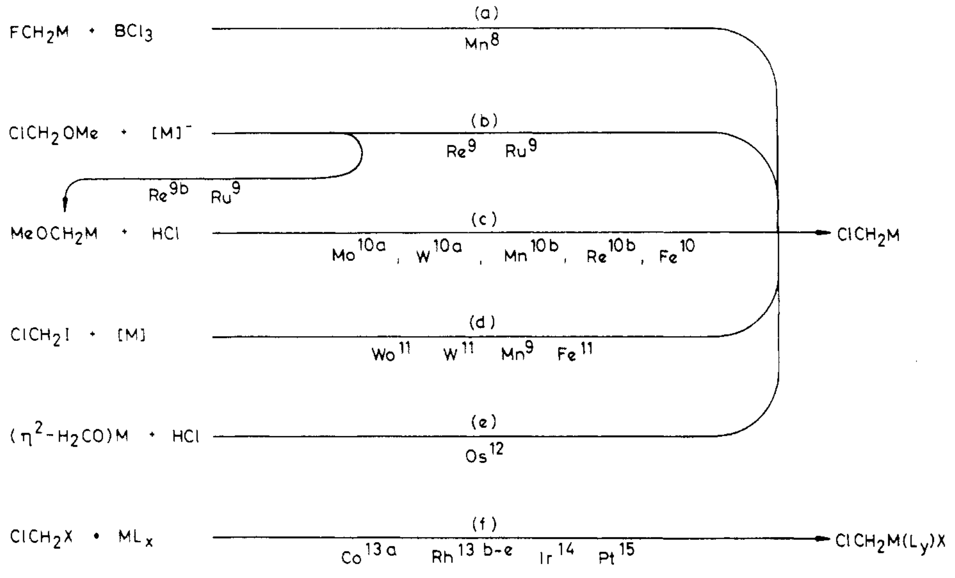
(5) $RCo(CO)_4$ (R = Me): (a) Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* 1960, *93*, 901. $RCo(CO)_4$ (R = $R'OC(O)CH_2$, R′ = various alkyl groups): (b) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* 1981, *209*, 183. (c) Pályi, G.; Galamb, V.; Röder, A. *Atti Accad. Sci. Bologna, Cl. Sci. Fis.* 1981, *269*(13/8), 67. $RCo(CO)_4$ (R = $NCCH_2$): (d) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1962, *84*, 2499. (e) Francalanci, F.; Gardano, A.; Abis, L.; Foá, M. *J. Organomet. Chem.* 1983, *251*, C5. $RCo(CO)_4$ (R = $[\eta^6\text{-}Cr(CO)_3]C_6H_5CH_2$): ref 1.

(6) The meaning of this word is often confused: we mean here the kinetic stability against CO insertion, decomposition, or β-elimination in the sense of: Wilkinson, G. *Chimia* 1972, *27*, 165.

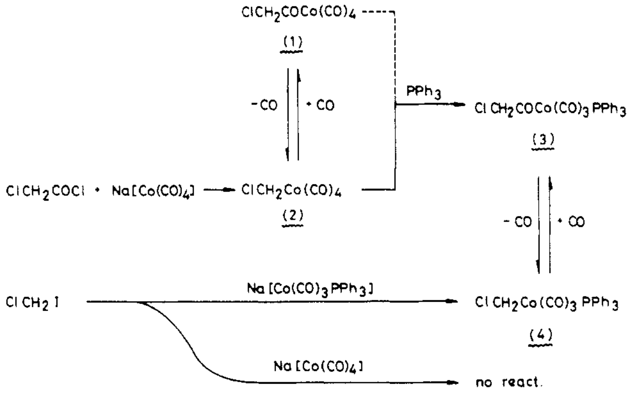
(7) $H_2CX_2 + ROH + CO \rightarrow H_2C(COOR)_2$ ($X_2 = Cl_2$ or ClBr) catalyzed by Co carbonyls: (a) Kato, I.; Takakura, M.; Ogawa, T.; Hiraoka, M. (Nippon Soda Co. Ltd.) Japan Kokai 7807613, 1978. (b) Sonoda, N.; Tanaka, H.; Hirano, A.; Haitani, H. (Nihon Nohyaku Co. Ltd.) Japan Kokai Tokkyo Koho 7955516, 1979. (c) Sonoda, N.; Tanaka, H.; Hirano, A.; Haitani, H. 7955515, 1979. $ArCH{=}CBr_2 + CO + OH^- \rightarrow ArCH{=}C(COOH)_2$, catalyzed by a Pd complex: (d) Galamb, V.; Gopal, M.; Alper, H. *Organometallics* 1983, *2*, 801.

0276-7333/87/2306-0861$01.50/0

Scheme I



Scheme II



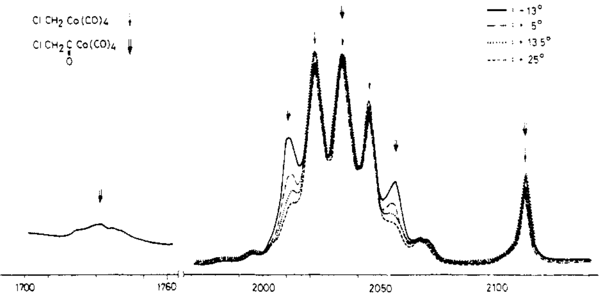


Figure 1. Infrared ν(CO) spectra of the equilibrium mixtures of **1** and **2** under 1 bar of CO (n-hexane) at different temperatures.

roacetyl)cobalt carbonyls: these are the first examples of the synthesis of a chloromethyl complex via decarbonylation of the corresponding acylmetal compound[17c] (of CO insertion into the metal–alkyl bond in a chloromethyl transition-metal complex), a ligand substitution reaction of a tertiary phosphine with a chloromethyl complex,[21] a structural study of a chloromethyl complex,[22,25] and an

---

(8) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305.

(9) (a) Botha, C.; Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1981**, *220*, C21. (b) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221.

(10) (a) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508. (b) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (c) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926. (d) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

(11) King, R. B.; Braitsch, D. M. *J. Organomet. Chem.* **1973**, *54*, 9.

(12) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Mardsen, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7.

(13) (a) Hofmann, L.; Werner, H. *J. Organomet. Chem.* **1985**, *289*, 141. (b) Werner, H.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C71. (c) Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* **1985**, *281*, 317. (d) Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261. (e) Paul, W.; Werner, H. *Chem. Ber.* **1985**, *118*, 3032.

(14) (a) Mango, F. D.; Dvoretzky, I. *J. Am. Chem. Soc.* **1966**, *88*, 1654. (b) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236. See also ref 17c.

