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STABLE ALKYLCOBALT CARBONYLS: [(ALKOXYCARBONYL)-METHYL]COBALT TETRACARBONYL COMPOUNDS *

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Summary

Stable alkylcobalt carbonyls of the general formula $ROOCCH_2Co(CO)_3L$ (R = alkyl, CH_2Ph; L = CO, EPh_3; E = P, As, Sb) were prepared. The molecular structure of $PhCH_2OOCCH_2Co(CO)_3(PPh_3)$ was determined by X-ray diffraction.

Introduction

Alkylcobalt carbonyls are believed to play a key role in hydroformylation and several related homogeneous catalytic reactions. However, in spite of their importance, they have been poorly characterizied because of their instability. In general, the alkylcobalt tetracarbonyls, $RCo(CO)_4$ (I), are almost immediately converted into the corresponding acyl derivatives (II) [3—5], and stable compounds of type (I) could be isolated only with fluorinated R groups [6—8]. Somewhat less stable solutions of I for R = CH_2Ph have also been characterized [9].

Our attention was turned to the title compounds as models of the α-formylation of acrylates.

Results and discussion

Preparative results

Almost two decades ago Heck and Breslow [4] studied the reaction between $Na[Co(CO)_4]$ and $BrCH_2COOEt$ (IVb) and identified the products as III, a

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[*] Some of the results described here were presented at Conferences [1,2].

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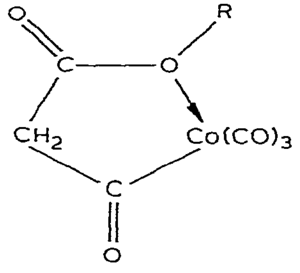
chelated acyl compound, on the basis of gas volumetric measurements (no CO was absorbed) and poorly resolved IR spectra [10].



(III)

In our experiments, the compounds IVa—IVf reacted according to eq. 1.

$$R'OOCCH_2X + Na[Co(CO)_4] \xrightarrow[0^\circ C]{Et_2O} R'OOCCH_2Co(CO)_4 + NaX \qquad (1)$$

(IVa, X = Cl, R' = Et;	(Va, R' = Et;
IVb, X = Br, R' = Et;	Vb, R' = CH_2Ph;
IVc, X = Br, R' = CH_2Ph;	Vc, R' = t-Bu;
IVd, X = Br, R' = t-Bu;	Vd, R' = (*S*)-(—)-2 MeBu;
IVe, X = Br, R' = (*S*)-(—)-2 Me-Bu;	Ve, R' = (1*R*, 3*R*, 4*S*)-(—)-menthyl)
IVf, X = Br, R' = (1*R*, 3*R*, 4*S*)-(—)-menthyl)	

Reaction 1 proceeded smoothly in Et_2O at —10 to 0° C to give almost quantitative yields. It made no difference whether an Ar or CO atmosphere (0.1 MPa) was used.

The products (V) are brownish-red oils, readily soluble in hydrocarbons. Their structures are based upon analysis (cf. Experimental), chemical and spectroscopic evidence as well as on an X-ray diffraction study.

The chemical evidence for our suggested structure is as follows.

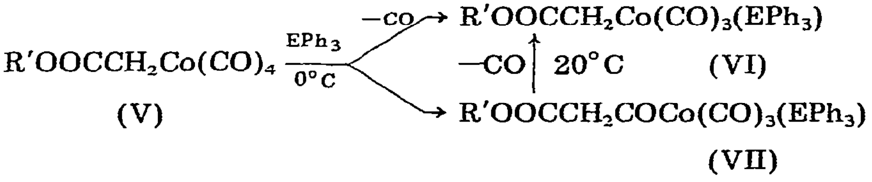
(i) No CO absorption was observed in reaction 1.

(ii) On decomposition of compounds V with I_2/EtOH, 4 mol of CO were evolved per Co atom.

(iii) Reaction of Va with $HCo(CO)_4$ led to the formation of 1 mol of CH_3COOEt *.

(iv) Treatment of Va with aniline yielded *N*-phenyl-glycine ethyl ester.

(v) Reaction of V with EPh_3 (E = P, As, Sb) ligands at 0° C give mixtures of the corresponding alkyl VI and acyl VII derivatives as shown by the IR spectra. VII decomposed to VI upon further stirring at 20° C for 6—8 h and the evolution of 1 mol of CO per Co atom was observed for the overall reaction eq. 2:



$$\begin{tikzcd}
 & & R'OOCCH_2Co(CO)_3(EPh_3) \\
\underset{(V)}{R'OOCCH_2Co(CO)_4} \arrow[r, "EPh_3", "0^\circ C"'] & {} \arrow[ur, "-CO"] \arrow[dr] & (VI) \\
 & & \underset{(VII)}{R'OOCCH_2COCo(CO)_3(EPh_3)} \arrow[uu, "-CO"', "20^\circ C"]
\end{tikzcd} \qquad (2)$$

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* This reaction represents the first example of a reaction between an alkylcobalt tetracarbonyl and $HCo(CO)_4$, and can be regarded as a two-step hydrogenolysis of the C—X bond in IVa and IVb.

