Journal of Organometallic Chemistry, 419 (1991) 205–217
Elsevier Sequoia S.A., Lausanne
JOM 22032

Alkylcobalt carbonyls

XI *. Ligand-assisted carbonylation–decarbonylation reactions of alkylcobalt carbonyls

Judit Somlyai-Haász [1], Ferenc Haász [1], Vilmos Galamb [1], Adriano Benedetti, Claudia Zucchi, Gyula Pályi *
Department of Chemistry, University of Modena, Via Campi 183, I-41100 Modena (Italy)

Thomas Krümmling [2], Berit Happ [2] and Tamás Bartik
Department of Organic Chemistry, University of Veszprém, H-8200 Veszprém (Hungary)

(Received April 29th, 1991)

Abstract

An [(alkoxycarbonyl)methyl]cobalt tetracarbonyl (**1**) derivative (alkyl = Et, **1a**) was treated with tertiary phosphorus ligands. A monosubstituted acyl derivative $EtOC(O)CH_2C(O)Co(CO)_3L$ (**2**), L = PPh_3 (**2f**) was isolated, and other new complexes of type **2** were detected spectroscopically (L = PEt_3, **2a**; $P(^iPr)_3$, **2c**; $P(^tBu)_3$, **2d**; $PMePh_2$, **2e**; $P(NEt_2)_3$, **2g**; $P(OMe)_3$, **2h**; $P(OEt)_3$, **2i**; $P(OSiMe_3)_3$, **2j**; $P(S^iPr)_3$, **2k**). The corresponding alkyl derivatives, $EtOC(O)CH_2Co(CO)_3L$ (**3**), were obtained by thermal decarbonylation. Disubstituted acyl-, $EtOC(O)CH_2C(O)Co(CO)_2L_2$ (**4**), and alkyl-, $EtOC(O)CH_2Co(CO)_2L_2$ (**5**) derivatives were obtained by direct substitution at ca. 30 °C and ca. 70 °C, respectively. The geometries of the new complexes were deduced from spectroscopic data. The monosubstituted derivatives **2** and **3** all show a trigonal bipyramidal array with axial organyl and PR_3 ligands. All the disubstituted complexes display a trigonal bipyramidal geometry with axial organyl groups, whereas an axial–equatorial distribution of the phosphines was assigned in the case of compounds **4a, b** and **5a, b, e, h, i**, and an equatorial-equatorial distribution in the case of complexes **4j** and **5g, j**. For the alkyl complexes **5** a solvation-like interaction between the ester group and the cobalt atom (autosolvation) was indicated by spectroscopic data.

Introduction

Cobalt carbonyls are the original and perhaps the most important type of carbonylation catalysts (e.g. for hydroformylation [2], hydroxy- and alkoxycarbonylation [3], homologation [4], cyclocarbonylation [5], etc.). A common feature of

---

* For Part X see ref. 1.

[1] Present address: Alkaloida Chemical Works, Tiszavasvári (Hungary).

[2] GDR Research Fellow, on the leave from the Humboldt-University of Berlin.

mechanistic speculations about all of these reactions is that in a first step the substrate (olefin, acetylene, functionalized alkyl- or aryl-derivatives) forms a cobalt–carbon bond. This bond subsequently reacts with a carbon monoxide molecule by a 1,1-(C,C)-addition; that is, the CO is formally "inserted" into the Co–C bond. The most generally accepted mechanistic scheme [6] for this reaction is based essentially on theoretical (EH-MO) considerations [7] and IR [8] and NMR [9] studies of related manganese complexes. In the scheme the "insertion" is described as a 1,2-migration of the (Co)-C-bonded group (alkyl, aryl, etc.) from the cobalt to the carbon of a coordinated CO.

In spite of the importance of this reaction only a very limited amount of relevant preparative work has been reported and, furthermore not all the results can be readily accommodated by the accepted scheme. A careful isotopic exchange (^{13}CO) study showed that the "inserted" carbon monoxide is in fact one of the coordinated carbonyls [10]. On the other hand the very few structural studies of phosphine-substituted acylcobalt carbonyls, $RC(O)Co(CO)_3L$ (R = 2,6-dichlorophenyl-methyl [11], chloromethyl [12], methoxy [13] and n-butoxy [14], $L = PPh_3$), and of the substituted alkylcobalt carbonyls, $RCo(CO_3)L$, (R = (benzyloxycarbonyl)methyl [15] and chloromethyl [12], $L = PPh_3$) which were prepared by decarbonylation of the corresponding acyl derivative, all show a *trans*-(bis-axial) [16*] array of the hydrocarbon and tertiary phosphorous ligands, not that (*cis*-axial-equatorial) which would be expected for the common accepted mechanism of CO insertion. This difficulty can easily overcome by assuming a fast rearrangement of a coordinatively unsaturated intermediate or of the end-product; such rearrangement is a fairly general feature of trigonal bipyramidal complexes [17a] and the suggestion gains support from an *ab initio* theoretical study [17b] of a representative of this type of compound. Experimental verification of this suggestion is still lacking, however.

The problems are due not only to the experimental difficulties of obtaining stereochemical information from reaction mixtures in which the main reaction is (or may be) accompanied by fast rearrangement(s) but also to the well-known instability of the alkylcobalt carbonyls [18] (especially towards CO insertion!).

These considerations prompted us to initiate a preparative study on the ligand-assisted carbonylation of one group of the rare, relatively stable, non-fluorinated alkylcobalt tetracarbonyls, namely the [(alkoxycarbonyl)methyl]cobalt tetracarbonyls **1** [15].