(15) (a) Young, B. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808. (b) Scherer, O. J.; Jungmann, H. *J. Organomet. Chem.* **1981**, *208*, 153. (c) Kermode, J. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698. (d) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. *J. Organomet. Chem.* **1982**, *232*, C78.

(16) The chemistry of (haloalkyl)cobalamin and related complexes is not within the scope of this paper. About a dozen $ClCH_2Co$ derivatives are reported in this field. Some reviews: (a) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1. (b) Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* **1973**, *11*, 332. (c) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 417; **1977**, *16*, 233. (d) Cardin, D. J. *J. Organomet. Chem. Libr.* **1978**, *6*, 397. (e) Kemmitt, R. D. W.; Russel, D. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 1–276.

(17) An early effort with Mn: (a) Calderazzo, F.; Nocack, K.; Schaerer, U. *J. Organomet. Chem.* **1966**, *6*, 265. A more recent systematic study: (b) Dilgassa, M.; Curtis, D. M. *J. Organomet. Chem.* **1979**, *172*, 177. Decarbonylation in the coordination sphere of a coordinatively unsaturated $ClCH_2C(O)IrL_x$ complex succeeded, yielding the saturated $ClCH_2Ir(CO)L_x$ derivative: (c) Blake, D. M.; Vinson, A.; Dye, R. *J. Organomet. Chem.* **1981**, *204*, 257.

(18) This could be expected on the basis of the behavior of fluoroalkyl complexes. Some relevant reviews: (a) Treichel, P. L.; Stone, F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143. (b) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177. (c) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. Key original papers: (d) Ref 8 of this paper. (e) Hieber, W.; Wagner, G. *Justus Liebigs Ann. Chem.* **1958**, *618*, 24. (f) Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, *618*, 24. (g) McClellan, W. R. *J. Am. Chem. Soc.* **1961**, *83*, 1595. (h) King, R. B. *Inorg. Chem.* **1963**, *2*, 531. (i) King, R. B.; *J. Am. Chem. Soc.* **1963**, *85*, 1918. (j) McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 4096. (k) King, R. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(19) Reference 5d reports the preparation of $ClCH_2C(O)Co(CO)_3PPh_3$ by a "one-pot" synthesis starting from $ClCH_2COX$ (X = Cl or Br (not specified)), $Na[Co(CO)_4]$, and PPh_3. The product was characterized by C and H analysis and a melting point of 88–90 °C dec.

(20) Two recent papers provide confirmation of this statement: (a) Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495. (b) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

(21) Chloromethyl transition-metal complexes are reported to react with PR_3 ligands yielding either the corresponding ylide ($M–CH_2PR_3$) or the 1,2-halogen shift ($M(PR_3)Cl$) product: ref 20a and Kaska, W. C. *Coord. Chem. Rev.* **1984**, *48*, 1. Perhaps the "one-pot" synthesis[13a] of $[(C_5H_5)Co(CH_2Cl)(PMe_3)L](PF_6)$ (L = PMe_3, $P(OMe)_3$, CNMe) complexes from $(C_5H_5)Co(CO)PMe_3$ in the presence of excess L represents another example of ligand substitution.

(22) Reference 15b cites an "unpublished" structural study[23] on a $PtCH_2Cl$ complex. This study has not been published yet.[24]

alkylcobalt vs. acylcobalt carbonyl pair with the same organic group II in both the alkyl and the acyl groups.[1,3c]

Results and Discussion

Preparative Observations. The preparative findings are summarized in Scheme II. Since our attempts to obtain (chloromethyl)cobalt tetracarbonyl from the reaction of $ClCH_2I$ with $Na[Co(CO)_4]$ failed,[26] we tried the acylcobalt/decarbonylation route although this did not seem very hopeful on the basis of published data.[5c,17] Surprisingly, the reaction of chloroacetyl chloride with $Na[Co(CO)_4]$ at low temperature (0 °C) yielded solutions containing a mixture of two mononuclear cobalt carbonyls, (chloroacetyl)- (**1**) and (chloromethyl)cobalt tetracarbonyls (**2**). The bands due to **2** were predominant already in the IR spectra of samples taken in the initial stage of the reaction (measured at room temperature).

The solutions that were believed to contain a mixture of **1** and **2** reversibly released and absorbed CO in quantities, exceeding changes in the solubility of CO with the variation of pressure or temperature. This was accompanied by characteristic and reversible changes in the infrared $\nu(CO)$ spectra (Figure 1) that allowed the identification of the band systems belonging to **1** and **2**, respectively. Application of $\sim$5 bar of CO pressure at room temperature had approximately the same effect as cooling to −10 °C.

Compound **1** was too unstable to be isolated, but **2** could be obtained analytically pure.

It is interesting to note that the decarbonylation of **1** was always accompanied by the formation of some $Co_2(CO)_8$. This may arise either from β-Cl elimination in **1**[17,27] and subsequent fast decomposition of $ClCo(CO)_4$[28] or from $Co_2(CO)_8$ elimination from a dinuclear compound that may be $(CO)_4CoCH_2COCo(CO)_4$.[29]

Both solutions containing predominantly **1** or **2** reacted with PPh_3 to yield (chloroacetyl)cobalt tricarbonyl triphenylphosphine (**3**). In the case of **1** it cannot be excluded that **1** first decarbonylates to **2** that then reacts with PPh_3. The reaction of **2** with PPh_3 represents the first example where a chloromethyl transition-metal complex reacts with tertiary phosphine yielding a ligand (CO) substitution product,[20a,21] and at the same time it is the first observation of a ligand-induced migratory insertion reaction in this compound class.[20,30]

Table I. IR and ^1H NMR Spectra of the New Compounds

compound	IR $\nu(CO)$,[a] cm^{-1}	^1H NMR δ[d]
$ClCH_2C(O)Co(CO)_4$ (**1**)	2112 w-m, 2058 s, 2040, 2012 s[b,f]	*c*
$ClCH_2Co(CO)_4$ (**2**)	2112.4 m, 2047.6 s, 2037.2 vs, 2024.8 vs[f]	3.76 (s, 2 H, CH_2)[e]
$ClCH_2C(O)Co(CO)_3PPh_3$ (**3**)	2056.5 w, 1990.5 vs, 1965.5 vs, 1702.0 m[g]	4.35 (s, 2 H, CH_2), 6.9–7.6 (m, 15 H, Ph)[e]
$ClCH_2Co(CO)_3PPh_3$ (**4**)	2050.0 vw, 1984.8 vs, 1972.1 vs[h]	4.60 (s, 2 H, CH_2), 6.9–7.6 (m, 15 H, Ph)

[a] Calibrated with the simultaneously registered spectrum of C_6H_6. [b] This compound could not be obtained in pure form; the absorption maxima were determined from the spectra of mixtures with **2** and some $Co_2(CO)_8$. [c] Decomposed during measurement. [d] Me_4Si as an internal standard. [e] In C_6D_6. [f] In *n*-hexane. [g] In cyclohexane. [h] In *n*-pentane.

