Trivalent Phosphorus Derivatives of Cobalt Carbonyls. II.

Syntheses and Physico-chemical Studies of new Cations

in the Hypothetical Pentacarbonyl Cobalt(I) Series

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*A general examination of the reactions of $Co_2(CO)_8$ with $P(OMe)_3$. Three main kinds of reaction noted:*

— classical substitution: $Co_2(CO)_{8-n}L_n$ series.

— formation of acyl derivatives.

— precipitation of the cation $Co(CO)_{5-n}L_n^+$.

The tetraphenylborates derivatives of these cations undergo substitution of their CO molecules by organophosphorus ligands, leading to a series $Co(CO)_{5-n}L_n^+$. Infrared and nmr spectrographical studies seem to provide proof of stereochemical non-rigidity in the case of the above cations.

Introduction

It is known that under the influence of a Lewis base, the dicobalt octacarbonyl can lead to two series of compounds whose respective basic formulae is $Co_2(CO)_{8-r}L_n$[1] and $Co_2(CO)_{9-n}L_n$.[2]

The first series of compounds is the result of classical substitutions such as:

$$Co_2(CO)_8 + nL \rightarrow Co_2(CO)_{8-n}L_n + nCO \qquad (a)$$
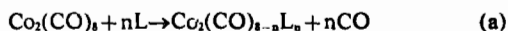
In this series, mono, di and tri substituted derivatives[3] can be quoted resulting from the substitution reaction (a), and also such complexes as $Co_2(CO)_2(PPh_3)_6$ and $Co_2[P(OEt)_3]_8$ resulting from more specific methods of preparation.

The second series seems to be the result of a global increase in the coordinance of cobalt. The cleavage of the Co–Co bond finally leads to the formation of ionic complexes consisting of a cation $Co(CO)_{5-n}L_n^+$ associated with the tetracarbonylcobaltate anion $Co(CO)_4^-$:

$$Co_2(CO)_8 + nL \rightarrow Co(CO)_{5-n}L_n^+, \ Co(CO)_4^- + (n-1) \ CO \qquad (b)$$
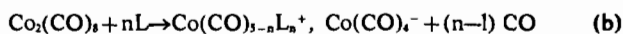
The cation series $Co(CO)_{5-n}L_n^+$, is well illustrated by the example of the $Co(CO)_3L_2^+$ derivatives of va-

rious phosphines[2] L and CoL_5^+ derivatives of phosphites[4] and isonitriles.[5]

An unusual reaction of $Co_2(CO)_8$ with $P(OMe)_3$ has been also found leading to an acyl derivative of the series $RCOCo(CO)_{4-n}L_n$.

In the present study, our main aim has been to examine comprehensively the possibilities of syntheses of cation derivatives. This was made possible firstly by extending reaction(b) to various types of ligands. Secondly, by carrying out successive substitutions of CO molecules on these ionic derivatives, according to the classical methods of metal carbonyl chemistry[6], we were able to complete the series for diverse values of n.

Finally, several observations are made concerning the structural study of pentacoordinated cations, using infra red, and nuclear magnetic resonance spectrographies.

Experimental Section

I.R. spectrography: the spectra were recorded on a Perkin-Elmer 225 spectrophotometer with a precision greater than ± 1 cm^{-1}, both for the whole range from 4000 to 200 cm^{-1}, and more particularly in the region of the CO stretching vibrations from 2200 to 1600 cm^{-1}. The compounds were observed in a weakly concentrated solution (10^{-3}mol) of acetone or methylene chloride.

N.M.R. spectrography: the spectra were recorded at room temperature on a Perkin-Elmer R 10 - 60 MHz, and at low temperature on a Varian H.A. 100 and a JEOL C60 HL at respectively 100 and 60 MHz, using saturated solutions in acetone, or methylene chloride; tetramethylsilane(TMS) was used mainly as an external reference. Practical difficulties appear at extremely low temperatures due evidently to the increase in viscosity and to the solidification of the solvent, and also to the insufficient solubility of the products.