TABLE 1

INFRARED ν*(C—O) SPECTRA OF THE ALKYL COBALT CARBONYLS PREPARED*

(Solvent: n-hexane; DCl calibration, values in cm^{-1})

Compound	ν(C—O) terminal			ν(C—O) organic	ν(C—O) organic [b]
Va	2111.5m; 2027.0vs;	2046.5s;	2036.5vs;	1720.0m	1748; 1764(sh)
Vb	2112.0m; 2028.5vs;	2047.0s;	2038.0vs;	1722.0w	1748; 1770(sh)
Vc	2111.0m; 2027.0vs;	2046.0s;	2036.0vs;	1710.5w	1740; 1760(sh)
Vd	2111.0m; 2027.0vs;	2046.0s;	2035.5vs;	1717.5m	1746; 1764(sh)
Ve	2111.0m; 2027.0vs;	2045.5s;	2036.0vs;	1712.0w	1743; 1758(sh)
VI(R = Et, E = P)	2050.5vw;	1985.5vs;	1973.5s	1712.0m	
VI(R = CH_2Ph, E = P) [a]	2048.0vw;	1983vs;	1971.0vs	1698.0w	
VI(R = t-Bu, E = P)	2048.0vw;	1983.5vs;	1972.0vs	1699.0w	
VI(R = 2 MeBu, E = P)	2050.0vw;	1985.0vs;	1974.5vs	1708.5w	
VI(R = Men. E = P)	2049.0w;	1985.0s;	1975.0s	1705.5w	
VI(R = Et, E = As)	—	1984.5s;	1973.0vs	1713.0w	
VI(R = Et, E = Sb)	—	1983.5s;	1972.0vs	1713.0w	

[a] in CCl_4 solution. [b] Data of the corresponding $BrCH_2COOR$ compounds. The higher wave number band corresponds to the *cis*-, the lower to the *gauche*-form [14].

Compounds VI precipitated out as powders, and after recrystallization from ether/pentane, gave greenish-yellow crystals.

Spectra

The IR ν(C—O) spectra (Table 1) of compounds V show four terminal CO absorptions. This indicates a reduction of the C_{3v} symmetry of compounds I [11,12] and excludes the presence of an acylcobalt tricarbonyl isomer (as e.g. III) with the same elemental composition.

Comparison of the terminal ν(C—O) spectra of some alkyl cobalt carbonyls, including V, in Table 2 leads to the surprising conclusion that the effect of the COOR group on the values of the average terminal ($\bar{\nu}_t$) and the $\nu(A_1^2)$ * frequencies must be approximately equal to that of a fluorine substituent. At the same time the "organic" ν(C—O) bands appear at 1720—1710 cm^{-1}, i.e., at surprisingly low frequencies compared with those in the corresponding (starting) bromoacetic acid esters, which absorb at ~45 cm^{-1} (*cis*-form [14]) or ~25 cm^{-1} (*gauche*-form [14]) higher wavenumbers.

Kahn and Bigorgne [13] deduced a group electronegativity value for the $Co(CO)_4$ group approximately equal to that of iodine (2.5). On this bases, a much higher organic ν(C—O) frequency was expected for compounds V. This was verified experimentally: we examined the ν(C—O) frequency of ICH_2COOEt (in n-hexane) and found only one band at 1743 cm^{-1} **.

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* As a first approximation this frequency can be assigned to the CO group *trans* to the organic ligand; and may be regarded as characteristic of the electronic effect of the latter.

** This band probably corresponds to the *gauche*-form; the absence of the *cis*-form is obviously due to the steric effect of the large iodine atom.

TABLE 2

COMPARISON OF THE TERMINAL ν(C—O) FREQUENCIES OF SOME I COMPOUNDS

Compound	Terminal ν(C—O) absorptions (cm^{-1}) [a]			$\bar{\nu}_t$ [b]	Ref.
	$A_1{}^1$	$A_1{}^2$	E		
$CF_3Co(CO)_4$	2135	2075	2050	2077.5	8
$CHF_2Co(CO)_4$	2122	2059	2042 2038	2065.3	23
$CH_2FCo(CO)_4$	2120	2048	2036 2034	2059.5	23
$HCo(CO)_4$	2116.1	2053.3	2029.8	2057.3	12
$EtOOCCH_2Co(CO)_4$	2111.5	2046.5	2036.5 2027.0	2055.4	c
$CH_3Co(CO)_4$	2104.6	2035.5	2018.5	2044.3	5,12
$(CH_3)_3CCo(CO)_4$	2104	2033	2015	2041.8	13

[a] Assignment according to ref. 12. [b] $\bar{\nu}_t = \nu(A_1{}^1) + \nu(A_1{}^2) + 2\,\nu(E)/4$. [c] This work, (Va).