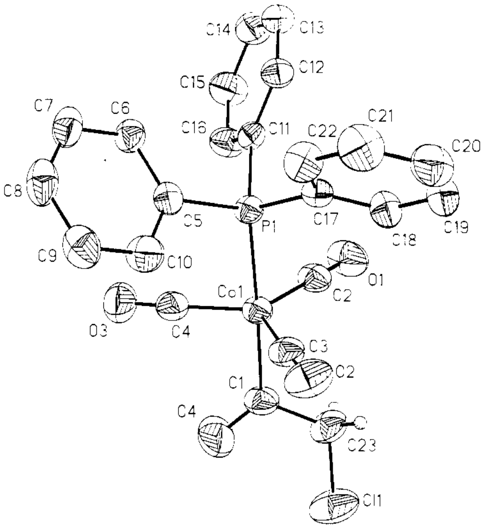


Figure 2. Structure of $ClCH_2C(O)Co(CO)_3PPh_3$ (**3**).

The chloroacetyl complex **3** could be smoothly decarbonylated ($\sim$40 °C) yielding the corresponding chloromethyl derivative $ClCH_2Co(CO)_3PPh_3$ (**4**). Both compounds **3** and **4** could be isolated in pure form and characterized by spectroscopic methods and X-ray diffraction.

The alkyl derivative **4** can easily be carbonylated under mild conditions (1 bar of CO, 20–40 min, room temperature, *n*-heptane). The carbonylation/decarbonylation experiment can be repeated 2–3 times without significant loss in concentration.

It is interesting to compare the relative stability of the **1**/**2** and **3**/**4** couples. Obviously the substitution of one CO by a phosphine increases the stability of the acyl more than that of the alkyl derivative. A reason for this may be that the acyl ligand is a better π-acceptor than the alkyl group.

Compound **4** could be obtained independently also from $ClCH_2I$ and $Na[Co(CO)_3PPh_3]$, following the "classical" route of King.[11a] In this case the carbonylate anion appears to be sufficiently nucleophilic.[31]

An attempt has been made[32] to see whether the chemistry described above can really be linked to the alkoxycarbonylation of dihalomethanes. It has been found that methoxide ion reacts with **2** yielding $[ClCH_2Co(COOMe)(CO)_3]^-$ (**5**)[33] at low temperature (−40 °C). This complex decomposes rapidly when the solution is warmed

---

(23) Krüger, C.; Tsay, Y. H., unpublished results, 1981.

(24) Krüger, C. personal communication, 1985.

(25) The only published structural study of an XCH_2ML_x (X = Cl, Br, or I; M = transition metal) complex concerns a (iodomethyl)platinum derivative.[15c]

(26) Most probably due to the very low nucleophility of $[Co(CO)_4]^-$: (a) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (b) King, R. B. *J. Organomet. Chem.* **1975**, *100*, 111. See also ref 18c.

(27) (a) Bevan, W. I.; Haszeldine, R. N.; Young, J. C. *Chem. Ind.* (*London*) **1961**, 1080. (b) Wilford, J. B.; Forrester, A.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 6519. (c) Clark, H. C.; Tsansg, W. S. *J. Am. Chem. Soc.* **1967**, 89, 529. (d) King, R. B.; Bisnette, M. S. *J. Organomet. Chem.* **1967**, 7, 311. (e) Lukas, J.; Visser, J. P.; Kouwenhoven, A. P. *J. Organomet. Chem.* **1973**, *50*, 349.

(28) $XCo(CO)_4$ (X = Cl, Br, or I) decomposes fast to CoX_2 and $Co_2(CO)_8$. The order of decreasing stability was found to be I > Br > Cl. (a) Pankowski, M.; Bigorgne, M. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264C*, 1382. (b) Tasi, M.; Pâlyi, G. *Organometallics* **1985**, *4*, 1523.

(29) A similar reaction is supposed to proceed quantitatively in reactions of $Na[(C_5H_5)Fe(CO)_2]$.[17b,18h]

(30) A marked difference from the behavior of the structurally similar alkoxymethyl complexes, for example: ligand substitution, ref 10d; CO insertion: Bodnar, T.; Coman, G.; LaCroce, T.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2471 and ref 20a.

(31) A dramatic preparative example: Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 1744.

(32) Sâmpâr-Szerencsés, E.; Galamb, V.; Pâlyi, G. unpublished results.

(33) This ionic species could not be isolated yet. Its structure is based on IR spectra, as described in the Experimental Section.

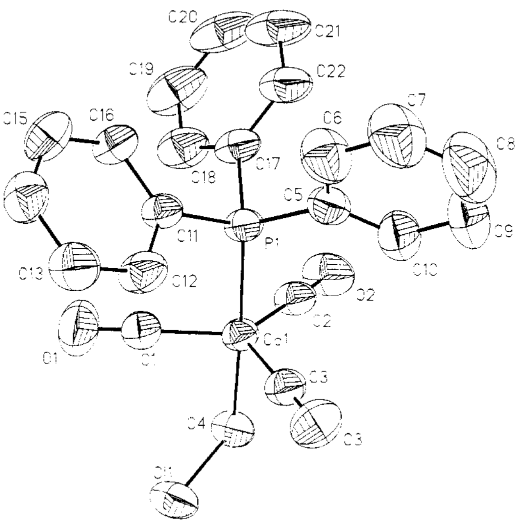


Figure 3. Structure of $ClCH_2Co(CO)_3PPh_3$ (4).

Table II. Comparison of Co–C(organic) Distances[a] of Alkyl- and Acylcobalt Carbonyls

compound	Co—C-(organic) dist, pm	ref
$ClCH_2Co(CO)_3PPh_3$ (4)	202.2 (3)	this work
$CHF_2CF_2Co(CO)_3PPh_3$	195 (3)	42
$PhCH_2OC(O)CH_2Co(CO)_3PPh_3$	210.9 (8)	5b
$[\eta^1\text{-}(\eta^6\text{-}4\text{-}MeC_6H_4CH_2)Cr(CO)_3]Co(CO)_4$	212.6 (7)	1
$ClCH_2C(O)Co(CO)_3PPh_3$ (3)	199.9 (5)	this work
$MeOC(O)Co(CO)_3PPh_3$	197.6 (*b*)	43
$(2,6\text{-}Cl_2C_6H_3)CH_2C(O)Co(CO)_3PPh_3$	199.6 (4)	1

[a] Esd's in parentheses. [b] Not given.

either in the absence or in the presence of $ClCH_2I$.[34] Reaction mixtures obtained in this way contained 10–55% (with respect to the Co) dimethyl malonate. Further studies are in progress in order to explore this aspect of (chloromethyl)cobalt carbonyls.