The analytical data of the different compounds were obtained through the aid of the Microanalysis ser-

(1) A. Sacco *Ann. Chim.*, *43*, 495 (1953); C. Pegot, *Thèse 3ème Cycle*, Toulouse (1969).
(2) A. Sacco and M. Freni, *J. Inorg. and Nuclear Chem.*, *8*, 566 (1954); W. Hieber and W. Freyer, *Chem. Ber.*, *91*, 1230 (1958); W. Hieber and W. Freyer, *Chem. Ber.*, *93*, 462 (1959).
(3) G. Capron-Cotigny, *These 3ème cycle*, Paris 1967.

(4) K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Adv. in Chem. Series*, 590 (1966).
(5) Y. Dartiguenave, M. Dartiguenave, and H. B. Gray, *Bull. Soc. Chim.*, *12*, 4225 (1969).
(6) G. R. Dobson, I. W. Stollz, and R. K. Sheline, *Adv. in Inorg. and Radio. Chem.*, *8*, 1 (1966).

Table I. Physical Data of some prepared compounds.

Compound	Aspect	Melting Point °C	δppm/TMS (cation)	$J_{p-H}Hz$ [a] (cation)	IR.ν(CO) cm^{-1}
Co(CO)₃[PMe₃]₂⁺,BPh₄⁻	White solid	207 (dec)	— 2.1 (CH₃)	9.5	1998
Co(CO)₃[PEt₃]₂⁺,BPh₄⁻	White solid	190 (»)			1995
Co(CO)₃[P(NMe₂)₃]₂⁺,BPh₄⁻	White solid	213 (»)	—3.18(CH₃)	10.2	1985
Co(CO)₃[PPh₃]₂⁺,BPh₄⁻	Orange-yellow solid	221 (»)		—	2010
Co(CO)₂[PMe₃]₃⁺,BPh₄⁻	Yellow solid	209 (»)	—2.1 (CH₃)	8	1995-1937
Co(CO)₂[PEt₃]₃⁺,BPh₄⁻	Yellow solid	136		—	1988-1945-1929 [b]
Co(CO)₂[P(OMe)₃]₃⁺,BPh₄⁻	White solid	160 (dec)	—3.28(OCH₃)	12	2037-1982
Co(CO)₂[P(OCH₂)₃CEt]₃⁺,BPh₄⁻	White solid	165 (»)	—4.55(OCH₂)	—	2062-2013-1978 [b]
Co(CO)[P(OMe)₃]₄⁺,BPh₄⁻	Yellow solid	170 (»)	—3.68(OCH₃)	11.4	1970
Co(CO)[P(OCH₂)₃CEt]₄⁺,BPh₄⁻	Yellow solid	200 (»)	—4.35(OCH₂)	—	2041-2003 [b]
Co(CO)[P(OMe)₃]₂[P(OCH₂)CEt]₂⁺,BPh₄⁻	Waxy solid	—	{ —4.05(OCH₂) { —3.55(OCH₃)	—	1980
Co[P(OMe)₃]₅⁺,BPh₄⁻	Yellow solid	115	—3.71(OCH₃)	9.4	
Co[P(OMe)₃]₂[P(OCH₂)₃CEt]₃⁺,BPh₄⁻	Waxy solid	—	{ —4.20(OCH₂) { —3.65(OCH₃)		
CH₃COCo(CO)₂[P(OMe)₃]₂	Yellow-white solid	35	{ —3.52(OCH₃) { —2.85(CH₃)	11	{ 2006-1995-1944 [b] { 1938-1660

[a] These NMR spectra are of second order type and the reported values J_{PH} are in fact the separation of the lines of the most intense doublet. [b] For these compounds it appears an anormal number of absorption frequencies. This has not been studied but would seem « a priori » due to the existence of isomers.

Table II. Analytical results.

Compounds	Carbon % Found	Calc.	Hydrogen % Found	Calc.	Phosphorus % Found	Calc.
Co(CO)₂[P(OMe)₃]₃⁺,BPh₄⁻	51.92	52.17	5.79	5.84	11.48	11.55
Co(CO)[P(OMe)₃]₄⁺,BPh₄⁻	50.52	49.28	6.38	6.21	13.45	13.76
Co[P(OMe)₃]₅⁺.BPh₄⁻	46.96	46.94	6.69	6.52	15.44	15.54
Co(CO)₂[PMe₃]₃⁺,BPh₄⁻	65.05	62.96	7.12	7.05	13.87	13.94
Co(CO)₂[PEt₃]₃⁺,BPh₄⁻	68.04	67.09	8.24	8.26	11.34	11.82
CH₃COCo(CO)₂[P(OMe)₃]₂	29.59	29.55	5.28	5.17	15.23	15.27

vice of the C.N.R.S. and the results arrived at in Carbon, Hydrogen and Phosphorus are satisfactory.

