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ALKYLCOBALT TETRACARBONYLS AND THEIR DERIVATIVES

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CONTENTS

A. INTRODUCTION

Alkylcobalt tetracarbonyls and some of their substituted derivatives are believed to play a key role in several important reactions. These include various carbonylations of olefins and other unsaturated substrates, "homologation" of alcohols, hydrogenations, etc. Among these, the hydroformylation of olefins (oxo-reaction) possesses exceptional importance since it is one of the few homogeneous catalytic reactions utilized industrially.

Mechanistic studies concerning these reactions often propose steps including the formation of alkylcobalt carbonyls despite the fact that: (a) only a

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** Throughout this paper those alkylcobalt carbonyls are considered in which the formal oxidation state of Co is +1 (thus the Co(III) alkyls will not be included even if they contain CO ligand(s)); on the other hand only those derivatives are treated which contain in addition to the η^1 alkyl group CO, PR_3, $P(OR)_3$ ligands (thus the NO, isonitrile, etc. complexes reported in the literature are not included).

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few alkylcobalt tetracarbonyls have been well characterized; (b) alkylcobalt tetracarbonyls are not detected under catalytic conditions; (c) attempts to obtain alkylcobalt tetracarbonyls from simple stoichiometric reactions, so modelling the proposed individual steps of the catalytic processes (e.g. olefin + $HCo(CO)_4$) are very rare.

The importance of alkylcobalt carbonyls from a theoretical standpoint can be best understood by considering that these compounds contain both the alkyl group and carbon monoxide in an activated form, just as $HCo(CO)_4$ represents activated hydrogen and CO in the same molecule.

These considerations prompted us to summarize the current state of accumulated knowledge regarding alkylcobalt carbonyls, with the intention of drawing attention to some challenging problems in this area.

B. PREPARATION OF ALKYLCOBALT CARBONYLS AND THEIR DERIVATIVES

The first alkylcobalt tetracarbonyl, the methyl derivative, was reported in 1960 as a part of the systematic exploratory effort of Hieber's school [1] having been obtained from the reaction of methyl iodide with sodium tetracarbonylcobaltate (1):

$$CH_3I + Na[Co(CO)_4] \rightarrow CH_3Co(CO)_4 + NaI \qquad (1)$$

The yield of this reaction is only ca. 2%, which can be attributed to the high kinetic lability of the product towards decomposition and a CO "insertion" reaction (cf. Section D of this review).

The method can theoretically be extended to the preparation of other alkylcobalt carbonyls but generally the rapid reaction and/or decomposition of the product prevents its isolation or even observation.

The reaction of alkyl halogenides with $Na[Co(CO)_4]$ was used recently to prepare some (functionalized) alkylcobalt tetracarbonyls. Thus haloacetic acid esters were found to provide (alkoxycarbonylmethyl)cobalt tetracarbonyls in good yield (80–90%) [2,3] (reaction (2)) *.

$$ROOCCH_2X + Na[Co(CO)_4] \rightarrow ROOCCH_2Co(CO)_4 + NaX \qquad (2)$$

$X = Cl, Br, I$; $R = Et, CH_2Ph, CMe_3$, (S)-$(-)$-2-MeBu, Men **.

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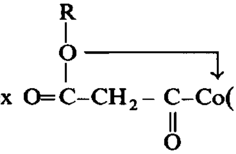
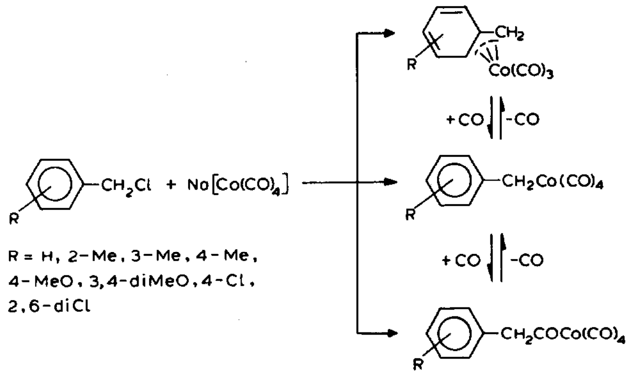
[*] Two decades ago the cobalt–organic product of reaction (2) was supposed to be the acyl-type chelate complex  $O{=}C(OR){-}CH_2{-}C({=}O){-}Co(CO)_3$ on the basis of IR spectra of low resolution [4].

[**] The hydrocarbon group of (1*R*, 3*R*, 4*S*)-*p*-menthane-3-ol (menthol) will be denoted as Men in this paper.

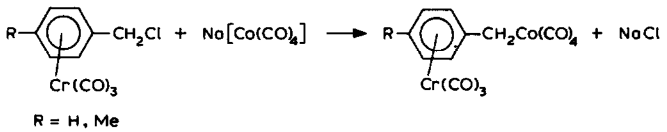
In the case when the alkoxycarbonylmethyl group contained one more substituent the corresponding alkylcobalt tetracarbonyls were not isolable [5,6]. These compounds ($R^1OOCCHR^2Co(CO)_4$, R^1 = Me, Et) could, however, be observed and characterized by IR spectroscopy for R^2 = Me, tBu, Ph and indicated through organic decomposition products for $R^2 = COOR^1$.

Benzyl halogenides also react with $Na[Co(CO)_4]$ but follow a more complicated reaction pattern (reaction (3)) [7,8]. The equilibria between the



(3)

products are in an intermediate position at one atmosphere CO pressure (cf. also Section D) and can be shifted to one or other side (i.e. to the π-benzyl- or to the acyl-complex) simply by bubbling Ar or CO through the reaction mixture. This behaviour prevented the isolation of the benzylcobalt carbonyl products which were identified only by their IR and ^1H NMR spectra. Complexation of the arene ring with $Cr(CO)_3$ gave pure benzylcobalt tetra-



(4)

carbonyls [7,8] (reaction (4)) by utilizing the following advantages offered by the $Cr(CO)_3$ group: (i) the increased electronegativity of the organic group increases the stability against CO "insertion" [9] (the electron withdrawing ability of the $Cr(CO)_3$ group is approximately equal to that of a p-NO_2 group [10]; (ii) the η^6 complexation of the aromatic ring inhibits π-benzyl formation; (iii) it is possible that the rigidity of the π-$arCr(CO)_3$ group enhances the tendency to form crystals which is favourable in purification and in obtaining good crystals for structure determination *.

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* In fact the molecular structure of the p-Me derivative could be determined by X-ray diffraction (cf. Section C).

The alkyl halogenide + $Na[Co(CO)_4]$ method has been used for the in situ preparation of alkylcobalt carbonyls under conditions where the product is immediately transformed [11]. Satisfactory overall yields could generally be obtained in this way.

The mechanism of the reactions ((1)–(4)) was found to be probably of S_N2 character [12,13]. This would account for the lack of data on the preparation of arylcobalt tetracarbonyls by this reaction (for an indirect synthesis see below, reaction (5)).

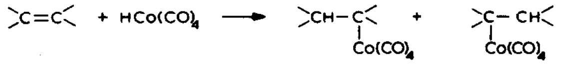
Reactions (5) and (6) represent modified variants of the syntheses starting from $Na[Co(CO)_4]$. These possibilities could however only be used for the

$$\begin{tikzcd} RCOCl + Na[Co(CO)_4] \arrow[r] & RCOCo(CO)_4 \arrow[d, "-CO"] & (5) \\ & RCo(CO)_4 & \\ (RCO)_2O + Na[Co(CO)_4] \arrow[r] & RCOCo(CO)_4 \arrow[u, "-CO"'] & (6) \end{tikzcd}$$

preparation of such $RCo(CO)_4$ compounds where the corresponding acyl derivative undergoes facile decarbonylation. Such systems are mostly the fluoroalkyl or perfluorophenyl groups [14–18] as well as the phenylacetylcobalt tetracarbonyls [7,8], which can in fact also be prepared by reaction (5).

The $[Co(CO)_4]^-$ anion can also be alkylated using dialkyl sulfates, alkyl sulfonates and trialkyloxonium salts [19–21]. $Zn[Co(CO)_4]_2$ reacts with perfluoroallyl iodide formally in an alkylation reaction giving η^3-perfluoroallylcobalt tricarbonyl and σ-$CF_3CF{=}CFCo(CO)_4$. The latter (which is unstable above 0°) is the only known σ-vinylcobalt tetracarbonyl. The intermolecular rearrangement of the presumed σ-perfluoroallyl derivative was proposed [157] to explain the formation of this compound.

The addition of $HCo(CO)_4$ to an olefinic double bond (reaction (7)) represents in principle [22,23] a clean and elegant method for the synthesis of

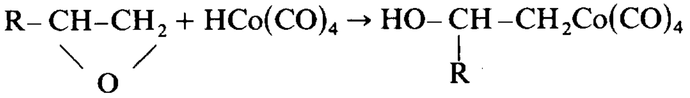


$$>C{=}C< + HCo(CO)_4 \longrightarrow >CH{-}\underset{Co(CO)_4}{C}< + >\underset{Co(CO)_4}{C}{-}CH< \qquad (7)$$

alkylcobalt tetracarbonyls. The actual application of this reaction has been reported only for the preparation of $CF_2HCF_2Co(CO)_4$ from tetrafluoroethylene [18]. Very recently alkylcobalt tetracarbonyls have been detected by IR ν(C–O) spectra from the reaction of conjugated dienes with $HCo(CO)_4$ [24,25]. Several papers have also reported various aspects of the reaction of

$HCo(CO)_4$ with olefins * but to the best of our knowledge none of these papers presented convincing proof of the actual presence (intermediacy) of alkylcobalt tetracarbonyls.

The reaction of epoxides with $HCo(CO)_4$ is believed to yield (2-hydroxyalkyl)cobalt tetracarbonyls (reaction (8)).

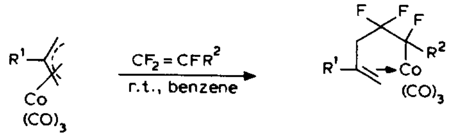


$$\mathrm{R-\underset{\diagdown\;O\;\diagup}{CH-CH_2} + HCo(CO)_4 \rightarrow HO-\underset{\overset{|}{R}}{CH}-CH_2Co(CO)_4} \qquad (8)$$

Oxetane gives (3-hydroxypropyl)cobalt tetracarbonyl in a similar reaction. However these cobalt alkyls were identified only through their derivatives and products of decomposition [31].