Although similar tendencies were observed for compounds VI, the effect of the Group V ligand was also present and thus the situation was not as clear-cut as with the unsubstituted compounds.

The high mean terminal and the low organic ν(C—O) values for V and VI suggest an electron transfer from the metal or/and from (one of) the equatorial carbonyl group(s) to the carbalkoxy group. *

The ^{1}H and ^{13}C NMR results (Tables 3 and 4) should provide some further structural information, but the absence of comparative data ** renders interpretation difficult. The $^3J(^1H, ^{31}P)$ and $^3J(^{13}C, ^{31}P)$ values of the "alkyl" CH_2 group indicate [16] a trigonal bipyramidal structure for compounds VI (cf. the X-ray results), with the organic and pnicogenic *** ligands in the axial positions.

The extreme low-field signal observed for the carboxylic carbon also suggest, a lower electronegativity of the $Co(CO)_4$ group. as expected from data given in ref. 13.

X-ray diffraction; the structure of $PhCH_2OOCCH_2Co(CO)_3(PPh_3)$

The greenish-yellow crystals of VI (R = CH_2Ph, E = P) are triclinic. 2547 independent reflections with $F > 2\sigma$ were obtained. The unit cell parameters were found to be a = 1037.0(1), b = 1060.1(2), c = 1289.1(2) pm, α 87.41(1), β 74.48(1), γ 80.62(1), V = 1347.3.10^6 pm^3; ^{d}calc. = 1.367 g cm^{-3}, $\mu(\lambda$ Mo—$K)$ = 7.6 cm^{-1}, Z = 2, the space group initially was assumed to be $P1$ or $P\bar{1}$.

Statistical distribution of normalized structure factors was close to the theoretical for an acentric model. The structure was solved by the direct method using a MULTAN program + under the assumption of space group $P1$. An

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* More information is needed about the nature of this interaction. Relevant MO studies are currently being performed (Prof. M. Bán, Szeged, and Dr. F. Cser, Budapest).

** The ^{13}C NMR spectrum of the carbonyl groups of $CF_3Co(CO)_4$ [15] provides the only relevant NMR data for alkylcobalt carbonyls.

*** "Pnicogenic" refers to the Group VA elements and their derivatives [24].

+ All calculations were performed with Syntex-EXTL programs and an Eclipse /S200 Computer.

TABLE 3

^{1}H NMR SPECTRA (TMS internal standard)

Compound	Solvent	δ (ppm)	Multiplicity	Intensity	Assignment	Note
$CH_3COOCH_2CH_3$	$CDCl_3$	1.25	t	3	$-\mathrm{CH_2}-CH_3$	
		2.03	s	3	$CH_3-\mathrm{CO}-$	
		4.12	q	2	$-CH_2-\mathrm{CH_3}$	
$BrCH_2COOCH_2CH_3$	CCl_4	1.26	t	3	$-\mathrm{CH_2}-CH_3$	
		3.86	s	2	$-CH_2-\mathrm{CO}-$	
		4.17	q	2	$-CH_2-\mathrm{CH_3}$	
$ICH_2COOCH_2CH_3$	CCl_4	1.20	t	3	$-\mathrm{CH_2}-CH_3$	
		3.55	s	2	$-CH_2-\mathrm{CO}-$	
		4.05	q	2	$-CH_2-\mathrm{CH_3}$	
$(CO)_4CoCH_2COOCH_2CH_3$	C_6D_6	0.95	t	3	$-\mathrm{CH_2}CH_3$	
		1.95	s	2	$-\mathrm{Co}-CH_2-$	
		3.90	q	2	$-CH_2-\mathrm{CH_3}$	
$PPh_3(CO)_3CoCH_2COOCH_2CH_3$	C_6D_6	0.98	t	3	$-\mathrm{CH_2}-CH_3$	
		2.35	d	2	$-\mathrm{Co}-CH_2-$	$^3J(^1\mathrm{H}-^{31}\mathrm{P})$: 3 Hz
		4.02	q	2	$-CH_2-\mathrm{CH_3}$	
$AsPh_3(CO)_3CoCH_2COOCH_2CH_3$	C_6D_6	1.01	t	3	$-\mathrm{CH_2}-CH_3$	
		2.38	s	2	$-\mathrm{Co}-CH_2-$	
		4.03	q	2	$-CH_2-\mathrm{CH_3}$	

TABLE 4

^{13}C NMR SPECTRA (TMS internal standard)