Experimental

All reactions were carried out under carefully dried, deoxygenated and CO_2-free Ar or CO at. Dried and deoxygenated solvents [19] were used. Infrared spectra were recorded on Philips PU 9716 and Bruker FT-IR IFS 113V instruments. ^{1}H-NMR spectra were recorded on Varian XL-200 (FT-220 MHz) and Bruker WP 80SY (FT-80 MHz) spectrometers.

Starting materials were of commercial origin except for of $Co_2(CO)_8$ [20a] and $EtOC(O)CH_2Co(CO)_4$ (**1a**) [20b], which were prepared by published methods.

---

* Reference number with asterisk indicates a note in the list of references.

[(Ethoxycarbonyl)acetyl] cobalt tricarbonyl triphenylphosphine (2f)

Complex **1a**, 129 mg (0.5 mmol) was dissolved in n-hexane, (10 mL) in a Schlenk vessel under Ar at room temperature, and this solution was stirred (by external magnetic stirrer) during the addition, all at once, of a solution of triphenylphosphine, 131 mg (0.5 mmol) in n-hexane, (5 mL). The solution was stirred for a further 10–20 min then examined by IR spectroscopy. The ν(C–O) region showed complete absence of the band system of **1a** [15], and the presence of a new band system attributed to **2f** [15]. Then the mixture was cooled to −40 ° C and two-thirds of the solvent were evaporated off under reduced pressure as a slow current of CO gas was bubbled into the solution through a G3 sintered glass filter (to maintain a CO partial pressure high enough to slow down decarbonylation). To the concentrated solution was added diethyl ether (1 mL), and the mixture was kept at −80 ° C for 3–5 days, during which greenish yellow crystals separated. These were filtered off while the liquid was still cold. They could not be washed even with cold (−80 ° C) solvents, and turned into an oil between −40 to −20 ° C when allowed to warmed to room temperature. This oil was dissolved in n-hexane, and the IR spectrum of the solution showed a ν(C–O) pattern expected for a $XCo(CO)_3L$ species [10–12,21] along with an "organometallic" acyl band that was attributed previously to **2f** [15]. Elemental analysis were consistent with the formation to $EtOC(O)CH_2C(O)Co(CO)_3PPh_3$. Found: C, 60.3; H, 4.4. $C_{26}H_{22}CoO_6P$ calcd.: C, 60.01; H, 4.26%. Yield 122 mg (47%).

Further derivatives of type **2** were characterized in solution by means of their characteristic IR ν(C–O) bands, details of which are given in Table 1.

[(Ethoxycarbonyl)methyl]cobalt tricarbonyl phosphine (**3**) derivatives were prepared essentially by the procedure described in refs. 15, 20b, 22, and characterized by the similarity of their IR ν(C–O) spectra (Table 1) to those of complexes of type **3** isolated [15] previously.

[(Ethoxycarbonyl)acetyl]cobalt dicarbonyl bis(tri-n-butyl-phosphine) (4b) and [(ethoxycarbonyl)methyl]cobalt dicarbonyl bis(tri-n-butylphosphine) (5b)

Method A. [(Ethoxycarbonyl)methyl]cobalt tricarbonyl tri-n-butylphosphine, **3b** $EtOC(O)CH_2Co(CO)_3(PBu_3)$ (130 mg, 0.3 mmol) was dissolved in n-hexane (10 mL) under Ar and the solution was thermostated at 30 ° C in a Schlenk vessel. The solution was stirred (by external magnetic stirring) as tri-n-butylphosphine, PBu_3, 61 mg (0.3 mmol) was added all at once. The progress of the reaction was monitored by IR spectroscopy. After 3–5 min time two new band systems had appeared, the dominant one was attributed to $EtOC(O)CH_2C(O)Co(CO)_2(PBu_3)_2$ (**4b**) (~ 90%), and the minor (~ 10%) to the corresponding alkylcobalt derivative $EtOC(O)CH_2Co(CO)_2(PBu_3)_2$ (**5b**). (Attempts to isolate **4b** (or other complexes of type **4**) failed; oils were obtained which could not be purified.) The solution was refluxed for 4 h (70 ° C), resulting in gradual decomposition of both complexes, but the ratio of the two band systems did not change. Similar behaviour was observed when the attempted decarbonylation was performed under reduced pressure.

Method B. [(Ethoxycarbonyl)methyl]cobalt tetracarbonyl, **1a** (129 mg, 0.5 mmol) was dissolved in n-hexane (20 mL) under Ar and the solution was stirred at room temperature as tri-n-butylphosphine (404 mg, 2 mmol) was added all at once. The mixture was stirred at 70 ° C for 6 h, after which IR spectroscopic examination showed the presence of 5–10% of $Co_2(CO)_6(PBu_3)_2$ [23*], 5–10% of EtOC(O)-

Table 1

Infrared ν(C–O) spectra of complexes **2**–**5** (n-hexane, cm^{-1}) ($R = EtOC(O)CH_2$)

