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Synthesis, characterization and reactions of acylcobalt carbonyl complexes, $RC(O)Co(CO)_{4-n}L_n$ ($n=0, 1, 2, 3$)

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Abstract

The synthesis, structural and spectroscopic features, and reactions of acylcobalt carbonyl complexes of the type $RC(O)Co(CO)_{4-n}L_n$ ($n=0$, 1, 2, 3) are comprehensively reviewed.

Keywords: Acylcobalt carbonyl complexes

1. Introduction

Acylcobalt carbonyl complexes of the general formula $RC(O)Co(CO)_{4-n}L_n$ ($n=$ 0, 1, 2, 3) are particularly important organometallic compounds from a practical point of view due to their relevance to a growing number of cobalt-catalyzed carbonylation (and decarbonylation) reactions [1]. Best known is the commercially successful hydroformylation of olefins [1a], but the hydroalkoxycarbonylation of butadiene to adipic acid [1a,2] and homologation of methanol to acetaldehyde [3] are also promising candidates for industrial application. In certain cases, acylcobalt carbonyls may contribute to the synergistic effect observed in carbonylations catalyzed by cobalt containing bimetallic systems [4]. In addition, many of them are useful starting materials in both stoichiometric and catalytic organic syntheses [5] as well as suitable models for structural and mechanistic studies. Accordingly, these compounds attracted considerable interest from different groups of the scientific community in the last four decades.

Note that the term "acylcobalt carbonyl complex" usually refers to compounds originating from the corresponding alkylcobalt carbonyl complexes via, at least formal, CO insertion into the C–Co bond. However, the less numerous alkoxycarbonyl ($R=R'O-$) and carbamoyl ($R=R'_2N-$) complexes can also be considered as acyl analogues since (1) their structure and reactions are similar to those of the typical acyl complexes (see below), (2) CO insertion into the O–Co [6–8] and N–Co bond [9], respectively, was suggested (although cobalt carbonyl complexes with O–Co and N–Co bonds are not known), and (3) they are plausible intermediates in several cobalt-catalyzed carbonylation reactions, as well [6,8–10]. In fact, there is a precedent where both the alkoxycarbonyl- and carbamoylcobalt carbonyls were treated as acyl complexes [11].

The first isolated and unambiguously identified acylcobalt carbonyl complex, $CH_3C(O)Co(CO)_4$, was reported by Breslow and Heck in 1960 [12]; the authors demonstrated the quantitative carbonylation of methylcobalt tetracarbonyl as a possible pathway to obtain its acyl counterpart. The most widely accepted mechanism of olefin hydroformylation, featuring the acylcobalt carbonyls as intermediates and the alkyl–acyl equilibrium, appeared in the same publication. Interestingly, Orchin et al. characterized a complex earlier by IR spectroscopy as a product of the reaction of 1-hexene, CO and $HCo(CO)_4$ (stoichiometric hydroformylation) [13], but failed to identify what appears to be heptanoylcobalt tetracarbonyl. Most of the research stimulated by these pioneering discoveries was then aimed at the synthesis and

reactions of new complexes including ligand substituted derivatives, their possible use in organic syntheses and the better understanding of catalytic reactions. As a result, the first alkoxycarbonylcobalt complex, $(CH_3)_3COC(O)Co(CO)_4$, was isolated in 1964 [6], while the first stable carbamoylcobalt complex, $C_5H_{10}NC(O)Co(CO)_3PPh_3$, was synthesized in 1969 [9].

After a decade of fruitful investigations, some aspects of which were repeatedly reviewed by Heck [5d–f], considerably less advance was made during the 1970s. However, a major breakthrough took place in the mid-eighties when high-resolution and high-pressure spectroscopic techniques as well as improved preparative methods became routinely available. Since that time a substantial amount of data has been accumulated, which merits attention. Furthermore, while the chemistry of alkylcobalt carbonyls has been thoroughly reviewed [14], no similar work fully covering the chemistry of acylcobalt carbonyls is available, although valuable sources of information do exist [11,15].

The purpose of this review, therefore, is to provide possibly complete information about the synthesis, structural characterization and reactions of complexes of the type $RC(O)Co(CO)_{4-n}L_n$ ($n=0$, 1, 2, 3) where R represents a C-, O- or N-bound group, with special emphasis on the most recent achievements. To our knowledge, Tables 1–3 list all compounds which were isolated and/or characterized by analytical methods. Since many reactions of the acylcobalt carbonyls were already known in the early years and summarized by Heck [5d], discussion in Section 4 is limited only to those reactions which were further studied or found later.

2. Synthesis and properties of acylcobalt carbonyl complexes

2.1. Acylcobalt tetracarbonyls

Evidently, the tetracarbonyls $RC(O)Co(CO)_4$ are the most important acylcobalt derivatives as catalytic intermediates, since the vast majority of cobalt-catalyzed carbonylation processes do not utilize ligands other than CO. In the catalytic cycles they are generated presumably by the carbonylation of $RCo(CO)_4$ intermediates, which is indeed a widely useful laboratory procedure for their synthesis (Eq. (1)). The $RCo(CO)_4$ precursors can be generated in various ways [14] and usually react in situ with CO. As an alternative, reaction of the tetracarbonylcobaltate(−I) anion with an appropriate carboxylic acid halide (Eq. (2)) is an expedient preparative method in many cases.

$$RCo(CO)_4 + CO \rightleftharpoons RC(O)Co(CO)_4 \quad (1)$$

$$[Co(CO)_4]^- + RC(O)X \rightarrow RC(O)Co(CO)_4 + X^- \quad (2)$$

Nevertheless, both reactions Eq. (1) and Eq. (2) find specific applications, depending on the nature of the alkyl group (Table 1). For the same reason, mixtures of alkyl

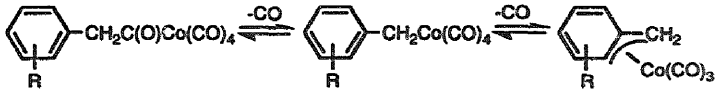
Table 1
Acylcobalt tetracarbonyls, $RC(O)Co(CO)_4$

R	Method of preparation (reaction no.)	Characterization	Lit.
CH_3–	(1), (2), (6), (8)	IR; ^1H, ^{13}C NMR	[12,17,21,25,29–32]
C_2H_5–	(1), (2), (6)	IR, ^1H NMR	[21,29,30]
n-C_3H_7–, iso-C_3H_7–	(2), (6)	A, IR; ^1H, ^{13}C, ^{59}Co NMR	[17,21,29,33]
n-C_nH_{2n+1}– (n=4, 7, 8)	(1)	IR	[30]
t-C_4H_9–	(2)	IR	[17,29]
n-C_5H_{11}–	(2)	IR	[17,29,34,35]
$(CH_3)_2CHCH_2$–, $(C_2H_5)_2CH$–, $CH_3CH{=}CH$–	(2)	IR	[17]
$CH_2{=}CHCH_2$–	(1), (2)	IR	[36]
$CH_2{=}CH(CH_2)_n$– (n=3, 4, 8), $CH_3CH{=}CH(CH_2)_3$–	(2)	IR	[20]
$CH_3CH{=}CHCH(CH_3)$–	(1)	IR, ^1H NMR	[37]
$C_6H_5CH_2$–	(1), (2)	IR; ^1H, ^{13}C NMR	[1,16,17]
$XC_6H_4CH_2$– (X=2-Me, 3-Me, 4-Me, 4-Cl)	(1), (2)	IR; ^1H, ^{13}C NMR	[1,16]
$XC_6H_4CH_2$– (X=4-MeO), 2,6-$Cl_2C_6H_3CH_2$–, 3,4-$(MeO)_2C_6H_3CH_2$–	(1), (2)	IR	[16]
2-$ClC_6H_4CH_2$–	(2)	A, IR; ^1H, ^{13}C NMR	[1]
$XC_6H_4CH_2$– (X=3-Cl, 2-F), $(CH_3)_5C_6CH_2$–	(2)	IR; ^1H, ^{13}C NMR	[1]
4-$BrC_6H_4CH_2$–, 1-$C_{10}H_7CH_2$–, 2-$C_{10}H_7CH_2$–	(2)	^1H, ^{13}C NMR	[1]
2,3-$O(CH_2CH_2O)_4C_6H_3CH_2$–	(8)	A, IR, ^1H NMR	[26]
$C_6H_5CH(CH_3)$–	(1), (6)	IR	[16,21,38]
$XC_6H_4CH(CH_3)$– (X=2-Me, 3-Me, 4-Me, 4-MeO, 4-Cl)	(1)	IR	[16]
$C_6H_5CH_2CH_2$–	(1)	IR	[38]
XC_6H_4– (X=H, 2-Me, 3-MeO, 4-MeO, 4-NO_2), 2,4,6-$(CH_3)_3C_6H_2$–	(2)	IR	[17,29]
$HOCH_2$–, Me_3SiOCH_2–	(1)	IR, ^1H NMR	[39,40]
$HOCH_2CH_2$–	(1)	IR	[41]
$CH_3CH(OH)CH_2$–	(1)	IR, ^1H NMR	[42]
$CH_3CH_2CH(OH)CH_2$–	(1)	IR; ^1H, ^{13}C NMR	[42]
CH_3OCH_2–	(1)	IR, ^1H NMR	[17,29,39]
$C_6H_5OCH_2$–, 2-$C(O)C_6H_4C(O)NCH_2$–	(2)	IR; ^1H, ^{13}C NMR	[43]
$CH_2{=}CHCH_2OCH_2$–	(2)	IR	[20]
$Me_3SiOCH_2CH_2$–	(1)	IR, ^1H NMR	[44]
$CH_3CH(OSiMe_3)CH_2$–, $CH_3CH(OSiEt_3)CH_2$–, $CH_3CH(OSiPh_3)CH_2$–, $CH_3CH(OSiEt_2Me)CH_2$–, $H_3CH(OSiMe_2Ph)CH_2$–, $CH_3CH(OSiMe_2Cl)CH_2$–	(1)	IR	[44]
$CH_3CH{=}CHCH(OSiMe_3)$–	(1)	IR	[40]

Table 1 (*continued*)