Structural Studies. The ν(CO) and ^1H NMR data of the complexes prepared in this work are collected in Table I. These indicate trigonal-bipyramidal structures with an axial alkyl or acyl group for compounds **1**–**4**[35,36] and a relative trans position of the organic and phosphine ligands in **3** and **4**.[37,38]

Considering the uncertainties in the structure assignment on the basis of IR and NMR data as well as the lack of structural studies on chloromethyl transition-metal complexes, the structures of compounds **3** and **4** were determined by X-ray crystallography. The structures are shown in Figures 2 and 3, respectively. The following conclusions can be made on the basis of the structural parameters (Tables II and III).

(i) The overall geometry of compounds **3** and **4** was confirmed as containing a trans bis-axial array of the non-carbonyl ligands. Since infrared studies of the reaction mixtures of the conversions **2** → **1** or **4** → **3** never showed the presence of any band system that could be attributed to another isomer of **1** or **3**; this structural result has an important implication in the mechanism of the 1,2-alkyl migration reaction of alkylcobalt carbonyls. The only relevant study[39] (isotopic labeling) suggests that CO insertion in alkylcobalt carbonyls proceeds by a 1,2-alkyl migration mechanism. This, however, would require an equatorial position of the acyl group in the primary product.[40] The actual structural and infrared results thus indicate that the formation of the acyl derivative is accompanied or followed by a fast rearrangement of (one of) the intermediate(s) or the primary (equatorial) reaction product.[41]

Table III. Bond Lengths (pm) and Bond Angles (deg) for 3 and 4

3		4	
	Bond Lengths		
Co(1)–P(1)	225.4 (1)	Co(1)–P(1)	222.3 (1)
Co(1)–C(2)	179.2 (4)	Co(1)–C(2)	179.3 (3)
Co(1)–C(4)	179.1 (5)	C3(1)–C(4)	202.2 (3)
P(1)–C(11)	181.8 (3)	P(1)–C(11)	182.4 (2)
Cl(1)–C(23)	171.4 (7)	Cl(1)–C(4)	179.4 (3)
C(1)–O(4)	118.0 (7)	C(2)–O(2)	113.0 (3)
C(3)–O(2)	114.0 (6)	Co(1)–C(1)	178.6 (3)
C(23)–H(23a)	68.4 (35)	Co(1)–C(3)	177.1 (3)
Co(1)–C(1)	199.9 (5)	P(1)–C(5)	181.7 (2)
Co(1)–C(3)	177.7 (5)	P(1)–C(17)	181.9 (2)
P(1)–C(5)	182.5 (3)	C(1)–O(1)	113.5 (4)
P(1)–C(17)	181.6 (3)	C(3)–O(3)	114.8 (3)
C(1)–C(23)	149.9 (8)		
C(2)–O(1)	112.8 (6)		
C(4)–O(3)	113.5 (7)		
C(23)–H(23b)	98.4 (53)		
	Bond Angles		
P(1)–Co(1)–C(1)	174.5 (1)	P(1)–Co(1)–C(1)	91.6 (1)
C(1)–Co(1)–C(2)	91.6 (2)	C(1)–Co(1)–C(2)	119.1 (1)
C(1)–Co(1)–C(3)	85.7 (2)	C(1)–Co(1)–C(3)	121.7 (1)
P(1)–Co(1)–C(4)	92.4 (2)	P(1)–Co(1)–C(4)	177.6 (1)
C(2)–Co(1)–C(4)	113.6 (2)	C(2)–Co(1)–C(4)	88.6 (1)
Co(1)–P(1)–C(5)	113.9 (1)	Co(1)–P(1)–C(5)	116.4 (1)
Co(1)–P(1)–C(17)	114.4 (1)	Co(1)–P(1)–C(17)	113.5 (1)
Co(1)–C(1)–O(4)	125.6 (4)	Co(1)–C(2)–O(2)	178.0 (2)
Co(1)–C(2)–O(1)	117.7 (4)	Co(1)–C(4)–Cl(1)	114.9 (1)
Co(1)–C(4)–O(3)	177.3 (4)	P(1)–C(5)–C(10)	119.3 (1)
P(1)–C(5)–C(10)	118.4 (1)	P(1)–C(11)–C(16)	122.0 (1)
P(1)–C(11)–C(16)	119.2 (1)	P(1)–C(17)–C(22)	121.6 (1)
P(1)–C(17)–C(22)	121.5 (1)	P(1)–Co(1)–C(2)	91.9 (1)
Cl(1)–C(23)–H(23a)	103.0 (33)	P(1)–Co(1)–C(3)	94.0 (1)
Cl(1)–C(23)–H(23b)	107.3 (37)	C(2)–Co(1)–C(3)	118.7 (1)
H(23a)–C(23)–H(23b)	118.2 (43)	C(1)–Co(1)–C(4)j	86.0 (1)
P(1)–Co(1)–C(2)	93.5 (2)	C(3)–Co(1)–C(4)	87.8 (1)
P(1)–Co(1)–C(3)	89.9 (2)	Co(1)–P(1)–C(11)	113.1 (1)
C(2)–Co(1)–C(3)	121.2 (2)	Co(1)–C(1)–O(1)	178.7 (3)
C(1)–Co(1)–C(4)	87.3 (2)	Co(1)–C(3)–O(3)	178.9 (2)
C(3)–Co(1)–C(4)	124.9 (2)	P(1)–C(5)–C(6)	120.6 (1)
Co(1)–P(1)–C(11)	115.7 (1)	P(1)–C(11)–C(12)	117.9 (1)
Co(1)–C(1)–C(23)	116.9 (4)	P(1)–C(17)–C(18)	118.4 (1)
C(23)–C(1)–O(4)	117.2 (5)		
Co(1)–C(3)–O(2)	177.4 (5)		
P(1)–C(5)–C(6)	121.6 (1)		
P(1)–C(11)–C(12)	120.8 (1)		
P(1)–C(17)–C(18)	118.5 (1)		
Cl(1)–C(23)–C(1)	117.9 (4)		
C(1)–C(23)–H(23a)	100.5 (34)		
C(1)–C(23)–H(23b)	110.3 (36)		

---

[34] Foá et al. observed that the presence of excess alkyl halide (RX) was favorable for obtaining RCOOR′-type products from alcoholic (R′OH) solutions of $[RCo(COOR')(CO)_3]^-$ (R = $EtOC(O)CH_2$, N≡CCH_2) complexes.[4g,5e]

[35] For the description and analysis of the spectra of $RCo(CO)_4$ compounds see ref 1, 3c, 5b, c, and 33.