L	$RC(O)Co(CO)_3L$ (**2**)	$RCo(CO)_3L$ (**3**)	$RC(O)Co(CO)_2L_2$ (**4**)	$RCo(CO)_2L_2$ (**5**)
PEt_3	2047w	2043vw	1952m	1955w
(**a**)	1981s	1977s	1894s	1896vs
	1959s	1965s		
	1744w	1703w	1744w	1632w
	1675w	–	1665w	–
P^nBu_3	2044w	2042vw	1953m	1968m
(**b**)	1978s	1974s	1893s	1904s
	1958s	1964s		
	1745m	1708m	1745w	1609w
	1675m	–	1667w	–
P^iPr_3	2046w	2043vw		
(**c**)	1978s	1974s		
	1956s	1962s		
	1747m	1710m		
	1677m	–		
P^tBu_3	2040w	2037w		
(**d**)	1972s	1968s		
	1951s	1956s		
	1748w	1711m		
	1679w	–		
$PMePh_2$	2050w	2047vw		1976m
(**e**)	1986s	1981s		1915s
	1966s	1971s		
	1747m	1709m		1690w
	1680m	–		–
PPh_3	2053w	2049vw		
(**f**)	1987s	1985s		
	1969s	1974s		
	1747m	1709m		
	1680m	–		
$P(NEt_2)_3$	2043w	2039vw		1934m
(**g**)	1975s	1971s		1899s
	1956s	1960s		
	1746m	1706m		1630w
	1672m	–		–
$P(OMe)_3$	2064w	2061vw		2010m
(**h**)	1998s	1994s		1954s
	1978s	1983s		
	1747m	1710m		1706w
	1684m	–		–
$P(OEt)_3$	2064w	2058vw		2005m
(**i**)	1999s	1992s		1950s
	1976s	1980s		
	1747m	1710m		1713m
	1684m	–		–

Table 1 (continued)

L	$RC(O)Co(CO)_3L$ (2)	$RCo(CO)_3L$ (3)	$RC(O)Co(CO)_2L_2$ (4)	$RCo(CO)_2L_2$ (5)
$P(OSiMe_3)_3$	2059w	2052vw	1987s	1989s
(j)	1990s	1984s	1939mw	1947w
	1969s	1976s		
	1746m	1708m	1707m	1650m
	1677m	–	1659m	–
$P(S^{i}Pr)_3$	2060w	2057vw		
(k)	1998s	1995s		
	1980s	1983s		
	1737m	1711m		
	1685m	–		

$CH_2C(O)Co(CO)_2(PBu_3)_2$ (**4b**) and 80–90% of $EtOC(O)CH_2Co(CO)_2(PBu_3)_2$ (**5b**). The solution was left to cool to room temperature and its volume was then reduced to 1/5th (2 mL) under reduced pressure. The concentrated solution was kept at −80 °C, and by the next day yellow crystals had formed, and these were identified as **5b** by their spectra (Table 1) and elemental analysis. Found: C, 59.5; H, 10.4. $C_{30}H_{61}CoO_4P_2$ calcd.: C, 59.39; H, 10.13%. Yield 204 mg (67%).

Other complexes of type **5** were prepared by essentially the same procedures. Three additional **5** derivatives, as follows were isolated in analytically pure form:

$EtOC(O)CH_2Co(CO)_2(PPh_2Me)_2$, **5e** (from n-hexane at −80 °C). Found: C, 63.9; H, 5.7. $C_{32}H_{33}CoO_4P_2$ calcd.: C, 63.79; H, 5.52%. Yield 190 mg (63%)

$EtOC(O)CH_2Co(CO)_2[P(OMe)_3]_2$, **5h** (from n-hexane/$Et_2O$ (1 : 1) at −80 °C). Found: C, 31.8; H, 5.6. $C_{12}H_{25}CoO_{10}P_2$ calcd.: C, 32.01; H, 5.60%. Yield 98 mg (44%).

$EtOC(O)CH_2Co(CO)_2[P(OEt)_3]_2$, **5i** (from n-hexane/$Et_2O$ (1 : 1) at −80 °C). Found: Co, 11.0; P, 11.1. $C_{18}H_{37}CoO_{10}P_2$ calcd.: Co, 11.03; P, 11.59%. Yield 192 mg (72%)

Carbonylation of [(ethoxycarbonyl)acetyl]cobalt dicarbonyl bis(tri-n-butylphosphine) (4b)

A solution of **4b**, 32 mg (0.05 mmol) in n-hexane (10 mL) was prepared as described above. The argon atmosphere was replaced by CO and the solution stirred at 30 °C for 1 h. After which the IR ν(C–O) bands of **4b** had disappeared completely and the band system of **3b** was dominant (~ 90%), alongside bands from some (unidentified) minor species.

Attempted preparation of bis(tertiary phosphine) complexes with two different PR_3 ligands

A solution of **3f**, 25 mg (0.05 mmol) in n-hexane (10 mL) was prepared as described above. This solution was stirred under Ar at 30 °C while tri-n-butylphosphine (20 mg, 0.1 mmol) was added all at once. The mixture was stirred for a further 3 h and changes in the IR ν(C–O) spectrum were monitored. After 3 h the band system of **3f** had disappeared completely but no new band had appeared that could have been assigned either to $EtOC(O)CH_2Co(CO)_2(PPh_3)(PBu_3)$ or to

$EtOC(O)CH_2C(O)Co(CO)_2(PPh_3)(PBu_3)$, and only the bands of $EtOC(O)CH_2Co(CO)_3(PBu_3)$ (**3b**) were present. The same result was obtained in the presence of an up to 10-fold excess of PPh_3.

^{1}H-NMR spectra

NMR spectra can be obtained for cobalt complexes only with some difficulty owing to the nuclear quadrupole moment of ^{59}Co. Thus addition of a relaxation agent, $Cr(acac)_3$ (~ 10%) was necessary, and a longer spectrum accumulation time used, but this caused decomposition of the samples during the recording of the spectrum and most of the spectra contained signals from unidentified decomposition products that prevented reliable assignment, which was also complicated by overlapping with strong ligand signals (in the ^{1}H-spectra) in the case of phosphines containing alkyl groups.

