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TERVALENT PHOSPHORUS DERIVATIVES OF COBALT CARBONYLS

IV*. COMPARISON OF THE REACTIONS OF PHOSPHITES AND PHOSPHINES WITH DICOBALT OCTACARBONYL

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Summary

The reaction of dicobalt octacarbonyl with tertiary phosphites gives several products, which have been interconverted by chemical means. Some cobalt—cobalt bonds have been formed from the nucleophilic attack by the anion $[Co(CO)_{4-n}L_n]^-$ on the cation $[Co(CO)_{5-n}(PR_3)_n]^+$ leading to known binuclear compounds. Such a reaction is not possible with tertiary phosphites because of a Michaelis—Arbuzov rearrangement, previously observed for complexes of manganese and molybdenum.

Introduction

Over many years the study of the reactivity of dicobalt octacarbonyl in the presence of organophosphorus ligands, has led to knowledge of the existence of three main series of compounds: $Co_2(CO)_{8-n}L_n$; $RCOCo(CO)_{4-n}L_n$ and $RCo(CO)_{4-n}L_n$; and $[Co(CO)_{5-n}L_n]^+[B(C_6H_5)_4]^-$.

The initial aim of this work was to obtain a series of complexes of the type $Co_2(CO)_{8-n}L_n$ with L = PA_3. Complexes where L = phosphine and n = 1[1], 2[2], 3, 4[3] and 6[4] are well known. However, for L = phosphite only those for which n = 1[1], 2[5], 4[6] and 8[7] have been reported.

Disproportionation of dicobalt octacarbonyl in the presence of PA_3 gives rise to a series of ionic complexes: $[Co(CO)_{5-n}(PA_3)_n]^+[Co(CO)_4]^-$ where n = 2 [2] or 3 [8], depending upon the nature of the Lewis base. The cations $[Co(CO)_{5-n}(PA_3)_n]^+$ may be isolated as their tetraphenylborates, in which further substitution of carbon monoxide can take place, giving an extended series of complexes $[Co(CO)_{5-n}(PA_3)_n]^+[B(C_6H_5)_4]^-$ [9]. In the case of

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* For Part I see ref. 27, Part II see ref. 9, Part III see ref. 6.

phosphites a third kind of reaction occurs leading to alkyl and acyl complexes of the type $RCo(CO)_{4-n}L_n$ and $RCOCo(CO)_{4-n}L_n$, which have been prepared by other reaction pathways [10].

The present work involved an investigation of the relationships between the various reactions quoted above and an explanation of the role of phosphites in the reaction steps. Moreover attempts have been made to obtain complexes containing metal—metal bonds by the combination of different types of cations and anions. The results observed are different with phosphines and trialkyl phosphites.

Discussion

Classical substitutions in dicobalt octacarbonyl

Mono-, di-, tri- and tetra-substituted derivatives can be obtained by direct replacement of carbon monoxide by phosphine ligands following the classical method used in the metal carbonyl chemistry.

$$Co_2(CO)_8 + nL \rightarrow Co_2(CO)_{8-n}L_n + n\,CO\uparrow$$

With phosphite, only mono- and di-substituted derivatives were obtained by this method although tetra- and octa-substituted complexes were prepared by special ways. Successive substitution of carbon monoxide in $Co_2(CO)_8$, observed for phosphines, does not occur with tertiary phosphites. Typically, a yellow precipitate of $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$ is formed in non-polar solvents which loses one mole of CO when refluxed in benzene to yield disubstituted derivatives $Co_2(CO)_6(PR_3)_2$ [2]. This reaction shows a possible relation between the ionic complexes $[Co(CO)_{5-n}L_n]^+[Co(CO)_4]^-$ and the substituted derivatives $Co_2(CO)_{8-n}L_n$. It was interesting to attempt such a reaction with phosphite, for which precipitation occurs at trisubstitution. The precipitate should give the unknown complex $Co_2(CO)_5L_3$ but this was not observed. The difference in reactivity of phosphines and phosphites prompted a study with substituted ligands of the type $P(OCH_3)_{3-n}(C_6H_5)_n$ ($n = 0, 1, 2$) which are intermediate between phosphines and phosphites.

