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Preparation and X-ray Structure of (1,2-Bis(methoxycarbonyl)ethyl)cobalt Tricarbonyl Triphenylphosphine and Its Acyl Precursor

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Summary: The sec-alkylcobalt carbonyl complex $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ (**3**) *and its acyl precursor* $MeO_2CCH_2CH(CO_2Me)C({=}O)Co(CO)_3PPh_3$ (**2**) *were prepared in 64 and 60% yields from* $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ (**1**) *and* PPh_3 *at room temperature and at 0 °C, respectively, and were characterized by IR,* ^1H, $^{13}C\{^1H\}$, *and* $^{31}P\{^1H\}$ *NMR spectroscopy. The solid-state structure of* **3** *was determined by a single-crystal X-ray diffraction technique. The compound crystallizes in monoclinic space group* $P2_1/n$ *with* $a = 1522.2(6)$ *pm,* $b = 1785.8(7)$ *pm,* $c = 988.0(4)$ *pm,* $\beta = 103.5(2)°$, $Z = 4$, *and* $R = R_w = 0.0995$.

Numerous phosphine-substituted alkylcobalt carbonyls are known.[1,2] The well-characterized examples are those in which a primary alkyl group is attached to the cobalt. They were prepared either by the reaction of an alkyl halide with phosphine-substituted carbonylcobaltate(1−) anion or, in cases where the alkyl group has electron-withdrawing substituent(s), by decarbonylation of the corresponding phosphine-substituted acyl complex.

Secondary alkylcobalt carbonyls have not been prepared by these methods. $NaCo(CO)_3PPh_3$ does not afford any carbon–cobalt-bonded species in reactions with several *sec*-alkyl (and allyl) halides.[3] Similar attempts were made with $NaCo(CO)_4$ earlier but failed to give stable alkyl- or acylcobalt tetracarbonyls.[4]

Alternatively, the reaction of $HCo(CO)_4$ with α,β-unsaturated carboxylic acid esters afforded fairly stable $RCH(CO_2R')Co(CO)_4$ complexes ($R = Me, Et, CH_2CO_2R'$; $R' = Me, Et$).[5] In this series $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ was successfully isolated,[5d] which is the parent compound of $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$, the first PPh_3-substituted secondary alkylcobalt carbonyl possessing hydrogen atoms in a position β to cobalt. Here we report the preparation and structure characterization of $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$.

Experimental Section

General Considerations. All manipulations involving air-sensitive compounds were carried out by standard Schlenk technique[6] using deoxygenated, dry solvents and gases. Infrared spectra were recorded on a Specord IR 75 (Carl Zeiss, Jena) spectrometer in a 0.061-mm solution cell with CaF_2 windows and were calibrated with benzene (1959.6 cm^{-1}) and polystyrene (1601.4 cm^{-1}). ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on Varian Unity 300 and Varian CFT 20 spectrometers. The chemical shifts were referenced to tetramethylsilane (TMS) (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P).

Preparation of (1,2-Bis(methoxycarbonyl)ethyl)cobalt Tetracarbonyl (1).[5d] A 16-mL amount of a 1 M pentane solution of $HCo(CO)_4$ (16 mmol, −60 °C) was added to a stirred solution of dimethyl fumarate (13.8 g, 96 mmol) in a CH_2Cl_2–pentane mixture (2.5:1 v/v, 400 mL) at 10 °C under CO. The CO pressure was raised to 900 mmHg, and the stirring was continued for 3 h. The resulting light brown solution was concentrated to 200 mL under vacuum at −20 °C and placed on dry ice overnight. Cold filtration at −79 °C on a P-2 glass frit gave 10.8 g of crystals (a mixture of dimethyl fumarate and $Co_2(CO)_8$) and a light reddish yellow filtrate. When the foregoing procedure was repeated twice, 1.0 and 0.2 g of solids were removed from 70- and 20-mL concentrates, respectively. The volume of the final filtrate was reduced to ca. 7 mL, 14 mL of pentane was added, and the product was crystallized at −79 °C. Cold filtering, washing with 3 × 4 mL of cold pentane, and drying under vacuum at −20 °C gave 3.27 g (65% yield) of $CH_3O_2CCH^aH^bCH^x(CO_2CH_3)Co(CO)_4$ as thermally sensitive light yellow crystals. IR (hexane): ν_{CO} 2111 m-s, 2046 s, 2036 vs, 2026 vs, 1744 m-w, 1720 w cm^{-1}. ^1H NMR ($CDCl_3$, −20 °C): δ 3.71 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 3.33 (dd, $J_{ax} = 12.45$ Hz, $J_{bx} = 3$ Hz, 1H, CH^x), 3.11 (dd, $J_{ax} = 12.45$ Hz, $J_{ab} = 17.2$ Hz, 1H, CH^a), 2.56 (dd, $J_{bx} = 3$ Hz, $J_{ab} = 17.2$ Hz, 1H, CH^b)