A noteworthy reaction of tetrafluoroethylene with dicobalt octacarbonyl was reported as early as 1960 [32,33] and refined later [34,35]: in a formally simple addition reaction 1,2-bis(tetracarbonylcobalt)-1,1,2,2-tetrafluoroethane was formed in high yields (up to 85% [35]) under relatively mild conditions (100°C, 1–3 h, 20–60°C, several days). Haszeldine and co-workers [35] studied some interesting reactions of this compound (c.f. also Section D) including that with HCl yielding $HCF_2CF_2Co(CO)_4$, reported earlier by Stone and co-workers [18] (see reaction (7)). The attempted addition of $Co_2(CO)_8$ to $CCl_2{=}CCl_2$ failed [35]. In an analogous experiment CF_3I was found to react with $Co_2(CO)_8$ giving $CF_3Co(CO)_4$ [36].

η^3-Allylcobalt tricarbonyls react with tetrafluoroethylene or hexafluoropropylene yielding products of (at least formal) insertion of the olefin into a terminal C–Co bond of the η^3-allylic ligand [37]. In these compounds the newly coupled C_5 chain is coordinated by a 1-η^1; 4,5-η^2 coordination mode to the cobalt (reaction (9)). The high regiospecificity of the insertion observed for $R^2 = CF_3$ is also a noteworthy feature of this reaction.



(9)

$R^1 = H, Me;\ R^2 = F, CF_3$

Under extreme conditions (12 K, $h\nu$) η^3-allylcobalt carbonyl reacted with a CO-matrix giving the σ-allyl derivative. The latter was characterized by its ν(C–O) spectrum [158].

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* Extensive (mostly kinetic) investigations on the mechanism of the stoichiometric reaction of olefins with $HCo(CO)_4$ have been published recently [26–30] but none of these works described preparative variants of reaction (7).

Alkylcobalt tetracarbonyls were not isolated or even detected by spectroscopic methods (e.g. high pressure IR studies [38]) in reaction mixtures under conditions identical or comparable to those of the technically important catalytic reactions (10–30 MPa H_2/CO, 50–150°C). IR observations about the presence of alkylcobalt tetracarbonyls in reaction mixtures of stoichiometric carbonylation and hydrogenation reactions became available recently [30,39,40].

The isolated or spectroscopically characterized alkylcobalt tetracarbonyls are summarized in Table 1.

The most important CO ligand-substituted derivatives of alkylcobalt tetracarbonyls are those containing one or more trialkyl- or -arylphosphine or -phosphite ligands. These compounds correspond to the general formula $R^1Co(CO)_n(PR^2_3)_{4-n}$ (R^1 = alkyl; R^2 = alkyl, aryl, alkoxy, aryloxy). The $n = 3$ derivatives are regarded as intermediates of the hydroformylation reactions with phosphine-modified cobalt catalysts [45,46]. Due to this aspect and their much higher stability, these compounds have been more extensively studied than the unsubstituted parent compounds. These studies resulted in the isolation and characterization of a large number of complexes.

$MeCo(CO)_2[P(OMe)_3]_2$ was found to be an excellent catalyst for the hydrogenation of terminal olefins under mild conditions [47].

The most generally used route [2–4,7,8,15–18,48] to obtain phosphine-substituted alkylcobalt carbonyls starts either from the unsubstituted alkylcobalt tetracarbonyls (reaction (10)) or from the corresponding acylcobalt tetracarbonyls (reaction (11)): both complex types react to give acylcobalt tricarbonyl phosphine (or phosphite) derivatives, which generally can be decarbonylated to the substituted alkyl complexes (reaction (12)).

$$R^1Co(CO)_4 + PR^2_3 \rightarrow R^1COCo(CO)_3PR^2_3 \qquad (10)$$

$$R^1COCo(CO)_4 + PR^2_3 \rightarrow R^1COCo(CO)_3PR^2_3 + CO \qquad (11)$$

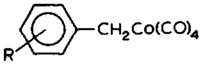
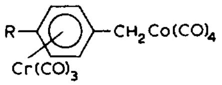
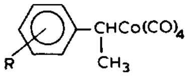
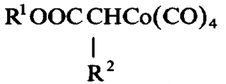
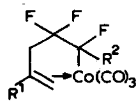
$$R^1COCo(CO)_3PR^2_3 \rightarrow RCo(CO)_3PR^2_3 + CO \qquad (12)$$

$R^1 = CH_2Ph$ [7,8,48], CH_2COOR^3 [2,3], $CH_2C{\equiv}N$ [4], CH_2F [16,49], CHF_2 [16,49], CF_3 [14], CF_2CHF_2 [18], C_nF_{2n+2} [50]; R^2 = alkyl, aryl, -*O*-alkyl, -*O*-aryl; R^3 = see R in reaction (2).

The decarbonylation takes place spontaneously (for perfluorinated complexes, the acyl intermediate cannot be observed directly) after some hours of standing at room temperature ($R^1 = CH_2COOR^3$ [2]), or after refluxing in benzene solution (R^1 = benzyl derivatives) [7,8,48]). In those cases (saturated, aliphatic alkyl-groups) where the alkylcobalt tetracarbonyl itself shows a high kinetic lability toward the CO "insertion" this method cannot be used; for these molecules other reaction paths had to be worked out (see reactions (15)–(17)).

TABLE 1

Reported alkylcobalt tetracarbonyls (isolated or characterized by direct methods)

Compound	Synthesis (reaction no.)[a]	Characterization[b]	Ref.
$CH_3Co(CO)_4$	(1), (5) (gas phase)	A, IR, UV/VIS	1, 41, 42
$(CH_3)_3CCo(CO)_4$	[c]	IR	43
 (R = 2-, 3-, 4-Me, 4-MeO, 3,4-diMe, 4-Cl, 2,6-Cl_2	(3), (5)	IR, ^1H NMR	7, 8
 (R = H, Me)	(4)	A, IR, ^1H NMR, X-ray diffr. (Me)	7, 8
	(7)	IR, ^1H NMR	30
$ROOCCH_2Co(CO)_4$ (R = Et, CH_2Ph, tBu, (*S*)-(−)-2-Me-Bu, Men*, CPh_3)	(2)	A, IR, ^1H-, ^{13}C NMR, UV/VIS, CD	2, 3
$N{\equiv}CCH_2Co(CO)_4$	(2)	IR, ^1H-, ^{13}C NMR	4, 44
 $R^1OOC\underset{R^2}{\underset{\mid}{C}}HCo(CO)_4$ (R^1 = Me, Et; R^2 = Me, tBu, Ph)	(2)	IR	5, 6
$CH_2FCo(CO)_4$	(6)	A, IR	16
$CHF_2Co(CO)_4$	(6)	A, IR	16
$CF_3Co(CO)_4$	(5) and $CF_3I + Co_2(CO)_8$	A, IR	14, 36
$HCF_2CF_2Co(CO)_4$	(7)	A, IR, NMR	18
$C_2F_5Co(CO)_4$	(5), (6)	A, IR	15, 17
σ-$C_3H_5Co(CO)_4$	η^3-$C_3H_5Co(CO)_4 + CO, h\nu$	IR	158
σ-$C_3F_5Co(CO)_4$	$Zn[Co(CO)_4]_2$ $+ CF_2{=}CF{-}CF_2I$	IR, ^{19}F NMR	157
n-$C_3F_7Co(CO)_4$	(5), (6)	A, IR	15, 17
n-$C_7F_{15}Co(CO)_4$	(6)	A, IR	15
$C_6F_5Co(CO)_4$	(5)	A, IR	18
$(CO)_4CoCF_2CF_2Co(CO)_4$	$C_2F_4 + Co_2(CO)_8$	A, IR	32–35
 (R^1 = H, Me R^2 = F, CF_3)	(9)	A, IR, ^1H-, ^{19}F NMR	37

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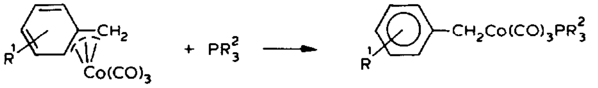
[a] The reaction no. of this review is given, or formula if the equation was not described.

[b] A = elemental analysis, IR = infrared spectroscopy (generally ν(C–O)).

[c] Only the IR ν(C–O) spectrum was reported; details of preparation or characterization with other methods were not found in the literature.

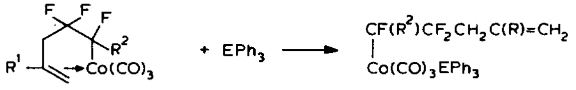
Reactions (10) and (12) were also observed for the $R^1 = CH_2COOR^3$ alkyl complexes with tertiary arsines and stibines [2]. The monosubstituted alkyl derivatives could be isolated in pure form but after redissolution of the products the presence of 10–20% of the corresponding unsubstituted alkyl derivative was always observed in the solutions.

There are only two cases, reactions (13) [7,8] and (14) [37], where "direct" substitution with a PR_3 ligand was found to lead to an alkylcobalt complex. These transformations are of limited preparative potential but illustrate well



(13)

R^1 = H, 2-Me, 3-Me, 4-Me, 4-MeO, 3,4-diMeO
R^2 = Ph



(14)

R^1 = H, Me; R^2 = F, CF_3; E = P, As

the view that the η^3-benzylcobalt and the 1-η^1; 4,5-η^2-pentenylcobalt tricarbonyls can be regarded (to a certain degree) as tricarbonyl intermediates of a dissociative substitution pathway stabilized by intramolecular coordination. (This view is also in line with the distribution of the Co,C(benzyl) bond distances in a related complex [51].)

In cases where the decarbonylation of the acyl complex does not proceed satisfactorily or if more than one phosphine ligand is required in the product, the alkylation of the corresponding anion was found to be useful (reaction (15)).

$$[Co(CO)_n(PR^1_3)_{4-n}]^- + R^2X \rightarrow R^2Co(CO)_n(PR^1_3)_{4-n} \qquad (15)$$

$n = 0$–3; R^1 = alkyl, aryl, –O-alkyl, –O-aryl; R^2 = Me, –COOMe *,
–COOEt *, n-Pr; X = Cl, Br, I.

This method was used for the preparation of mono- [52–54], di- [52–55], tri- [52] and tetra-substituted [13] derivatives of $MeCo(CO)_4$, while other applications were published only to a limited extent [56,57].

Taking into consideration other preparative approaches [58–60] to the R^2 = COOMe and COOEt derivatives they should be regarded rather as derivatives of the hypothetic alkoxycobalt tetracarbonyls which are supposed

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* These compounds are discussed in this review because of some analogies, in spite of the fact that they are formally acylcobalt complexes.

to be intermediates in some important reactions [61–65] but which have never been prepared.