Compound	Solvent	δ(ppm)	Multi-plicity	Assignment	Note
$CH_3COOCH_2CH_3$	—	13.80	s	$-CH_2-CH_3$	
		20.00	s	CH_3-CO-	$^1J(^{13}C-^1H) = 130$ Hz
		59.80	s	$-CH_2-CH_3$	
		170.00	s	$-COO-CH_2$	
$BrCH_2COOCH_2Ph$	—	26.40	s	$-CH_2-COO-$	$^1J(^{13}C-^1H) = 155$ Hz
		67.40	s	$-CH_2-Ph$	
		166.80	s	$-COO-CH_2$	
$(CO)_4CoCH_2COOCH_2Ph$	C_6D_6	7.60	s	$-CoCH_2-$	
		66.50	s	$-CH_2-Ph$	
		177.20	s	$-COO-CH_2-$	
		196.10	br	$Co-CO$	
$PPh_3(CO)_3CoCH_2COOCH_2Ph$	C_6D_6	5.60	d	$-Co-CH_2-$	$^1J(^{13}C-^1H) = 143.2$ Hz $^3J(^{13}C-^{31}P) = 16.8$ Hz
		66.70	s	$-CH_2-Ph$	
		179.80	s	$-CO-CH_2-$	
		199.50	d	$Co-CO$	$^3J(^{13}C-^{31}P) = 22.0$ Hz
$AsPh_3(CO)_3CoCH_2COOCH_2CH_3$	C_6D_6	5.90	s	$-CO-CH_2$	
		15.20	s	$-CH_2-CH_3$	
		60.50	s	$-CH_2-CH_3$	
		180.60	s	$-COOCH_2$	
		200.30	s	$Co-CO$	

TABLE 5

ATOMIC COORDINATES OF Va

Atom	G	*X*(SD)	*Y*(SD)	*Z*(SD)	*B*(SD)
Co	1.0	0.53416(9)	0.30496(9)	0.31913(8)	—
P	1.0	0.3327(2)	0.2821(2)	0.3021(1)	—
O(1)	1.0	0.5058(7)	0.1417(6)	0.5099(6)	—
O(2)	1.0	0.6618(6)	0.1933(6)	0.1061(5)	—
O(3)	1.0	0.4681(7)	0.5788(6)	0.3604(6)	—
O(4)	0.5	0.889(1)	0.2355(9)	0.1876(8)	4.7(2)
O(5)	0.5	0.840(1)	0.126(1)	0.341(1)	4.2(3)
O(4′)	0.5	0.796(1)	0.115(1)	0.423(1)	7.3(3)
O(5′)	0.5	0.889(1)	0.146(1)	0.253(1)	6.8(3)
C(1)	1.0	0.5163(7)	0.2039(7)	0.4342(7)	—
C(2)	1.0	0.6112(8)	0.2365(7)	0.1902(7)	—
C(3)	1.0	0.4910(8)	0.4717(8)	0.3432(7)	—
C(4)	1.0	0.7254(7)	0.3301(8)	0.3354(8)	—
C(5)	0.5	0.829(1)	0.238(1)	0.277(1)	3.1(3)
C(5′)	0.5	0.811(2)	0.183(2)	0.345(2)	4.4(4)
C(6)	1.0	0.9500(9)	0.0170(9)	0.278(1)	—
C(7)	1.0	0.883(1)	−0.0643(9)	0.2212(9)	—
C(8)	1.0	0.948(1)	−0.102(1)	0.116(1)	—
C(9)	1.0	0.892(1)	−0.181(1)	0.0639(9)	—
C(10)	1.0	0.777(1)	−0.227(1)	0.114(1)	—
C(11)	1.0	0.707(1)	−0.186(1)	0.221(1)	—
C(12)	1.0	0.765(1)	−0.1071(9)	0.2744(9)	—
C(13)	1.0	0.2692(7)	0.3926(7)	0.2058(5)	—
C(14)	1.0	0.3567(8)	0.4719(7)	0.1419(6)	—
C(15)	1.0	0.306(1)	0.5564(8)	0.0680(7)	—
C(16)	1.0	0.178(1)	0.5580(9)	0.0559(8)	—
C(17)	1.0	0.0938(9)	0.4769(9)	0.1203(8)	—
C(18)	1.0	0.1392(8)	0.3930(8)	0.1959(6)	—
C(19)	1.0	0.1942(6)	0.3008(6)	0.4266(5)	—
C(20)	1.0	0.2004(7)	0.3797(7)	0.5085(6)	—
C(21)	1.0	0.0962(8)	0.3978(8)	0.6008(7)	—
C(22)	1.0	−0.0174(9)	0.3379(8)	0.6136(7)	—
C(23)	1.0	−0.0258(8)	0.2590(8)	0.5342(7)	—
C(24)	1.0	0.0837(7)	0.2372(7)	0.4374(7)	—
C(25)	1.0	0.3293(6)	0.1240(6)	0.2534(6)	—
C(26)	1.0	0.3342(8)	0.1086(7)	0.1446(6)	—
C(27)	1.0	0.3395(9)	−0.0161(9)	0.1074(8)	—
C(28)	1.0	0.3359(9)	−0.1201(9)	0.1797(9)	—
C(29)	1.0	0.3315(8)	−0.1017(8)	0.2885(8)	—
C(30)	1.0	0.3283(7)	0.0202(7)	0.3258(7)	—

E-synthesis and a number of successive Fourier series identified 72 atoms out of 74 ($R = 20.1\%$). However, further attempts to refine the structure by isotropic least squares decreased the *R*-factor by only 2%.