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ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, −15 °C): δ 194.1 (s, 3*C*O), 177.6 (s, *C*OO), 169.9 (s, *C*OO), 50.0 (s, *C*H_3), 49.8 (s, *C*H_3), 39.6 (s, *C*H_2), 20.0 (s, *C*H) ppm.

Preparation of (2,3-Bis(methoxycarbonyl)propanoyl)-cobalt Tricarbonyl Triphenylphosphine (2). To a freshly prepared light yellow solution of 1 (474 mg, 1.5 mmol) in a CO-saturated pentane–CH_2Cl_2 mixture (10:1 v/v, 12 mL) at 0 °C was added powdered PPh_3 (393 mg, 1.5 mmol) at once with stirring under a CO atmosphere. The PPh_3 dissolved within a few seconds, and the solution became pale yellow. Crystallization was initiated by scratching the inside wall with a glass rod. After 20 min the separated solid was filtered and washed with 3 × 2 mL of cold pentane and dried under vacuum at 0 °C to give 520 mg (60% yield) of light ocher crystals of $CH_3O_2CCH^aH^bCH^x(CO_2CH_3)C(=O)Co(CO)_3PPh_3$. IR ($CH_2Cl_2$): ν_{CO} 2053 w, 1987 vs, 1968 vs, 1737 s, 1663 m, 1650 m cm^{-1}. IR (KBr): ν_{CO} 2050 w, 1984 s, 1966 vs, 1736 s, 1665 m cm^{-1}. ^1H NMR ($CDCl_3$, −20 °C): δ 4.75 (dd, J_{ax} = 6 Hz, J_{bx} = 8 Hz, 1H, CH^x), 3.74 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 2.91 (dd, J_{ax} = 6 Hz, J_{ab} = 17 Hz, 1H, CH^a), 2.79 (dd, J_{bx} = 8 Hz, J_{ab} = 17 Hz, 1H, CH^b) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0 °C): δ 236.1 (d, J_{PC} = 38.6 Hz, Co*C*(=O)C), 196.9 (d, J_{PC} = 22.3 Hz, 3*C*O), 169.8 (s, *C*OO), 166.7 (s, *C*OO), 131.0 (d, J_{PC} = 11.3 Hz, *o*-C_6H_5), 130.3 (d, J_{PC} = 45 Hz, *ipso*-C_6H_5), 129.1 (d, J_{PC} = 1.8 Hz, *p*-C_6H_5), 126.9 (d, J_{PC} = 10.5 Hz, *m*–C_6H_5), 69.6 (d, J_{PC} = 23.3 Hz, *C*H), 50.5 (s, *C*H_3), 50.0 (s, *C*H_3), 31.1 (s, *C*H_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 0 °C): δ 48.9 ppm. Anal. Calcd for $C_{28}H_{24}CoO_8P$: Co, 10.2; P, 5.36. Found: Co, 10.54; P, 5.35.