Arylation of $[Co(CO)_3PPh_3]^-$ did not afford the phenyl derivative but treatment of the corresponding iodo complex with PhLi was successful [66]

$$ICo(CO)_3PPh_3 + PhLi \rightarrow PhCo(CO)_3PPh_3 + LiL \qquad (16)$$

(reaction (16)). It is noteworthy that no non-fluorinated arylcobalt tetracarbonyl has yet been isolated. The treatment of benzoyl halogenides with $Co_2(CO)_8$ (80°C, benzene, 24 h) unexpectedly yielded trinuclear derivatives ($ArCCo_3(CO)_9$ in which Ar = Ph [67], 2,4,6-triMeC_6H_2 [68]).

An ingenious variant of reaction (16) was used for the synthesis of $MeCo(PMe_3)_4$ (reaction (17)) [69].

$$ClCo(PMe_3)_3 + LiMe + PMe_3 \rightarrow MeCo(PMe_3)_4 + LiCl \qquad (17)$$

It would be of interest to use the $XCo(CO)_4$ (X = Cl, Br, I) compounds [70] for the synthesis of unsubstituted alkyl- or arylcobalt carbonyls. The instability of the halogencobalt tetracarbonyls, however, represents a major obstacle to such an attempt.

Tri- and disubstituted alkylcobalt carbonyls can be obtained by the carbonylation of the tetrasubstituted analogs (reaction (18)) [13].

$$MeCo[P(OMe)_3]_4 \xrightarrow{CO} MeCo(CO)[P(OMe)_3]_3 \xrightarrow{CO} MeCo(CO)_2[P(OMe)_3]_2 \qquad (18)$$

If the ligands of the tetrasubstituted complex are tertiary phosphines (as PMe_3 or $Ph_2PCH_2CH_2PPh_2$ (dpe)) both coordinative carbonylation and CO "insertion" can be observed [69,71].

Higher valent cobalt complexes can be reduced and carbonylated in the presence of CO, phosphines and proper reductive agents, as shown in reactions (19) [71] and (20) [72].

$$Co(acac)_3 + AlMe_2(OMe) + 2\ dpe \rightarrow MeCo(dpe)_2 \qquad (19)$$

$$Co(OOCC_{16}H_{33})_2 + RMgX + PPh_3 \xrightarrow{CO} R(CO)_nCo(CO)_3PPh_3 \qquad (20)$$

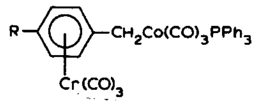
R = alkyl, phenyl, $n = 1$; R-mesityl, $n = 0$.

The mechanism of these reactions is most likely very complicated, probably involving the intermediate formation of $HCo(CO)_4$ or its phosphine derivatives [73,74].

The formation of substituted alkylcobalt complexes containing more than one phosphorus ligand was observed in a direct substitution reaction only in the case of the preparation of the disubstituted phosphite derivatives $R^1OOCCH_2Co(CO)_2[P(OEt)_3]_2$ (R^1 = Et, Men) [2].

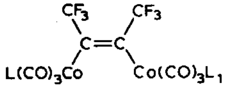
TABLE 2

Substituted derivatives of alkyl- and arylcobalt tetracarbonyls

Compound	Synthesis (reaction no.) [a]	Characterization [b]	Ref.
$CH_3Co(CO)_3PPh_3$	(15)	A, IR	53, 54
$CH_3Co(CO)_3P(p\text{-}MeOC_6H_4)_3$	(15)	IR	52
$CH_3Co(CO)_3P(OPh)_3$	(15)	A	53, 54
$CH_3Co(CO)_3(tmpp)$ [c]	(15)	A, IR	52
$CH_3Co(CO)_2(PPh_3)_2$	(15)	A	55
$CH_3Co(CO)_2[P(OMe)_3]_2$	(15)	A, IR	52
$CH_3Co(CO)_2(tmpp)_2$ [c]	(15)	A, IR	52
$CH_3Co(CO)(PMe_3)_3$	(17) $CH_3Co(PMe_3)_4 + CO_2$ $CH_3Co(PMe_3)_4 + CH_3COCo(CO)_2(PMe_3)_2$	A, IR, MS, ^1H-, ^{31}P NMR	
$CH_3Co(CO)(tmpp)_3$	(15)	A, IR	52
$CH_3Co(MPe_3)_4$	(17)	A, IR, ^1H-, ^{31}P NMR	69
$CH_3Co(dpe)_2$ [d]	(19)	A	71
$CH_3Co[P(OMe)_3]_4$	(15)	A, ^1H-, ^{31}P NMR	13
$CH_3CH_2CH_2Co(CO)_3PPh_3$	(15)	A, IR	56
$RC_6H_4CH_2Co(CO)_3PPh_3$ (R = H, 2-Me, 3-Me, 4-Me, 4-MeO, 3,4-$(MeO)_2$, 2,6-Cl_2)	(10)–(13)	A, IR, ^1H NMR	7, 8, 48
 (R = H, Me)	(10)+(12)	A, IR, ^1H NMR	7, 8
$ROOCCH_2Co(CO)_3PPh_3$ (R = Et, tBu, CH_2Ph, Men*, (*S*)-(−)-2-MeBu)	(10)+(12)	A, IR, ^1H, ^{13}C NMR UV/VIS, CD [e] X-ray (R = CH_2Ph)	2, 3
$ROOCCH_2Co(CO)_3PPh_2Men*$ (R = Et, Men*)	(10)+(12)	IR, CD	3

$EtOOCCH_2Co(CO)_3AsPh_3$	(10)+(12)	A, IR, ^1H-, ^{13}C NMR	2
$EtOOCCH_2Co(CO)_3SbPh_3$	(10)+(12)	A, IR	2
$EtOOCCH_2Co(CO)_2[P(OMe)_3]_2$	(10)+(12)	A, IR, ^1H NMR	2
$ROOCCH_2Co(CO)_2[P(OEt)_3]_2$ (R = Et, Men*)	(10)+(12)	A, IR, ^1H NMR, CD [e]	2
$N{\equiv}CCH_2Co(CO)_3PPh_3$	(10)+(12)	A, IR	4
$R^1C(=NR^2)Co(CO)_3PPh_3$ (R^1 = Et, Ph, *p*-anisyl; R^2 = Me, *p*-toluyl, *p*-ClC_6H_4)	(1) in the presence of PPh_3	A, IR	76
$ROOCCo(CO)_3PPh_3$ (R = Me, Et, tBu)	(15)	A, IR, ^1H NMR X-ray (R = Me)	57, 58, 59, 60
$EtOOCCo(CO)_3P(OPh)_3$	(15)	A, IR	57
$ROOCCo(CO)_2(PPh_3)_2$ (R = Me, Et)	$[Co(CO)_3(PPh_3)_2]Cl + KOR$	A, IR	57
$PhC{\equiv}CCo(PMe_3)_4$	$MeCo(PMe_3)_4 + PhC_2H$	A, ^1H NMR	69
$RC{\equiv}CCo(dpe)_2$ [d] (R = Me, Ph)	$MeCo(dpe)_2 + RC_2H$	A, IR	71
$C_6H_5Co(CO)_3PPh_3$	(16)	A	66
$C_6H_5Co[P(OMe)_3]_4$	$K[CoL_4] + PhN_2BF_4$ $L = P(OMe)_3$	^1H-, ^{31}P NMR	13
$2,4,6\text{-}Me_3C_6H_2Co(CO)_3PPh_3$	(20)	A, IR	72
$CH_2FCo(CO)_3PPh_3$	(10), (11), (12)	A, IR	16, 49
$CH_2FCo(CO)_3P(OPh)_3$	(5), (6)+(12) (11), (12)	A, IR	16
$CHF_2Co(CO)_3PPh_3$	(5), (6)+(12) (11), (12)	A, IR	16, 49
$CHF_2Co(CO)_3P(OPh)_3$	(6)+(12)	A, IR	16
$CF_3Co(CO)_3PPh_3$	(12)	A, IR	14
$CF_3Co(CO)_3P(OPh)_3$	(10), (12)	A, IR	50, 45
$HCF_2CF_2Co(CO)_3PPh_3$	(10)+(12)	A, IR, X-ray	18, 77
$C_2F_5Co(CO)_3PPh_3$	(12)	A, IR	15
$C_2F_5Co(CO)_3P(OPh)_3$	(10)+(12)	A, IR	50

TABLE 2 (continued)

Compound	Synthesis (reaction no.)[a]	Characterization[b]	Ref.
σ-$C_3F_5Co(CO)_3PPh_3$ (*trans*)	3-$C_3F_5Co(CO)_3 + PPh_3$	A, IR, ^{19}F NMR	157
σ-$C_3F_5Co(CO)_3PPh_3$ (*cis*)		A, IR	157
n-$C_3F_7Co(CO)_3PPh_3$	(12)	A, IR	50
n-$C_3F_7Co(CO)_3P(OPh)_3$	(12)	A, IR	50
$R_FCo(CO)_{4-n}(PF_3)_n$ ($R_F = CF_3, C_2F_5, C_3F_7$; $n = 1$–4)	$R_FCOCo(CO)_4 + PF_3$	IR, ^{19}F NMR	145, 146
$CH_2{=}C(R^1)CH_2CF_2CF(R^2)Co(CO)_3PPh_3$ ($R^1 = H, Me$; $R^2 = F, CF_3$)	Analogous to (13)	A, IR, ^1H-, ^{19}F NMR	37
$CH_2{=}C(Me)CH_2CF_2CF_2Co(CO)_3AsPh_3$	Analogous to (13)	A, IR, ^1H-, ^{19}F NMR	37
 ($L = PPh_3, AsPh_3, L_2 = dpe$)	$Co_4(CO)_{12}(C_4F_6)_2 + L$	A, IR, ^{19}F NMR	75

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[a] Refering to no. in this review.

[b] A = analysis; IR = infrared (generally ν(C–O)).

[c] tmpp = (1,2,3-trimethylolpropan)phosphite.

[d] dpe = $Ph_2PCH_2CH_2PPh_2$.

[e] With the optically active derivatives.