R	Method of preparation (reaction no.)	Characterization	Lit.
$C_2H_5OC(O)CH_2CH_2$–	(1)	IR	[45]
$CH_3OC(O)CH_2CH(C(O)OCH_3)$–	(1)	^1H, ^{13}C NMR	[46]
$C_2H_5OC(O)$–	(2)	IR	[27]
$ClCH_2$–	(1)	IR	[47]
$ClCH_2(CH_2)_2$–	(2)	IR	[17,29]
FCH_2–	(7)	IR	[24]
CF_2H–	(7)	A, IR	[24]
CF_3–	(7)	A, IR	[17,22]
C_2F_5–	(7)	A	[23]
$(CO)_4CoCF_2$–, $(CO)_4CoC(O)CF_2$–	(2)	^{19}F NMR	[48]
$C_5H_{10}N$–	(10)	IR	[9]
CH_3O–	(9–11)	A, IR, ^1H NMR	[7,10,49]
C_2H_5O–	(9), (11)	IR, UV-VIS; ^1H, ^{13}C NMR	[10,27,49]
iso-C_3H_7O–	(11)	IR	[10,49]
t-C_4H_9O–	(1), (11)	IR	[6,10]
n-$C_5H_{11}O$–, *n*-$C_{10}H_{21}O$–, CH_2=$CHCH_2O$–, XC_6H_4O–(X=H, 2-Me, 4-*t*-Bu, 4-MeO, 4-MeC(O), 4-Br), $C_6H_5CH(CH_3)CH_2O$–, 1-$C_{10}H_7O$–, 2-$C_{10}H_7O$–,	(11)	IR	(10)
(η^6-$C_6H_5CH_2O$–)$Cr(CO)_3$	(11)	A, IR	[10]
c-$C_6H_{11}O$–,	(10–11)	IR	[10,49,50]
$C_6H_5CH_2O$–	(11)	IR	[10,49,50]

and acyl complexes are often formed under ambient conditions and thus, most of the acylcobalt tetracarbonyls cannot be isolated as pure compounds. In addition, irreversible transformations of the alkyl counterpart, such as π-allyl formation from σ-allylcobalt tetracarbonyls, may consume all the acyl complex present initially in the equilibrium mixture. In the particular case of phenylacetylcobalt tetracarbonyls, however, a unique three-component acyl–alkyl–π-allyl equilibrium was observed (Eq. (3)), which could be shifted to



(3)

either side by changing the CO pressure [1]g[16]. Specific to α,β-unsaturated acylcobalt tetracarbonyls is that they form an equilibrium mixture with their π-acrylyl derivatives (Eq. (4), R≠H) [17,18]. In addition, those containing the olefinic function more distant from the acyl group (n=2, 3, 4) may consist of an equilibrium

Table 2
Monosubstituted acylcobalt carbonyl complexes, $RC(O)Co(CO)_3L$

R	Method of preparation (reaction no.)	Characterization	Lit.
$RC(O)Co(CO)_3PPh_3$			
CH_3–	(13), (14), (18)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[8,29,56–59]
C_2H_5–, iso-C_3H_7–	(14)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[29,56,59,60]
n-C_3H_7–	(14)	IR; ^1H, ^{13}C, ^{31}P NMR	[59,60]
n-C_5H_{11}–	(14)	A, IR	[29,56,61]
t-C_4H_9–	(14)	IR; ^1H, ^{13}C, ^{17}O, ^{31}P NMR	[59]
c-C_3H_5–	(17)	IR	[62]
CH_2=$CHCH_2$–	(13), (14)	A, IR	[19,56]
CH_3CH=CH–, 2,4,6-$(CH_3)_3C_6H_2$–	(14)	A, IR	[17]
CH_3CH=$CHCH_2$–	(13)	A, IR	[19]
CH_2=$CH(CH_2)_n$– (*n*=3, 4), CH_3CH=$CHCH_2CH_2$–	(14)	A, IR	[20]
$CH_3C(CH_3)$=$C(CH_3)CH_2$–	(13)	A, IR, ^1H NMR	[19,63]
CH_2=CHCH=CH–, CH_3CH=CHCH=CH–,			
CH_2=CHCH=$CHCH_2CH_2$–	(14)	A, IR	[18]
$(CH_3)_2C$=$C(CH$=$CH_2)$–	(19)	A, IR, ^1H NMR, MS	[51]
CH_3C≡CCH_2–, C_6H_5C≡CCH_2–, $ClCH_2C$≡CCH_2–,	(13), (18)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[64]
$C_6H_5CH_2$–	(13), (14)	A, IR, ^1H NMR	[16,58,65]
2-$CH_3C_6H_4CH_2$–	(13), (14)	IR, ^1H NMR	[16,58]
3-$FC_6H_4CH_2$–	(13)	–	[66]
2,6-$Cl_2C_6H_3CH_2$–	(13), (14)	IR, ^1H NMR, X-ray	[16]
3,4-$(CH_3O)_2C_6H_3CH_2$–, $XC_6H_4CH_2$– (X=3-Me, 4-Me,			
4-MeO), (η^6-4-$CH_3C_6H_4CH_2$–)$Cr(CO)_3$,	(13), (14)	IR, ^1H NMR	[16]
2,3-$O(CH_2CH_2O)_4C_6H_3CH_2$–	(13), (14)	IR	[26]
2,4,6-$(CH_3)_3C_6H_2CH_2$–, $XC_6H_4CH_2$– (X=4-Br, 3-CN),			
2-$C_{10}H_7CH_2$–	(14)	IR	[58]
$C_6H_5CH(CH_3)$–, $C_6H_5CH_2CH_2$–	(13)	IR, ^1H NMR	[16,38]
XC_6H_4– (X=H, 4-MeO)	(14), (21)	A, IR, ^1H NMR	[29,54]
XC_6H_4– (X=2-Me, 4-Me, 4-Cl, 4-F)	(21)	IR, ^1H NMR	[54]
4-$PPh_3(CO)_3CoC(O)C_6H_4$–	(13)	A	[29]
2-$C(O)C_6H_4C(O)NCH_2$–	(14)	IR, ^1H NMR	[67]
$HOCH_2$–	(14)	IR, ^1H NMR	[39]
$HOCH_2CH_2$–, $HOCH_2CH_2CH_2$–, $(CH_3)_2C(OH)CH_2$–,			
$HOCH(CH_2)_4CH$–, $C_6H_5CH(OH)CH_2$–	(14)	A, IR	[41]
$CH_3CH(OH)CH_2$–	(14)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[41,42,59]

Table 2 (*continued*)

R	Method of preparation (reaction no.)	Characterization	Lit.
CH_3OCH_2–	(14), (18)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[29,39,57]
$C_2H_5OCH_2$–, $C_2H_5OCH(CH_3)$–	(18)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[57]
Me_3SiOCH_2–	(14)	IR, ^1H NMR, MS	[39,40]
$(CH_3)_3CCH(OSiMe_3)$–	(13)	IR, ^1H NMR	[40]
$CH_3OC(O)CH_2$–	(13)	IR; ^1H, ^{13}C, ^{31}P, ^{17}O NMR	[46]
$C_2H_5OC(O)CH_2$–	(13)	A, IR	[29,68]
$CH_3OC(O)CH(CH_3)$–, $CH_3OC(O)CH_2CH_2$–	(13), (14)	A, IR	[61]
$C_2H_5OC(O)CH(CH_3)$–	(13)	^1H NMR	[45]
$C_2H_5OC(O)CH_2CH_2$–	(13)	A, ^1H NMR	[29,45]
$CH_3OC(O)CH_2CH(CO_2CH_3)$–	(13)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[46,69]
$CH_3OC(O)CH{=}CHCH_2$–	(13)	A, IR	[70]
$\overline{OCH(CH_2OH)CH(OH)CH(OH)CH(OH)CH}$–, $\overline{OCH(CH_2OC(O)CH_3)CH(OC(O)CH_3)CH(OC(O)CH_3)}$–$-CH(OC(O)CH_3)CH$–	(13)	–	[71]
$ClCH_2$–	(13), (14)	A, IR, ^1H NMR, X-ray	[29,47]
$Cl(CH_2)_3$–	(14)	A	[29]
FCH_2–, CF_2H–	(20)	A, IR, ^1H NMR, MS	[24,53]
CF_2Cl–		IR; ^1H, ^{19}F, ^{31}P NMR	[72]
CF_3–	(20)	A, IR	[22,24,29]
C_2F_5–	(20)	IR	[23]
n-C_3F_7–	(20)	A, IR	[52]
$(CH_3)_2N$–	(22)	A, IR	[55]
$C_5H_{10}N$–, $(n\text{-}C_3H_7)_2N$–	(14)	A, IR	[9]
CH_3O–	(14)	IR, ^1H NMR, X-ray	[7,10]
C_2H_5O–	(14), (17)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[6,10,27,49,73]
iso-C_3H_7O–	(14)	A, IR, ^1H NMR	[10,49,50]
n-C_4H_9O–	(14)	A, IR, ^1H NMR, X-ray	[10,74]
t-C_4H_9O–	(14)	IR	[6,10]
n-$C_5H_{11}O$–, XC_6H_4O– (X=4-*t*-Bu–, 4-MeO–, 4-Br–),			
2-$C_{10}H_7O$–	(14)	IR	[10]
n-$C_{10}H_{21}O$–	(14)	IR, ^1H NMR	[10]
c-$C_6H_{11}O$–, $C_6H_5CH_2O$–	(14)	IR, ^1H NMR	[10,49]
$C_6H_5CH(CH_3)CH_2O$–	(14)	IR, ^1H NMR	[10,16]
$RC(O)Co(CO)_3L$ ($L \neq PPh_3$)			

Table 2 (*continued*)

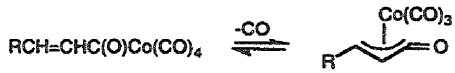
R	Method of preparation (reaction no.)	Characterization	Lit.
CH_3–; L=PBu_3, PPh_2Me, $P(4\text{-}MeOC_6H_6)_3$, $P(OMe)_3$,	(13), (14), (17)		
ETPO, $PPh_2(CH_2)_2SiMe_2\text{-}\eta^5\text{-}C_5H_4ZrCl_2\text{-}\eta^5\text{-}C_5H_5$	(18)	A, IR; ^1H, ^{13}C, ^{31}P NMR,	[8,75–79]
CH_3–; L=I^-	(15)	A, IR, ^1H NMR, X-ray	[25,80]
C_2H_5–; L=PBu_3,	(17)	A, IR	[76]
CH_2=$CHCH_2CH_2$–[a]	(14)	IR	[19]
$C_6H_5CH_2$–; L=Cl^-, I^-, Br^-, 2,3-$\overbrace{O(CH_2CH_2O)_4}C_6H_3CH_2$–; L=$Cl^-$, I^-	(15)	A, IR	[26]
$\overbrace{C(C_6H_5)=C(C_6H_5)}CH$–; L=$PEt_3$	(17)	IR	[62,81]
C_6H_5–; L=PMe_3, PCy_3	(17)	A, IR, ^{13}C NMR	[82]
$H_2NCH_2CH_2$–[b]	(13)	IR	[83]
$Ph_2PCH_2CH_2CH_2$–, $Cy_2PCH_2CH_2CH_2$–[c]	(18)	A, IR; ^1H, ^{13}C, ^{31}P NMR, MS	[84]
$HOCH_2$–; L=PPh_2Cl	(14)	IR, ^1H NMR	[39]
CH_3OCH_2–; L=PPh_2Me	(18)	IR; ^1H, ^{13}C, ^{31}P NMR	[77]
$CH_3OC(O)CH_2$–; L=PPh_2Me	(13)	^{13}C, ^{31}P NMR	[59]
$C_2H_5OC(O)CH_2$–; L=$P(OMe)_3$, PEt_3, $P(OEt)_3$, $P(i\text{-}Pr)_3$,			
$P(S\text{-}i\text{-}Pr)_3$, $P(OSiMe_3)_3$, PBu_3, $P(t\text{-}Bu)_3$, $P(NEt_2)_3$	(13)	IR	[68]
$C_2H_5OC(O)CH_2$–; L=PPh_2Me	(13), (17)	IR; ^1H, ^{13}C, ^{31}P NMR	[68,77]
CH_2F–, CF_2H–; L=$P(OPh)_3$	(20)	A, IR; ^1H, ^{19}F NMR, MS	[24]
CF_3–, C_2F_5–, $n\text{-}C_3F_7$–; L=$P(OPh)_3$	(20)	A, IR	[52]
$Cp(CO)_2FeCH_2$–; L=PMe_2Ph	(17)	A, IR; ^1H, ^{13}C NMR	[85]
$C_5H_{10}N$–; L=$C_5H_{10}N$	(14)	IR	[9]
CH_3O–; L=I^-	(16)	IR	[10]
C_2H_5O–; L=$P(OPh)_3$	(17)	A, IR	[73]
$n\text{-}C_4H_9O$–; L=$P(OMe)_3$, PEt_3, $P(OEt)_3$, PMe_2Ph, $P(i\text{-}Pr)_3$, PEt_2Ph, $P(OEt)_2Ph$, PEt_2Bz, $P(i\text{-}Pr)_2Ph$, PMe_2Menth, PBu_3, $P(t\text{-}Bu)_3$, $P(OBu)_3$, $P(O\text{-}t\text{-}Bu)_3$, $P(NEt_2)_3$, PPh_2Me, $P(t\text{-}Bu)(Menth)Cl$, $PPh_2(i\text{-}Pr)$, $PPh_2(SiMe_3)$, $P(O\text{-}c\text{-}Pent)_3$, $PNeopent_3$, $PPh_2(O\text{-}t\text{-}Bu)$, $P(O\text{-}c\text{-}Pent)_2Ph$, $PNeopent_2Ph$, $PPh_2Neopent$, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, PCy_2Ph, PCy_3, $PPh_2(o\text{-}Tol)$,			