Preparation of (1,2-Bis(methoxycarbonyl)ethyl)cobalt Tricarbonyl Triphenylphosphine (3). To a freshly prepared solution of 1 (680 mg, 2.15 mmol) in CO-saturated CH_2Cl_2 (8 mL) at 0 °C was added a solution of PPh_3 (620 mg, 2.36 mmol) in pentane (40 mL). After 24 h at room temperature a red-brown precipitate ($Co_2(CO)_6(PPh_3)_2$) was removed by filtration on a P4 glass frit, and the clear yellow filtrate was kept at −22 °C for crystallization. Crystals obtained in 52 h were separated from the light yellow solution with a P2 glass frit, washed with 2 × 5 mL of pentane, and dried under vacuum. This gave 570 mg (48.2% yield) of golden yellow air-stable crystals of $CH_3O_2CCH^aH^bCH^x(CO_2CH_3)Co(CO)_3PPh_3$. A second crop (193 mg, 16.3%) could be collected after concentrating the solution to about 20 mL and crystallizing at −22 °C. IR (CH_2Cl_2): ν_{CO} 2046 vw, 1981 vs, 1970 vs, 1736 m, 1697 m cm^{-1}. IR (KBr): ν_{CO} 2043 vw, 1980 vs, 1967 vs, 1729 s, 1696 m cm^{-1}. ^1H NMR ($CDCl_3$, room temperature): δ 3.68 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 3.3 (dd, J_{ax} = 11.7 Hz, J_{bx} < 5 Hz, 1H, CH^x), 3.2 (dd, J_{ax} = 11.7 Hz, J_{ab} = 16.5 Hz, 1H, CH^a), 2.7 (dd, J_{bx} < 5 Hz, J_{ab} = 16.5 Hz, 1H, CH^b) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature): δ 197.1 (d, J_{PC} = 23.1 Hz, 3*C*O), 179.8 (s, CH_2*C*OO), 170.9 (d, J_{PC} = 6 Hz, CH*C*OO), 131.1 (d, J_{PC} = 10.9 Hz, *o*-C_6H_5), 130.9 (d, J_{PC} = 47.5 Hz, *ipso*-C_6H_5), 129.2 (d, J_{PC} = 2.0 Hz, *p*-C_6H_5), 126.9 (d, J_{PC} = 10.7 Hz, *m*-C_6H_5), 49.5 (s, *C*H_3), 48.9 (s, *C*H_3), 40.2 (s, *C*H_2), 17.0 (d, J_{PC} = 19.6 Hz, *C*H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature): δ 58.2 ppm. Anal. Calcd for $C_{27}H_{24}CoO_7P$: Co, 10.72; P, 5.64. Found: Co, 10.66; P, 5.62.

Crystallographic Analysis of 3. Single crystals for structure determination were obtained by slow cooling of a solution prepared from 309 mg of 3 in 2.5 mL of CH_2Cl_2, which was diluted at 30 °C with 30 mL of pentane, to room temperature. The crystal used for data collection was mounted inside a sealed glass capillary and transferred to a Philips PW1100 automated diffractometer equipped with graphite-monochromated Mo Kα radiation. Weissenberg recordings showed a primitive lattice of monoclinic symmetry. Reflections $h0l$ only present for $h + l = 2n$ and $0k0$ only present for $k = 2n$, respectively, restrict the choice of space group to $P2_1/n$. Unit cell constants were determined by the least-squares fit of the diffractometer setting angles for 25 reflections. Intensities were measured by the θ–2θ scan method out to a maximum 2θ value of 40°. A total of 2890 unique intensities was measured, with 1654 of these satisfying the condition $F_o^2 > 4\sigma(F_o^2)$. Corrections for Lorentz and polarization effects were made in the usual manner. The positions of Co, P, C1, and O4 atoms were determined by direct phase determination methods (SHELXS-86); those of the other C and O atoms resulted from Fourier and difference Fourier syntheses (SHELX-76), where position criteria have been taken into consideration. Absorption was taken into account by a computationally supported method (DIFABS). The heavy atoms Co and P were anisotropically handled. Further crystallographic details are given in Table I. The final positions and the thermal parameters for 3 are shown in Table II. Selected bond lengths and bond angles are collected in Table III.

Table I. Crystal Data and Data Collection and Refinement Details for $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ (3)

	Crystal Data
formula	$C_{27}H_{24}CoO_7P$
fw	550.37
cryst size, mm	0.25 × 0.20 × 0.12
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, pm	1522.2(6)
b, pm	1785.8(7)
c, pm	988.0(4)
β, deg	103.5(2)
V, 10^6 pm^3	2611.5
Z	4
D_{calc}, g cm^{-3}	1.40
μ, cm^{-1}	7.45
	Data Collection and Refinement
diffractometer used	Philips PW1100
temp, K	298
radiation	Mo Kα, graphite monochromated
2θ limits, deg	5–40
scan speed, deg min^{-1}	3.6
no. of unique rflns	2890
no. of obsd rflns ($F_o^2 \geq 4\sigma(F_o)^2$)	1654
method of phase determination	direct
program	SHELXS-86 (for Co, P, C1, O4), SHELX-76 (for C and O atoms)
no. of variables	155
$R(F)^a = R_w(F)^b$	0.0995