Synthesis: Co₂(CO)₈ was prepared under carbon monoxide at normal pressure, according to the method evolved by Clark and coll.;[7] PMe₃ and PEt₃ were prepared following the method of Mann and ells.[8]. The other ligands P(OMe)₃, P[N(CH₃)₂]₃, and PPh₃, were obtained from commercial sources.

The solvents used., methylenechloride, pentane, acetone, methylethylketone, benzene had been distilled just before use.

Co₂(CO)₈ was handled in the absence of direct light and air, in order to avoid the risks of photochemical degradation or oxydation.

Although we considered it preferable for diverse reasons to perform reactions on metal carbonyls in inert solvents, insofar as this was possible, in the case of the cationic derivatives we studied, the acetone and the methylethylketone maintained their effectiveness because of their strong dissolving power.

PENTACOORDINATED CATIONS DERIVED FROM COBALT(I) Co(CO)₅₋ₙLₙ⁺.

1) *Derivatives of P(OMe)₃.*

Tris(trimethylphosphite)dicarbonyl Cobalt(I) tetra-

(7) R. J. Clark, S. E. Whiddon, and R. E. Serfass, *J. Organometal. Chem.*, **2**, 637 (1968).
(8) F.G. Mann and A.F. Wells, *J. Chem. Soc.*, 702 (1938).
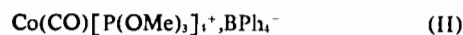
phenylborate.

$$Co(CO)_2[P(OMe)_3]_3{}^+,BPh_4{}^- \qquad (I)$$

3.5 g of Co₂(CO)₈ dissolved in a minimum of pentane at 0°C were added to a solution of 4 g of P(OMe)₃ in pentane cooled to –20°C.

The reaction was very vigorous, exothermic giving an abundant yellow precipitate separated at –20°C from the overlying solution. The latter was then eliminated by filtration and the precipitate was washed with pentane, then vacuum dried.

Afterwards the product was treated with 7 g of NaBPh₄ in acetone and precipitated by an abundance of nitrogen saturated distilled water.

The white precipitate obtained was filtered, washed several times with methanol, dried, and recrystallised in acetone.[2]

Tetrakis.(trimethylphosphite)monocarbonyl Cobalt-(I) tetraphenylborate.

$$Co(CO)[P(OMe)_3]_4{}^+,BPh_4{}^- \qquad (II)$$

A solution of(I) in pure P(OMe)₃ was kept at 100°C for 2 days. The excess of ligand was extracted in a vacuum and the yellow residue obtained recrystallized in acetone.

Pentakis(trimethylphosphite)Cobalt(I) tetraphenylborate.

$$Co[P(OMe)_3]_5{}^+BPh_4{}^- \qquad (III)$$
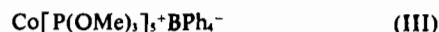
(I) was dissolved in $P(OMe)_3$ and exposed to ultra-violet radiation from a mercury arc lamp at 366 mμ, together with several milliliters of pentane; the latter through its low boiling point (35°C) enables overheating to be avoided. This irradiation lasted about 1 day and finally leads to the precipitation of golden yellow flakes, which were then extracted and recristallized in acetone.
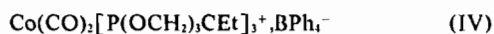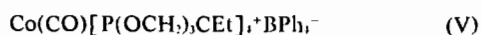
2) Derivatives of $P(OCH_2)_3CEt$.

Tris (4 Ethyl 2,6,7 trioxa 1 phosphabicyclo 2,2,2 octane) dicarbonyl Cobalt(I) tetraphenylborate.

$$Co(CO)_2[P(OCH_2)_3CEt]_3{}^+, BPh_4{}^- \qquad (IV)$$

This compound was isolated by Booth and Coll.[9] during a reaction of $Co_2(CO)_8$ both with butadiene and with the ligand. Using our own method, we prepared it in the same way as the trisubstituted derivative in $P(OMe)_3$, from 5 g of $P(OCH_2)_3$ CEt and 3.5 g of $Co_2(CO)_8$ dissolved at −20°C in pentane. The mixture was exposed to the action of an acetone solution of $NaBPh_4$ and released through water, giving a white precipitate.