A centrosymmetrical version of the structural model and a further refinement within the $P\bar{1}$ space group gave $R = 14.3\%$. At this stage, some previously missing atoms (of the ester group) were identified, though still unsatisfactorily, in both ordinary and acentric space groups. Moreover, bond distances and angles in the ester group were far from their standard values.

Another attempt, assuming a $P\bar{1}$ space group with an ester group occupying two equally populated positions, led to a considerably better *R*-factor of 6.7%. The atomic coordinates obtained in this manner are summarized in Table 5.

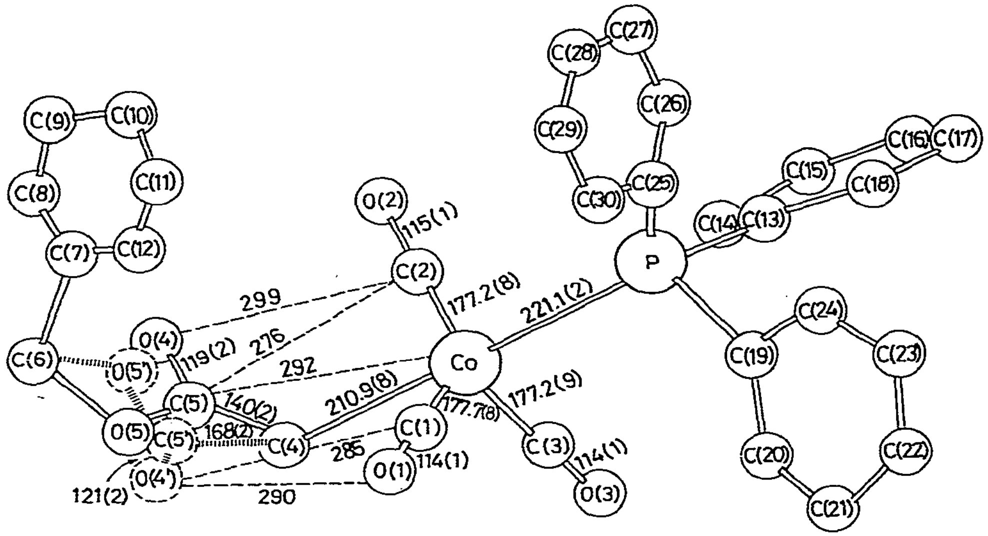

Fig. 1. ORTEP representation of the structure of $PhCH_2OOCCH_2Co(CO)_3(PPh_3)$. (Full and dotted lines in the ester group indicate the two conformers.)

The overall geometry and additional important geometric data are shown in Fig. 1.

The two "isomers" depecited in Fig. 1. are, however, still approximations of a more or less continuous series of conformers between these limiting cases. This supposition is based on continuous "trajectories" of atoms C(5), O(4) and O(5) in the Fourier maps between their positions given in Fig. 1. Moreover, it is in accordance with the still non-standard values of the C—C and C—O distances within the ester group. This observation can be interpreted as the first direct evidence of a tunnelling-type solid state rearrangement [17].

Despite the interesting crystallographic evidence of disorder in the ester group, the structural data do not support the spectroscopic conclusion based on geometric parameters within the ester group. Nevertheless, even if these uncertainties are taken into account it can be stated that the C(5)—Co distances in all possible C(5) positions, and the C(5)—C(2); O(4)—C(2) and O(4)—O(2), as well as the C(5')—C(1); O(4')—C(1) and O(4')—O(1) distances are within the sums of the standard values of the Van der Waals radii (C—C 370 pm, C—O 370 pm, Co—C 385 pm, Co—O 354 pm [18]). These distances are short enough to be consistent with, but not short enough to prove unambigously, interaction(s) between the organic carbonyl group and the cobalt carbonyl part of the molecule as suggested on the basis of the spectroscopic observations.

A further noteworthy feature of the structure is the long Co—C(sp^3) distance, which exceeds the sum of the covalent radii (202 pm [19]). This value, when viewed in the light of the stability of compounds V and VI with respect to intramolecular CO-insertion, implies that the mechanism of the stabilization of the cobalt-alkyl system must be different from that proposed [8,20] for the fluorinated alkylmetal carbonyls. The possibilities include those deduced from the spectroscopic data.

The overall shape of the molecule supports the trigonal bipyramidal structure, with *trans* P and C(sp^3) atoms, as concluded from the spectroscopic data.

Experimental

All operations were performed with careful exlusion of air under dry, deoxygenated Ar or CO.

The starting materials were mostly of commercial origin with the exception of $Co_2(CO)_8$, which was made using the high-pressure method of Szabó et al. [21], and of some haloacetic acid esters, which were synthesized by conventional methods.