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Results and Discussion

The addition of PPh_3 either to the isolated $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ (1) or to the *in situ* prepared reaction product of dimethyl fumarate and $HCo(CO)_4$ in pentane–CH_2Cl_2 solvent mixtures at 0 °C gave $MeO_2CCH_2CH(CO_2Me)C(=O)Co(CO)_3PPh_3$ (2) (eq 1), which was isolated as

$$\underset{1}{MeO_2CCH_2CH(CO_2Me)Co(CO)_4} + PPh_3 \rightarrow$$

$$\underset{2}{MeO_2CCH_2CH(CO_2Me)C(=O)Co(CO)_3PPh_3} \rightleftarrows$$

$$\underset{3}{MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3} + CO \quad (1)$$

light yellow crystals in 60% yield. Complex 2 was found to be stable at room temperature as a solid under CO atmosphere but decarbonylated slowly in solution into $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ (3) and CO. The decarbonylation was facilitated by purging the solution with argon. According to the IR spectra of the reaction mixture, 24 h was necessary under argon at room temperature to achieve a complete decarbonylation. The decarbonylation was always accompanied by some decomposition, leading to a minor amount of $Co_2(CO)_6$-

Table II. Positional and Thermal Parameters for $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ (3)

atom	x^a	y	z	U_{eq},[b] Å^2
Co	0.3663(2)	0.0884(1)	0.1343(3)	392(14)
P1	0.2201(3)	0.0575(3)	0.0820(5)	376(28)
O1	0.3523(9)	0.1650(7)	0.3919(14)	604(39)
O2	0.4068(10)	0.9287(9)	0.1194(15)	805(47)
O3	0.3571(11)	0.1784(10)	0.8869(18)	934(54)
O4	0.5579(9)	0.0837(8)	0.4228(14)	658(40)
O5	0.6881(13)	0.1985(11)	0.2905(20)	1170(64)
O6	0.5755(8)	0.0019(7)	0.2645(13)	565(37)
O7	0.6275(11)	0.2409(9)	0.0810(17)	906(51)
C1	0.1303(11)	0.9204(11)	0.0915(18)	433(48)
C2	0.1769(12)	0.0424(10)	0.8948(18)	408(47)
C3	0.3574(15)	0.1399(13)	0.9821(24)	699(66)
C4	0.3598(12)	0.1343(10)	0.2940(19)	438(50)
C5	0.3939(13)	0.9921(12)	0.1241(20)	521(54)
C6	0.1966(12)	0.9692(10)	0.1637(18)	416(49)
C7	0.0278(15)	0.2313(13)	0.2042(23)	722(67)
C8	0.1426(12)	0.1239(10)	0.1337(18)	415(48)
C9	0.0893(15)	0.2537(13)	0.1279(22)	687(64)
C10	0.2291(13)	0.8851(11)	0.3617(21)	567(57)
C11	0.1133(13)	0.8539(11)	0.1561(21)	559(57)
C12	0.5481(12)	0.0692(10)	0.2994(19)	452(51)
C13	0.0800(13)	0.1010(12)	0.2093(20)	575(57)
C14	0.1609(14)	0.8373(12)	0.2884(21)	604(59)
C15	0.5269(13)	0.1984(11)	0.2066(19)	515(54)
C16	0.5057(11)	0.1145(10)	0.1784(18)	389(47)
C17	0.6232(15)	0.2096(13)	0.1973(24)	680(65)
C18	0.2465(13)	0.9530(11)	0.2989(20)	570(57)
C19	0.1497(13)	0.1998(11)	0.0984(20)	568(58)
C20	0.2177(15)	0.9844(13)	0.8379(23)	710(66)
C21	0.0218(15)	0.1571(13)	0.2448(22)	693(65)
C22	0.6046(14)	0.9448(12)	0.3721(22)	681(64)
C23	0.1868(17)	0.9721(14)	0.6877(26)	867(77)
C24	0.1056(14)	0.0845(13)	0.8170(23)	703(64)
C25	0.1190(16)	0.0153(14)	0.6093(25)	803(73)
C26	0.7218(20)	0.2530(17)	0.0530(30)	1131(97)
C27	0.0768(19)	0.0708(16)	0.6684(30)	1087(95)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses. [b] The anisotropic thermal parameter is $U_{eq} = {}^1/_3 = (\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j))$.