Precipitation of the ionic complexes with $P(OCH_3)_{3-n}(C_6H_5)_n$

It is known that $P(C_6H_5)_3$ reacts with $Co_2(CO)_8$ to give $[Co(CO)_3\{P(C_6H_5)_3\}_2]^+[Co(CO)_4]^-$ [2]. The replacement of only one phenyl group by a methoxy group causes a change in the reactivity, and the resulting complexes are of the type: $[Co(CO)_2\{P(OCH_3)_{3-n}(C_6H_5)_n\}_3]^+[Co(CO)_4]^-$ ($n = 1,2$). These complexes are characterized by infrared and NMR measurements on their tetraphenylborate salts. They all show two absorption bands in the carbonyl region which increase in frequency as n decreases. The presence of two CO stretching vibrations shows a structure in which one ligand is in a different environment from the other two. The NMR spectrum of the cation $[Co(CO)_2L_3]^+$, however, shows a single resonance for the methyl protons, indicating apparent equivalence of the three ligands. These observations tend to show rapid intramolecular exchange between the two possible structures, trigonal bipyramid or square based pyramid [11].

The purpose of using the other ligands $P(OCH_3)_2C_6H_5$ and $P(OCH_3)(C_6$-

$H_5)_2$ was to obtain more stable complexes and also to discover whether the Michaelis-Arbuzov rearrangement depends upon the number of methoxy groups around phosphorus. In general, studies of the reactions of $Co_2(CO)_8$ with these ligands show that the ligands react in the same manner as $P(OCH_3)_3$. In these circumstances, the ligand $P(OCH_3)_3$, which gives the least experimental difficulty, has been retained.

Nucleophilic attack on the cations $[Co(CO)_{5-n}(PA_3)_n]^+$

Substitution of carbon monoxide by phosphorus ligands has been previously reported [9]. It would be interesting to know if other nucleophilic groups such as $[Co(CO)_4]^-$ or X^- can react with these cations to give either binuclear complexes or pentacoordinate derivatives.

(1) Attack by $Co(CO)_{4-m}(PA_3)_m^-$

(a) $PA_3 = P(CH_3)_3$ *or* $P(C_2H_5)_3$; $n = 2,3$; $m = 0$. The first reaction observed was the combination of $[Co(CO)_3(PA_3)_2]^+$ and $[Co(CO)_4]^-$ with loss of one mole of carbon monoxide to give $Co_2(CO)_6(PA_3)_2$ [2]. The following reactions were attempted in the light of this behaviour.

The cations $[Co(CO)_2(PA_3)_3]^+$ have been obtained as tetraphenylborate derivatives [12]. The possibility of reaction with $MCo(CO)_4$ depends upon the precipitation of $[B(C_6H_5)_4]^-$ with an alkali metal ion, M^+. The isolation of $M[B(C_6H_5)_4]$, allows association of the ion pair $[Co(CO)_2(PA_3)_3]^+[Co(CO)_4]^-$ and probably promotes, as a kinetic factor, the formation of metal—metal bonds. This has been possible by using $KCo(CO)_4$ giving precipitation of $K[B(C_6H_5)_4]$ which is less soluble than $Na[B(C_6H_5)_4]$. The reaction mixtures have been studied by infrared spectroscopy. The spectra show typical absorption bands of the trisubstituted derivatives $Co_2(CO)_5(PA_3)_3$ and also those of the well known disubstituted complex $Co_2(CO)_6(PA_3)_2$ which is a stable degradation product.

(b) $PA_3 = P(CH_3)_3$ *or* $P(C_2H_5)_3$; $n = 2$; $m = 1$. The reactions of $KCo(CO)_3PA_3$ with $[Co(CO)_3(PA_3)_2]^+[B(C_6H_5)_4]^-$ gives the trisubstituted derivatives $Co_2(CO)_5(PA_3)_3$. In fact the characterization of the substituted anions was not possible because of their great instability. However, the products obtained after a reaction without decomposition, provide proof of the identity of the initial complexes.