Sufficiently clean ^{1}H-NMR spectra were obtained only for three of the new complexes:

$EtOC(O)CH_2Co(CO)_2(PMePh_2)_2$, (**5e**) (THF-$d_8$, δ_{TMS}, ppm): 1.19 (t, J(H–H) 7.1 cps, 3H, CH_2–CH_3); 1.53 (t, J(P–H) 4.1 cps, 2H, Co–CH_2); 1.67 (d, J(P–H) 6.7 cps, 6H, P–CH_3); 3.96 (q, J(H–H) 7.1 cps, 2H, CH_2–CH_3); 7.32 (m, 20H, P–C_6H_5).

$EtOC(O)CH_2Co(CO)_2[P(OMe)_3]_2$, (**5h**) ($C_6D_6$, δ_{TMS}, ppm): 1.27 (t, J(H–H) 7.1 cps, 3H, CH_2–CH_3); 2.22 (t, J(P–H) 3.3 cps, 2H, Co–CH_2); 3.32 (m, 18H, P–CH_3); 4.3 (q, J(H–H) 7.1 cps, 2H, CH_2–CH_3).

$EtOC(O)Co(CO)_2[P(OEt)_3]_2$, (**5i**) ($C_6D_6$, δ_{TMS}, ppm): 0.98 (t, J(H–H) 7.0 cps, 18H, $POCH_2CH_3$); 1.12 (t, J(H–H) 7.1 cps, 3H, OCH_2CH_3); 2.00 (t, ^3J(P–H) 3 cps, 2H, Co–CH_2); 3.80 (m, ^3J(P–H) 4 cps, 12H, $POCH_2CH_3$); 4.14 (q, J(H–H) 7.0 cps, 2H, OCH_2CH_3).

Results and discussion

Preparative results

The main results of the preparative work are summarized in Scheme 1.

The stable alkylcobalt tetracarbonyl **1a** reacted with the phosphines PR_3 under mild conditions to give the monosubstituted acylcobalt complexes **2**, which underwent relatively easy thermal decarbonylation, yielding the monosubstituted alkylcobalt compounds **3**. Infrared spectroscopic analysis of the mixtures revealed that initially no **3** was formed in detectable quantities, and moreover **2** was the only product present up to 30–40% conversion of **1a**. In some cases an enrichment of the kinetic product **2** up to ~ 90% (e.g. **2f**) could be achieved. Essentially qualitatively the same result was obtained when a variety of solvents (C_6H_6, $C_6H_5CH_3$, Et_2O, THF, CH_3CN, CH_2Cl_2, $CHCl_3$, CCl_4) were used.

The results indicate that the formation of the monosubstituted alkylcobalt complex **3** proceeds through a ligand-promoted CO insertion/deinsertion mechanism, and not through a "one-step" dissociative pathway. This picture seems to be in accordance with the generally accepted view of the behaviour of alkylcobalt carbonyls towards PR_3 ligand [11,12,18,22,24], and accounts for the slight phosphine dependence of the rate of formation of **3f** [25].

Addition of 2–10 molar equivalents of PR_3 ligand to the monosubstituted alkylcobalt complexes **3** gave an entirely different result. At lower temperature

(25–30 °C) the disubstituted acylcobalt complexes **4** were the major products along with minor amounts of the disubstituted alkylcobalt derivatives **5**, while at higher temperature (70 °C) the complexes **5** became dominant. Additional experiments showed the acylcobalt complexes **4** to be surprisingly resistant towards thermal decarbonylation, showing that at ~ 70 °C the formation of complexes **5** does not proceed via thermal decarbonylation of **4** (in contrary to compounds **3**) but apparently via CO-dissociation followed by PR_3 addition.

Neither complexes **3** nor **5** could be carbonylated at 1 bar CO pressure. Interestingly the acylcobalt complexes **4** reacted under 1 bar CO to yield the monosubstituted alkyl derivatives **3** by expulsion of a PR_3 ligand followed by thermal decarbonylation. Complex **3f** was found not to react with PBu_3 to form the mixed-ligand acylcobalt derivative $EtOC(O)CH_2C(O)Co(CO)_2(PPh_3)(PBu_3)$, but instead to give the *mono*substituted **3b** by a phosphine exchange reaction (probably involving a CO insertion-deinsertion sequence).

These results demonstrate that the reactivity of the monosubstituted alkyl-complex **3** is to be markedly different from that of complex **1a**. Apparently the substitution of complexes **3** at lower temperatures proceeds by a ligand-promoted CO insertion pathway but switches over to a dissociative mechanism at higher temperatures. Another important difference in the behaviour of the mono- and disubstituted complexes is that monosubstitution (still) allows thermal decarbonylation, but disubstitution inhibits this reaction.

It should be pointed out that this radical change in the mechanism upon substitution of one CO by a PR_3 ligand is the first clear example of a ligand-induced switch-over of the mechanism [26] in the chemistry of cobalt carbonyls. This gains further importance from the fact that cobalt catalysts modified by excess PR_3 ligands were shown to have advantages in hydroformylation [27].

Beyond the mechanistic interest on the formation of complexes **4** and **5**, it should be pointed out that these are the first representatives of disubstituted alkylcobalt and acylcobalt carbonyls obtained by direct substitution.