Table 2 (*continued*)

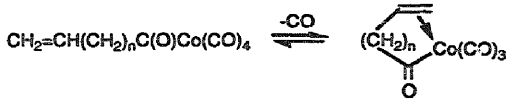
R	Method of preparation (reaction no.)	Characterization	Lit.
$P(o\text{-Tol})_2Ph$, $P(2\text{-MeOC}_6H_4)_2Cy$, $P(o\text{-Tol})_3$,			
$P(O\text{-}o\text{-Tol})_3$, PPh_2Menth	(14)	IR	[74]
XC_6H_4O– (X=H, 4-Br), $XC_6H_4CH_2O$– (X=H, 2-Me); L=I^-	(16)	IR	[10]

[a]The olefinic double bond acts as L in the metallacycle.
[b]The NH_2 group acts as L in the metallacycle.
[c]The PR_2 group acts as L in the metallacycle.

mixture with their cyclic counterparts as shown in Eq. (5) [19,20], but the intermediacy of an alkyl complex is also plausible in the latter reaction.



(4)



(5)

It was reported recently that the reaction of hydridocobalt tetracarbonyl with ketenes (Eq. (6)) results in the formation of acylcobalt tetracarbonyls in high yields at

$$HCo(CO)_4 + R^1R^2C{=}C{=}O \rightarrow R^1R^2CHC(O)Co(CO)_4 \quad (6)$$

temperatures as low as −79 °C [21]. This method is particularly suitable for the preparation of acetyl-, propionyl, and iso- and *n*-butyrylcobalt tetracarbonyls which were isolated >95% pure, but cannot be applied to ketenes containing electron-withdrawing substituents.

A series of fluoroacylcobalt tetracarbonyls were synthesized with good yield by treating $[Co(CO)_4]Na$ with the corresponding fluorocarboxylic acid anhydride according to Eq. (7) [22–24].

$$[Co(CO)_4]Na + (R^fCO)_2O \rightarrow R^fC(O)Co(CO)_4 + R^fCO_2Na \quad (7)$$

Although ligand replacement by CO in monosubstituted acylcobalt carbonyls, $RC(O)Co(CO)_3L$, usually does not take place, the weakly coordinating halide ligand makes a rare exception. The halide ligand in acyl complexes of the type $[RC(O)Co(CO)_3(X)]^-$ (R=CH_3, $PhCH_2$ etc.; X=Cl, I) is easily replaced by a CO

Table 3
Di- and trisubstituted acylcobalt carbonyls, $RC(O)Co(CO)_{4-n}L_n$ ($n=2$, 3)

R	Method of preparation (reaction no.)	Characterization	Lit.
$RC(O)Co(CO)_2L^1L^2$			
CH_3–; $L^1=L^2=PMe_3$, PPh_2Me, DPPE, $P(OMe)_3$, ETPO, Pom-Pom;[a] $L^1=PPh_3$, $L^2=P(OMe)_3$	(23)	A, IR; ^1H, ^{13}C, ^{31}P NMR	[75,77,86] [88–92]
CH_3–; $L^1=PPh_2H$, $L^2=PPh_2(OMe)$	(23)	A, IR, X-ray	[93]
$CH_2=CHCH_2CH_2$–; $L^1=PPh_3$[b]	(23)	A, IR	[19]
$C(C_6H_5)=C(C_6H_5)CH$–; $L^1=L^2=PPh_2$	(25)	IR	[62]
$H_2NCH_2CH_2$–; $L^1=PPh_3$[c]	(23)	A, IR	[83]
$Cy_2PCH_2CH_2CH_2$–;[c] $L^1=PPh_3$	(24)	A, IR; ^1H, ^{31}P NMR, MS	[84]
$CH_2=CHOCH(CH_3)$–; $L^1=PPh_3$[b]	(23)	A, IR	[20]
CH_3OCH_2–; $L^1=L^2=$DPPE, PPh_2Me	(26)	IR; ^1H, ^{13}C, ^{31}P NMR	[77,87]
CH_3OCH_2–; $L^1=PPh_3$, $L^2=P(OMe)_3$	(23)	A	[75]
$C_2H_5OCH_2$–; $L^1=L^2=$DPPE	(26)	–	[87]
$C_2H_5OCH(CH_3)$–, $CH_3OCH_2CH(OC_2H_5)$–, $C_2H_5OCH_2CH(OC_2H_5)$–; $L^1=L^2=$DPPE	(26)	IR; ^1H, ^{13}C, ^{31}P NMR	[87]
$C_2H_5OCH(CH_3)CH(OC_2H_5)$–; $L^1=L^2=$DPPE	(26)	A, IR; ^1H, ^{13}C, ^{31}P NMR, X-ray	[87]
$C_2H_5OC(O)CH_2$–; $L^1=L^2=PEt_3$, $P(OSiMe_3)_3$, PBu_3	(23)	IR	[68]
2-$(C_6H_5N=N)C_6H_4C(CF_3)=C(CF_3)$–[d]	(24)	A, IR; ^1H, ^{19}F NMR, MS, X-ray	[94,95]
2-(3′-$RC_6H_4N=N)C_6H_4C(CF_3)=C(CF_3)$– (R=$CH_3$, CF_3, CH_3O, EtOC(O))[d]	(24)	IR	[95]
H_2N–; $L^1=PPh_3$, $L^2=NH_3$	(29)	A, IR	[55]
CH_3O–, C_2H_5O–; $L^1=L^2=PPh_3$;	(28)	A, IR	[73]
n-C_4H_9O–; $L^1=L^2=P(OMe)_3$, PEt_3	(23)	IR	[74]
(η^4-2,3-Ph_2C_4HO–)$(CO)_2CoC(O)$O-2,3-Ph_2C_4H[e]	(30)	IR	[62]
$RC(O)Co(CO)L_3$			
H_2N–: L=$(Ph_2PCH_2)_3CCH_3$, $(Ph_2PCH_2)_3CCH_2PPh_2$)	(22)	A, IR	[96,97]
CH_3–; L=$P(OMe)_3$, ETPO	(23)	A	[75]

[a]Pom-Pom: 1,2-bis(dimethoxyphosphino)ethane.
[b]The olefinic C=C bond acts as L^2 in the metallacycle.
[c]The NH_2 group acts as L^2 in the metallacycle.
[d]The PCy_2 groups acts as L^2 in the metallacycle.
[e]Both the olefinic C=C bond and an azido nitrogen coordinate to cobalt.
[f]The η^4-cyclobutadienyl ligand is considered as both L^1 and L^2.

ligand under ambient conditions (Eq. (8)), providing alternative pathways to obtain these particular compounds [25,26].

$$[RC(O)Co(CO)_3(X)]^- + CO \rightarrow RC(O)Co(CO)_4 + X^- \quad (8)$$

(Alkoxycarbonyl)cobalt tetracarbonyls are formed very slowly or not at all in

reactions of the weakly nucleophilic tetracarbonylcobaltate(−I) anion with chloroformate esters in reaction Eq. (2). Alternative ways were therefore explored to provide access to this class of compounds. Individual species were obtained earlier in reactions Eq. (1) [6,7] and Eq. (9) [7,27], but the general synthetic methods outlined in Eq. (10) and Eq. (11) were elaborated

$$[Co(CO)_4]Na + ROC(O)C(O)Cl \rightarrow ROC(O)C(O)Co(CO)_4 \rightarrow ROC(O)Co(CO)_4 + CO \quad (9)$$

$$Co_2(CO)_8 + RO^- \rightarrow ROC(O)Co(CO)_4 \quad (10)$$

$$ICo(CO)_4 + RO^- \rightarrow ROC(O)Co(CO)_4 \quad (11)$$

only recently [10]. Note that so far only a single representative of the unstable (alkoxyoxalyl)cobalt tetracarbonyls, i.e. $EtOC(O)C(O)Co(CO)_4$, was characterized briefly as an intermediate in Eq. (9) [27]. Furthermore, a possible model intermediate of reaction Eq. (10) was isolated in the form of $[\mu\text{-OEt})(B)CoCo(CO)_4]_2$ (B=py, THF), which was transformed into a stoichiometric amount of (ethoxycarbonyl)cobalt tetracarbonyl under CO pressure according to Eq. (12) [28]. The reaction of dicobalt octacarbonyl with

$$[(\mu\text{-OEt})(B)CoCo(CO)_4]_2 + 10CO \rightarrow 2EtOC(O)Co(CO)_4 + Co_2(CO)_8 \quad (12)$$

alkoxides in Eq. (10) can also be applied to nitrogen bases. Such a reaction of piperidine, for instance, resulted in the formation of the unstable carbamoyl complex $C_5H_{10}NC(O)Co(CO)_4$ [9].