IR spectra were taken with a UR-20 (Carl Zeiss, Jena, GDR) spectrophotometer, using simultaneous DCl calibration [22]. ^1H NMR spectra were recorded with a BS-487 (Tesla, Brno, CSSR) 80 MHz instrument, and ^{13}C NMR spectra with a XL-100 FT (Varian, Palo Alto, USA) 25.2 MHz spectrometer. The NMR measurements were taken from 100—250 mg/ml solutions (including 3—5 mg/

TABLE 6

ANISOTROPIC TEMPERATURE FACTORS OF VA

Atom	B_{11}(SD)	B_{22}(SD)	B_{33}(SD)	B_{12}(SD)	B_{13}(SD)	B_{23}(SD)
Co	0.0078(1)	0.0069(1)	0.00546(8)	—0.0039(2)	—0.0041(1)	—0.0013(1)
P	0.0082(2)	0.0066(2)	0.0052(2)	—0.0031(3)	—0.0045(3)	—0.0008(3)
O(1)	0.023(1)	0.0175(9)	0.0107(6)	—0.010(2)	—0.016(1)	0.009(1)
O(2)	0.0173(9)	0.0156(8)	0.0069(5)	—0.004(1)	—0.002(1)	—0.004(1)
O(3)	0.025(1)	0.0080(7)	0.0181(8)	—0.006(1)	—0.009(2)	—0.004(1)
C(1)	0.0100(9)	0.0097(9)	0.0082(7)	—0.005(1)	—0.008(1)	0.001(1)
C(2)	0.0105(9)	0.0094(9)	0.0070(7)	—0.006(1)	—0.005(1)	0.000(1)
C(3)	0.011(1)	0.0093(9)	0.0096(8)	—0.005(2)	—0.004(1)	—0.000(1)
C(4)	0.0089(9)	0.012(1)	0.0144(9)	—0.005(2)	—0.009(2)	—0.006(2)
C(6)	0.015(1)	0.011(1)	0.029(2)	0.003(2)	—0.024(3)	—0.007(2)
C(7)	0.013(1)	0.012(1)	0.013(1)	—0.002(2)	—0.009(2)	0.004(2)
C(8)	0.016(2)	0.018(2)	0.018(2)	—0.000(3)	—0.013(3)	0.012(3)
C(9)	0.020(2)	0.024(2)	0.011(1)	0.009(3)	—0.000(3)	0.006(2)
C(10)	0.024(2)	0.018(2)	0.013(1)	0.006(3)	—0.017(3)	—0.006(2)
C(11)	0.017(2)	0.017(1)	0.018(1)	—0.010(2)	—0.015(3)	0.002(2)
C(12)	0.017(1)	0.014(1)	0.015(1)	—0.013(2)	—0.008(2)	0.001(2)
C(13)	0.012(1)	0.0082(8)	0.0045(5)	0.003(1)	—0.006(1)	—0.001(1)
C(14)	0.017(1)	0.0094(9)	0.0067(7)	—0.005(2)	—0.005(2)	0.004(1)
C(15)	0.024(2)	0.011(1)	0.0073(7)	—0.001(2)	—0.009(2)	0.004(1)
C(16)	0.018(2)	0.015(1)	0.0091(9)	0.007(2)	—0.011(2)	—0.005(2)
C(17)	0.014(1)	0.016(1)	0.0091(8)	0.003(2)	—0.008(2)	—0.004(2)
C(18)	0.011(1)	0.013(1)	0.0073(7)	0.003(2)	—0.012(1)	—0.001(1)
C(19)	0.0067(8)	0.0079(8)	0.0054(5)	—0.000(1)	—0.000(1)	—0.000(1)
C(20)	0.011(1)	0.0105(9)	0.0061(6)	—0.003(2)	—0.002(1)	—0.006(1)
C(21)	0.011(1)	0.015(1)	0.0079(7)	—0.05(2)	0.000(2)	—0.006(1)
C(22)	0.014(1)	0.012(1)	0.0079(7)	—0.000(2)	—0.004(2)	—0.002(1)
C(23)	0.012(1)	0.014(1)	0.0090(8)	—0.005(2)	—0.001(2)	0.001(2)
C(24)	0.0075(9)	0.0117(9)	0.0092(7)	—0.005(2)	—0.003(1)	0.001(1)
C(25)	0.0064(8)	0.0069(8)	0.0069(6)	—0.003(1)	—0.003(1)	—0.004(1)
C(26)	0.011(1)	0.0108(9)	0.0073(7)	—0.004(2)	—0.004(1)	—0.008(1)
C(27)	0.016(1)	0.013(1)	0.0112(9)	—0.004(2)	—0.004(2)	—0.009(2)
C(28)	0.013(1)	0.011(1)	0.016(1)	—0.004(2)	—0.007(2)	—0.007(2)
C(29)	0.014(1)	0.0093(9)	0.014(1)	—0.004(2)	—0.011(2)	0.000(2)
C(30)	0.0105(9)	0.0059(8)	0.0115(8)	—0.005(1)	—0.009(1)	0.000(1)

ml $Cr(acac)_3$ as a relaxation-accelerating reagent in the case of ^{13}C NMR measurements). A MAT-111 (Varian-MAT, Bremen, GFR) GC—MS system was used for the gas chromatographic and mass spectrometric measurements.