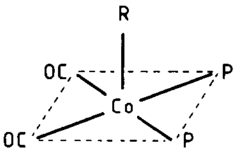
Spectra and structures

The structures of compounds **2** and **3** can be described as trigonal bipyramidal with a *trans*-(bis-axial) array of the organyl and phosphine ligands on the basis of the close analogy between their IR ν(C–O) spectra and those of alkylcobalt tricarbonyl phosphine complexes with structures known from X-ray studies [11–16,28]. The splitting of the lowest two terminal ν(C–O) bands (E species in the parent C_{3v} point group) can be attributed to a somewhat hindered rotation of the alkyl- or acyl-group around the Co–C(alkyl, acyl) axis [15,17,29].

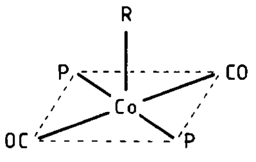
This hindrance is ascribed to a $d\pi$–$p\pi$ (or $p\pi^*$) interaction between the Co atom and the attached acyl carbonyl group for complexes **2**. The origins of the same effect in complexes **3** will be discussed later, together with that in compounds **5**.

Careful spectroscopic monotoring of the reaction mixtures from the initiation of the reaction did not reveal the presence of any intermediate that could be assigned to either a trigonal bipyramidal or tetragonal pyramidal *cis* geometry; no species showing the spectroscopic characteristics of the only know such compound [30], *cis*-$CF_2CFCF_2Co(CO)_3(PPh_3)$ (which, however, was characterized only in solution and prepared from an η^3-allylcobalt precursor).

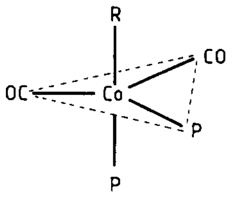
The geometries of compounds **4** and **5** are based on spectroscopic data (Table 1), since no crystals suitable for an X-ray diffraction study could be obtained. Theoretically 11 types of geometry are possible (5 trigonal bipyramidal, 6 tetragonal pyramidal). It can reasonably be assumed that the strong tendency of alkyl- and acylcobalt tetracarbonyls and their mono- and tetra-substituted derivatives to have direct the σ-organyl ligand in an axial position will be retained [11–16*,29,31*]. Thus, after the isomers with non-axial R have been discarded, only structures A–D remain. Since the IR spectra show 2 terminal ν(C–O) bands of unequal intensity in all cases, the more symmetric **A** (C_s with 2 CO ligands in identic environment) and **B** (C_{2v}) structure can be eliminated.



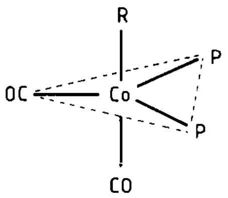
A(C_S)



B(C_{2v})



C(C_1)



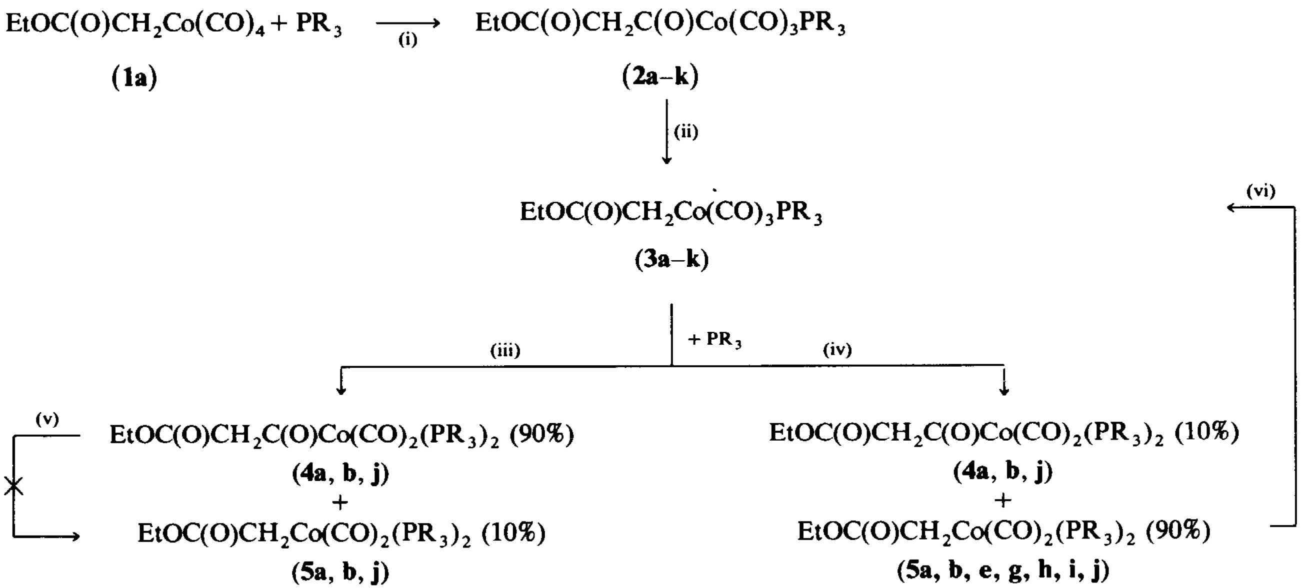
D(C_S)

Regarding the shapes of the terminal ν(C–O) bands two types can be distinguished: (a) in complexes **4a**, **b**, and **5a**, **b**, **e**, **h**, **i** the splitting (Δν) of the two terminal bands is within the range 50–64 cm^{-1} and the relative intensity of the higher wave number band ** is less than 50% of that of the lower energy one; (b) in the group of compounds consisting of **4j**, and **5g**, **j** the Δν values are in the range 35–50 cm^{-1}, and the relative intensity of the higher energy band exceeds 50% of that of the lower energy one. Both features prompt us to assign type (a) to structure **C** and type (b) to structure **D**. This assignment is consistent with recent findings [33*] on equatorial-axial and equatorial-equatorial isomers of disubstituted derivatives of $HCo(CO)_4$.