(c) $n = 3$; $m = 1$. Attempts to obtain the tetrasubstituted derivatives $Co_2(CO)_4(PA_3)_4$ starting from $KCo(CO)_3PA_3$ and $[Co(CO)_2(PA_3)_3]^+[B(C_6H_5)_4]^-$, were unsuccessful. Indeed the precipitation of $K[B(C_6H_5)_4]$ occurs facilitating the ion pair formation and probably the Co—Co bond, but the infrared spectrum shows the typical absorption bands of $Co_2(CO)_5(PA_3)_3$. This would seem in agreement with the loss of one mole of PA_3 instead of the usual loss of carbon monoxide.

This study of the anion—cation combination shows the possibility of obtaining derivatives of the type $Co_2(CO)_{8-n}(PA3)_n$ from various anions and cations substituted by phosphine ligands. But unfortunately the preparation of compounds with high values of n following such a method seems to be prevented by the difficulty of obtaining stable anions that are more than monosubstituted, and stable cations that are more than trisubstituted.

(2) Attack by X^- (X = Cl or I)

Since the cations could be attacked by nucleophilic groups, it was interesting to try the reaction with other simple nucleophilic reagents such as the halides X^- [13]. In all cases Cl^- or I^-, substituted either one mole of carbon monoxide or one of phosphine in the cation and combined with the metal to give a neutral pentacoordinated complex: $[XCo(CO)_2(PA_3)_2]$. This substitution may be driven by the fact that the disubstituted halide derivative is the most stable; this explains why attack on $[Co(CO)_3\{P(CH_3)_3\}_2]^+$ and $[Co(CO)_2\{P(CH_3)_3\}_3]^+$ by KI gives in both cases the new complex $[ICo(CO)_2\{P(CH_3)_3\}_2]$; the latter is characterized by comparison of its CO stretching bands with those of analogous complexes with triphenylphosphine [14].

Nucleophilic attack with anions and cations substituted by trialkylphosphite ligand

Following the results described above with phosphine ligands which show the formation of the derivatives $Co_2(CO)_{8-n}(PA_3)_n$, it was interesting for two reasons to study the same reactions with trialkylphosphite. Firstly, with the ionic complex $[Co(CO)_2\{P(OCH_3)_3\}_3]^+[Co(CO)_4]^-$, it was reasonable to expect the trisubstituted derivative $Co_2(CO)_5[P(OCH_3)_3]_3$. Secondly, the pentasubstituted cation $[Co\{P(OCH_3)_3\}_5]^+$ exists [8] and could give high degrees of substitution in the series $Co_2(CO)_{8-n}(PA_3)_n$.

In a first attempt $[Co(CO)_2\{P(OCH_3)_3\}_3]^+[Co(CO)_4]^-$ was allowed to react in benzene. Two phases were obtained: one viscous, containing the ion pair, the other light, containing the products soluble in benzene. When the mixture was stirred under nitrogen the ionic complex was transformed into a product which dissolved in the upper benzene phase. The infrared spectrum in the carbonyl region showed several bands (2020, 1995, 1970, 1965 and 1680 cm^{-1}). The particular band at 1680 cm^{-1} is attributed to an acyl group; thus a Michaelis—Arbuzov rearrangement is needed to explain the mechanism.

Such a phenomenon has been observed by Haines [15] in the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with trialkyl phosphite. The products obtained are $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ and $\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_3)_3]P(O)(OCH_3)_2$. The proposed mechanism involves the nucleophilic attack of the anion $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ on the cation $[\pi\text{-}C_5H_5Mo(CO)_2\{P(OCH_3)_3\}_2]^+$.