[36] (a) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184. (b) Bor, G. *Inorg. Chim. Acta* **1967**, *1*, 81.

[37] The ν(CO) spectrum is in accord with a bis-axial C_{3v} geometry,[3c,5b,c] but it is far from proving it. A further argument can be deduced from the P–H coupling between the PPh_3 ligand and the α-CH_2 group.[35].

[38] Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944. See also ref 1 and 5b.

[39] The "inserted" carbonyl is coming from the coordination sphere: Nagy-Magos, Z.; Bor, G.; Markó, L. *J. Organomet. Chem.* **1968**, *14*, 205.

[40] The following excellent reviews cover all basic information in this field: (a) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Markó, L. *Fundam. Res. Homogeneous Catal.* **1984**; 4, 1. (d) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

(ii) The Co–C(organic) distances of compounds **3** and **4** (Table II) are very similar. This may be one reason for the relatively easy interconversion of these compounds. Both values are nearer to those measured for the two known acylcobalt carbonyl structures than to the nonfluorinated alkylcobalt carbonyls.

(iii) The Cl–C distance in **3** falls between the ranges expected for Cl–C(sp^2) and Cl–C(sp)[44] bonds. This can be explained by a conjugative-type interaction[45] between the acyl CO group (or even the metal carbonyl fragment) and the chlorine atom. This is in agreement also with the fact that the C(H$_2$)–C(O) distance is somewhat shorter than that in the only comparable acylcobalt carbonyl structure.[1b]

The low value of the Cl–C bond distance is in good agreement with the absence of β-halogen elimination in **3**, which is an important reaction path for other (chloroacetyl)metal complexes.[17]

(iv) The Cl–C bond distance in **4** is essentially that expected for Cl–C(sp^3) bonds.[44] This is in marked difference to the situation in fluorinated alkylcobalt carbonyls. For example, $CHF_2CF_2Co(CO)_3PPh_3$ shows a lengthening of the F–C bonds in the α-position with respect to the standard F–C(sp^3) values or to those found in the β-position. This situation was explained[46] by the assumption that beyond the Co–alkyl σ-bond formed by the overlap of the Co(dsp) (hybrid) and the C(sp^3) (hybrid) orbitals, another dπ → σ* component is also of importance, one which increases the stability of the Co–alkyl bond, resembling to some extent the well-known retrodative bond. This is also reflected in the short Co–C(alkyl) distance (Table II) in this compound. The relatively short Co–C(alkyl) bond in compound **4** indicates a similar situation, where, however, the electron density from the cobalt is taken up not only by a σ* (antibonding) but (due to the more accessible p and d orbitals of the chlorine than those of the fluorine) also by a π-type (bonding) interaction. This picture would serve to attribute some sp^2 character to the methylene carbon that is in fact well-reflected by the relatively large low-field shift of the protons (Table I) on this carbon with respect to the value of the comparable compound EtOOC*C*H$_2$Co(CO)$_3$PPh$_3$ (2.35 ppm).[5b]

It should be added to this analysis that more structural knowledge on other chloromethyl and chloroacetyl transition-metal complexes would be of fundamental importance to gain a better understanding of the reactivity consequences of the structure in this compound class.[47]

Experimental Section

All reactions were carried out under deoxygenated CO or Ar by using carefully dried (Na) solvents. The IR spectra were run on Specord 75 (Carl Zeiss, Jena, GDR), ^{1}H NMR spectra on 80-MHz BS-487 (Tesla, Brno, CSSR), and mass spectra on JMS-01 SG-2 (JEOL, Tokyo, Japan) instruments. GC measurements were performed by using a Hewlett-Packard (Avondale, PA, USA) 5830/A instrument and a 25-m glass capillary column[48] coated with SP 2340. Starting compounds were of commercial origin with the exception of $Co_2(CO)_8$[49] and $ClCH_2I$,[50] which were prepared by published procedures.

Reaction of Chloroacetyl Chloride with Na[Co(CO)$_4$]. Dicobalt octacarbonyl, $Co_2(CO)_8$ (340 mg, 1.0 mmol), in 30 mL of dry Et$_2$O was vigorously stirred with 1.5% Na[Hg] (ca. 30 g) until a colorless solution was observed. After 20 min of standing, the clear solution was decanted into a Schlenk tube under Ar and cooled to 0 °C. With stirring, chloroacetyl chloride, $ClCH_2COCl$ (143 μL, 203 mg, 1.80 mmol), was added at once. The solution immediately turned red-brown, and a white precipitate (NaCl) separated. After 15 min of stirring the ether was removed at 0 °C in vacuo, and the residue was dissolved in 30 mL of *n*-pentane.

The *n*-pentane solution was filtered under Ar, and then the filtrate was cooled to −78 °C for 1 h to remove the byproduct $Co_2(CO)_8$ (if it was present, as checked by IR). The supernatant liquid was decanted and the solvent removed under high vacuum at −10 to −15 °C, giving a brown oil that gave satisfactory Co analysis for **2**, yield, 350–375 mg (88–95%) of ($ClCH_2Co(CO)_4$ (**2**). Anal. Calcd for $C_5ClCoH_2O_4$: Co, 26.73. Found: Co, 26.6. If the *n*-pentane solution was cooled to −78 °C under CO for a prolonged period, large needlelike light green crystals were formed that melted at 5–8 °C with vigorous CO evolution to give a brown oil. This crystalline material is believed to be **1**.

Preparation of ClCH$_2$C(O)Co(CO)$_3$PPh$_3$ (3). To a stirred ethereal solution (30 mL) of **2** (prepared as described before from 1.8 mmol of $ClCH_2COCl$) was added PPh$_3$ (472 mg, 1.8 mmol) at 0 °C under CO. CO evolution started immediately, and some brown precipitate was formed while the solution turned greenish yellow. After 10–15 min of stirring, the mixture was filtered rapidly and the clear solution cooled to −78 °C. An equal volume of cold *n*-pentane was layered over the ethereal solution. After 1–2 days of standing on dry ice, greenish yellow crystals formed. These were filtered in the cold and dried by vacuum as quickly as possible: yield 146–205 mg (17–24% based on PPh$_3$); mp 105–108 °C dec (compare ref 5d and 19).