As mentioned above the majority of known acylcobalt tetracarbonyl complexes were not isolated as pure compounds owing mainly to various decarbonylation reactions, but were characterized by spectroscopic methods. All compounds which were isolated and/or characterized at least in solution are listed in Table 1. The few compounds isolated in pure form are air-sensitive oils or low melting solids, which are well soluble in common organic solvents and exhibit moderate thermal stability under an atmosphere of CO. A number of others were generated in situ, but were transformed into more tractable phosphine-substituted derivatives without any characterization; these are discussed in Section 2.2 and Tables 2 and 3.

2.2. *Substituted acylcobalt carbonyl complexes*

The major group of ligand substituted acylcobalt carbonyls, $RC(O)Co(CO)_{4-n}L_n$ ($n=1, 2, 3$), consists of monosubstituted derivatives. Although they can occur as intermediates in a few catalytic cycles that use additional ligands (phosphines, phosphites, amines, iodide), the real importance of this class of complexes (particularly that of monophosphine-substituted derivatives) lies in their stability and direct availability from unstable alkyl- and acylcobalt tetracarbonyls, which thus can easily be identified.

The most straightforward way to obtain monosubstituted acylcobalt carbonyls uses addition of one or more equivalents of the appropriate ligand to either an

alkyl- or acylcobalt tetracarbonyl, or to an equilibrium mixture of the two (Eq. (13) and Eq. (14)).

$$RCo(CO)_4 + L \rightarrow RC(O)Co(CO)_3L \quad (13)$$

$$RC(O)Co(CO)_4 + L \rightarrow RC(O)Co(CO)_3L + CO \quad (14)$$

Substitution of the first CO ligand is usually facile and results in the formation of compounds of the type $RC(O)Co(CO)_3L$ where the entering ligand L is typically a neutral tertiary phosphine (in particular PPh_3) or phosphite. However, derivatives containing arsine ($AsPh_3$), stibine ($SbPh_3$) and amines are also known (Table 2).

Monosubstituted, halide ion containing acylcobalt complexes, $[RC(O)Co(CO)_3(X)]^-$ ($R=CH_3$, $PhCH_2$; X=Cl, I), were also generated either by treating the tetracarbonylcobaltate(−I) anion with alkyl halides (Eq. (15)) [25,26] or reacting iodocobalt tetracarbonyl with alkoxides (Eq. (16)) [10]. There is speculation, however, that reaction Eq. (15) may proceed through direct halide ion substitution of a preformed acylcobalt tetracarbonyl intermediate [25].

$$[Co(CO)_4]^- + RX \rightarrow [RC(O)Co(CO)_3(X)]^- \quad (15)$$

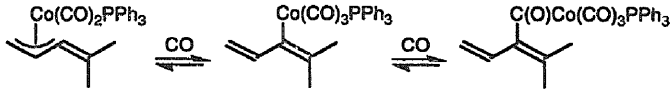
$$ICo(CO)_4 + RO^- \rightarrow [ROC(O)Co(CO)_3(I)]^- \quad (16)$$

A less convenient method, limited to the preparation of phosphine- and phosphite-substituted compounds, uses the reaction of acyl or alkyl halides with the corresponding substituted anion $[Co(CO)_3L]^-$ and, in the latter case, carbonylation of the resulting alkyl complex $RCo(CO)_3L$ (Eq. (17) and Eq. (18)). The carbonylation of $RCo(CO)_3L$ is

$$[Co(CO)_3L]^- + RC(O)X \rightarrow RC(O)Co(CO)_3L \quad (17)$$

$$RCo(CO)_3L + CO \rightleftharpoons RC(O)Co(CO)_3L \quad (18)$$

reversible similar to that of $RCo(CO)_4$, but the substituted acyl complexes are reasonably stable and in most cases can be isolated. It is also similar to the tetracarbonyl systems that $RC(O)Co(CO)_3L$ ($R=\sigma$-allyl, $L=PR_3$) complexes irreversibly decompose to stable π-allyl complexes through alkyl intermediates. There is one exception, however, where this two-step CO loss was found to be reversible as shown in Eq. (19) [51].



(19)

Monophosphine-substituted fluoroacyl compounds were isolated from the reaction of $[Co(CO)_3L]^-$ and fluorocarboxylic acid anhydrides according to Eq. (20) [22–24,52,53].

$$[Co(CO)_3L]^- + (R^fCO)_2O \rightarrow R^fC(O)Co(CO)_3L + R^fCOO^- \quad (20)$$

Most recently, Hidai et al. reported the $Pd(PPh_3)_4$-catalyzed formation of aroylcobalt tricarbonyl triphenylphosphines from iodoarenes, $[Co(CO)_4]^-$ and PPh_3 [54]. It was demonstrated in model experiments that the aroylcobalt products originate from the thermolysis of mixed Pt–Co complexes (Eq. (21)), which are stable analogues of the possible intermediates of the catalytic process.

$$PPh_3(CO)ArPt-Co(CO)_3PPh_3 \rightarrow ArC(O)Co(CO)_3PPh_3 \quad (21)$$

A different approach to the synthesis of carbamoyl complexes not involving simple phosphine substitution included the reaction of $[Co(CO)_4PPh_3]Cl \cdot HCl$ with Me_2NH (Eq. (22)) [55].

$$[Co(CO)_4PPh_3]^+ + 3Me_2NH \rightarrow (CH_3)_2NC(O)Co(CO)_3PPh_3 + 2[Me_2NH_2]^+ \quad (22)$$

The isolated and/or spectroscopically characterized monosubstituted acylcobalt carbonyl compounds are compiled in Table 2. The PPh_3-substituted derivatives are fairly stable, mostly yellow crystalline solids and therefore can be isolated and studied conveniently. Many of them are moderately air-stable as well. The monosubstituted compounds containing substituents other than PPh_3 are usually oily, readily soluble substances but less stable and more difficult to purify.

Di- and trisubstituted acylcobalt carbonyl complexes are much less in number (Table 3) than the monosubstituted ones probably because further substitution of both the monosubstituted alkyl or acyl compounds proceeds only with a few small ligands, such as $P(OMe)_3$ and PEt_3. Nevertheless, direct substitution is the most general path to obtain $RC(O)Co(CO)_2L_2$ and $RC(O)Co(CO)L_3$ derivatives (Eq. (23)). Some mixed

$$RC(O)Co(CO)_3L + L \rightarrow RC(O)Co(CO)_2L_2 + CO \xrightarrow{L} RC(O)Co(CO)L_3 + 2CO \quad (23)$$

ligand-substituted derivatives of the type $RC(O)Co(CO)_2(PR_3)L$ are also known, which contain a different phosphine, phosphite, halide ion or amine beside a tertiary phosphine (typically PPh_3). Only sporadic reports mention different synthetic procedures: CO insertion into a monosubstituted alkyl complex promoted by a second entering substituent (Eq. (24)) [84], reaction of acyl halides with the properly substituted carbonylcobaltate(−I) anions (Eq. (25)) [62], and carbonylation of $RCo(CO)_2L_2$ (Eq. (26)) [86,87] or $(CH_3)_3Co(PMe_3)_3$ (Eq. (27)) [88]. Probably also reaction Eq. (26) was the ultimate step

$$RCo(CO)_3L + L \rightarrow RC(O)Co(CO)_2L_2 \quad (24)$$

$$[Co(CO)_2L_2]^- + RC(O)X \rightarrow RC(O)Co(CO)_2L_2 + X^- \quad (25)$$

$$RCo(CO)_2L_2 + CO \rightarrow RC(O)Co(CO)_2L_2 \quad (26)$$

$$(CH_3)_3Co(PMe_3)_3 + 4CO \rightarrow CH_3C(O)Co(CO)_2(PMe_3)_2 + CH_3COCH_3 \quad (27)$$

leading to the formation of $CH_3C(O)Co(CO)_2(PMe_3)_2$ when two phosphines were

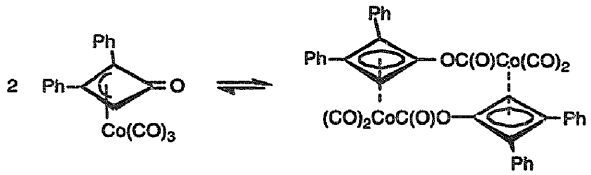
replaced with CO ligands in $CH_3Co(PMe_3)_4$ [89]. In addition, this experiment demonstrates that starting either from tetracarbonyls by phosphine substitution or from tetrakis-phosphine complexes by CO substitution, disubstituted acylcobalt carbonyl complexes are the common products, suggesting optimum stability of these particular species.

Reaction of $[Co(CO)_3(PPh_3)_2]Cl \cdot HCl$ with an alkoxide (Eq. (28)) [73] or that of $ICo(CO)_3PPh_3$ with excess ammonia (Eq. (29)) [55] represent examples of the syntheses of disubstituted alkoxycarbonyl and carbamoyl complexes, respectively.

$$[Co(CO)_3(PPh_3)_2]^+ + RO^- \rightarrow ROC(O)Co(CO)_2(PPh_3)_2 \quad (28)$$

$$ICo(CO)_3PPh_3 + 3NH_3 \rightarrow H_2NC(O)Co(CO)_2(PPh_3)NH_3 + NH_4I \quad (29)$$

Finally, the binuclear η^4-cyclobutadienyl complex formed by dimerization of the corresponding η^3-cyclobutenonyl complex in Eq. (30) can be considered as a special representative of disubstituted alkoxycarbonylcobalt carbonyls [81].



(30)

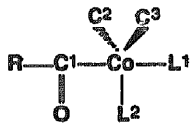
Upon substitution of the second CO ligand, the acylcobalt complexes become even more robust crystalline materials, and are better candidates for studying reactions of the alkyl chain. However, the access to $RC(O)Co(CO)_2L^1L^2$ type compounds is severely limited by the low number of suitable ligands. Di- and trisubstituted acylcobalt carbonyl compounds are listed in Table 3.