The Michaelis—Arbuzov rearrangement of tertiary phosphites in presence of alkyl halides is:

$$P(OR)_3 + R'X \rightarrow [R'P(OR)_3]X \rightarrow R'P(O)(OR)_2 + RX$$

In the case of molybdenum, the phosphonium intermediate should be the ionic derivative: $[\pi\text{-}C_5H_5Mo(CO)_2\{P(OCH_3)_3\}_2]^+[\pi\text{-}C_5H_5Mo(CO)_3]^-$. Another similar reaction occurs in the fission of tertiary phosphite by $Mn(CO)_5Si(C_6H_5)_3$ [16].

In accord with these results, it seems reasonable to propose the same mechanism in the case of cobalt since $Co_2(CO)_8$ gives, with excess of phosphite, a disproportionation reaction leading to an acylcobalt complex [9]. But no cobalt phosphonate was obtained in the mixture, perhaps because of extensive decomposition. The nature of the intermediate ionic complex can be revealed by the study of the association of the ion pair $[Co(CO)_2\{P(OCH_3)_3\}_3]^+[Co(CO)_4]^-$

The main product is $CH_3COCo(CO)_3[P(OCH_3)_3]$. It is clear that this acyl compound is derived from the anion $[Co(CO)_4]^-$ and not from the cation. The methyl group comes from one of the three phosphites coordinated to the Co^I; $CH_3Co(CO)_4$ is thus obtained and reacts immediately with free phosphite from the degradation of the cation, to give $[CH_3COCo(CO)_3\{P(OCH_3)_3\}]$.

The insertion of CO is well known following one of the mechanisms proposed by Noack [17] and Bor [18] or by Heck [10]. This acylcobalt compound should be the first relatively stable intermediate complex. Nevertheless it is well known that alkyl- and acyl-cobalt carbonyls are rather unstable, and give rise to isomerisation and disproportionation reactions [19]. This is a reason why the final product is the alkyl compound $CH_3Co(CO)_3L$, obtained with low yields because of extensive decomposition. The instability of these acyl and alkyl complexes [20] prevents any crystallization and elementary analysis. However, the formation of $CH_3COCo(CO)_3[P(OCH_3)_3]$ as the initial product of the reaction between $[Co(CO)_4]^-$, and $[Co(CO)_2\{P(OCH_3)_3\}_3]^+$ is supported by two further pieces of evidence. (i) If the reaction is performed in the presence of $P(C_6H_5)_3$, the intermediate $CH_3Co(CO)_4$ is trapped by this ligand which competes with $P(OCH_3)_3$ leading to the much more stable complex $CH_3COCo(CO)_3[P(C_6H_5)_3]$ [21]. (ii) If the reaction is performed in the presence of an excess of phosphite, $CH_3COCo(CO)_2[P(OCH_3)_3]_2$ is obtained as the result of CO substitution. All these compounds are characterized by their infrared spectra [10].

As the reactivity of the strong nucleophile $[Co(CO)_4]^-$ towards the cation $[Co(CO)_2\{P(OCH_3)_3\}_3]^+$ is clearly demonstrated, it seemed interesting to extend the reaction to the more substituted cation $[Co\{P(OCH_3)_3\}_5]^+$. The isolation of $K[B(C_6H_5)_4]$ from the mixture allows the ion pair $[Co\{P(OCH_3)_3\}_5]^+[Co(CO)_4]^-$ to react. In fact the infrared spectrum of the benzene solution shows the same absorption bands as does the solution of the trisubstituted cation, viz. 2020, 1995, 1972, 1960 and 1680 cm^{-1}. Bands at 2020, 1960, and 1680 cm^{-1} are attributed to $CH_3COCo(CO)_3[P(OCH_3)_3]$ (A) [10], those at 1995 and 1972 cm^{-1} are attributed to $Co_2(CO)_6[P(OCH_3)_3]_2$ (B) [5] which is a well known non-bridged disubstituted complex of $Co_2(CO)_8$.

A carbonyl complex cannot probably derive from the $[Co\{P(OCH_3)_3\}_5]^+$ cation; thus both derivatives (A) and (B) are formed from $[Co(CO)_4]^-$ through the intermediate $CH_3Co(CO)_4$. The cation is only the source of methyl groups and free phosphite. The formation of compound (B) can only be explained starting from $CH_3COCo(CO)_3[P(OCH_3)_3]$.