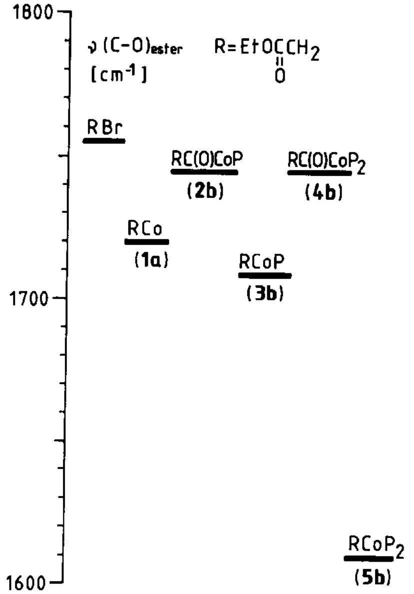
The "organic" (ester) ν(C–O) band shows characteristic alternating changes in the sequence **1a** → **2** → **3** → **4** → **5** as shown for the PBu_3 (**b**) derivatives in Scheme 2. The changes amount to 20–40 cm^{-1} for the first three (formal) steps, while a large jump of ~ 100 cm^{-1} accompanies the (formal) decarbonylation **4b** → **5b**.

By comparison of these values with each other and with the changes in the "acyl" ν(C–O) band it can be concluded that these large changes cannot be due to the electronic effect of the phosphine ligand introduced, at least not as transmitted by the σ-bond system between the ester carbonyl group and the PR_3 ligand.

** This band can be confidently assigned to the "totally symmetric" vibration of the CO ligands [32*].



Scheme 1. **2–5**, R = Et (**a**); ^{n}Bu (**b**); ^{i}Pr (**c**); ^{t}Bu (**d**); $R_3 = MePh_2$ (**e**); R = Ph (**f**); NEt_2 (**g**); OMe (**h**); OEt (**i**); $OSiMe_3$ (**j**); $S^{i}Pr$ (**k**). (i) 25–30 °C; 10–60 min; Co : P = 1 : 1; n-hexane, n-pentane, benzene, toluene, Et_2O, THF, AN, CH_2Cl_2, $CHCl_3$, CCl_4 (Ar or CO). (ii) as (i) complete after 30–300 min. (iii) 25–30 °C, 10–60 min, Co : P = 1 : 2–10, n-hexane, Ar. (iv) 70 °C, 300–400 min, Co : P = 1 : 2–10, n-hexane, Ar. (v) 70 °C and/or reduced pressure, 240 min, n-hexane, Ar. (vi) 25–30 °C, 60 min, n-hexane, 1 bar CO.



Scheme 2. Positions of the ν(C–O) ester bands of $EtOC(O)CH_2Br$, **1a**, **2b**, **3b**, **4b**, and **5b**.

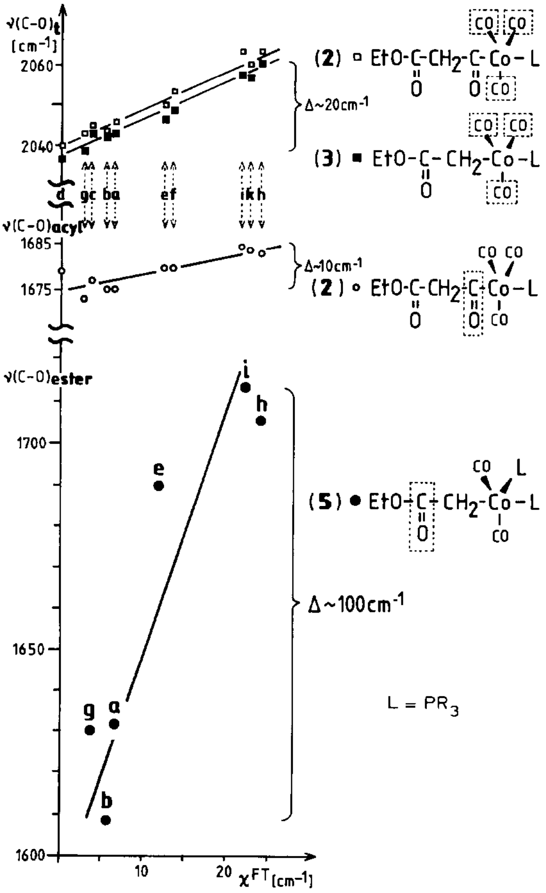


Fig. 1. Plots of ν(C–O) vs. χ^{FT} for various types of carbonyl groups in species **2**, **3** and **5**.

Another aspect of this effect can be seen from Fig. 1. The ν(C–O) vs. χ^{FT} parameter [35] diagrams show an acceptable linearity for the (highest) ν(C–O) frequencies of compounds **2** and **3** as well as for the acyl-CO group in compounds **2**, but a fairly irregular behaviour for the ester-CO group in compounds **5**. Even more surprising, the changes in this latter case are 5–10 times as large as those for the other complexes.

We suggest that these differences can be explained in terms of an outer-sphere type chelating interaction of the ester group with the cobalt carbonyl part of the molecule. Such an interaction, termed by one of us autosolvation [36], was previously suggested for similar systems on the basis of structural and spectroscopic [IR, CD) [15,36] data. The interaction could involve (i) electron density transfer from the carbonyl or ether oxygen of the ester group to the metal or coordinated carbonyl π^* orbitals, or (ii) charge transfer from the non-bonding (a) metal d or (b) carbonyl p orbitals to the π^* orbital of the ester carbonyl group. The fact that the changes in the ν(C–O) shift indicates decreasing strength of the C=O vibrator with increasing number of phosphines [37*] somewhat favours the possibility (ii)/(a).