$(PPh_3)_2$[7] as a red-brown precipitate, which could be removed by filtration. The formation of $Co_2(CO)_6(PPh_3)_2$ occurred only as long as complex **2** was present. On the other hand, **3** is thermally stable in chlorinated hydrocarbon or alkane solutions at least up to 50 °C under argon (temperature limits of the stability were not determined). When such solutions were cooled, golden yellow crystals of **3** were obtained in good yield. The formation of **3** by the decarbonylation of **2** is reversible; keeping a CH_2Cl_2 solution of **3** under 120 atm of CO pressure at room temperature resulted in a quantitative transformation into **2**.

The new cobalt complexes were characterized by a combination of elemental analysis, IR and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectroscopy, and, in the case of **3**, X-ray crystallography.

Both the solution and solid-state IR spectra in the ν_{CO} region are similar to those reported for $RCo(CO)_3PR'_3$ (R = alkyl, acyl; R′ = alkyl, aryl, alkoxy, aryloxy), having a distorted-trigonal-bipyramidal structure with three equatorial CO ligands and axial PPh_3 and R groups.[1] According to the overall symmetry-lowering effect of the bulky and asymmetric R group in **2** and **3**, three instead of two terminal ν_{CO} bands are present. The appearance of two acyl ν_{CO} bands in the solution spectrum of **2** indicates a hindered rotation about the "alkyl" carbon–"acyl" carbon axis[8] similar to the established case of $CH_2FC(=O)Co(CO)_3PPh_3$.[9] In the solid state, however, only one rotamer exists, as shown by a single band at 1665 cm^{-1}.

Table III. Selected Bond Distances (pm) and Bond Angles (deg) for $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ (3)

Co–P1	223.3(5)	C12–C16	146.2(24)
Co–C3	174.1(24)	C12–O4	122.0(20)
Co–C4	180.1(19)	C12–O6	134.4(20)
Co–C5	177.9(21)	C22–O6	146.4(23)
Co–C16	211.6(17)	P1–C2	183.2(18)
Co–C15	308.6	P1–C6	184.4(18)
Co–C12	288.7	P1–C8	182.8(18)
C4–O1	114.1(19)	C1–C11	140.1(25)
C5–O2	115.3(21)	C6–C1	139.7(27)
C3–O3	116.3(24)	C6–C18	140.4(24)
C7–C9	139.1(29)	C10–C14	140.7(26)
C7–C21	139.4(29)	C10–C18	141.5(26)
C8–C13	140.1(24)	C11–C14	137.1(25)
C8–C19	141.0(25)	C2–C20	139.2(26)
C9–C19	140.8(28)	C2–C24	139.4(26)
C13–C21	143.5(25)	C20–C23	146.4(29)
C15–C16	154.4(25)	C23–C25	137.4(30)
C15–C17	150.3(28)	C24–C27	145.1(32)
C17–O5	120.0(24)	C25–C27	138.3(33)
C17–O7	129.3(24)	O7–C26	153.9(31)
P1–Co–C3	93.3(7)	O6–C12–C16	112.9(16)
P1–Co–C4	93.4(6)	O4–C12–C16	128.8(17)
P1–Co–C5	89.0(6)	C12–C16–Co	106.1(12)
P1–Co–C16	177.8(5)	C12–C16–C15	110.8(15)
C2–P1–Co	112.0(6)	C16–C15–C17	106.4(16)
C6–P1–Co	113.3(6)	C15–C17–O7	111.4(20)
C6–P1–C2	104.7(8)	C15–C17–O5	124.8(22)
C8–P1–Co	116.7(6)	O5–C17–O7	123.3(23)
C8–P1–C2	105.9(8)	C17–O7–C26	154.8(16)
C8–P1–C6	103.2(8)	Co–C3–O3	174.1(21)
C22–O6–C12	119.7(15)	Co–C4–O1	176.9(17)
O6–C12–O4	118.3(17)	Co–C5–O2	175.9(18)