Previous studies of new ketone and aldehyde syntheses, show reactions of type:

$R\,COCo(CO)_{4-n}L_n + RCo(CO)_{4-n}L_n \rightarrow RCOR + [Co(CO)_{4-n}L_n]_2$ [ref. 22]

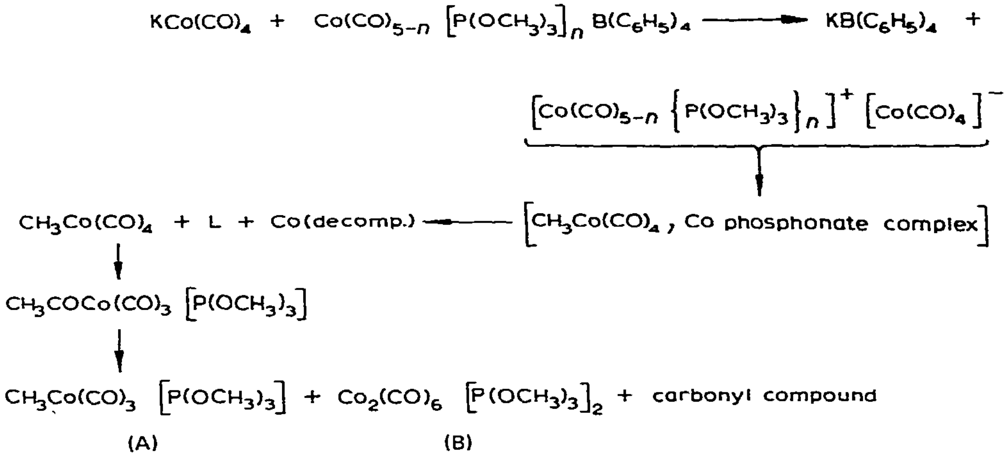
and

$2RCOCo(CO)_n \rightarrow RCHO + R_{-H} + Co_2(CO)_{2n}$ [ref. 19]

Hieber and colleagues [23] found that acetone could be obtained by a degradation reaction of alkylcobalt carbonyl. The formation of $Co_2(CO)_6L_2$ can thus be explained as follows:

$$2CH_3COCo(CO)_3[P(OCH_3)_3] \rightarrow Co_2(CO)_6[P(OCH_3)_3]_2 + 2CH_3CO\cdot$$

The $CH_3CO\cdot$ radicals probably combine to give an aldehyde or ketone [23]. The infrared spectrum of the mixture shows an absorption band at 1730 cm^{-1} which could be characteristic of a carbonyl compound (aldehyde, ketone or even diketone). Such mechanisms are in agreement with the ability of alkyl- and acyl-cobalt carbonyls to give isomerisation and disproportionation reactions. In conclusion, the nucleophilic attack of the anion $[Co(CO)_4]^-$ on the phosphite-substituted cations, leads to the following reactions:



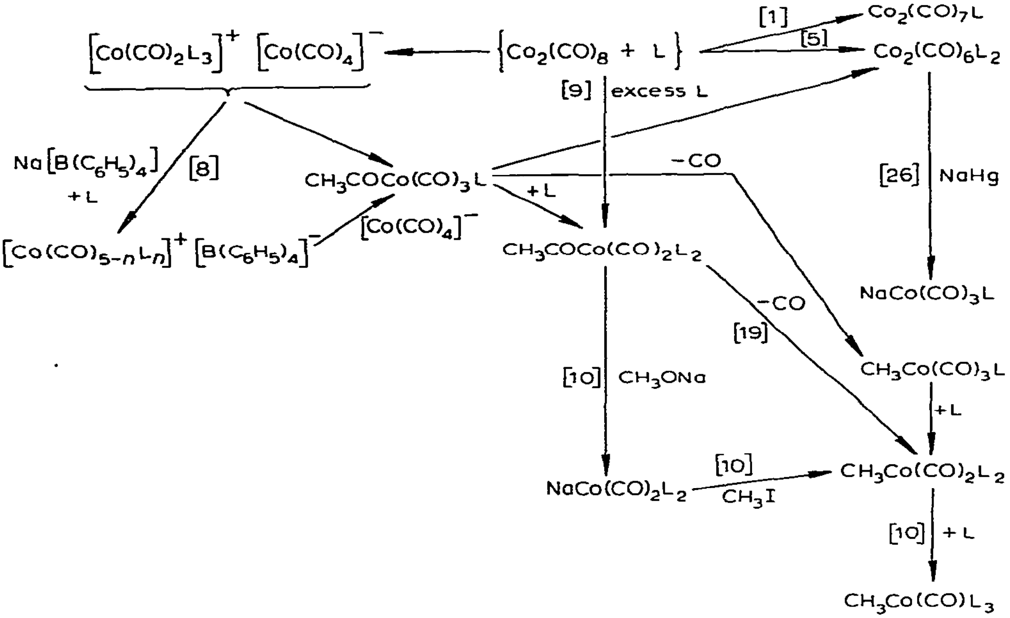
The reaction of $Co_2(CO)_8$ with excess phosphite leading directly to the acylcobalt dicarbonyl bis(trimethylphosphite), can now be explained:

$$\begin{tikzcd}
Co_2(CO)_8 + 3L \arrow[r, "fast"] & {[Co(CO)_2L_3]^+[Co(CO)_4]^- + 2CO\uparrow} \arrow[d, "fast"] \\
CH_3COCo(CO)_3L \arrow[d, "slow"] & CH_3Co(CO)_4 + \text{decomp. (green heavy phase)} \arrow[l, "excess\ L"', "fast"] \\
CH_3COCo(CO)_2L_2 \rightarrow CH_3Co(CO)_2L_2 + CO\uparrow \text{ (yellow, light phase)} &
\end{tikzcd}$$

At room temperature the ionic form is very labile. The first steps are fast. After the formation of $CH_3COCo(CO)_3L$, the substitution of CO, to give the disubstituted derivative, is slower. Thus under nitrogen the mixture obtained contains both alkyl- and acyl-cobalt dicarbonyl bis(trimethylphosphite), while under carbon monoxide the decarbonylation is inhibited.

In conclusion, the Michaelis—Arbuzov transposition of the trialkylphosphite prevents the formation of the highly substituted complexes $Co_2(CO)_{8-n}(PA_3)_n$ through the loss of one ligand in the anion—cation pairs. The relationship between various reactions is summarised in Scheme 1.

SCHEME 1. REACTIONS BETWEEN $Co_2(CO)_8$ AND $P(OCH_3)_3$



Experimental

Infrared spectra were obtained using a Perkin—Elmer model 225 instrument; frequencies are given Table 1. NMR spectra were recorded on a Varian A60 model. Reactions were carried out under nitrogen. Solvents were distilled and stored over molecular sieves; tetrahydrofuran was treated specially to remove water, peroxides and oxygen.

All the ligands were synthesised, except for $P(OCH_3)_3$, which was purchased from Fluka. $P(CH_3)_3$ and $P(C_2H_5)_3$ were made by the method of Mann and Wells [24] and $P(OCH_3)_2C_6H_5$ and $P(OCH_3)(C_6H_5)_2$ by reaction of chlorophenylphosphines with sodium methoxide. Dicobalt octacarbonyl was purchased from Pressure Co.

$KCo(CO)_4$

This was prepared by the disproportionation of $Co_2(CO)_8$ in the presence of KOH, in THF [25]. The filtered yellow solution was dried under vacuum and the white solid was washed several times with methylene chloride, dried and used immediatly to avoid decomposition.

$KCo(CO)_3(PA_3)$; $PA_3 = P(CH_3)_3$ and $P(C_2H_5)_3$

$Co_2(CO)_6(PA_3)_2$ was reduced by potassium amalgam in THF following a method adapted from the known reduction [26] by sodium amalgam. The crude product was not isolated from its solution which was immediately mixed with the cation solution.