It can readily be appreciated that in the acyl derivatives **2** and **4** the ester group cannot get close enough to the metal to permit such an interaction. On the other hand, it should be recalled that the ester group in the closely related alkyl complex, $PhCH_2OC(O)CH_2Co(CO)_3PPh_3$ [14], was found to be close enough (Co–C(ester) 292 pm) to allow an interaction stronger than that of the van der Waals type [37*].

The more interesting side of this effect lies not in the spectroscopic effects but its influence on the reactivity [39*] or the stereochemistry [36c,40*] of intermediates of catalytic cycles. Carbonylation studies with acrylates as substrates are in progress to provide additional information on this effect.

Acknowledgements

The authors acknowledge stimulating discussions by Prof. L. Markó (Veszprém) as well as help in the preparative and analytical work by Dr. E. Halmos-Galambos and Mr. T. Werk. Fellowships are acknowledged from the German (GDR) Ministry of Education (T.K.) and the Italian National Research Council (CNR, Rome) (to J.S.-H., F.H., V.G. and T.B.).

References and notes

1 F. Haász, V. Galamb, T. Bartik and G. Pályi, Organometallics, 9 (1990) 2773.

2 (a) P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley-Interscience, New York, 1977, p. 43; (b) J. Falbe, New Syntheses with Carbon Monoxide, Springer, Heidelberg, 1980; (c) L. Markó, Fund. Res. Homogeneous Catal., 4 (1984) 1; (d) G. Henrici-Olivé and S. Olivé, The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide, Springer, Berlin, 1984.

3 (a) P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley-Interscience, New York, 1977, p. 233; (b) H. Alper, Fund. Res. Homogeneous Catal., 4 (1984) 79; idem, J. Organomet. Chem., 300 (1986) 1.

4 (a) M. Röper and H. Loevenich, in W. Keim (Ed.), Catalysis in C_1 Chemistry, D. Riedel, Dordrecht, 1983, p. 105; (b) M. Tasi and G. Pályi, Magy. Kém. Lapja, 41 (1986) 190.

5 G. Pályi, G. Váradi and L. Markó, in I. Bernal (Ed.), Stereochemistry of Organometallic and Inorganic Compounds Elsevier, Amsterdam, 1986, p. 358.

6 (a) F. Calderazzo, Angew. Chem., 89 (1977) 305; Angew. Chem., Int. Ed. Engl., 16 (1977) 299; (b) L.J. Kuhlman and J.J. Alexander, Coord. Chem. Rev., 33 (1980) 195; (c) J.C. Flood, Top. Inorg. Organomet. Stereochem., 12 (1981) 37.

7 (a) H. Berke and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 7224; (b) M.E. Ruiz, A. Flores-Riveros and O. Novaro, J. Catal., 64 (1980) 1.

8 (a) F. Calderazzo and F.A. Cotton, Inorg. Chem., 1 (1962) 30; (b) F. Calderazzo and F.A. Cotton, Chim. Ind. (Milano), 46 (1964) 1165; (c) R.J. Mawby, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 86 (1964) 3994; (d) K. Noack and F. Calderazzo, J. Organomet. Chem., 10 (1967) 101.

9 J.C. Flood, J.E. Jensen and J.A. Statler, J. Am. Chem. Soc., 103 (1981) 4410.

10 Z. Nagy-Magos, G. Bor and L. Markó, J. Organomet. Chem., 14 (1968) 105.

11 V. Galamb, G. Pályi, F. Ungváry, L. Markó, R. Boese and G. Schmid, J. Am. Chem. Soc., 108 (1986) 3344.

12 V. Galamb, G. Pályi, R. Boese and G. Schmid, Organometallics, 6 (1987) 861.

13 D. Milstein and J.L. Huckaby, J. Am. Chem. Soc. 104 (1982) 6150.

14 T. Krümmling, T. Bartik, L. Markó, R. Boese, G. Schmid, P. Vivarelli and G. Pályi, J. Organomet. Chem., JOM22209.

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

16 A similar, *trans*-(bis-axial) geometry was observed recently in the X-ray diffraction structure of $[PPN][MeC(O)Co(CO)_3I]$: M. Röper and C. Krüger, J. Organomet. Chem., 339 (1988) 159.

17 (a) J.A. Altman, K. Yates and I.G. Csizmadia, J. Am. Chem. Soc., 98 (1976) 1450; (b) J. Demuynck, A. Strich and A. Viellard, Nuov. J. Chim., 1 (1977) 217.

18 V. Galamb and G. Pályi, Coord. Chem. Rev., 59 (1984) 203.

19 (a) S. Herzog and J. Dehnert, Z. Chem., 4 (1964) 1; (b) D.F. Shriver, Manipulation of Air Sensitive Compounds, McGraw-Hill, New York, 1969.

20 (a) P. Szabó, L. Markó and G. Bor, Chem. Techn. (Berlin), 13 (1961) 549; (b) V. Galamb and G. Pályi, in R.B. King and J.J. Eisch (eds.), Organometallic Syntheses Vol. 3, Elsevier, Amsterdam, 1986, p. 142.