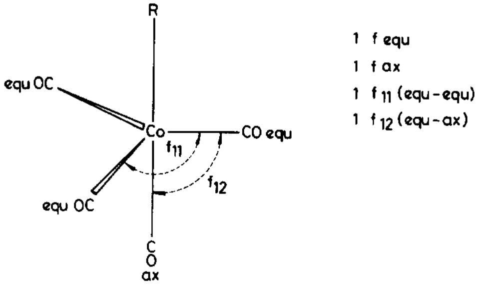

Fig. 1. Idealized trigonal bipyramidal structure of the alkylcobalt carbonyls.

Fluorinated substituted alkylcobalt carbonyls were obtained from the reactions of η^3-$C_3F_5Co(CO)_3$ [157], $(CF_3CCF_3)Co_4(CO)_{12}$ [75] and phosphines. The former gave two isomeric forms of the monosubstituted derivative.

The isolated and characterized substituted alkylcobalt carbonyls are collected in Table 2.

C. SPECTRA AND STRUCTURE OF ALKYLCOBALT CARBONYLS

The structure of alkylcobalt carbonyls and their derivatives have been investigated mostly by spectroscopic methods. The analysis of the ν(C–O) spectra offers outstanding potential in this respect, providing valuable information about the geometry with relatively simple computational apparatus [78,79].

The cobalt core of the alkylcobalt tetracarbonyls (and of the derivatives) is pentacoordinated. Tetragonal pyramidal (C_{4v} or C_s point group *) or trigonal bipyramidal (C_{3v} or C_{2v} point group) structures can be assumed. The infrared ν(C–O) spectra generally show 3 bands ($2A_1 + E$) which correspond to the number required by the selection rules of C_{3v} symmetry (Fig. 1).

The IR spectroscopic data have been subjected to different analysis. The uncertainty in the mathematical description of the vibration (in an isolated CO force field) is due to the greater number of force constants (2) and interaction constants (2) than parameters in the measurable data. This difficulty has been overcome by neglecting the f_{12} interaction constant [80] or (in more sophisticated studies) by properly choosing the value of f_{12} [80,81].

A further ^{13}CO isotopic IR study enabled determination of a more precise value of Bor's cos β which caused an increased separation of the k_{ax} and k_{eq}

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* The local symmetry of the $Co(CO)_n$ unit will be considered; the actual overall symmetry of the molecule is generally lower.

values [82]. The analysis of the IR spectra enabled further conclusions about the geometry (at least in solution) to be made: the equatorial CO groups and the Co atom are not in one plane, the CO ligands are slightly bent towards the alkyl group [81].

The shape (and symmetry) of the alkyl group does not exert much influence on the spectra; if strongly electronegative substituents are bound to the α-C atom the E-band broadens or slightly splits into two components [2,7,8,16,18].

One X-ray diffraction structure is available: that of η^1-[η^6-(4-$MeC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$ [8] (Fig. 2; Table 3). Some important aspects of this study are as follows:

(i) The trigonal bipyramidal geometry of the $RCo(CO)_4$ molecule with the alkyl group in an axial position was confirmed.

(ii) The Co-C(alkyl) bond length is longer (213 pm) than the sum of the covalent radii (202 pm).

(iii) The equatorial CO ligands are in fact slightly bent towards the (rather bulky!) alkyl group as predicted by the IR studies [81].

MO descriptions of alkylcobalt carbonyls have been reported. The hydroformylation of propylene has been studied by MO methods [83]. Two further papers present the ab initio description of $MeCo(CO)_4$ [84,85] aimed at clarifying the mechanism of its pseudorotation and calculating the rotation energy of the Co–Me bond.

A series of extended Hückel (Wolfsberg–Helmholz) UV/VIS parametrized MO calculations was performed [9,42] for the $RCo(CO)_4$ ($R = Me$,

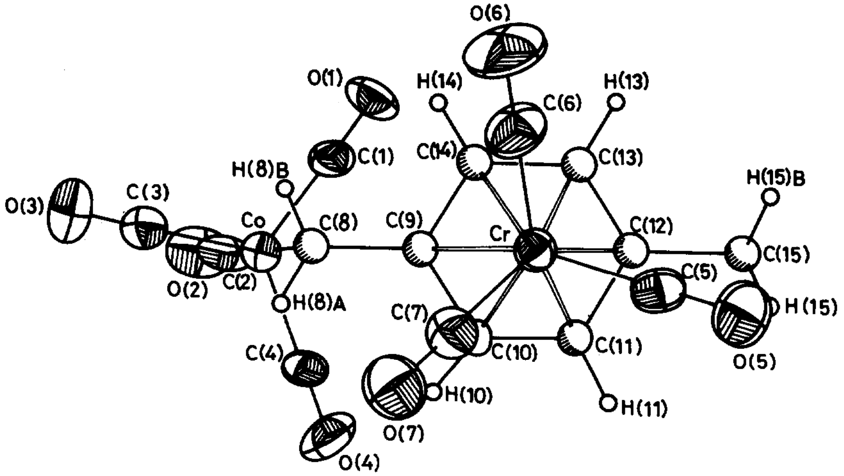

Fig. 2. The X-ray structure of η^1-[η^6-(4-$MeC_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$ [8].

TABLE 3

Characteristic geometric data for alkyl- and acylcobalt carbonyls (A, η^1-[η^6-(4-MeC_6H_4-CH_2)Cr$(CO)_3$]Co$(CO)_4$ [8]; B, $PhCH_2OOCCH_2Co(CO)_3PPh_3$ [2]; C, $C_2HF_4Co(CO)_3$-PPh_3 [77]; D, (2,6-$Cl_2C_6H_3$)$CH_2COCo(CO)_3PPh_3$ [8])

Atoms	Bond lengths (pm)			
	A	B	C	D
Co, α-C(org.)	212.6(7)	210.9(8)	195(3)	199.6(4)
Co, equ.C(O)	179.1(6)	177.2(8)	189(3)	177.8(5)
	178.8(8)	177.2(9)	171(3)	177.7(4)
	184.8(6)	177.7(8)	181(3)	179.8(6)
Co, ax. C(O) or P	180.6(8)	221.1(2)	227(1)	225.9(1)
α-C(org.), β-C(org.)	149.8(9)	140(2)	159(4)	153.7(7)
Equ. C, O	141.1(8)	115(1)	108(4)	114.3(6)
	113.8(10)	114(1)	119(4)	113.9(5)
	108.5(8)	114(1)	110(4)	113.2(7)
Ax. C, O	113.2(10)			
Acyl C, O				119.3(5)
	Bond angles (deg.)			
Equ. C(O), Co, α-C(org.)(av.)	85.2(3)	87.8(4)	88(1)	88.0(2)
α-C(org.); Co, ax. C(O) or P	179.2(3)	179.0(2)	117(1)	178.9(1)
Co, α-C(org.), β-C(org.)	112.3(4)	109.0(8)[a]	119(2)	116.1(3)
Equ. C(O), Co, equ. C(O)(av.)	119.6(3)	117 124(4)	114 124(1)	[b]
Co, α-C(org.), O				124.0(4)

[a] Average of 106.5(8) and 111.5(8) for the two conformers.
[b] Not determined.

Et *, iPr *, tBu *, Ph *, CH_2Ph, CH=CH_2 *, CF_3) compounds. The most important qualitative results of this study are as follows:

(i) The electron density on the α-carbon of the alkyl (aryl) group seems to decrease with increasing stability against the CO "insertion". This picture is in accord with the view that the migratory insertion can be regarded as a nucleophilic attack of the α-(alkyl)-carbon on one of the (equatorial) carbonyl-carbon atoms.

(ii) No significant charge density differences were found between the axial and equatorial carbonyl groups and between the carbonyl groups of the various molecules.

(iii) 3-3 MOs can be regarded as HOMO and LUMO. The HOMOs are predominantly of σ character and are localized on the α-alkyl carbon, while the LUMOs are of π* character and are mostly localized on the equatorial CO groups. This picture is again in good accord with the 1,2-alkyl migration mechanism of the CO "insertion".

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* These compounds were not prepared and characterized (cf. Section B, Table 1).

(iv) The Co–C(alkyl) bond consists of a bonding σ orbital and another orbital of π symmetry where there is low electron density on the bonding and a much higher electron density on the antibonding (π^*) component. This picture however still needs further clarification *.

An interesting explanation of the stability of the fluoroalkyl cobalt carbonyls has been advanced [88]. It was suggested that beyond the Co–alkyl σ bond formed from the overlap of the Co *dsp* (hybrid) and C sp^3 (hybrid) orbitals another $d\pi \rightarrow \sigma^*$ component is also formed which increases the stability of the Co–alkyl bond, resembling to some extent the well known retrodative bond. A comparison of the Co–C(alkyl) bond lengths (Table 3) known from the few X-ray studies seems to support this view.

Monosubstituted derivatives of the type $RCo(CO)_3L$ were assumed also to be of trigonal bipyramidal structure with bis-axial distribution of the non-CO ligands (R and L), on the basis of the D_{3h} IR ν(C–O) spectrum. This picture was confirmed by the two published X-ray diffraction structures for $HCF_2CF_2Co(CO)_3PPh_3$ [77] and $PhCH_2OOCCH_2Co(CO)_3PPh_3$ [2] (Table 3 and Figs. 3 and 4) **. The structure of these compounds permits some "through space" interaction [87,89] between the polar atoms of the alkyl group and the Co and/or the equatorial CO groups. It should be noted that the structural data permit, but do not prove, such an interaction. This is, however, supported by IR, NMR and CD evidence [2,3].

The structure of $PhCH_2OOCCH_2Co(CO)_3PPh_3$ shows a further interesting feature. The structure could be solved by assuming the existence of two independent molecules with different positions of the COO grouping. The electron density maps, however, show density trajectories between these two limiting positions indicating a quasi-continuous transition [90] even in the solid state [2].

In the case of the disubstituted derivatives, the IR data yield little structural information. If the trigonal bipyramidal structure with the axial alkyl ligand is retained, a diequatorial or axial/equatorial configuration can be assumed for the remaining ligands. These situations would mean C_s or C_1 point groups, both requiring two ν(C–O) bands in the IR which is actually observed. An X-ray structure determination has not yet been made. The configuration is similarly uncertain in the case of the trisubstituted derivatives.

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* A CNDO/2 study is in progress [86] for $MeCo(CO)_4$ and $MeOOCCH_2Co(CO)_4$ to investigate this problem and eventually to study organic carbonyl vs. Co or coordinated carbonyl interactions [87].

** Two exceptions were claimed: the configuration of $CH_2{=}C(R^1)CH_2CF_2(R^2)Co(CO)_3EPh_3$ (R^1 = H, Me; R^2 = F, CF_3; E = As, P) and one of the isomeric forms of $CF_3CF{=}CFCo(CO)_3PPh_3$ complexes were suggested to be of the axial–alkyl, equatorial-ER_3 type on the basis of NMR [37] and IR [157] data.