X-ray diffraction experiments were performed with single crystals sealed in thin-walled glass capillaries. A Syntex $P2_1$ diffractometer was used with Mo-K_α radiation and graphite monochromator with $\theta/2$ scan in the $1 \leqslant 2\theta \leqslant 48°$ range. The aniosotropic temperature factors are listed in Table 6.

Preparation of $R'OOCCH_2Co(CO)_4$ (V) compounds

A solution of 0.342 g (1 mmol) $Co_2(CO)_8$ in 40 cm^3 Et_2O was shaken with 40 g 1.5% Na amalgam until a colourless solution was obtained. This was left to stand for a few hours and then transferred to a Schlenk-type vessel, cooled to 0° C, and treated dropwise with a solution of 1.9 mmol of $BrCH_2COOR$ in 5 cm^3 Et_2O. Precipitation of NaBr started almost immediately and the solution turned orange (or brownish-red in the case of R' = Men). The 1890 cm^{-1} band of the $Na[Co(CO)_4]$ disappeared in 10—20 min, and 30 min later the NaBr was filtered off. The solvent of the filtrate was evaporated at —10° C under reduced pressure. The products are brownish-red oils, readily soluble in non polar solvents (e.g. n-hexane). Yields were almost quantitative. Analyses are shown in Table 7.

Preparation of $R'OOCCH_2Co(CO)_4(EPh_3)$ (VI) compounds

To a solution of 1 mmol of the corresponding $R'OOCCH_2Co(CO)_4$ (V) compound in 20 cm^3 Et_2O, 1.05 mmol of EPh_3 was added at room temperature. Vigorous gas evolution began at once, and the colour of the solution changed from orange-red to light yellow, as a green precipitate separated. After 6—8 h stirring, CO evolution stopped, most of the precipitate redissolved, and the solution became a somewhat deeper yellow. An IR ν(C—O) band which appeared at 1690 cm^{-1} in the initial stages was attributed to the intermediate formation of $ROOCCH_2COCo(CO)_3(PPh_3)$ (VII) and stirring was continued until this band disappered. The conversion was complete for E = P, but for E = As or Sb, despite high E/Co ratios, the solutions always contained some unreacted compound V. Nevertheless, the products VI were obtained pure by crystallization.

When n-hexane was used, the decarbonylation of the primary acyl derivatives were markedly accelerated by heating to 40—50° C.

The product VI was isolated by cooling the etheral solution to —78° C and adding an equal volume of cold n-pentane. The precipitated powders were recrystallized to give greenish-yellow crystals for E = P. Repetition of this operation 2 or 3 times gave pure products. Yields: E = P, 30—40%; E = As, Sb, 15—30%. Analyses are tabulated in Table 7.

Reactions of Va

With I_2. To 1.00 cm^3 of a 0.065—0.075 molar solution of Va (at a known concentration) in Et_2O contained in a thermostated (25° C) reaction vessel was added 5 cm^3 of Et_2O and 1 cm^3 of EtOH. The solution was stirred under a CO atmosphere until equilibrium was reached between the gas and liquid phases,

TABLE 7

ANALYTICAL DATA

Compound	Formula	Molecular weight	Analyses, Found (calcd.) (%)					
			Co	P	C	H	As	Sb
$EtOOCCH_2Co(CO)_4$	$CoC_8H_7O_6$	255.05	21.2 [a] (23.11)					
$EtOOCCH_2Co(CO)_3PPh_3$	$PCoC_{25}H_{22}O_5$	492.33	12.3 (11.97)	6.6 (6.30)	61.1 (60.99)	4.4 (4.51)		
$tBuOOCCH_2Co(CO)_3PPh_3$	$PCoC_{27}H_{26}O_5$	520.43	10.8 (11.32)	6.0 (5.95)				
$PhCH_2OOCCH_2Co(CO)_3PPh_3$	$PCoC_{30}H_{24}O_5$	544.44	10.5 (10.63)	5.7 (5.59)	65.5 (64.98)	4.5 (4.37)		
$EtOOCCH_2Co(CO)_3AsPh_3$	$AsCoC_{25}H_{22}O_5$	536.28	11.3 (11.00)				13.3 (13.97)	
$EtOOCCH_2Co(CO)_3SbPh_3$	$SbCoC_{25}H_{22}O_5$	583.11	10.2 (10.11)					21.6 (20.88)

[a] The unsubstituted compounds were oils which decomposed when attempts at further purification by TLC or distillation were made.

then 0.25 g I_2 contained in a sealed glass tube was added. The level of a gas burette connected to the reaction vessel was recorded before the tube was broken with a stirrer. An immediate vigorous gas evolution began, but this stopped after ~20 min. The volume of the evolved CO was 4.2 ± 0.3 mol/Co atom. Experiments conducted under Ar gave the same results.