3. Structural and spectroscopic characterizations

3.1. X-ray diffraction

Unfortunately no crystal structure data are available to date for acylcobalt tetracarbonyls. However structures of five monosubstituted derivatives, $MeOC(O)Co(CO)_3PPh_3$ [7], $2,6\text{-}Cl_2C_6H_3CH_2C(O)Co(CO)_3PPh_3$ [16], $ClCH_2C(O)Co(CO)_3PPh_3$ [47], $n\text{-}BuOC(O)Co(CO)_3PPh_3$ [74] and $[MeC(O)Co(CO)_3I)]^-$ [80], as well as two disubstituted derivatives, $EtOCH(Me)CH(OEt)C(O)Co(CO)_2DPPE$ [87] and $MeC(O)\text{–}Co(CO)_2(PPh_2H)PPh_2OMe$ [93], have been reported. Characteristic bond distances and angles of these compounds are compiled in Table 4. All of them possess a trigonal bipyramidal coordination geometry at the cobalt atom, with carbonyls (in disubstituted derivatives with one of the phosphorus ligands as well) in the equatorial plane and the non-carbonyl ligands in trans bis-axial positions. As the data in Table 4 clearly demonstrate, the main structural parameters do not change with the alkyl

Table 4
Characteristic bond distances and angles of phosphine-substituted acylcobalt carbonyl complexes

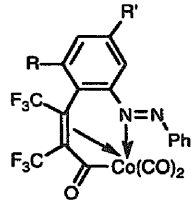


Compound [Lit.]	C(1)–O	C(1)–Co	Co–L(1)	C(2)–Co C(3)–Co L(2)–Co	C(1)–Co–L(1)	C(1)–Co–C(3) C(2)–Co–L(2) C(3)–Co–L(2)
2,6-$Cl_2C_6H_3CH_2C(O)Co(CO)_3PPh_3$ [16]	1.193	1.996	2.259	1.777 1.778 1.798	178.9	-
$ClCH_2C(O)Co(CO)_3PPh_3$ [47]	1.180	1.999	2.254	1.777 1.792 1.792	174.5	113.6 121.2 124.9
$CH_3OC(O)Co(CO)_3PPh_3$ [7]	1.196	1.976	2.232	1.786	174.7	-
n-$C_4H_9OC(O)Co(CO)_3PPh_3$ [74]	1.201	1.967	2.229	1.770 1.785 1.810	177.1	116.7 119.8 122.9
$[CH_3C(O)Co(CO)_3(I)]^-$ [80]	1.201	1.961	2.684	1.804 1.807 1.813	175.9	116.5 120.2 123.4
$CH_3C(O)Co(CO)_2(PPh_2H)P(Ph_2OMe)$ [93]	1.196	1.985	2.208	1.739 1.878 2.204	178.1	117.6 120.0 122.1
$EtOCH(CH_3)CH(OEt)C(O)Co(CO)_2DPPE$ [87]	1.181	1.979	2.240	1.742 1.764 2.233	177.1	125.6 127.6

chain or the substituent ligand, except that the Co–I bond is relatively long in $[MeC(O)Co(CO)_3(I)]^-$, consistent with the lability of the iodide [25]. Although no such structural information is available for acylcobalt tetracarbonyls, a similar trigonal-bipyramidal structure is assumed by analogy of the above well-characterized derivatives, and on the basis of IR and NMR spectroscopic observations (see below).

3.2 *Infrared spectroscopy*

Infrared spectroscopy is the oldest and most generally used, and often the only spectroscopic technique for the identification and characterization of acylcobalt carbonyl complexes (Tables 1–3). The spectra exhibit characteristic ν(CO) absorbances in the $\sim$2130–1890 cm^{-1} range for terminal CO ligands and in the $\sim$1750–1590 cm^{-1} range for the organic C=O group. Both types of absorbances are found at higher wave numbers for tetracarbonyls and shifted to lower values upon substitution owing to stronger basicity of the substituting ligands relative to CO. Recent systematic investigations demonstrated a direct relationship between these data and both the steric and electronic parameters of phosphorus ligands in the complexes $RC(O)Co(CO)_3L$ (R=$EtOC(O)CH_2$–, *n*-BuO–) [68,74]. However, the electronic and steric influences of the alkyl group on the acyl ν(CO) absorbance are far less understood, which is interesting since the absorbances of the terminal CO ligands not directly connected to the alkyl group are more sensitive at least to the electronic effects, e.g. they shift to higher wave numbers when an electron-withdrawing group is present. Nevertheless, on the basis of an analysis of available infrared data, it seems to be a trend that the bands attributable to acyl C=O groups attached to an electron-withdrawing alkyl moiety appear at lower positions. Drawing a general conclusion is further complicated by the fact that hindered rotation of some alkyl groups (for example, Me2CH– [21], CH_2F– [24,53], CH_2Ph– [65], $MeO_2CCH_2CH(CO_2Me)$– [69]) around the C(O)–C axis can split this band. To our knowledge, there is only one notable exception which escapes all attempts at generalization: the acyl CO absorbance of compound A appears between 1850–1860 cm^{-1} [95], an extraordinarily high position rather characteristic to bridging CO ligands, which may arise from high strain in the chelating system. It is also worth mentioning that although the acyl ν(CO) band of $MeCH(OEt)C(O)Co(CO)_3PPh_3$ fits in the above range (1647 cm^{-1}), there is about a 25 cm^{-1} reduction in frequency in comparison with analogous primary compounds [57], but no explanation was given for this discrepancy.



A

The IR spectroscopic data of terminal CO ligands are also in accord with the structures established by X-ray diffraction analyses and allow structural generalization for all acylcobalt carbonyl complexes. The trigonal bipyramidal structure possesses a local C_{3v} symmetry, which results in a three-band pattern ($2A_1+E$) for $RC(O)Co(CO)_4$ type and a two-band pattern (A_1+E) for $RC(O)Co(CO)_3L$ complexes. The A_1 ("total symmetric") band is weak and the E band is very strong [24]. The E band in both types of compounds is usually split into two well-separated bands, this is attributed to hindered rotation of the acyl group around the Co–C axis due to a $d\pi$–$p\pi$ interaction between the cobalt atom and the acyl group [68].

The complexes $RC(O)Co(CO)_{4-n}L_n$ ($n=2$, 3) exhibit two and one ν(CO) absorbances, respectively, those in the former being due to non-equivalent CO groups. Although the crystal structure data of both $EtOCH(Me)CH(OEt)C(O)Co(CO)_2$ DPPE [87] and $MeC(O)Co(CO)_2(PPh_2H)PPh_2OMe$ [93] show that the terminal CO ligands occupy two equatorial positions, there is infrared spectroscopic evidence that $EtO_2CCH_2C(O)Co(CO)_2[P(OSiMe_3)_3]_2$ contains both equatorial and axial CO groups (C_s symmetry) [68], while the structure of PEt_3- and PBu_3-substituted derivatives appears to be similar to that seen in the above crystal structures (C_1 symmetry) [68].

3.3. NMR spectroscopy

In contrast with the abundance of infrared spectroscopic information on acylcobalt carbonyl complexes, multinuclear NMR data are relatively scarce and more recent in vintage, though ^1H and/or ^{19}F NMR investigations were carried out occasionally to confirm the identity of new compounds, rather than to provide structural information (Tables 1–3). The lack of NMR data was explained by a line-broadening effect of the quadrupole moment of ^{59}Co [68], but more recent investigations [46] suggested that probably paramagnetic Co(II) impurities, generated by accidental oxidation, are responsible for poor quality spectra. ^{17}O and ^{59}Co NMR studies were attempted recently as well, but failed probably also because of significant line broadening [46].

^{13}C and ^{31}P NMR spectroscopy, however, proved to be a valuable tool to acquire additional structural and electronic information. $^{13}C\{^1H\}$ NMR measurements indicate that the four terminal CO ligands in tetracarbonyls undergo fast exchange and thus exhibit a broad singlet resonance in the narrow range of 193.5–198.5 ppm, while that attributable to the acyl C=O group appears at low field in the much wider range of 212–232 ppm. It is evident from these data that the shielding of the acyl carbon is strongly influenced probably by both the electronic and steric properties of the alkyl group, but the more distant terminal CO carbons are less sensitive. This complements the infrared spectroscopic observations. The only ^{13}C NMR study on alkoxycarbonyl derivatives [27] shows that the acyl carbon resonance of $EtOC(O)Co(CO)_4$ (177.9 ppm) is similar to that of organic esters.

In monophosphine-substituted derivatives, both types of resonances exhibit characteristic coupling constants to the phosphorus nucleus being in trans position to the acyl group (~31 Hz) and *cis* position to the CO ligands (~21 Hz). The terminal CO resonances typically appear in the 196.5–201.5 ppm range, while those of the

acyl C=O group are observed at low field in the 232–250 ppm range and indicate similar alkyl group effects to those in the tetracarbonyl derivatives, as well as no significant dependence on the nature of the phosphine. Again, the acyl resonance of $EtOC(O)Co(CO)_3PPh_3$ at δ 186.1 indicates organic ester-like properties and has a large J_{PC} (41 Hz) [27]. A P–C coupling is usually observed at the C_α nucleus as well. A unique type of monosubstituted acylcobalt carbonyl complexes is represented by the phosphacobaltacycloacyl complexes $CH_2(CH_2)_2C(O)Co(CO)_3PR_2$ (R=Ph, Cy) [84], which probably contain the phosphorus substituents in cis position to the acyl group. Accordingly, the ^{13}C NMR spectra exhibit small J_{PC} (0–3 Hz) at the acyl carbon which resonates at high field (~205 ppm) compared to the carbons of the CO ligands (~225 ppm). The only doublet resonance attributed to both the *cis* and trans CO ligands suggest fast exchange between these positions and the J_{PC} ~22 Hz coupling constant is not different from that of trans-acyls. The ^{31}P NMR data listed in Table 5 are characteristic of the basicity of the phosphine and do not indicate effects of the remote alkyl group. For PPh_3-substituted compounds, the singlet ^{31}P resonances appear in the narrow range of 48–51 ppm. Thus, the δ 53.5 value of $EtC(O)Co(CO)_3PPh_3$ (as well as a small (J_{PC}=22 Hz) coupling with C=O and the absence of coupling with C_α [59]) points to unusual structural properties of this particular compound. The phosphorus T_1 relaxation times of some PPh_3-substituted compounds appear to be ~7 s and the line widths are ~15 Hz (~5 Hz for free PPh_3). The T_1 relaxation time of free phosphine (~26 s) becomes much shorter upon coordination to the metal, which is mainly due to the increased contribution of the chemical shift anisotropy.

Unfortunately, very little is known about the NMR behaviour of double and triple substituted acylcobalt carbonyl complexes. Nevertheless, it is evident from the available data that both types of CO resonances further shift to low field when a second phosphine enters the coordination sphere. Interestingly, no coupling of the terminal CO ligands to phosphorus was reported, while the acyl carbon resonance appears as a triplet (J_{PC} ~12 Hz). The ^{31}P NMR data are compiled in Table 5 and do not distinguish between the phosphorus nuclei coordinating in cis or trans positions to the acyl group if otherwise they are identical.

3.4. Miscellaneous

There are very few examples found in the literature where different spectroscopic methods other than IR, NMR or X-ray diffraction were used for the characterization of acylcobalt carbonyl complexes. In one instance, the UV–vis spectrum of $EtOC(O)Co(CO)_4$ was reported [27] without further discussion. There has been a unique attempt recently to use ^{57}Co-doped $CH_3C(O)Co(CO)_3PPh_3$ for emission Mössbauer spectroscopic studies [98].