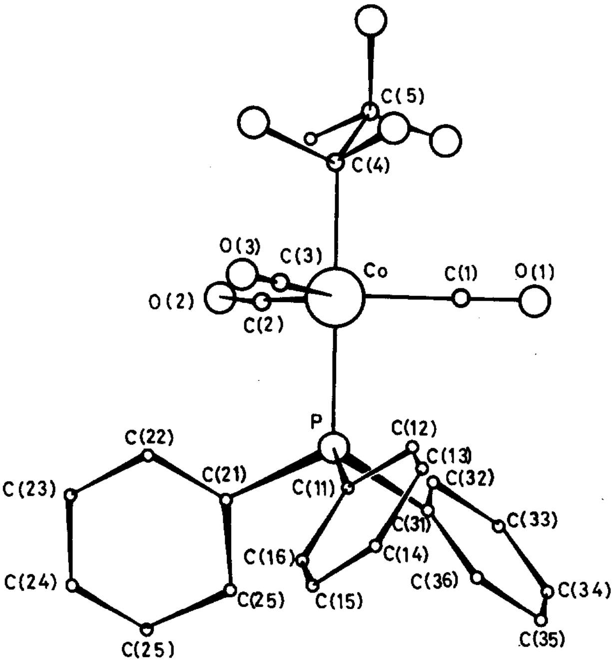


Fig. 3. The X-ray structure of $HCF_2CF_2Co(CO)_3PPh_3$ [77].

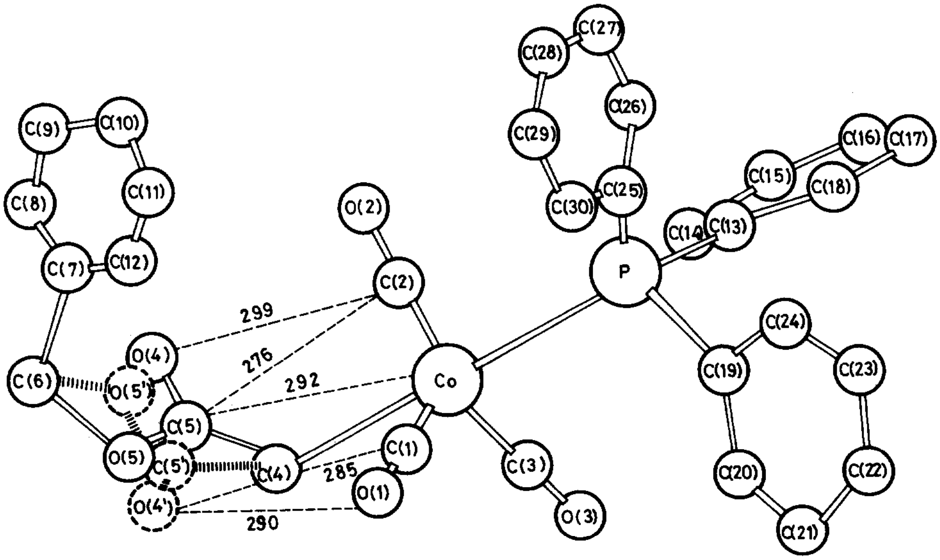


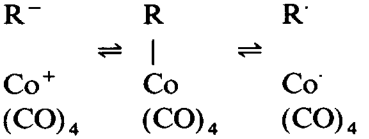
Fig. 4. The X-ray structure of $PhCH_2OOCCH_2Co(CO)_3PPh_3$ [2].

More recently ^{1}H-, ^{13}C-, ^{19}F-, ^{31}P NMR and CD [2,3,7,8,13,44,71,91–93] spectroscopic results have been reported. However a lot of systematic work is still needed to draw generalizable conclusions from these data.

Fluxional behaviour of the carbonyl ligands has been detected by ^{13}C NMR spectra of $CF_3Co(CO)_4$ [91] and of the $ROOCCH_2Co(CO)_4$ complexes [2]. The ^{31}P and ^{3}H NMR spectra of $MeCo(dpe)_2$ and $MeCo[P(OMe)_3]_4$ indicate that these complexes are either fluxional or their structure is different from the usually supposed trigonal bipyramid [13,71].

Finally, it should be mentioned that in some reactions where according to the generally accepted view, alkylcobalt carbonyls would form, the presence of alkyl–CoL_x radical pairs has been detected by spectroscopy (CIDNP) [92,93], kinetic measurements [30,40] and deduced from product analysis [6]. Some recent reviews analyse this question [94–96]. Here we would like only to point out two important consequences:

(i) The alkylcobalt carbonyls can be regarded * as being in equilibrium with products of both heterolytic and homolytic cleavage of the alkyl



$$\begin{array}{c} R^- \\ Co^+ \\ (CO)_4 \end{array} \rightleftharpoons \begin{array}{c} R \\ | \\ Co \\ (CO)_4 \end{array} \rightleftharpoons \begin{array}{c} R^\cdot \\ Co^\cdot \\ (CO)_4 \end{array} \qquad (21)$$

carbon–cobalt bond. The position of equilibria (21) surely depends very critically on the nature of R.

(ii) Due to what is probably a facile equilibrium between these species, it is difficult to infer what the actual intermediate(s) are in catalysis. Certainly this remains a question under intensive study, in which the importance of radical pairs is increasingly evident.

D. REACTIONS OF ALKYLCOBALT CARBONYLS

The alkylcobalt carbonyls are very reactive compounds. Most of their reactions were studied with complexes prepared in situ. It should however be noted in this connection that the results obtained with in situ generated reaction products generally contain some uncertainty, especially if the compound to be studied has not been detected directly.

The most important reaction types of these compounds are summarized in Table 4.

Before going into details of the reactions of alkylcobalt carbonyls the importance of equilibrium (22) [19] should be stressed. This equilibrium

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* cf. Ref. 95.

$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \tag{22}$$

produces a coordinatively unsaturated 16-electron species and therefore its detection met extraordinary experimental difficulties; in fact it has not yet been proved by direct methods. Nevertheless the existence of this equilibrium is generally accepted and it plays a key role in the presently accepted mechanism of hydroformylation [95,97–99]. The fact that many of the reactions of alkyl- and acylcobalt carbonyls are leading to the same product can also be explained by eqn. (22).

(i) Substitution reactions

(a) Substitution by Lewis bases

Alkylcobalt carbonyls can be easily substituted by soft Lewis bases: phosphines, phosphites, arsines, stibines. The primary product is the substituted acyl derivative. The reaction is generally fast and almost quantitative (cf. Section B). The mechanism is probably an S_N1 (eqns. (22) and (23)) type

$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \tag{22}$$

$$RCOCo(CO)_3 \xrightarrow{PR'_3} RCOCo(CO)_3PR'_3 \tag{23}$$

but an S_N2 path (eqn. (24)) cannot be ruled out. No kinetic studies are known concerning this problem.

$$RCo(CO)_4 + PR'_3 \rightarrow RCOCo(CO)_3PR'_3 \tag{24}$$

TABLE 4

A summary of the reactions of alkylcobalt carbonyls

Substitution reactions		Reactions of the Co,C(alkyl) bond			
		Various		Insertions	
D(i)(a)	Substitution with Lewis bases	D(ii)(a)	Oxidative fission	D(ii)(h)	CO insertion
D(i)(b)	Intramolecular substitution	D(ii)(b)	Reductive fission	D(ii)(h)	Insertion of unsaturated compounds
D(i)(c)	Oxidative addition	D(ii)(c)	Reaction with CH acids		
		D(ii)(d)	β-Elimination		
		D(ii)(e)	Isomerization		
		D(ii)(f)	Thermal degradation		
		D(ii)(g)	Radical reactions		

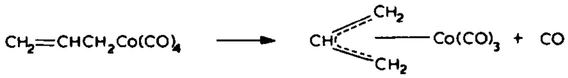
Higher than monosubstituted derivatives could not be obtained by direct substitution except with phosphites [2].

The carbonylation of the tetrakis-phosphine (or phosphite) compounds (reaction (18)) can be regarded as substitution by CO [45,71].

(b) Intramolecular substitution

Only a few examples were reported for cases where a function in the alkyl group substitutes for a CO ligand of the Co–carbonyl complex.

Allyl halogenides react with $[Co(CO)_4]^-$ presumably yielding η^1-allylcobalt tetracarbonyls which are converted by CO loss into the corresponding stable η^3-allylcobalt tricarbonyl [100,101,156,160] (reaction (25)).



(25)

The formation of η^3-benzylcobalt tricarbonyls [5,7,8] and η^3-oxallyl-tricarbonyls [159] can be regarded as a special case of reaction (25).

The formation of the 1-η^1; 4,5-η^2-pentenylcobalt tricarbonyls (reaction (9)) [37] can also be regarded as substitution of a CO by an olefin. The corresponding tetracarbonyls are not known but the tricarbonyl EPh_3 (E = P, As) derivatives could be prepared and isolated.

The supposition of formation of a five-membered acylmetallocycle from the reaction of $[Co(CO)_4]^-$ with haloacetic acid esters [4] later turned out to be erroneous [2,3] (cf. Section B, reaction (2)).

(c) Oxidative addition

Very recently it has been shown [44] that $N{\equiv}CCH_2Co(CO)_4$ or $R^1OOCCH_2Co(CO)_4$ (R^1 = alkyl) react with $NaOCH_3$ yielding the mononuclear cobalt carbonyl anions, $[R^2Co(COOCH_3)(CO)_3]^-$ ($R^2 = N{\equiv}CCH_2$ or R^1OOCCH_2). This reaction can formally be regarded as an addition of the alcoholate on an alkylcobalt carbonyl carbon. Although full characterization of the new anions is still to be achieved this discovery is one of the more important recent findings in the field covered by this review.

(ii) Reactions of the Co–C(alkyl) bond

(a) Oxidative fission

The alkylcobalt carbonyls (particularly the non-substituted derivatives) are sensitive to O_2 (or air). The oxidation products were not analyzed, but are assumed to be cobalt oxide and carboxylic acids [11].

Dihalogens are widely used as oxidation agents for organometallics. This oxidation can be used principally for the determination of the alkyl group (as halogenide) and the number of coordinated carbonyl groups at an alkylcobalt carbonyl. In fact the reaction of substituted alkylcobalt carbonyls with Cl_2 [80] or Br_2 [48,56] led to the formation of the corresponding alkyl chlorides or bromides.