Preparation of ClCH$_2$Co(CO)$_3$PPh$_3$ (4). To a solution of **2** in Et$_2$O (30 mL) (prepared from 1.8 mmol of $ClCH_2COCl$) were added *n*-heptane (30 mL) and PPh$_3$ (472 mg, 1.8 mmol). The mixture was stirred at 40–50 °C for 2–3 h. A brown precipitate was formed, and the solution turned pale yellow. After the solution was cooled to room temperature, the brown precipitate ($Co_2(CO)_6(PPh_3)_2$ as identified by its IR ν(CO) spectrum[51]) was filtered and the filtrate cooled to −78 °C. The off-white crystalline material was separated and dried under vacuum. A further crop could be obtained by evaporating the ether from the mother liquor and cooling the solution again. The separated crude crystals could be recrystallized by using hot *n*-heptane: yield (of almost colorless crystals), 350–420 mg (43–51% based on PPh$_3$): mp 153–155 °C dec (turned green at 122–125 °C). Anal. Calcd for $C_{22}ClCoH_{17}O_3P$: Cl, 7.80; Co, 12.96; P, 6.81. Found: Cl, 7.3; Co, 12.9; P, 7.0.

Low-Temperature and High Pressure IR Studies. Low-temperature experiments were carried out in a thermostated reaction flask/flow-through infrared cell closed system under atmospheric pressure of CO.[52] Spectra under pressure were registered by using a common high-pressure infrared cell.

(a) Detection of 1. To an ethereal solution of 2 mmol of Na[Co(CO)$_4$] (prepared as above from 2 mmol of $Co_2(CO)_8$ in 30 mL of Et$_2$O) was added 1.8 mmol of chloroacetyl chloride at −9 °C in a thermostated reaction flask. The formation of a white precipitate started immediately. From time to time the stirring was interrupted, the precipitate left to settle, and the clear liquid pumped through the infrared cell. The spectra showed a single broad band at ca. 1725 cm^{-1} (attributed[1,36a] to the acyl ν(CO) band of **1**) that gradually disappeared on warming the solution to room temperature. Additionally, the broad band centered at ca. 2040

---

[41] In the case of manganese both *cis*- and *trans*-MeC(O)Mn(CO)$_4$L could be identified: (a) Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1965**, *4*, 250. (b) Kraihanzel, C. S.; Maples, P. K. *J. Am. Chem. Soc.* **1965**, *87*, 5267.

[42] Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1967**, 2092.

[43] Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

[44] Accepted characteristic Cl–C(sp^n) bond distances: $n = 3$, 178 ppm; $n = 2$, 174 ppm; $n = 1$, 164 ppm. Trotter, J. *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Wiley: London, 1973; Part 1, pp 49–62.

[45] Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *11*, 96.

[46] (a) Churchill, M. R. *Inorg. Chem.* **1967**, *6*, 185. (b) Einstein, F. W. B.; Luth, H.; Trotter, J. *J. Chem. Soc. A* **1965**, 89. (c) van den Berg, G. C.; Oskam, A. *J. Organomet. Chem.* **1975**, *81*, 1.

[47] Structural studies of $ClCH_2COMn(CO)_5$, $ClCH_2Mn(CO)_5$, and $ClCH_2Mn(CO)_4PPh_3$ will be started in the near future. Moss, J. R., personal communication, 1985.

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

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

[50] Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2864.

[51] (a) Vohler, O. *Chem. Ber.* **1958**, *91*, 1235. (b) Palágyi, J.; Pályi, G.; Markó, L. *J. Organomet. Chem.* **1968**, *14*, 238.

[52] Constructed by C. D. Hoff and M. Tasi.

cm^{-1} gradually sharpened on increasing the temperature ($\nu_{1/2}$ at -9° = 49 cm^{-1} and $\nu_{1/2}$ at +22° - 38 cm^{-1}).

(b) 1 ⇌ 2 Equilibrium at Different Temperatures. A *n*-hexane solution (~0.1 M) of **2** was prepared. This solution was gradually cooled (from room temperature) under CO in the reaction vessel/flow-through cell equipment. As the temperature was lowered (to a minimum of -13 °C), two new bands appeared in the 2000–2140 cm^{-1} region at 2012 and 2058 cm^{-1} with increasing intensities. The relative intensity of the bands at 2037.2 and 2024.8 cm^{-1} (which is 1:1 at room temperature) showed a small change (1.05:1 at -13 °C). Additionally a new broad band appeared at ~1730 cm^{-1}.

The observed changes were reversible; when the solution was warmed, again to room temperature, the original spectrum was observed.

(c) 1 ⇌ 2 Equilibrium under CO Pressure. A *n*-hexane solution (~0.1 M) of **2** was filled into a high-pressure infrared cell and pressurized by 5.5 bars of CO at room temperature. The spectrum had exactly the same shape as that at low temperature (-10 to -13 °C) under atmospheric pressure, i.e. new bands appeared at 2012, 2058, and 1730 cm^{-1}. As could be estimated from the relative intensities, roughly one-third of **2** was converted to **1** under 5.5 bars of CO. When the pressure was released, the starting spectrum of **2** was observed again.

Detection of the 3 ⇌ 4 Equilibrium by IR Spectroscopy. The saturated solution of **4** in *n*-hexane was stirred under a CO atmosphere at room temperature. After a few minutes, a greenish yellow substance started to precipitate. This precipitate was pure **3** as shown by its ν(CO) spectrum. The spectrum of the solution showed the presence of both **3** and **4**. The ratio of these compounds did not change afterwards, but more and more greenish yellow precipitate was formed. On the other hand, when the atmosphere was changed to Ar, the precipitate gradually redissolved and finally only the presence of **4** was observed in the infrared spectra. Decarbonylation could be accelerated either by bubbling Ar through the solution or by heating the reaction mixture to 40–50 °C.

The Reaction of Na[Co(CO)$_3$PPh$_3$] with ClCH$_2$I. $Co_2(CO)_6(PPh_3)_2$ (810 mg, 1 mmol) was suspended in THF (50 mL). The suspension was stirred with 1.5% Na[Hg] (~30 g) until a light yellow solution was observed. After 1 h of standing, the clear solution was decanted into a Schlenk tube and chilled to 0 °C, under Ar. To the stirred solution was added dropwise (~10 min) $ClCH_2I$ (330 mg, 1.9 mmol), dissolved in 20 mL of THF. Then the cooling bath was removed, and the reaction mixture was gently refluxed for 1 h. During this period the color turned green, and some precipitate was formed. In the reaction mixture **4** was identified by its infrared ν(CO) spectrum (THF, 1946.5 w, 1983.4 vs br cm^{-1}).