Mass spectrometric analysis of acylcobalt complexes was also rarely performed. The sporadic reports include CH_2F– and $CF_2HC(O)Co(CO)_3PPh_3$ [53], CH_2F– and $CF_2HC(O)Co(CO)_3P(OPh)_3$ [24], as well as $CH_2(CH_2)_2C(O)Co(CO)_2(L)PR_2$ (L=CO, PPh_3; R=Ph, Cy) [84]. Since the molecules readily lose CO ligands, usually no molecular peaks could be observed (electron impact) but the frag-

Table 5
$^{31}P\{^1H\}$ NMR data for phosphine-substituted acylcobalt carbonyl complexes

R	L	δ (ppm)[a]	Solvent	Lit.
$RC(O)Co(CO)_3L$				
CH_3–	PPh_3	48.2	$CDCl_3$	[57]
C_2H_5–	PPh_3	53.5	$CDCl_3$	[59]
n-C_3H_7–	PPh_3	48.5 (6.9 s, 15 Hz)[b]	$CDCl_3$	[59]
i-C_3H_7–	PPh_3	49.0 (7.25 s, 18 Hz)[b]	$CDCl_3$	[59]
t-C_4H_9–	PPh_3	50.6 (6.8 s, 13 Hz)[b]	$CDCl_3$	[59]
$CH_3C{\equiv}CCH_2$–	PPh_3	48.9	CD_2Cl_2	[64]
$C_6H_5C{\equiv}CCH_2$–	PPh_3	48.9	CD_2Cl_2	[64]
$ClC{\equiv}CCH_2$–	PPh_3	48.8	CD_2Cl_2	[64]
$CH_3CH(OH)CH_2$–	PPh_3	49.8 (7.3 s, 30 Hz)[b]	$CDCl_3$	[59]
CH_3OCH_2–	PPh_3	49.1	$CDCl_3$	[57]
$C_2H_5OCH_2$–	PPh_3	50.2	$CDCl_3$	[57]
$C_2H_5OCH(CH_3)$–	PPh_3	49.5	$CDCl_3$	[57]
$CH_3OC(O)CH_2$–	PPh_3	49.9 (6.28 s, 14 Hz)[b]	$CDCl_3$	[46]
$CH_3OC(O)CH_2CH(C(O)OCH_3)$–	PPh_3	48.9	$CDCl_3$	[69]
CF_2Cl–	PPh_3	50.2	$CDCl_3$	[72]
C_2H_5O–	PPh_3	51.3	C_6D_6	[27]
CH_3–	PPh_2Me	33.4	$CDCl_3$	[77]
CH_3OCH_2–	PPh_2Me	33.4	$CDCl_3$	[77]
$CH_3OC(O)CH_2$–	PPh_2Me	34.4	$CDCl_3$	[59]
$C_2H_5OC(O)CH_2$–	PPh_2Me	34.5	$CDCl_3$	[77]
$PPh_2(CH_2)_3$–	[c]	21.3	THF (−50 °C)	[84]
$PCy_2(CH_2)_3$-	[c]	36.6	THF (−50 °C)	[84]
CH_3–	PPh_2R[d]	49.6	C_6D_6	[79]
$RC(O)Co(CO)_2L_2$				
CH_3–	PPh_2Me	26.5	$CDCl_3$	[77]
CH_3OCH_2–	PPh_2Me	26.0	$CDCl_3$	[77]
$C_2H_5OCH(CH_3)CH(OC_2H_5)$	DPPE	66.1	Toluene	[87]
$PPh_2(CH_2)_3$–	PPh_3^c	19.2, 50.8 (J_{PP} = 34 Hz)	Toluene (−70 °C)	[84]

[a] Recorded at room temperature (20 °C), relative to 85% H3PO4.
[b] T_1 relaxation time and line width are given in parentheses.
[c] Metallacyclic compound.
[d] R = $CH_2CH_2SiMe_2$–η^5–C_5H_4ZrCp.

ments formed via stepwise CO loss were identified. Using the soft field desorption technique, however, allowed determination of the molecular peak of $CH_2(CH_2)_2C(O)Co(CO)_2(L)PR_2$ [84].

4. Reactions of acylcobalt carbonyl complexes

4.1. Reactions at the central cobalt atom

The reactions discussed in this section have the common feature of requiring dissociation of a terminal CO ligand to generate an empty coordination site which

allows various reactants to interact directly with the central cobalt atom. Due to the considerable lability of the ligand sphere of cobalt carbonyl complexes, such type of reactions frequently occur and are central to most catalytic processes involving acyl cobalt carbonyl complexes.

4.1.1. Ligand exchange and substitution

The most general reaction of acylcobalt carbonyls, like those of all other metal carbonyl complexes, is the exchange or replacement of one or more coordinated ligands by an external ligand(s). So far the only exchange reaction was reported for CO and ^{13}CO and usually a coordinated CO can also be substituted by other ligands. A well established exception is the substitution of halide ions by CO or PPh_3 in $[RC(O)Co(CO)_3(X)]^-$ [25,26]. The molecular mechanism of both reactions has been studied by kinetic and spectroscopic methods in recent years.

An infrared spectroscopic study was conducted on the ^{13}CO exchange reaction of $EtOC(O)Co(CO)_4$ and led to the conclusion that CO dissociation must be the first step, creating a 16-electron, coordinatively unsaturated species which is then stabilized by an entering ligand, i.e. ^{13}CO (Eq. (31) and Eq. (32)) [99]. The first-order rate constant of

$$RC(O)Co(CO)_4 \rightleftharpoons RC(O)Co(CO)_3 + CO \quad (31)$$

$$RC(O)Co(CO)_3 + L \rightarrow RC(O)Co(CO)_3L \quad (32)$$

dissociation was found to be $4.7 \times 10^{-4}\ s^{-1}$ at 15 °C, which indicates considerable stability in comparison with other cobalt tetracarbonyl complexes. Although CO exchange of the terminal ligands took place three orders of magnitude faster than that of the acyl group, slow incorporation of ^{13}CO into the O–Co bond strongly supports the equilibrium in Eq. (33) [6–8].

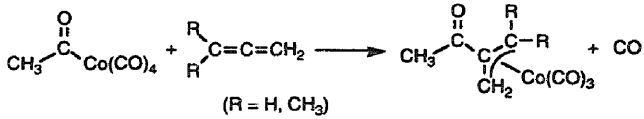
$$ROC(O)Co(CO)_4 \rightleftharpoons ROCo(CO)_4 + CO \quad (33)$$

Kinetics and thermodynamics of the CO exchange reaction of $CH_3C(O)Co(CO)_4$ with ^{13}CO were investigated subsequently by high-pressure ^{13}C NMR spectroscopy [31]. Activation parameters for the CO dissociation step (Eq. (31)) were obtained as $\Delta H^{\ddagger} = 22.0(0.2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8(0.5)$ eu. Comparative analysis of these data suggested that the coordinatively unsaturated intermediate in Eq. (31) might be stabilized by transient coordination of the acyl oxygen to cobalt. This assumption was supported by reactivity studies of matrix isolated $CH_3C(O)Co(CO)_3$, which proved to be surprisingly inert toward both H_2 and CO, and this photochemically generated unsaturated species could be thoroughly characterized by IR spectroscopy for the first time [100]. Theoretical calculations on the electronic and molecular structure of $CH_3C(O)Co(CO)_3$, utilizing the density functional theory, also point to possible stabilization by the acyl oxygen since its lone-pair electrons may interact with low-lying empty orbitals of the metal, polarized along the axis of the empty coordination site [101], although the authors emphasize that it is not the case under catalytic conditions.

Kinetics and mechanism of the PPh_3 substitution reaction of $EtOC(O)Co(CO)_4$

[27], $(CH_3)_2CHC(O)Co(CO)_4$ and $CH_3(CH_2)_2C(O)Co(CO)_4$ [102] were also investigated in detail and the results were in good agreement with those mentioned above for the ^{13}CO exchange reaction, that is, (1) intermediacy of an $RC(O)Co(CO)_3$ species was confirmed (Eq. (31) and Eq. (32)), (2) $k=3.9\times10^{-4}\ s^{-1}$ first-order rate constant was calculated for the CO dissociation of $EtOC(O)Co(CO)_4$ at 15 °C and (3) the activation parameters for CO dissociation of the iso- and *n*-butyryl complexes are respectively $\Delta H^{\ddagger}=19.2(0.3)$ kcal mol^{-1} and $\Delta S^{\ddagger}=0(1)$ eu as well as $\Delta H^{\ddagger}=19.6(0.1)$ kcal mol^{-1} and $\Delta S^{\ddagger}=0.1(0.4)$ eu. Prior to these measurements Heck determined the *k* values of a large number of acylcobalt tetracarbonyls for their PPh_3 substitution reactions and demonstrated unambiguous steric and electronic effects of various alkyl groups [17].

Acetylcobalt tetracarbonyl was found to react with allene leading to (2-acetyl-η^3-allyl)cobalt tricarbonyl and carbon monoxide [103]. The analogous reaction with 3-methyl-1,2-butadiene resulted in (2-acetyl-η^3-3,3-dimethylallyl) cobalt tricarbonyl (Eq. (34)) [104].



(34)

The kinetic behaviour of reaction Eq. (34) ($R=CH_3$) was found to be in accordance with a reversible dissociation of carbon monoxide from acetylcobalt tetracarbonyl, followed by a reaction with 3-methyl-1,2-butadiene [104].

4.1.2. Oxidative addition and reductive elimination

Acylcobalt carbonyl complexes of the type $RC(O)Co(CO)_{4-n}L_n$ ($n=0$, 1) generally undergo carbon-cobalt bond cleavage reactions with HX (X=H, ML_n (M= transition metal), SnR_3, SiR_3, halogen) type compounds resulting in the formation of the corresponding aldehyde (formate from alkoxycarbonyls) and $XCo(CO)_{4-n}L_n$ (Eq. (35)).

$$RC(O)Co(CO)_{4-n}L_n + HX \rightarrow RCHO + XCo(CO)_{4-n}L_n \quad (35)$$

Examples for reduction by H_2 and/or $HCo(CO)_4$ are well known [5d,8,12,25,34,75,76] mainly due to the interest in the mechanism of the cobalt-catalyzed hydroformylation of olefins; both reactions were presumed as possible product forming steps in the catalytic cycle. However, continuing controversy over the molecular mechanism and identity of the product forming step under catalytic conditions led to renewed kinetic and mechanistic investigations in recent years. Kinetic studies were performed on the reactions of $EtOC(O)Co(CO)_4$ [27], $CH_3(CH_2)_2C(O)Co(CO)_4$ and $(CH_3)_2CHC(O)Co(CO)_4$ [102,105] with both H_2 and

$HCo(CO)_4$, and suggested the mechanism in Eq. (31) and Eqs (36)–(38).

$$RC(O)Co(CO)_3 + HX \rightleftharpoons RC(O)CoHX(CO)_3 \quad (36)$$

$$RC(O)CoHX(CO)_3 \rightarrow RCHO + XCo(CO)_3 \quad (37)$$

$$XCo(CO)_3 + CO \rightarrow XCo(CO)_4 \quad (38)$$

This mechanism involves rate determining oxidative addition of the H–X molecule to the same coordinatively unsaturated acylcobalt tricarbonyl intermediate, which has been assumed in the ligand exchange and substitution reactions, followed by reductive elimination of the aldehyde or formate. In contrast to this theory, Orchin et al. found the rate of the reaction of $CH_3(CH_2)_4C(O)Co(CO)_4$ with $HCo(CO)_4$ to be independent of the carbon monoxide partial pressure and, for the rate dependence on carbon monoxide concentration is considered as a key evidence for the intermediacy of a coordinatively unsaturated species, suggested an alternative radical pathway [35]. However, Hidai et al. later proved that this particular reaction rate is indeed dependent on the carbon monoxide concentration [106], consistent with the general mechanism outlined in Eq. (31) and Eqs (36)–(38). In addition, on the basis of further kinetic measurements, the same mechanistic pathway was suggested for the reaction of $EtOC(O)Co(CO)_4$ with $HMn(CO)_5$ [107], $(CH_3)_2CHC(O)Co(CO)_4$ and $(CH_3)_2CHC(O)Co(CO)_3PPh_3$ with hydrogen halides [108], as well as for that of $CH_3C(O)Co(CO)_3PPh_3$ with $HSnR_3$ and $HSiR_3$ [109].