The I_2/MeOH reagent was used to analyze some reaction mixtures obtained by the reaction of $HCo(CO)_4$ and olefins and the presence of acylcobalt derivatives was detected [102,103]. Later it was shown that this reagent leads to the "detection" of acyl derivatives even starting from pure solutions of stable alkylcobalt carbonyls [104].

In quantitative studies reaction of the halogen (I_2 was investigated) with both the low-valent metal and the phosphine should be taken into account [105,106].

Oxidatively induced CO insertion into alkyl–metal bonds has been observed with some Fe and Mo complexes [107–109]. This interesting aspect has not yet been studied with cobalt carbonyls.

(b) Reductive fission

The carbonylation of olefins is always accompanied by hydrogenation of the starting compound to alkane. In some cases this is the main reaction. It is supposed that the saturated product was formed by the reductive fission of the Co–C bond of an alkylcobalt carbonyl.

The reducing agent may be either dihydrogen or $HCo(CO)_4$ (or its phosphine derivative(s)) the latter always being present in such reaction mixtures (see, for example, ref. 95). In spite of the importance of this reaction in the hydroformylation and other reactions it has been surprisingly neglected by studies in this field.

Only one example is known where an isolated Co(I) alkyl complex reacted with dihydrogen (reaction (26)) [71].

$$MeCo(dpe)_2 + H_2 \xrightarrow[20°C]{0.1\ MPa} HCo(dpe)_2 + CH_4 \tag{26}$$

In contrast to the dpe complex $MeCo[P(OMe)_3]_4$ does not react with H_2 even under higher pressure [13].

The lack of data on the reaction of alkylcobalt carbonyls with $HCo(CO)_4$ is even more striking. Only recently the discovery of the $ROOCCH_2Co(CO)_4$ type of cobalt alkyls permitted a quantitative study of this problem. It was shown that $EtOOCCH_2Co(CO)_4$ reacts with $HCo(CO)_4$ in a clean and quantitative reaction to give ethyl acetate and $Co_2(CO)_8$ [2]. A kinetic study of this reaction [110] provided data which are compatible with an oxidative addition/reductive elimination type mechanism (reactions (27)–(30)).

$$EtOOCCH_2Co(CO)_4 \rightleftharpoons EtOOCCH_2Co(CO)_3 + CO \tag{27}$$

$$EtOOCCH_2Co(CO)_3 + HCo(CO)_4 \xrightarrow{slow} [EtOOCCH_2Co_2(CO)_7H] \quad (28)$$

$$[EtOOCCH_2Co_2(CO)_7H] \xrightarrow{fast} EtOOCCH_3 + Co_2(CO)_7 \quad (29)$$

$$Co_2(CO)_7 + CO \rightleftharpoons Co_2(CO)_8 \quad (30)$$

It is however far from proven that this picture could be generalized. Under different conditions and/or with different structural features in the alkyl group the mechanism may show dramatic changes (e.g. direct protonation of the Co–C(alkyl) bond, radical reaction pathways, etc.).

The reductive fission of the Co–C(alkyl) bond of an intermediate cobalt alkyl species by $HCo(CO)_4$ (generated in situ) is proposed in the hydrogenolysis of organic halides [111] or in the stoichiometric hydrogenation of various olefins [30,95,112–114]. An analogous mechanism is accepted for the catalytic hydrosilylation of olefins [97]: in this case the $HSiR_3$ component is regarded as the reducing agent.

(c) Reactions with CH and NH acids

The tetrasubstituted methylcobalt compounds react with terminal acetylenes yielding the corresponding Co–acetylide and methane. Similarly, the formation of methane was observed in the reaction of these complexes with mineral acids [13,69,71].

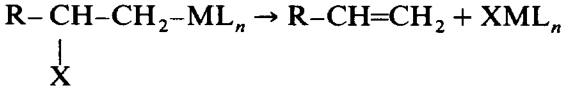
The $ROOCCo(CO)_3L$ ($L = PPh_3$, $P(OPh)_3$) compounds (which can be regarded as "alkyl"-complexes only in a very general sense) react with HCl to give the corresponding cationic cobalt complexes: $[Co(CO)_4L]^+Cl^-$ [57].

$CH_3Co(dpe)_2$ shows an interesting reaction with the CH–acid acetaldehyde: methane and CO are evolved [71]. This is noteworthy since the carbonylation of this complex is accompanied by CO insertion (cf. refs. 69, 71 and Section B).

Only one example is known for the reaction with an NH acid: $EtOOCH_2Co(CO)_4$ reacts with aniline to give *N*-phenylglycine ethylester [2].

(d) β Elimination

β Elimination is a characteristic reaction of organometallics which correspond to the structural criteria shown in eqn. (31).



$$\underset{\displaystyle X}{R\text{-}\overset{}{CH}}\text{-}CH_2\text{-}ML_n \rightarrow R\text{-}CH{=}CH_2 + XML_n \quad (31)$$

X = H, halogen, etc.

Such processes are often encountered in the chemistry of alkylcobalt carbonyls, especially with β-H atoms. On the other hand the best characterized case of β elimination of these compounds is that possessing a β-fluorine atom.

It has already been mentioned that $(CO)_4CoCF_2CF_2Co(CO)_4$ reacts with dry HCl at 65°C yielding $CHF_2CF_2Co(CO)_4$ (13%) (Section B) [35]. The main product of this reaction was trifluoroethylene (53%). These products can be rationalized by the reaction sequence (32) [35]. It is an interesting

$$(CO)_4CoCF_2CF_2Co(CO)_4 \xrightarrow{HCl} CHF_2CF_2Co(CO)_4 + CF_2{=}CHF$$

$$+ FCo(CO)_4 \rightarrow \text{decomp.} \tag{32}$$

feature of this reaction that it clearly shows the preference of β elimination of fluorine over hydrogen.

There is still one more case for β elimination of H, but here the alkylcobalt carbonyl has only been characterized by IR spectroscopy. The thermal decomposition (at 0–25°C) of $EtOOCCH(CH_3)Co(CO)_4$ always yields ethylacrylate (with other organic products) independent of the atmosphere (CO or Ar) used [6].

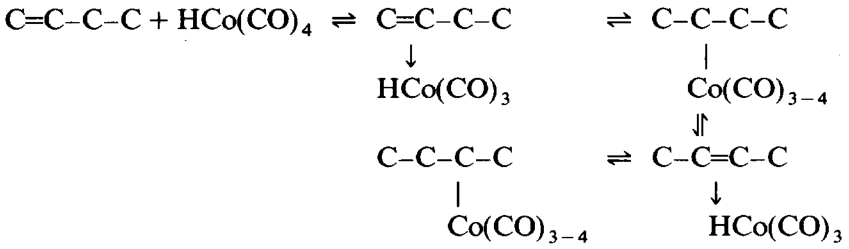
β Elimination steps are assumed in the isomerization of alkylcobalt carbonyls (see Section D(ii) (e)). In the reaction of $K\{Co[P(OMe)_3]_4\}$ and EtCl, the formation of ethylene and the corresponding cobalt hydride was observed [13] and again explained by β elimination. The $n\text{-}PrCo(CO)_3PPh_3$ complex which was isolated however did not show this reaction [56].

(e) Isomerization

The formation of all possible isomeric aldehydes in the cobalt-catalyzed OXO reaction can be explained well by the isomerization of the alkylcobalt carbonyl intermediates. However no direct experimental proof of this generally accepted hypothesis has yet been presented [95,97].

In situ prepared alkylcobalt carbonyls were treated under OXO conditions in an ingenious experiment [115] but only the non-isomerized aldehydes were obtained. The oxidative fission of an analytically pure sample of $n\text{-}PrCo(CO)_3PPh_3$ with Br_2 yielded only n-PrBr [56]. These observations do not favour the supposition of the isomerization of alkylcobalt carbonyls.

On the other hand, in stoichiometric reactions of olefins and $HCo(CO)_4$ where the formation of alkylcobalt carbonyls is generally supposed (and in some cases even detected [18,24,25]) extensive isomerization of the olefins was observed [95,116–120]. This observation has been rationalized with the equilibria (33).



$$\begin{array}{lcccc} C{=}C{-}C{-}C + HCo(CO)_4 & \rightleftharpoons & \underset{\overset{\downarrow}{HCo(CO)_3}}{C{=}C{-}C{-}C} & \rightleftharpoons & \underset{\overset{|}{Co(CO)_{3-4}}}{C{-}C{-}C{-}C} \\ & & & & \Updownarrow \\ & & \underset{\overset{|}{Co(CO)_{3-4}}}{C{-}C{-}C{-}C} & \rightleftharpoons & \underset{\overset{\downarrow}{HCo(CO)_3}}{C{-}C{=}C{-}C} \end{array} \qquad (33)$$

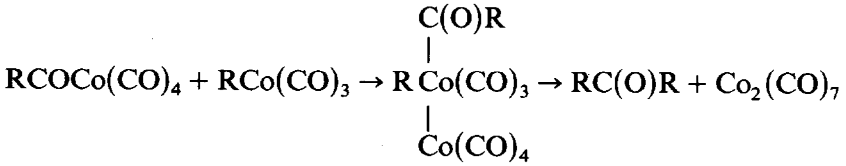
It was proposed recently that in certain cases the equilibria (33) should be reinterpreted in terms of geminate (alkyl/CO) radical pairs [30,94–96].

(f) Thermal degradation

Hydrocarbon–alkylcobalt carbonyls decompose generally in a fast reaction above 0°C even in dilute solutions. The most characteristic reaction product is the corresponding acylcobalt carbonyl [41]. The reaction can be regarded (formally) as disproportionation

$$2\ RCo(CO)_4 \rightarrow RCOCo(CO)_4 + RCo(CO)_3 \qquad (34)$$

Upon heating an isolated alkylcobalt carbonyl or its solution, the formation of dialkyl ketones can be observed (eqn. (35)) [121]. A Co(III) acyl–alkyl complex was regarded as a key intermediate in this reaction.



$$RCOCo(CO)_4 + RCo(CO)_3 \rightarrow R\,\underset{\overset{|}{Co(CO)_4}}{\overset{\overset{C(O)R}{|}}{Co(CO)_3}} \rightarrow RC(O)R + Co_2(CO)_7 \qquad (35)$$

The formation of ketones was also investigated [122] under OXO conditions. A bimolecular mechanism was proposed *.