Alkoxycarbonylation Experiments. (a) Complex **2** was prepared (as described earlier) from $ClCH_2COCl$ (1.8 mmol) in Et_2O (30 mL) at 0 °C under Ar atmosphere. Then the solvent (Et_2O) was drawn off at -5 °C, and the residue was dissolved in THF (or methanol) (30 mL). This solution was thermostated to -40 °C. Sodium methoxide, $NaOCH_3$ (290 mg, 5.4 mmol, 3-fold excess with respect to **2**), was dissolved in methanol (3.6 mL). The solution of the methoxide was added to the cold solution of **2** in six equal parts, while the reaction mixture was stirred at -40 °C. Infrared spectra were taken after each portion. These indicated the presence of $[Co(CO)_4]^-$ and an other band system of about roughly $^1/_3$ to $^1/_{10}$ intensity of the former. These weaker bands were relatively better developed in THF. The new band system consisted of a weak band at ~2020 cm^{-1} and a strong broad band centered at 1960 cm^{-1}. This band pattern and the circumstances of the formation of the new species are quite similar to those of the $[XCH_2Co(COOMe)(CO)_3]^-$ (X = N≡C–, EtOC(O)–),[4g,5e,53] $[ICo(COOR)(CO)_3]^-$ (R = alkyl, aryl),[28b] and $[Co(COOR)_2(CO)_3]^-$ (R = Me, $PhCH_2$)[28b] anionic complexes,[54] Thus the new band system was attributed to $[ClCH_2Co(COOMe)(CO)_3]^-$ (**5**).

Table IV. Crystal Data and Details of the Structure Determination of 3 and 4

	3	4
	Crystal Data	
formula	$C_{23}H_{17}ClCoO_4P$	$C_{22}H_{17}ClCoO_3P$
space group	$P2_1/c$	$P4_3$
cryst system	monoclinic	tetragonal
a, pm	1212.3 (2)[55]	1086.3 (1)[56]
b, pm	928.9 (3)	
c, pm	2029.9 (4)	1815.5 (4)
α, deg	90	90
β, deg	104.15 (2)	90
γ, deg	90	90
V, 10^9 pm^3	2.216.8 (8)	2.142.3 (6)
Z	4	4
d(calcd), g/cm^3	1.36	1.41
F(000)	984	928
μ, cm^{-1}	9.86	10.16
	Data Collection and Reduction	
diffractometer	Nicolet R3	Nicolet R3
radiatn, pm	Mo Kα (71.069)	Mo Kα (71.069)
temp, K	294–296	294–296
cryst dimens, mm	0.31 × 0.24 × 0.18	0.32 × 0.28 × 0.46
scan technique	$2\theta/\omega$	2θ–ω[57]
2θ (min–max), deg	2–55	2–50
scan speed, deg/min	2–30	2–30
no. of unique reflctns	5084	5041
no. of unique obsd reflctns	3305	4358
σ criterion	4.5	3.5
emp absorptn correctn[58] min/max transmissn	0.16/0.20	none
R(Merg) (before and after correctn)	0.026 and 0.010	
	Structure Determination and Refinement	
method of phase determination	Patterson	direct
programs	SHELXTL[59]	SHELXTL[59]
scattering factors	neutral[60]	neutral[60]
R and R_w[61]	0.057 and 0.056	0.033 and 0.033
weight (w)	$1/(\sigma^2(F) + 0.00045F^2)$	$1/(\sigma^2(F) + 0.00035F^2)$
no. of parameters	243	219
ratio of observns to parameters	13.6:1	19.9:1
max shift/error	0.005	0.027
residual electron density, e/Å^3	0.53	0.38
goodness of fit	1.67	1.11

After the last portion of the methoxide solution had been added the temperature of the reaction mixture was gradually raised to room temperature in 2 h. The resulting solution was analyzed

---

(53) Vlaic, G.; Bart, J. C. J.; Foá, M.; Francalanci, F.; Clement, R. *J. Organomet. Chem.* **1985**, *287*, 369.

(54) Some further examples of addition of ionic species to mononuclear complexes. Co: (a) Foá, M.; Cassar, L. *J. Organomet. Chem.* **1971**, *30*, 123. Mn: (b) Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1965**, *4*, 250. (c) Casey, C. P.; Bunnel, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.

(55) Same as for **4**, reflections in the 2θ range 5–23°.

(56) Cell dimensions were determined by a constraint least-squares fit of 25 automatically centered and indexed reflections in the 2θ range 20–25°.

(57) The 96 step–scan technique with subsequent profile fitting and a background to scan ratio of 0.2:1 (Clegg, W. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 22. Diamond, R. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1969**, *A25*, 43).

(58) Psi scans in 10° steps of eight reflections, distributed in the 2θ range up to 35°, were measured, and an ellipsoid, close to the crystal shape was fitted to minimize the R(Merg) of the psi-scan data set. The final parameters of the ellipsoid were taken for the absorption correction of the whole data set.

(59) Sheldrick, G. M. SHELXTL, a complete system for solving, refining, and displaying crystal structures from diffraction data (Rev. 4.1); University of Göttingen: Göttingen, Federal Republic of Germany, 1983.

(60) Scattering factors were taken as incorporated in SHELXTL.

(61) $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. $R_w = \sum((|F_o - F_c|)w^{1/2})/\sum(|F_o|w^{1/2})$.

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^{-1}) for 3

atom	*x*	*y*	*z*	U^b
Co(1)	1517 (1)	3055 (1)	1010 (1)	44 (1)
P(1)	2824 (1)	1789 (1)	631 (1)	41 (1)
Cl(1)	−1172 (1)	4394 (2)	2140 (1)	94 (1)
C(1)	480 (4)	4237 (6)	1422 (2)	56 (2)
C(2)	350 (4)	2006 (5)	537 (2)	55 (2)
C(3)	2217 (4)	2599 (5)	1860 (3)	55 (2)
C(4)	1780 (4)	4654 (6)	580 (3)	57 (2)
C(5)	4148^a	2764^a	677^a	46 (1)
C(6)	4688 (2)	2733 (3)	145 (1)	52 (2)
C(7)	5722^a	3447^a	208^a	64 (2)
C(8)	6214^a	4191^a	804^a	70 (2)
C(9)	5673^a	4222^a	1337^a	72 (2)
C(10)	4640^a	3509^a	1273^a	66 (2)
C(11)	2387^a	1190^a	−248^a	41 (1)
C(12)	2827 (2)	−71 (3)	−456 (1)	49 (2)
C(13)	2489^a	−507^a	−1133^a	56 (2)
C(14)	1709^a	318^a	−1602^a	68 (2)
C(15)	1269^a	1579^a	−1394^a	71 (2)
C(16)	1608^a	2015^a	−717^a	58 (2)
C(17)	3294^a	149^a	1103^a	44 (1)
C(18)	2479 (2)	−737 (3)	1275 (2)	60 (2)
C(19)	2809^a	−2015^a	1630^a	77 (2)
C(20)	3955^a	−2406^a	1812^a	84 (3)
C(21)	4770^a	−1520^a	1639^a	85 (3)
C(22)	4440^a	−242^a	1285^a	65 (2)
C(23)	−394 (4)	3439 (7)	1689 (3)	68 (2)
O(1)	−393 (3)	1383 (4)	224 (2)	82 (2)
O(2)	2647 (3)	2255 (5)	2401 (2)	83 (2)
O(3)	1908 (4)	5657 (4)	288 (2)	89 (2)
O(4)	554 (4)	5489 (4)	1520 (3)	106 (2)