The NMR spectra confirm the presence of the expected ligands around the cobalt atom. The ^1H NMR spectra of both **2** and **3** show a typical ABX spin–spin coupling pattern for the substituted ethyl group, as found for **1** and dimethyl chlorosuccinate,[10] respectively (see Experimental Section and Table IV). The J_{ab} value of each compound fits the characteristic values of a geminal coupling of diastereotopic methylene protons. The J_{ab}, J_{ax}, and J_{bx} coupling constants show considerable parallels in the **1**–**3** and **2**–dimethyl chlorosuccinate pairs. The poor resolution observed in the case of **3** did not allow us to determine the value of the small J_{bx} coupling constant, which might be obscured by the superposition of an expected additional small coupling of the methine proton to the phosphorus, as well. The different sets of vicinal coupling constants (J_{ax} = 12.45 Hz and J_{bx} = 3 Hz in **1**, J_{ax} = 11.7 Hz and J_{bx} < 5 Hz in **3**, J_{ax} = 6 Hz and J_{bx} = 8 Hz in **2**, and J_{ax} = 7.5 Hz and J_{bx} = 6.8 Hz in dimethyl chlorosuccinate) indicate that a free rotation around the $-CH_2CH-$ axis is only slightly hindered in **2** and dimethyl chlorosuccinate but probably strongly hindered in **3** and **1**. The number of resonances in the $^{13}C\{^1H\}$ NMR spectra of **2** and dimethyl chlorosuccinate, as well as in **3** and **1**, corresponds to the number of different carbon nuclei in these compounds in the corresponding chemical shift range. In addition to

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(10) The preparation of dimethyl chlorosuccinate has been published elsewhere.[3] Data for $CH_3O_2CCH^aH^bCH^xClCO_2CH_3$ are as follows. IR (hexane): ν_{CO} 1761, 1749 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.63 (dd, J_{ax} = 7.5 Hz, J_{bx} = 6.8 Hz, 1H, CH^x), 3.80 (s, 3H, CH_2COOCH_3), 3.70 (s, 3H, $CHCOOCH_3$), 3.15 (dd, J_{ax} = 7.5 Hz, J_{ab} = 17.0 Hz, 1H, CH^a), 2.93 (dd, J_{bx} = 6.8 Hz, J_{ab} = 17.0 Hz, 1H, CH^b) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.6 (s, CHCOO), 169.0 (s, CH_2COO), 53.2 (s, $CHCOOCH_3$), 52.1 (s, CH_2COOCH_3), 51.1 (s, CH), 39.3 (s, CH_2) ppm.

Table IV. Selected ^1H and $^{13}C\{^1H\}$ NMR Data[a] for the CH_2CH Fragment of Complexes 1–3 and Dimethyl Chlorosuccinate

	CH^aH^b		CH^x	
compd[b]	^1H δ, ppm[c]	$^{13}C\{^1H\}$ δ, ppm[d]	^1H δ, ppm[c]	$^{13}C\{^1H\}$ δ, ppm[d]
R—Co(CO)$_4$ (**1**)	3.11 dd, 2.56 dd, J_{ab} = 17.2 Hz	39.6 s	3.33 dd, J_{ax} = 12.45 Hz, J_{bx} = 3 Hz	20.0 s
R—Co(CO)$_3$PPh$_3$ (**3**)	3.2 dd, 2.7 dd, J_{ab} = 16.5 Hz	40.2 s	3.3 dd, J_{ax} = 11.7 Hz, J_{bx} < 5 Hz	17.0 d, J_{PC} = 19.6 Hz
R—C(═O)Co(CO)$_3$PPh$_3$ (**2**)	2.91 dd, 2.79 dd, J_{ab} = 17 Hz	31.1 s	4.75 dd, J_{ax} = 6 Hz, J_{bx} = 8 Hz	69.6 d, J_{PC} = 23.3 Hz
R—Cl	3.15 dd, 2.93 dd, J_{ab} = 17.0 Hz	39.3 s	4.63 dd, J_{ax} = 7.5 Hz, J_{bx} = 6.8 Hz	51.1 s

[a] In $CDCl_3$. [b] R = $CH_3O_2CCH_2CH(CO_2CH_3)$. [c] Recorded at −20 °C for **1** and **2**, but at room temperature for **3** and RCl. [d] Recorded at −15 °C for **1**, at 0 °C for **2**, and at room temperature for **3** and RCl.