The thermal decomposition of solutions of $EtOOCCH(R)Co(CO)_4$ (R = Me, tBu, Ph, COOEt) complexes inferred the involvement of radical pathways (from product analysis) [6,123]. Although these complexes are thermally unstable they seem to be stable against the "insertion" of carbon monoxide.

Heating of the "bis-alkyl" $(CO)_4CoCF_2CF_2Co(CO)_4$ under various conditions showed a series of interesting transformations [34,35] which are summarized in eqn. (36). The formation of the bridged carbene complex ((A) → (C)) represents, to the best of our knowledge, the first example of the 1–2 shift of a non-hydrogen substituent on a C_2 moiety coordinated to a transition metal **.

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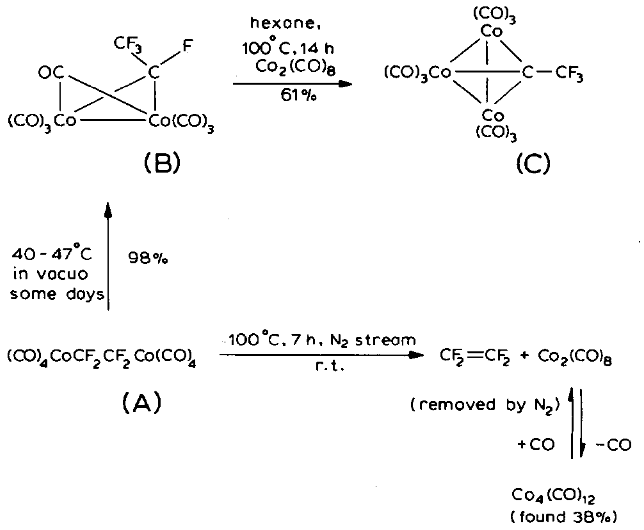
* The results of Bergman and co-workers [149–152] obtained recently with cyclopentadienyl–Co(III) complexes are certainly of great importance in this respect (cf. Section E).

** Some further examples of this reaction type were found recently with acetylenes and cobalt carbonyls [124–126].



(36)

(g) Radical reactions

The alkylcobalt carbonyls are, or are proposed to be, involved in some reaction mechanisms in which transient radicals are formed. Solvent caged organic/metallorganic radical pairs are believed to have great importance in this chemistry. We refer here only to some recent reviews which cover this field [94–96].

(h) CO "insertion"

The insertion reactions are the most important among the reactions of the alkylcobalt carbonyls.

In general terms, any species, L, which has two electrons (not necessarily a lone pair) of proper energy and/or symmetry (L may be CO, olefin, acetylene, SO_2, etc.) can undergo insertion (reaction (37)). The primary

$$RCo(CO)_4 + :L \rightarrow R\text{–}L\text{–}Co(CO)_4 \qquad (37)$$

insertion product is not isolated in all cases: sometimes the insertion event was only hypothesized on the basis of the structure of the end product of a multistep reaction. The isolation of the primary product has the best chances at the insertion of CO, due to its higher stability.

The CO insertion of the alkylcobalt carbonyls and their derivatives can be described by the overall process (38). In spite of the great importance of

$$RCo(CO)_nL_{4-n} + CO \rightleftharpoons RCOCo(CO)_nL_{4-n} \qquad (38)$$

equilibrium (38) very few studies have appeared. Kinetic studies are almost entirely lacking.

The equilibrium shown in eqn. (38) can be approached reversibly from both sides, and the position of equilibrium depends critically on R. The most important event of the CO insertion is the C–C bond formation between the α-(alkyl)C and the "inserted" CO-carbon. This is suggested by the IR observation of $CH_3COCo(CO)_4$ in solutions of $CH_3Co(CO)_4$ as well as of $CH_3Co(CO)_4$ vapours over the acetyl derivative [41]. The decisive chemical proof was obtained by the easy carbonylation/decarbonylation of the benzylcobalt or phenylacetylcobalt derivatives respectively [7,8,48]. The substituent dependence of the equilibria shown in (3) was studied recently [8] (Fig. 5).

Equilibria of type (38) ($n = 4$) are overwhelmingly on the acyl side for hydrocarbon alkyls, while shifted to the alkyl side for the fluorinated alkyls or the $ROOCCH_2$-type; the benzyl derivatives show an intermediary behaviour.

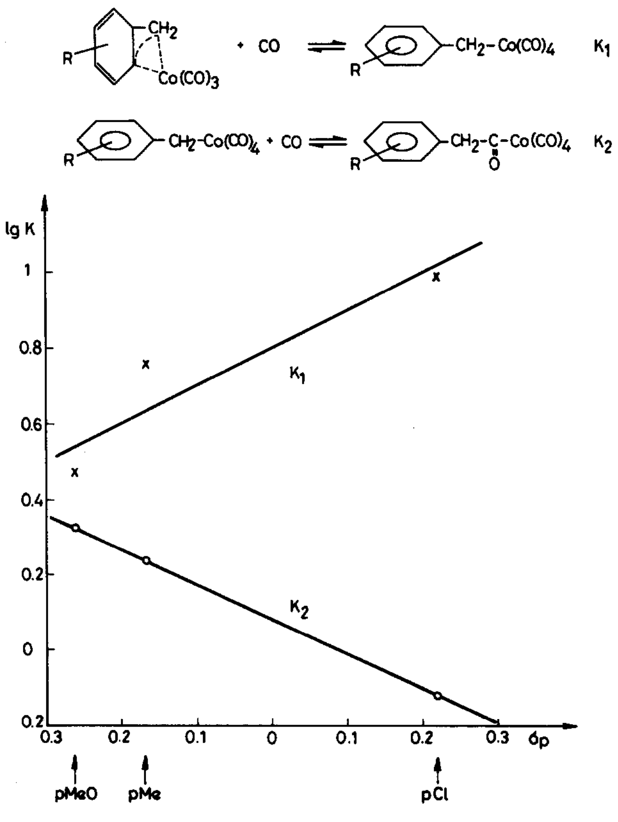
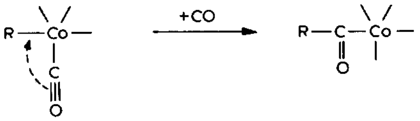


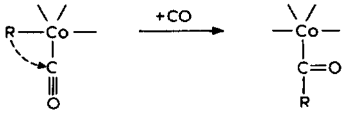
Fig. 5. The substituent dependence of the equilibria between η^3-, η^1-benzyl and η^1-phenylacetylcobalt carbonyls [8].

Principally, two types of intramolecular acyl formation can be imagined. At the true insertion one CO ligand was moved into the R–CO bond



(39)

However in a 1–2 alkyl shift the alkyl group migrates to one of the (equatorial) carbonyl-carbon atoms

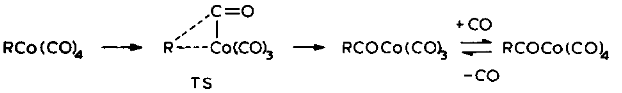


(40)

The two mechanisms could be differentiated for example by (i) using a labelled (^{13}CO or $C^{18}O$) atmosphere or (ii) carrying out the reaction in the presence of non-CO Lewis bases such as for example phosphines, if there were no rearrangement in the primary product, no isotopic exchange reaction of the starting molecule and no fluxionality of the CO ligands in the alkyl- or acylcobalt carbonyls.

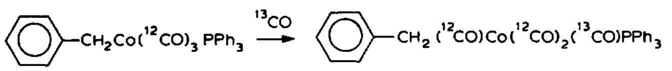
The only acylcobalt carbonyl structure known ($2,6\text{-}Cl_2C_6H_3CH_2\text{-}COCo(CO)_3PPh_3$ [8]) shows a bis-axial distribution of the acyl and the phosphine ligands, which would favour the "insertion" type mechanism. However, the fact that the non-CO ligands are in *trans* positions might indicate that a rearrangement of the ligands has occurred either in the transition state or in the product.

A 1–2 alkyl shift (from Co to the carbonyl carbon) is nowadays the most generally accepted mechanism (reaction (41)) [95,98,127–131]. The mechanism is therefore called migratory insertion. A surprising example (however for an Fe complex) which seems to support another mechanism (perhaps the true "insertion" type) was presented recently [132,133]. It should be stressed that most of the mechanistic studies were made with metals other than Co (Mn, Ir, Ru, Fe) and the results obtained (generally using mixed ligand complexes) with these metals were hypothesized to be true also for cobalt.

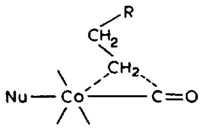


$$RCo(CO)_4 \longrightarrow \underset{TS}{R\text{---}\overset{C=O}{Co}(CO)_3} \longrightarrow RCOCo(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCOCo(CO)_4 \qquad (41)$$

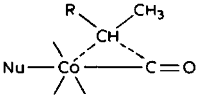
The belief that alkyl migration is intramolecular and that the $RCOCo(CO)_3$ unsaturated intermediate took up CO from the environment (dissolved, atmosphere) was supported by isotopic studies [48] (reaction (42)).



(42)



TS/a



TS/b

The stereochemistry of the transition state (TS) in reaction (41) is also very important from a technical viewpoint (distribution of straight and branched chain OXO products). The five coordinate TS depicted in (41) shows no prominent steric preference. However in the presence of a high concentration of a nucleophile, this can coordinate to the cobalt simultaneously with the migration and thus the six-coordinate TS(a) and TS(b) intermediates can be formed. The TS(b) form is crowded and therefore a strong preference for the TS(a) form develops which enhances the formation of the straight chain products, which are predominant [95,98]. The problem of the S_N1 or S_N2 character of the insertion is therefore a challenging important question which merits further studies.

It was shown recently in a kinetic study [30] that $Co_2(CO)_8$ catalyses the CO uptake in the stoichiometric reaction of olefins with $HCo(CO)_4$. These results can also be interpreted by radical pathways.

Another challenging aspect of the CO insertion reactions is the problem why the (at least formal) CO insertion into the acylcobalt Co–C bond is so rarely observed; the problem of the "insertive polymerization" of CO.

There are reports on organic products of catalytic or semicatalytic experiments where double CO insertion can be supposed in the course of the overall reaction [134–138]. These observations are however too sporadic to draw general conclusions.

In one particular case, at the carbonylation of α-phenethyl halides sufficient evidence has been accumulated to construct a picture of the possible mechanism (eqn. (43)) [138,139]. The possibility of the existence of the supposed enol intermediate has been further supported using optically active and deuterated substrates [137]. Taking into regard the presence of hard Lewis acids (Na^+, Ca^{2+}) in systems leading to double carbonylations the enol-type mechanism might be more general *.