In agreement with the above experimental results, recent theoretical studies [110,111] proved on the basis of density functional theory that acetaldehyde is formed in the reaction of dihydrogen and $CH_3C(O)Co(CO)_3$ most probably through the oxidative addition/reductive elimination pathway. While an energy barrier of 36.3 kJ mol^{-1} was calculated for the whole process, the oxidative addition step itself required 30.5 kJ mol^{-1} activation energy, confirming that the latter is rate determining [111].

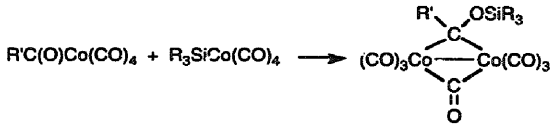
Kinetic data indicated that both $CH_3(CH_2)_2C(O)Co(CO)_4$ and $(CH_3)_2CHC(O)Co(CO)_4$ react faster with $HCo(CO)_4$ than H_2 at room temperature, but an analysis of the temperature dependence of the activation enthalpies led to the conclusion that H_2 must be the primary reducing agent under high pressure, high temperature catalytic hydroformylation conditions [102,105]. Room-temperature reactions of various acylcobalt complexes are generally slower with H_2 in comparison with transition metal or metalloid hydrides [27,102,112,113] probably due to the high H–H bond dissociation energy. A comparison of the rates of reactions of $EtOC(O)Co(CO)_4$ with $HMn(CO)_5$ and $HCo(CO)_4$ [107] as well as those of $C_5H_{11}C(O)Co(CO)_4$ with $[HRu(CO)_4]^-$ and $HCo(CO)_4$ [106] revealed that the heterobimetallic systems are more active in both cases, which may provide a possible explanation for the origin of synergistic activity in certain bimetallic hydroformylation catalyst systems.

When the hydrogenolysis of $EtOC(O)Co(CO)_4$ was carried out in the presence of an excess of 1-heptene, exclusive formation of $C_7H_{15}C(O)Co(CO)_4$ and octanal isomers was observed, that is, no $HCo(CO)_4$ and negligible $Co_2(CO)_8$ could be

detected among the products. This result suggested that $HCo(CO)_3$ formed according to Eq. (37) (X=H), is quenched by the olefin instead of being stabilized by CO uptake. and, once again, H_2 is the real reducing agent under catalytic hydroformylation conditions [114].

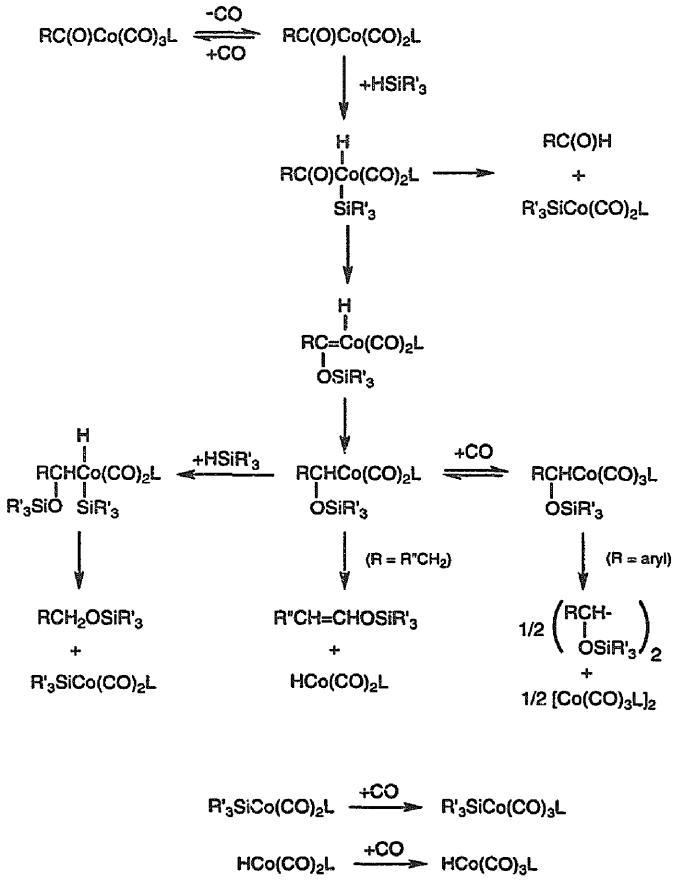
The reactions of acylcobalt complexes with hydrosilanes as HX in Eq. (35), however, merit further discussion. Although formation of acetaldehyde as sole organic product from $CH_3C(O)Co(CO)_3PPh_3$ and $HSiR_3$ (R=Et, Ph) under CO was established in the first such study [109], there is growing evidence that the product distribution can be quite complicated, depending on the reaction conditions and the nature of the starting acyl complex. Thus, in the absence of CO the same reaction did not afford any acetaldehyde but instead produced ethoxysilanes [78]. Similarly, no aldehyde was detected in the reaction mixture of phosphine-substituted aroylcobalt carbonyls, $ArC(O)Co(CO)_3PPh_3$, and $HSiEt_3$ when the experiment was performed under nitrogen, but the corresponding 1,2-disiloxyethanes appeared in addition to the alkoxysilanes [4]a. Applying different CO pressures and temperatures, aldehydes also formed and the ratio of the three organic products could be controlled. Furthermore, a kinetics study of the cleavage of $(CH_3)_2CHC(O)Co(CO)_4$ by $HSiEt_3$ revealed that $(CH_3)_2CHO$, $(CH_3)_2C{=}CHOSiEt_3$ and $(CH_3)_2CHCH_2OSiEt_3$ formed under 1 atm of CO [113]. In spite of different outcomes of these reactions, the mechanistic suggestions feature the same key intermediates (Scheme 1). While the general transformations outlined in Eq. (31) and Eqs. (36)–(38) might be responsible for the formation of aldehydes, the Co(III) intermediate $RC(O)Co(H)(SiR'_3)(CO)_2L$ is expected to undergo a competitive 1,3-silatropic shift due to the extreme oxophilic character of silicon, followed by hydride migration to result in the formation of a coordinatively unsaturated *sec*-alkyl intermediate, $RCH(OSiR'_3)Co(CO)_2L$ (L=CO, phosphine). The latter species in equilibrium with its saturated congener is then accountable for the formation of alkoxysilanes via cleavage by another molecule of hydrosilane, for that of silyl enol ethers via β-elimination and 1,2-disiloxyethanes via homolytic dissociation (Scheme 1).

Formally, an interesting reaction of acylcobalt tetracarbonyls with a variety of silylcobalt tetracarbonyls [115] outlined in Eq. (39) also belongs to this group owing to similarities to that with hydrosilanes (Scheme 1). Since formation of a coordinatively



(39)

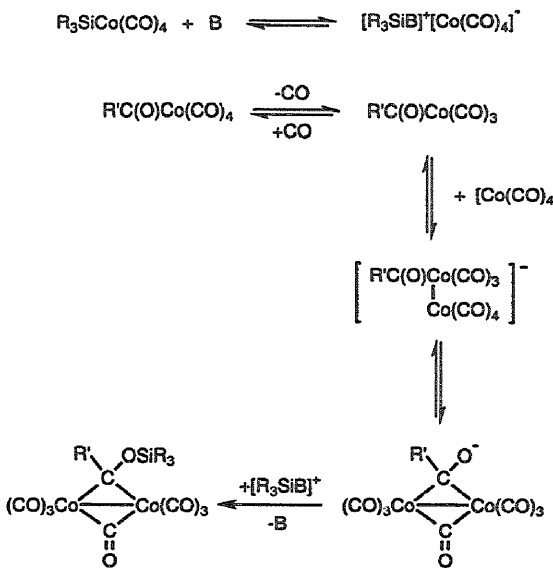
unsaturated intermediate $R'C(O)Co(CO)_3$ (Eq. (31)) is a necessity again, one would easily envisage the oxidative addition of $R_3SiCo(CO)_4$ to this species, followed by a 1,3-silatropic shift and rearrangements of the cobalt carbonyl moieties to form the binuclear siloxycarbene type product in Eq. (39). However, since such reactions are catalysed by bases (pyridine, PBu_3), the mechanism shown in Scheme 2 was suggested instead 115; this features an anionic Co(0) but not a neutral Co(III) intermediate.



Scheme 1.

4.1.3. Decarbonylation (acyl–alkyl equilibrium)

Most acylcobalt complexes exist in equilibrium with their alkyl counterparts in solution under a CO atmosphere (Section 2.1). The equilibrium can be shifted to either side depending on the electronic parameters of the alkyl group as well as the CO pressure and temperature. The electron withdrawing alkyl groups, an inert atmosphere and high temperatures all facilitate decarbonylation to an alkyl complex. Phosphorus donor ligands, however, kinetically stabilize the acyl complexes by reducing the decarbonylation rate by strengthening the coordination of the terminal CO ligands. Two phosphine substituents retard the decarbonylation process more significantly [68]. An interesting qualitative observation is that the relatively rare secondary acylcobalt tetracarbonyls exhibit susceptibility to decarbonylation which appears to be an average of that of the corresponding primary derivatives. Principal



Scheme 2.

examples are $CH_3CH{=}CHCH(CH_3)$– [37], $PhCH(CH_3)$– [16], $CH_3CH{=}CHCH(OSiMe_3)$– [40] and $CH_3O_2CCH_2CH(CO_2CH_3)C(O)$–$Co(CO)_4$ [46].

The mechanism of decarbonylation was never studied on cobalt complexes but was adapted from studies of analogous compounds of other metals (manganese, iron, etc.). In fact, the mechanism of the reverse process, CO insertion into alkyl complexes of these metals was thoroughly investigated and assumed to be identical with that of decarbonylation [116]. According to this widely accepted view, a pre-equilibrium CO dissociation should generate a coordinatively unsaturated intermediate as pointed out previously in Eq. (31) and migration of the alkyl group to the cobalt centre follows.