21 M. Tasi and G. Pályi, Organometallics, 4 (1985) 1523.

22 R.F. Heck, J. Am. Chem. Soc., 85 (1963) 1220.

23 Infrared ν(C–O) spectra: (a) D.J. Thornhill and A.R. Manning, J. Chem. Soc., Dalton Trans., (1974) 6; assignment based on X-ray diffraction: (b) R.F. Bryan and A.R. Manning, Chem. Commun., (1968) 1316; (c) J.A. Ibers, J. Organomet. Chem., 14 (1968) 423.

24 (a) R.F. Heck and D.E. Breslow, J. Am. Chem. Soc., 82 (1960) 4438 and 84 (1962) 2499; (b) R.F. Heck, J. Am. Chem. Soc., 85 (1963) 651.

25 C.D. Hoff, F. Ungváry, R.B. King and L. Markó, J. Am. Chem. Soc., 107 (1985) 666.

26 "Umpolung"; c.f. e.g.: D. Seebach and D. Enders, Angew. Chem., 87 (1975) 1; Angew. Chem., Int. Ed. Engl., 14 (1975) 15.

27 (a) L.H. Slaugh and R.D. Mullineaux, J. Organomet. Chem., 13 (1968) 469; (b) F. Asinger, B. Fell and W. Rupilius, Ind. Eng. Chem., Prod. Res. Dev., 8 (1969) 214; (c) E.R. Tucci, ibid., 7 (1968) 32, 125 and 9 (1970) 516; (d) M. Bianchi, E. Benedetti and F. Piacenti, Chim. Ind. (Milano), 51 (1969) 613; (e) G.F. Pregaglia, A. Andereetta, G.F. Ferrari and R. Ugo, J. Organomet. Chem., 30 (1971) 387.

28 J.B. Wilford and H.M. Powell, J. Chem. Soc. (A), (1967) 2092.

29 Acylcobalt tetracarbonyls: (a) L. Markó, G. Bor, G. Almásy and P. Szabó, Brennst. Chem., 44 (1963) 184; (b) E. Lindner and M. Zipper, Chem. Ber., 107 (1974) 1444.

30 K. Stanley and D.W. McBride, Can. J. Chem., 53 (1975) 2537.

31 (a) P.B. Hitchcock and R. Mason, Chem. Commun., (1966) 503; (b) H.-F. Klein and H.H. Karsch, Chem. Ber., 108 (1975) 944; (c) E.L. Muetterties and P.L. Watson, J. Am. Chem. Soc., 100 (1978) 6978; (d) R. Hammer and H.-F. Klein, Z. Naturforsch. B, 32 (1977) 138. It should also be mentioned that a trisubstituted derivative of $HCo(CO)_4$ contains all PR_3 groups in equatorial position, *trans*-$HCo(CO)(PPh_3)_3$: (e) J.M. Whitfield, S.F. Watkins, G.B. Tupper and W.H. Baddley, J. Chem. Soc., Dalton Trans., (1977) 407.

32 The highest wave-number band should be always assigned to the so-called "totally symmetric" vibration; this band gains intensity with increasing asymmetry of the CO ligands: (a) G. Bor, Spectrochim. Acta, 19 (1963) 1209; (b) S.F.A. Kettle and I. Paul, Adv. Organomet. Chem., 10 (1972) 199.

33 At $HCo(CO)_2L_2$ complexes $\Delta\nu \approx 50$–70 cm^{-1} corresponds to ax-eq-L_2, while $\Delta\nu \approx 30$–50 cm^{-1} to eq-eq-L_2 distribution [34].

34 T. Bartik and T. Krümmling, XXVth [Hungarian] Colloquium on Coordination Chemistry, Keszthely (Hungary), May 30–June 1, 1990.

35 (a) T. Bartik, T. Himmler, H.G. Schulte and K. Seevogel, J. Organomet. Chem., 272 (1984) 29; (b) P. Heimbach, T. Bartik, R. Boese, H. Schenkluhn, G. Szczendzina and E. Zeppenfeld, Z. Chem., 28 (1988) 121; (c) P. Heimbach and T. Bartik, An Ordering Concept on the Basis of Alternative Principles in Chemistry, Springer, Heidelberg, 1989.

36 (a) G. Pályi and G. Váradi, J. Organomet. Chem., 86 (1975) 119; (b) G. Pályi, Transition Met. Chem., 2 (1977) 273; (c) G. Pályi, M. Kovács-Toplak, G. Váradi, Atti Accad. Sci. Bologna, Rend. Cl. Sci. Fis., 266 (13/5) (1978) 139; (d) V. Galamb, G. Pályi and M. Kajtár, Inorg. Chim. Acta, 55 (1981) L113.

37 Similar "through-the-space" interactions were suspected at other Co [28] complexes and at Fe [38] carbonyls too.

38 Termed also as β-effect: (a) J.D. Duncan, J.C. Green, M.L.H. Green and R.A. McLauchlan, J. Chem. Soc., Chem. Commun., (1968) 721; (b) J.K.P. Ariyaratne, A.M. Bierrum, M.L.H. Green, M. Ishaq, C.K. Prout and M.G. Swanwick, J. Chem. Soc. (A), (1969) 1309; (c) A. Cutler, S. Raghu and M. Rosenblum, J. Organomet. Chem., 77 (1974) 381.

39 E.g. the unusual stability of compounds **1** against CO insertion may be due (in part) to this effect.

40 In case of coordinatively unsaturated intermediates such "outer sphere coordination" may go over into a true (twofold inner sphere) chelation, which can provide an important stabilizing factor for this intermediate, as it was suspected for the dissociative substitution of **1a** [25].