(i) Insertion of other unsaturated compounds

The insertion reactions of unsaturated compounds other than CO can generally be understood only by assuming prior insertion of CO. Thus these reactions are most probably in fact reactions of $RCOCoL_n$ complexes.

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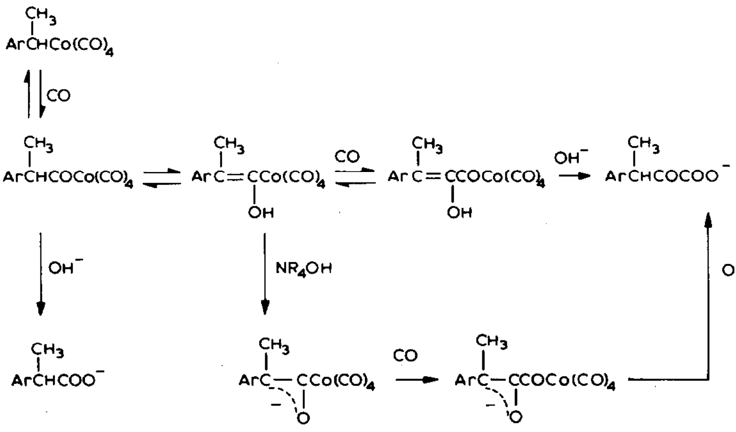
* One of the authors (G.P.) acknowledges a discussion with W. Keim and B. Fell (Aachen, G.F.R.) in 1981 which contributed to the formation of this opinion.

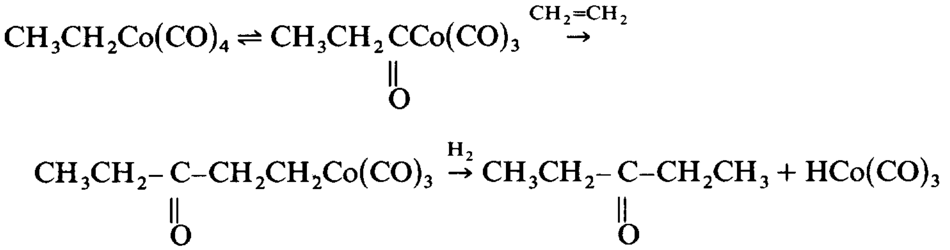


(43)

Therefore these reactions will only be summarized very briefly here.

In the presence of some unsaturated compounds the primary acyl complex generally cannot be observed, only (organic or organometallic) products of multistep reactions involving also the insertion of the unsaturated molecule can be detected or isolated.

The insertion of olefins provides an alternative mechanism for the formation of ketones (e.g. for ethylene reaction (44) (cf. also reaction (35)).



$$CH_3CH_2Co(CO)_4 \rightleftharpoons CH_3CH_2\underset{\underset{O}{\|}}{C}Co(CO)_3 \xrightarrow{CH_2=CH_2}$$

$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_2Co(CO)_3 \xrightarrow{H_2} CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3 + HCo(CO)_3 \qquad (44)$$

This mechanism was supported by the cyclization of acylcobalt carbonyls containing olefinic unsaturation in the acyl group [140].

Alkyl- (or better acyl-) cobalt carbonyls were also reacted with conjugated homo- and heterodienes and acetylenes [11,141]. These reactions are summarized in Fig. 6.

E. ALKYLCOBALT CARBONYLS AS INTERMEDIATES IN CATALYTIC AND OTHER IMPORTANT SYNTHETIC REACTIONS

In the previous sections of this review several hints were made at the importance of alkylcobalt carbonyls as supposed or proven intermediates of various organic syntheses. A series of excellent books and reviews

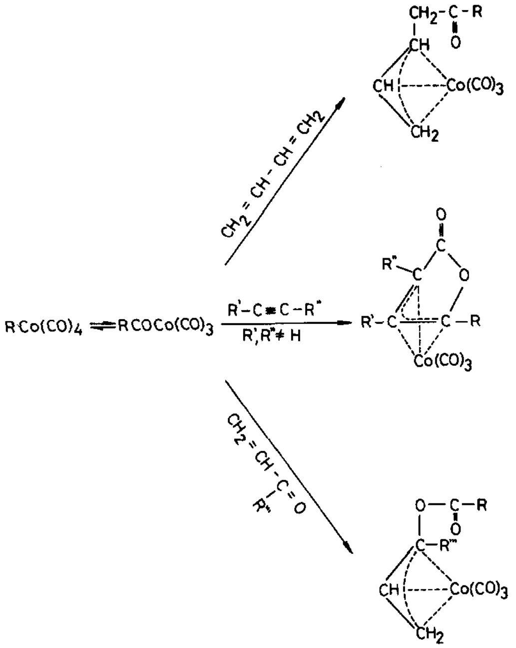


Fig. 6. Subsequent insertions of CO and homo- and heterodienes or acetylenes into the cobalt–carbon bond of the alkylcobalt carbonyls.

[11,46,62,63,78,94–99,127,128,142–144,156] deals with these reactions. Therefore we only summarize these reactions, not from the chemical viewpoint of the reaction mechanisms but from the practical viewpoint of the synthetic applications. The most important of these reactions are shown in Fig. 7.

The reactions of some Co(II) and Co(III) alkyl compounds (which were not discussed in this review) contribute considerably to the understanding of the reactions of the Co(I) alkyls. Therefore we give here some leading references in this field [147–153]. It remains however still to be proven how far the mechanistic results obtained with these compounds are applicable to the alkyl-Co(I) carbonyls.

F. CONCLUDING REMARKS

The survey presented in this paper is intended not only to summarize the results obtained with alkylcobalt carbonyls but also to focus the attention of the reader on the unsolved problems.

Alkylcobalt carbonyls can be prepared by several published procedures among which the alkyl halide + $[Co(CO)_4]^-$ and the olefin + $HCo(CO)_4$ routes seem to be of general utility. The exploration of their mechanisms is

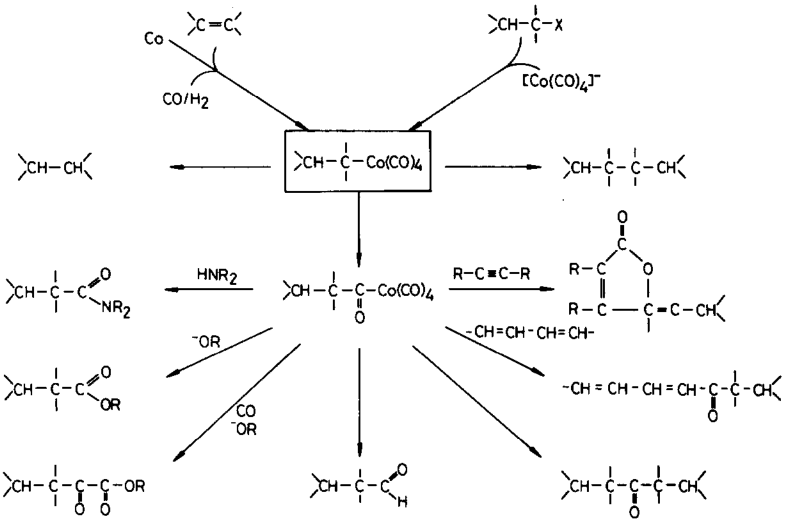


Fig. 7. Alkylcobalt carbonyls as intermediates of organic syntheses.

essential especially for the latter, which is of special importance because of its applications in catalysis. Preparative efforts to prepare arylcobalt tetracarbonyls would be important.

The kinetic and/or thermodynamic stability of the alkylcobalt carbonyls to be prepared is enhanced by (i) the absence of β-hydrogen atoms in the alkyl group and (ii) the presence of polar electron withdrawing group(s) on the α-carbon atom. Efforts are necessary to prepare some further examples of this group of compounds to enable a more comprehensive study of their properties.

The phosphine substituted derivatives of alkylcobalt carbonyls are preparatively much more easily accessible. Due to their importance in catalysis a detailed kinetic study of their formation would be important.

The most important reaction of alkylcobalt carbonyls is the CO "insertion" (or 1–2 alkyl shift, or migratory insertion). Its chemistry and stereochemistry is fairly well understood; however further investigation is necessary in the following areas: mechanistic (especially regarding the possibility of radical paths); thermodynamic (bond strength, equilibrium studies); stereochemical (S_N2 type alkyl migration, isomerization preference, asymmetric induction); theoretical (a high-level approximation MO study *); to get a better insight into this important reaction. At the present stage too

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* The authors are aware that an ab initio investigation of this problem has been recently initiated by F. Bernardi (Bologna, Italy) and his group.

many analogies are generalized from results obtained with other metals. Special attention should be devoted to reaction possibilities which are going through reaction steps other than a 1–2 alkyl shift.

Other reactions of the alkylcobalt carbonyls are explored only to a preliminary level. Here much chemical and mechanistic work is necessary.

Special attention should be paid to problems such as: the possibility of radical reactions; the formation of binuclear (see e.g. the alkyl-acyl–Co_2 intermediate in ketone formation) or trinuclear (the predicted existence of the alkyl analogue of $HCo_3(CO)_9$ [154] or its phosphine substituted derivative [155]) intermediates.

The main structural features of alkylcobalt tetracarbonyls and their monosubstituted phosphine derivatives are understood through X-ray diffraction. Further structural studies would be necessary to compare an alkyl- and acylcobalt tetracarbonyl pair (with the same alkyl group) and for molecules which contain more than one phosphine.

The infrared ν(C–O) spectra of alkylcobalt carbonyls are well interpreted. ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P NMR studies are relatively rare. Further efforts in this field are necessary to study configurational (bis tertiary phosphine derivatives), conformational ("stable" rotamers, etc.), and fluxionality (dependence of stereochemical non-rigidity on the electronic effects of the alkyl group) problems.

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Notes added in proof

Some further relevant work.

(i) η^1-[η^3-2,3,4-Tricarbonylcobalt)-perfluorcyclopentadiene-1-yl] cobalt tetracarbonyl has been prepared [161] and its structure determined by X-ray diffraction [162].

(ii) η^1-Cobalt tricarbonyl triphenylphosphine derivatives of some carbohydrates has been prepared [163].

(iii) $ClCF_2Co(CO)_4$ has been detected by ^{19}F NMR and mass spectra [164].

(iv) $PhCH_2Co(CO)_4$ has been postulated as an intermediate in PTC carbonylation of benzyl halides [165].

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