In spite of the enormous interest in the carbonylation/decarbonylation reactions of alkyl- and acylcobalt carbonyl complexes, quantitative investigations are almost entirely lacking. The only notable exception has been reported recently [117]; thermodynamic parameters for the decarbonylation of $CH_3C(O)Co(CO)_4$ (Eq. (40)) were

$$CH_3C(O)Co(CO)_4 \rightleftharpoons CH_3Co(CO)_4 + CO \qquad (40)$$

determined independently by using IR, NMR and gas volumetric methods and found to be $\Delta H = 11.2 \pm 0.6$ kcal mol^{-1} and $\Delta S = 19.5 \pm 2.0$ eu, indicating that this process is endothermic and the acyl complex represents ~99% of the total cobalt concentration under atmospheric pressure of carbon monoxide at 25 °C. The ratio of the rates of CO deinsertion (methyl migration) and CO uptake of the coordinatively unsaturated acyl tricarbonyl intermediate formed in Eq. (31) was estimated to be 21 in an earlier high-pressure ^{13}C NMR investigation [31]. Note that theoretical

calculations predicted the activation enthalpy of the decarbonylation of $CH_3C(O)Co(CO)_4$ to be 27 kcal mol^{-1} [118], considerably higher than that found experimentally [117].

4.1.4. Isomerization

The true reason for the changing *iso*-/*n*-butyraldehyde product ratio as a function of p_{CO} in the hydroformylation of propene has long been an unsolved mystery. A possible isomerization of *iso*- and *n*-butyrylcobalt tetracarbonyl intermediates seemed to be the most obvious explanation and indeed some indirect studies established that such a transformation occurs [119,120]. All the early work was carried out with acyl complexes generated in situ and the results were based on the analysis of mixtures of ester and aldehyde isomers as products of I_2/MeOH cleavage [119] and disproportionation [120], respectively. In contrast, no evidence for isomerization was found later, even at higher temperatures, when pure, isolated acyl complexes were investigated [102].

Recent investigations on octane solutions of pure iso- and *n*-butyrylcobalt tetracarbonyls showed that these complexes do interconvert, however, in the presence of added olefins (ethene, propene, 1-heptene) [60]. The equilibrium in Eq. (41), starting

$$CH_3CH_2CH_2C(O)Co(CO)_4 \rightleftharpoons (CH_3)_2CHC(O)Co(CO)_4 \quad (41)$$

from each side, was directly monitored by infrared spectroscopy and kinetic measurements allowed calculation of the activation energy of the iso→*n* transformation as $E_a = 41.2 \pm 0.4$ kcal mol^{-1}. The equilibrium composition at 25 °C was also determined by ^{1}H NMR spectroscopy after it was "frozen" in the form of PPh_3-substituted derivatives and showed that the normal isomer was the favoured product ($n/i \approx 1.3$). The equilibrium constant at 110 °C (catalytic hydroformylation conditions) was estimated to be 1.56, which coincides with the *n*-/*iso*butyraldehyde product ratio 1.6 obtained under 2.5 bar CO pressure. According to the proposed mechanism, the olefin may help to shift the acyl–alkyl equilibrium (see decarbonylation) to the alkyl side, which is normally far on the acyl side. Once an $RCo(CO)_3$(olefin) species is present in high enough steady-state concentration, isomerization of the alkyl group through a classic β-elimination pathway may proceed [60].

Prior to such detailed investigations, several other examples of non-equilibrium acyl isomerizations had already been demonstrated. The reaction of $HCo(CO)_4$ with styrene and ethyl acrylate below 10 °C resulted in the formation of the branched complexes $PhCH(CH_3)C(O)Co(CO)_4$ [38] and $EtOC(O)CH(CH_3)Co(CO)_4$ [45], respectively, as kinetic products, which slowly transformed at 25 °C into the thermodynamically more stable corresponding straight-chain acyl derivatives $PhCH_2CH_2C(O)Co(CO)_4$ and $EtOC(O)CH_2CH_2C(O)Co(CO)_4$. Both isomerizations were also reported much earlier by Takegami et al. [121], who identified the corresponding ethyl esters after treating the in situ generated acylcobalt tetracarbonyl isomers with I_2/EtOH, but the complexes were never characterized. The isomerization of n-$C_4H_9OCH(CH_3)C(O)Co(CO)_4$ to n-$C_4H_9OCH_2CH_2C(O)Co(CO)_4$ [119],

as well as that of α-ethylbutyryl- and α-methylvalerylcobalt tetracarbonyls to the straight-chain *n*-caproyl isomer and α-methylbutyrylcobalt tetracarbonyl to the *n*-valeryl derivative [122] were established in a similar manner.

In addition to these chain isomerizations, the ring isomerization of $PhCH_2C(O)Co(CO)_4$ to $2\text{-}MeC_6H_4C(O)Co(CO)_4$ was also reported [123]. The reaction proceeded easily only at higher temperatures and in the presence of $HCo(CO)_4$, and an inert atmosphere was also beneficial. However, the mechanism of this transformation and the role of $HCo(CO)_4$ remained unanswered.

4.2. Reactions of coordinated CO ligands

Efforts have been made to understand the molecular mechanism of the homogeneous "double carbonylation" reaction, which led to the discovery that powerful nucleophiles, such as alkoxides [10,82] and dialkylamides [82], can attack at the carbon atom of coordinated CO ligands and form anionic bisacyl compounds according to Eq. (42) and Eq. (43). The resulting unstable compounds usually have a limited lifetime only to

$$RC(O)Co(CO)_3L + R'O^- \rightarrow [RC(O)Co(COOR')(CO)_2L]^- \rightarrow RC(O)C(O)OR' \quad (42)$$

$$RC(O)Co(CO)_3L + R'_2N^- \rightarrow [RC(O)Co(CONR'_2)(CO)_2L]^- \rightarrow RC(O)C(O)NR'_2 \quad (43)$$

allow in situ characterization by IR spectroscopy and readily decompose into the corresponding α-keto acid derivatives. In one instance, however, a stable bisacyl derivative was prepared (Eq. (44)) and characterized by X-ray crystallography [124].

$$CH_3OC(O)Co(CO)_4 + CH_3OCs \rightarrow [Co(COOCH_3)_2(CO)_3]Cs \quad (44)$$

A brief study of the chemistry of the latter complex revealed that dimethyl carbonate was eliminated under an inert atmosphere, $CsOC(O)OCH_3$ and $CH_3OC(O)Co(CO)_4$ were formed upon reaction with CO_2, and a methoxy group was liberated upon treating with strong electrophiles, which was captured by $Co_2(CO)_8$ in the form of $CH_3OC(O)Co(CO)_4$ and $[Co(CO)_4]Cs$ [124].

4.3. Reactions of the acyl group

All reactions of the acyl group in acylcobalt complexes, not associated with the formation of a coordinatively unsaturated intermediate, involve the polarized carbonyl functionality and accordingly are divided into two subgroups (see below). However, there is one exception which does not fit into this picture, namely the decarboxylation of alkoxycarbonyl complexes [10,125]. This particular reaction is essentially a thermal decomposition that generates carbon dioxide, $Co_2(CO)_8$

and various oxygenated products (alcohols, carboxylic acids and their salts and esters) bearing the alkyl moiety (Eq. (45)). Starting from $CH_2{=}CHCH_2OC(O)Co(CO)_4$, η^3-allylCo(CO)$_3$ was obtained as

$$ROC(O)Co(CO)_3L \rightarrow 1/2Co_2(CO)_6L_2 + CO_2 + \text{“R”} \quad (45)$$

the product containing both the cobalt carbonyl and alkyl moieties [10]. Systematic investigations revealed a strong dependence of the yield of CO_2 on the electronic parameter of the alkyl group [125]. Evolution of high quantities of CO_2 hinted that the reverse reaction, insertion of CO_2 into a C–Co, bond might also be possible, although never was detected. In spite of such detailed investigations, however, no mechanistic pathway was suggested for the decarbonylation itself which, on the basis of the complicated product mixture, could be different than a simple CO_2 deinsertion.

4.3.1. Nucleophilic attack on the carbon atom

In order to understand better the mechanism of the cobalt/pyridine-catalyzed methoxycarbonylation of olefins, the product forming step of which is the reaction of an acylcobalt tetracarbonyl with methanol (Eq. (46)), a detailed kinetic investigation was

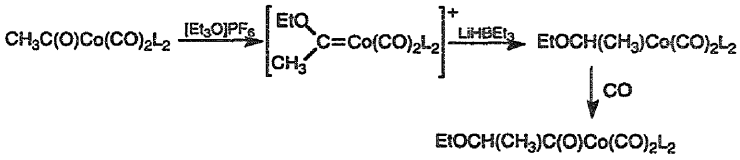
$$RC(O)Co(CO)_4 + CH_3OH \rightarrow RC(O)OCH_3 + HCo(CO)_4 \quad (46)$$

carried out on model reactions of $RC(O)Co(CO)_4$ (R=Me, *n*-Pr, i-Pr) [32]. It was established that the methanolysis is susceptible to both acid (HCl) and base (*i*-Pr_2EtN) catalyses and its rate is independent of CO pressure, which led to the conclusion that the most reasonable mechanism could be a nucleophilic attack of the methanol oxygen on the acyl carbon atom. This observation partly contradicts that of Heck [5]d who found base but no acid catalysis previously in similar systems.

According to a brief note of Heck [5]d, ammonolysis of acylcobalt carbonyls takes place in a similar manner and results in the formation of the corresponding amide and ammonium salt of the carbonylcobaltate(I) anion. The only relevant system that attracted considerable attention in the following years was the reaction of carbomoyl complexes with ammonia [126]. Although the products $HCo(CO)_{4-n}L_n$ (or its ammonium salt) and carbamide are consistent with the above results, ammonium cyanate was also formed, which led to the conclusion that ammonia rather deprotonated the NH_2-group than attacked the C=O group of the carbamoyl moiety.

4.3.2. Electrophilic attack on the oxygen atom

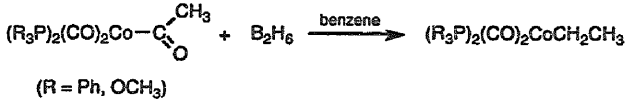
Conversion of CO into poly(alkoxymethylene)acyl ligands was achieved via consecutive electrophilic activation of the acyl group in $CH_3C(O)Co(CO)_2L^1L^2$ (L^1=CO, L^2=PPh_3; L^1=L^2=DPPE) complexes, hydride transfer to the oxycarbenoid intermediate and carbonylation of the resulting alkyl derivative [57,87] as shown in Eq. (47). The first two steps in this reaction sequence represent net reduction of an acyl



(47)

functionality. Furthermore, preparation of diethoxybutanoyl complexes, the products of two consecutive reduction–carbonylation sequences, took place in a *threo*-diastereoselective manner. Also worth mentioning is the fact that the alkoxycarbene intermediate appears to be the first fully characterized cationic cobalt Fischer-carbene complex.

An electrophilic attack on the acyl-oxygen has been assumed to be the first step in the reaction of disubstituted acetylcobalt dicarbonyl complexes with diborane leading to a rapid reduction to the corresponding ethyl complexes (Eq. (48)) [127].



(48)

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