TABLE 1

INFRARED ABSORPTION FREQUENCIES IN THE CO STRETCHING REGION

Compound	Frequency (cm^{-1})				Solvent
$KCo(CO)_4$	1888vs(br)				THF
$Co(CO)_3[P(C_6H_5)_3]_2^+B(C_6H_5)_4^-$	2010vs				$(CH_3)_2CO$
$Co(CO)_3[P(CH_3)_3]_2^+B(C_6H_5)_4^-$	1998vs				$(CH_3)_2CO$
$Co(CO)_3[P(C_2H_5)_3]_2^+B(C_6H_5)_4$	1995vs				$(CH_3)_2CO$
$Co(CO)_2[P(OCH_3)_3]_3^+B(C_6H_5)_4^-$	2040m	1985vs			CH_2Cl_2
$Co(CO)_2[P(OCH_3)_2C_6H_5]_3{}^+B(C_6H_5)_4^-$	2028m	1975vs			CH_2Cl_2
$Co(CO)_2[P(OCH_3)(C_6H_5)_2]_3^+B(C_6H_5)_4^-$	2015m	1964vs			CH_2Cl_2
$Co(CO)_2[P(CH_3)_3]_3^+B(C_6H_5)_4^-$	1995w	1937vs			$(CH_3)_2CO$
$Co(CO)_2[P(C_2H_5)_3]_3^+B(C_6H_5)_4^-$	1988w	1945s	1929s		$(CH_3)_2CO$
$ICo(CO)_2[P(CH_3)_3]_2$	1978m	1912s			CH_2Cl_2
$ICo(CO)_2[P(C_2H_5)_3]_2$	1977m	1910s			Hexadecane
$ClCo(CO)_2[P(C_2H_5)_3]_2$	1972m	1905s			CH_2Cl_2
$CH_3Co(CO)_3[P(OCH_3)_3]$	2020m	1960vs			Hexadecane
$CH_3COCo(CO)_3[P(OCH_3)_3]$	2057w	1996	1964vs	1686m	$(C_2H_5)_2O$
$CH_3Co(CO)_2[P(OCH_3)_3]_2$	1996s	1934vs			CCl_4
$CH_3COCo(CO)_2[P(OCH_3)_3]_2$	2000s	1938vs	1658m		CCl_4
$Co_2(CO)_6[P(OCH_3)_3]_2$	1995m	1972vs			Hexadecane
$Co_2(CO)_6[P(CH_3)_3]_2$	1972w	1950vs			Hexadecane
$Co_2(CO)_6[P(C_2H_5)_3]_2$	1972w	1951vs			Hexadecane
$Co_2(CO)_5[P(CH_3)_3]_3$	2000m	1947vs	1772w	1753m	Hexadecane
$Co_2(CO)_5[P(C_2H_5)_3]_3$	1992m	1942vs	1904vw		Hexadecane
$Co_2(CO)_4[P(OCH_3)_3]_4$	1950s	1885s			CH_2Cl_2

$[Co(CO)_{5-n}(PA_3)_n]^+[B(C_6H_5)_4]^-$

The following tetraphenylborate cations were prepared by already published procedures [9]. $[Co(CO)_3(PA_3)_2]^+[B(C_6H_5)_4]^-$; PA_3=$P(CH_3)_3$, $P(C_2H_5)_3$. $[Co(CO)_2(PA_3)_3]^+[B(C_6H_5)_4]^-$; PA_3=$P(CH_3)_3$, $P(C_2H_5)_3$ and $P(OCH_3)_3$. $[Co(PA_3)_5]^+[B(C_6H_5)_4]^-$; PA_3=$P(OCH_3)_3$.

The new cations substituted by $P(OCH_3)_2(C_6H_5)$ and $P(OCH_3)(C_6H_5)_2$ were obtained by similar methods. They were identified by infrared and NMR spectra.