$HCo(CO)_4$. To 5.00 cm^3 of a 0.06 molar Va solution (in Et_2O) was added 2.00 cm^3 of a 0.3—0.4 molar solution of $HCo(CO)_4$ in n-heptane. The mixture immediately turned dark brown. After 2 h of stirring at room temperature the IR bands of Va disappeared. The volume was made up to 10.00 cm^3 with Et_2O and 10 μl of butylacetate was added as a gas chromatographic standard. The solution was analysed by GLC (3% PEG on a 3 m Chromosorb P (80/100 mesh) column, 100°C column temperature, TC detector); 0.91 mol ethyl acetate/Co atom were found.

$C_6H_5NH_2$. To 50 cm^3 of a 0.2 molar solution of Va in n-hexane containted in a thermostatted vessel was added 1.5 g of aniline. The mixture was stirred at 60°C for 2 h in a CO atmosphere. Vigorous gas evolution occurred and a precipitate separated. The mixture was filtered, and the solvent evaporated from the filtrate to give a light brown oil. This oil was analysed by GC-MS using a 3 m 3% SE 30/Chromosorb Q (80/100 mesh) column at 200°C. Besides several minor components, *N*-phenylglycine ethyl ester was identified by its mass spectrum.

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References

1 V. Galamb and G. Pályi, (a) XIIth (Hungarian) Colloquim on Coordination Chemistry, Sopron, May 23—25, 1977; (b) XIXth Internat. Conf. Coord. Chem. (ICCC) Prague, (Czechoslovakia), Sept. 4—8, 1978, Abstr. Vol. II. p. 46.
2 Yu.T. Struchkov, M.G. Furmanova, F. Cser, V. Galamb and G. Pályi, (a) XIIIth (Hungarian) Colloquim on Coordination Chemistry, Mátrafüred, May 22—24, 1979; (b) IXth Internat. Conf. Organometal. Chem. (ICOMC), Dijon (France), Sept. 3—7, 1979, Abstr. P32W.
3 D.S. Breslow and R.F. Heck, Chem. Ind. (London), (1960) 467.
4 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 84 (1962) 2499.
5 L. Markó, G. Bor, G. Almásy and P. Szabó, Brennst. Chem., 44 (1963) 184.
6 W. Hieber, W. Beck and E. Lindner, Z. Naturforsch, 16b (1961) 229; W. Hieber and E. Lindner, Chem. Ber., 95 (1960) 2042.
7 P.M. Treichel and F.G.A. Stone, Adv. Organometal. Chem., 1 (1964) 143.
8 G.C. van der Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 69 (1974) 169.
9 Z. Nagy-Magos, G. Bor and L. Markó, J. Organometal. Chem., 14 (1969) 205; A. Moro, M. Foá and L. Cassar, J. Organometal. Chem., 185 (1980) 79.

10 R.F. Heck, personal communication, 1976.
11 G. Bor, C.Sc. Thesis, Veszprém, 1966.
12 G. Bor, Inorg. Chim. Acta, 1 (1967) 82.
13 O. Kahn and M. Bigorgne, J. Organometal. Chem., 10 (1967) 137.
14 T.L. Brown, J. Amer. Chem. Soc., 80 (1958) 3513.
15 D.L. Lichtenberger and T.L. Brown, J. Amer. Chem. Soc., 99 (1977) 8187.
16 B.E. Mann, Adv. Organometal. Chem., 12 (1974) 135.
17 V.I. Gol'danski, Annu. Rev. Phys. Chem., 27 (1976) 85.
18 G. Capaccio, P. Giacomello and E. Giglio, Acta Cryst. A, 27 (1971) 229; A.I. Kitaigorodski: Organic Chemical Crystallography. Consultant Bureau, New York, 1961; F. Cser, Acta Chim. (Budapest), 80 (1974) 317; N.L. Allinger, J.A. Hirsch, M.A. Miller and I.J. Tyminsky, J. Amer. Chem. Soc., 91 (1969) 337.
19 J. Demuynck, A. Strich and A. Veillard, Nouv. J. Chim., 1 (1977) 217.
20 F.A. Cotton and R.M. Wing, J. Organometal. Chem., 9 (1967) 511.
21 P. Szabó, L. Markó and G. Bor, Chem. Techn., 13 (1961) 549.
22 G. Bor, Acta Chim. (Budapest), 39 (1962) 315.
23 E. Lindner and M. Zipper, Chem. Ber., 107 (1974) 1444.
24 E.F. Westrum, Jr., Progr. Sci. Technol. Rare Earths, 2 (1966) 76.