[a] Only one C of the phenyl rings was determined; the rest were treated as rigid moieties; cf. Experimental Section. [b] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

by infrared spectroscopy and GC. The infrared spectra revealed the presence of $[Co(CO)_4]^-$ and sometimes a weak band system that was similar to that of the starting complex **2**. GC analyses showed the presence of dimethyl malonate as the only major organic product. 1,2-Dichloroethane, 1,3-dichloroacetone, dimethyl succinate, or methyl chloroacetate were not present. Quantitative GC analysis was carried out by using dimethyl succinate as internal standard. Yields: 0.17 mmol, 9.5% (THF solvent); 0.45 mmol, 25% (methanol solvent). (Yields are calculated with respect to the starting complex **2**).

(b) The procedure was the same as that described under (a) with the difference being that when the THF (or methanol) solution of **2** was already thermostated to −40 °C, $ClCH_2I$ (635 mg, 3.6 mmol) was added. Yields: 0.44 mmol, 24.4% (THF solvent); 1.025 mmol, 56.9% (methanol solvent). (Yields of dimethyl malonate with respect to the starting complex **2**). Other organic substances mentioned under (a) were absent.

X-ray Structural Analysis of 3 and 4. Both crystals were sealed under nitrogen in glass capillaries and mounted on the diffractometer. The Laue symmetries were checked by oscillation photos. Details of the crystal data, experimental conditions, and a summary of the solution and refinement are given in Table IV. The three check reflections, measured every 100 reflections, did not show any significant variation of intensity in both data collections.

The structure solution of **3** with direct methods failed, but the position of the heavy atom could be taken from a Patterson map. Subsequent difference density maps showed the complete molecule. The phenyl groups were treated as for **4**; the methylene hydrogen atoms were free of all constraints in a final model.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^{-1}) for 4

atom	*x*	*y*	*z*	U^b
Co(1)	6924 (1)	9561 (1)	0	42 (1)
P(1)	5013 (1)	9019 (1)	296 (1)	44 (1)
Cl(1)	8838 (1)	10510 (1)	−1228 (1)	64 (1)
C(1)	6409 (3)	11000 (3)	−362 (2)	60 (1)
C(2)	7414 (2)	9482 (3)	942 (2)	54 (1)
C(3)	7164 (2)	8264 (2)	−574 (1)	51 (1)
C(4)	8636 (2)	10128 (3)	−274 (1)	53 (1)
C(5)	4726^a	7381^a	403^a	56 (1)
C(6)	3566 (2)	6890 (2)	254 (1)	83 (1)
C(7)	3337^a	5644^a	382^a	104 (2)
C(8)	4268^a	4890^a	658^a	127 (2)
C(9)	5428^a	5381^a	806^a	115 (2)
C(10)	5657^a	6626^a	678^a	81 (1)
C(11)	3876^a	9504^a	−383^a	46 (1)
C(12)	4121 (1)	9263 (2)	−1124 (1)	65 (1)
C(13)	3309^a	9672^a	−1666^a	70 (1)
C(14)	2252^a	10322^a	−1469^a	66 (1)
C(15)	2007^a	10564^a	−729^a	68 (1)
C(16)	2819^a	10155^a	−186^a	57 (1)
C(17)	4476^a	9700^a	1153^a	55 (1)
C(18)	4647 (2)	10961 (2)	1259 (1)	75 (1)
C(19)	4226^a	11520^a	1903^a	97 (2)
C(20)	3635^a	10819^a	2441^a	102 (2)
C(21)	3464^a	9558^a	2335^a	100 (2)
C(22)	3385^a	8999^a	1690^a	73 (1)
O(1)	6102 (3)	11924 (2)	−587 (2)	106 (1)
O(2)	7688 (2)	9420 (2)	1541 (1)	79 (1)
O(3)	7339 (2)	7428 (2)	−947 (1)	79 (1)

[a] Only one C of the phenyl rings was determined; the rest were treated as rigid moieties; cf. Experimental Section. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The *E* maps of **4**, derived from direct methods, showed all non-hydrogen atoms, which were clearly visible in a difference electron density map, calculated after anisotropic refinement of all non-hydrogen atoms. The phenyl groups were treated as rigid bodies (C–C distances of 139.5 ppm and C–H distances of 96 pm; C–C–C and C–C–H angles of 120°) as well as the methylene group (a C–H distance of 96 pm; a H–C–H angle of 109°). All hydrogen atoms were refined with isotropic temperature factors, riding on the 1.2-fold of the orthogonalized $\mathbf{U}_{ij}$ tensor of the corresponding C atom.

Acknowledgment. This work was supported by the Hungarian Ministry of Industry. We acknowledge discussions with and support of this work by Profs. L. Kapolyi (Budapest) and L. Markó (Veszprém) as well as Dr. G. Szilágyi (Kazincbarcika) and discussions with Profs. C. Krüger (Mülheim/Ruhr) and J. R. Moss (Rondebosch). Help in the experimental work by Mrs. E. Sâmpár-Szerencsés is gratefully acknowledged.

Registry No. **1**, 106865-86-5; **2**, 106865-85-4; **3**, 105045-07-6; **4**, 106865-87-6; **5**, 106865-88-7; $Co_2(CO)_6(PPh_3)_2$, 24212-54-2; $Co_2(CO)_8$, 10210-68-1; $[Co(CO)_4]^-Na^+$, 14878-28-5; $ClCH_2COCl$, 79-04-9; $ClCH_2I$, 593-71-5; dimethyl malonate, 108-59-8.

Supplementary Material Available: Listings of observed and calculated structure factors for **3** and **4** (60 pages). Ordering information is given on any current masthead page.