The reactions noted below concern the nucleophilic attack of the cations by various anions and were studied on the basis of the easily interpretable infrared spectra of the mixtures.

$KCo(CO)_4$ or $KCo(CO)_3PA_3$ + $Co(CO)_{5-n}(PA_3)_nB(C_6H_5)_4$.

$PA_3 = P(CH_3)_3$ or $P(C_2H_5)_3$; $n = 2, 3$. A solution of the cation in THF was added to an equimolar amount of $KCo(CO)_4$ also in THF. The mixture was stirred; the yellow solution turned orange and a white precipitate of $K[B(C_6H_5)_4]$ slowly appeared. After a few hours, the solution was filtered and the solvent was removed under vacuum giving an orange powder. The latter showed infrared bands characteristic of the anion and the cation, giving a proof of the ion pair association. A suspension of the solid was refluxed in benzene until the spectrum showed the absence of the initial ions.

Finally the typical frequencies of the known binuclear compounds $Co_2(CO)_{8-n}(PA_3)_n$ [3]: $n = 2$ or 3, were found.

$[Co(CO)_2\{P(OCH_3)_3\}_3]^+[Co(CO)_4]^-$

This ionic complex was obtained from the reaction of $Co_2(CO)_8$ with $P(OCH_3)_3$ in pentane at − 20°. The yellow precipitate was washed, dried and put in suspension in benzene. The stirred solution separated immediatly into two phases: one yellow which turned rapidly to yellow-green, the other viscous which became dark green. The infrared spectrum of the upper solution in which alkyl and acyl species are soluble, showed the disappearance of the acyl band, and that the final products were $CH_3Co(CO)_3[P(OCH_3)_3]$ and $Co_2(CO)_6[P(OCH_3)_3]_2$. Attempts to crystallize the products and to separate them were unsuccessful.

If the same reaction is performed in presence of $P(C_6H_5)_3$, the isolation of the stable acyl compound $CH_3COCo(CO)_3[P(C_6H_5)_3]$ is possible and its crystallisation is easy.

It is also easy to obtain the disubstituted derivative $CH_3COCo(CO)_2[P(OCH_3)_3]_2$ mixed with $CH_3Co(CO)_2[P(OCH_3)_3]_2$ by adding an excess of phosphite to the mixture instead of $P(C_6H_5)_3$.

$KCo(CO)_4 + Co[P(OCH_3)_3]_5B(C_6H_5)_4$

Equimolar quantities of both salts in THF were mixed. The stirred solution changed from yellow to orange and a white precipitate of $KB(C_6H_5)_4$ appeared. After filtration the solvent was evaporated and the resulting solid $[Co\{P(OCH_3)_3\}_5]^+[Co(CO)_4]^-$ was refluxed in benzene. The initial infrared spectrum of the red solution, showed the bands of $CH_3Co(CO)_3[P(OCH_3)_3]$ and $Co_2(CO)_6[P(OCH_3)_3]_2$ and an additional one at 1730 cm^{-1}. A red powder was isolated of which the infrared spectrum presents only the typical bands of $Co_2(CO)_6[P(OCH_3)_3]_2$.

$KI + Co(CO)_{5-n}(PA_3)_n[B(C_6H_5)_4]$

$PA_3 = P(CH_3)_3$ *or* $P(C_2H_5)_3$, $n = 2, 3$. An excess of potassium iodide in acetone was added to an acetone solution of the cation. The mixture was refluxed for several hours until the infrared spectrum showed the absence of initial products. The complex formed in all cases $ICo(CO)_2(PA_3)_2$ was crystallized and identified by its infrared spectrum [13,14].

$ClN(CH_3)_4 + Co(CO)_{5-n}(PA_3)_n\ B(C_6H_5)_4$

$PA_3 = P(C_2H_5)_3$, $n = 3$. Both salts were dissolved in acetone, and the solution refluxed during several hours. Some decomposition occurred but it was possible to extract the complex $ClCo(CO)_2(PA_3)_2$, with hexane The product was identified by its infrared spectrum [13,14].

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