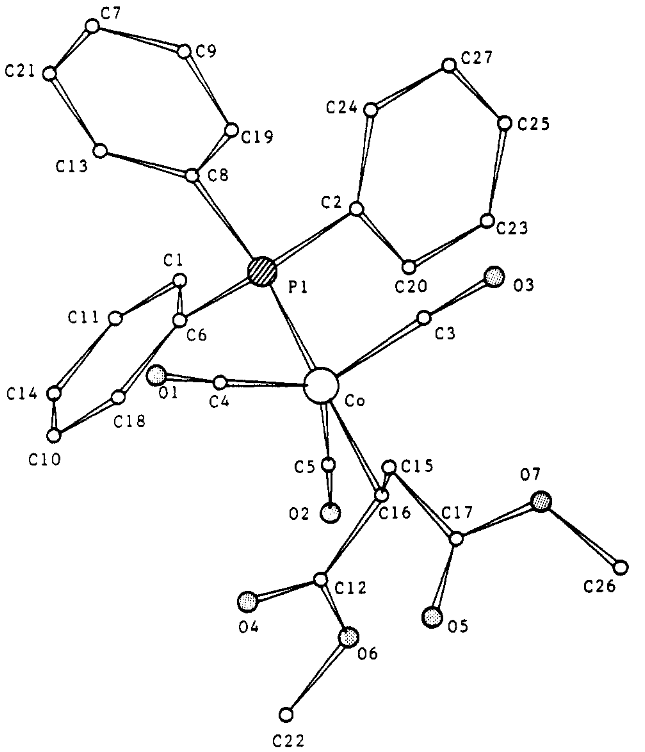

Figure 1. Solid-state structure of $MeO_2CCH_2CH(CO_2Me)$-$Co(CO)_3PPh_3$ (**3**).

the expected carbon–phosphorus couplings, one of the carboxylic carbon resonances of **3** shows a doublet at 170.9 ppm (J_{PC} = 6 Hz). This signal probably belongs to the carboxylic carbon adjacent to the methine group, which is three bonds away from the phosphorus. An unequivocal assignment of the ^{13}C resonances to the corresponding methoxycarbonyl groups could be made only in the case of dimethyl chlorosuccinate by performing an INEPT long-range experiment.[11]

Although PPh_3 is the most widely used ligand for stabilizing alkyl- and acylcobalt carbonyls, the ^{31}P NMR data for these complexes have been published only in a few cases. Considering the few data available, we find that the ^{31}P signals of both **2** and **3** are at the same chemical shift as found for propargyl acyl and propargyl complexes, respectively.[2i] Some further observations[2c,d,12,13] also support that varying the steric and electronic properties of the alkyl chain in both types of complexes does not influence the ^{31}P chemical shifts in solution.

The crystal structure of **3** is shown in Figure 1. In accord with the IR structures both in solution and in the solid state, the X-ray structure confirms a trigonal-bipyramidal geometry with the CO ligands and cobalt in the equatorial plane and phosphorus and C16 in axial positions. Structures of three PPh_3-substituted alkylcobalt[2a,b,f] and three PPh_3-substituted acylcobalt carbonyl complexes[2e,f,14] have been reported to date and may be used for comparison. The Co–P distance (223.3(5) pm) is practically the same as in the reported examples, but it is shorter than the "σ-only" value.[15] The Co–C_{ax} distance is 211.6(17) pm. A similar bond length was observed in $PhCH_2O_2CCH_2Co$-$(CO)_3PPh_3$ (210.9(8) pm).[2b] In all other cases the Co–C_{ax} distance is significantly shorter.[2a,e,f,14] The conformation of the substituted ethyl group is staggered with C17 and Co in *anti* and C12 and C17 in *gauche* positions.

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[13] A complete NMR investigation of a series of alkyl- and acylcobalt carbonyl complexes is currently in progress in our laboratories. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of Y–$Co(CO)_3PPh_3$ (Y = MeC(═O) EtC(═O), *n*-PrC(═O), *i*-PrC(═O), *t*-BuC(═O), $NCCH_2$) have been recorded. The ^{31}P chemical shifts of **2** and **3** show good agreement with these values, as well: Szalontai, G.; Kovács, I.; Ungváry, F. Unpublished results.

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