Tetrakis (4 Ethyl 2,6,7 Trioxa 1 phosphabicyclo 2,-2,2 octane) monocarbonyl Cobalt(I) tetraphenylborate.

$$Co(CO)[P(OCH_2)_3CEt]_4{}^+BPh_4{}^- \qquad (V)$$

This derivative was prepared directly through the action of the phosphite on $Co_2(CO)_8$ at 60°C in a solid state.[9] It was also obtained from (IV) in methylethylketone in the presence of an excess of ligand.

In order to identify these two derivatives of $P(OCH_2)_3$ CEt we limited ourselves to their infrared absorption spectra in the region of 2200-1600 cm^{-1}. The CO stretching frequencies are in fact identical to those reported by Booth and Coll.

3) Derivatives of $P(OMe)_3$ and $P(OCH_2)_3CEt$.

Bis(trimethylphosphite) bis (4 Ethyl 2,6,7 trioxa 1 phosphabicyclo 2,2,2 octane) monocarbonyl Cobalt(I) tetraphenylborate.

$$Co(CO)[P(OMe)_3]_2[P(OCH_2)_3CEt]_2{}^+, BPh_4{}^- \qquad (VI)$$
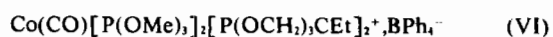
A methylethylketone solution of (V) was brought to boiling temperature in presence of an excess of $P(OMe)_3$ and kept there for three days. The compound (VI) was then precipitated through water.

Bis (trimethylphosphite) tris (4Ethyl 2, 6, 7 trioxa 1 phosphabicyclo 2,2,2 octane) Cobalt(I) tetraphenylborate.

$$Co[P(OMe)_3]_2[P(OCH_2)_3CEt]_3{}^+, BPh_4{}^- \qquad (VII)$$
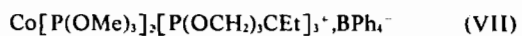
0.2 g of (III) react with 0.06 g of $P(OCH_2)_3$ CEt when boiling in methylethylketone for 1 day giving (VII).

Obtaining purified forms of the preceding mixed compounds presents several difficulties. The products obtained display a waxy consistency and being unable to obtain in security chemically analysable samples we determined their molecular composition in protonic resonance by integrating the relative peaks of the groups $(OCH_2)_3$, $(OMe)_3$ and (BPh_4).

4) Derivatives of the alkyl phosphines.

Tris (trialkylphosphine) dicarbonyl Cobalt(I) tetraphenylborate

$$Co(CO)_2[PR_3]_3{}^+, BPh_4{}^-$$

(VIII): R = Me
(IX) : R = Et

By boiling the known disubstituted derivatives $Co(CO)_3(PR_3)_2{}^+$, $BPh_4{}^-$ in methylethylketone in presence of a ligand excess, we managed to prepare for the first time the trisubstituted complexes.

We tried without succeeding to isolate the tetrasubstituted derivatives starting from (VIII) and (IX) both by thermic and by photochemical activation. However, we observed on the spectra in the CO stretching region new bands of absorption at a lower frequency which could be attributed to these tetrasubstituted derivatives.

ACYL COMPOUND

Acetyl cobalt dicarbonyl bis (Trimethylphosphite).

$$CH_3COCo(CO)_2[P(OMe)_3]_2 \qquad (X)$$

A benzene solution of $Co_2(CO)_8$ was brought to 60°C in presence of a large excess (10:1) of $P(OMe)_3$, for six hours. The yellow solution in then vacuum dried and the residue recristallized in pentane giving pale yellow crystals.

Results and Discussion

From a general point of view, this synthetic approach and the methods of preparation which we developed bring into evidence the fact that $P(OMe)_3$ reacts with $Co_2(CO)_8$ giving three series of products.

(a) If a stoichiometric quantity of the ligand is added at room temperature, the formation can be observed of a "non bridged" disubstituted derivative[3] of the $Co_2(CO)_8$ series: 1,2 bis (trimethylphosphite) hexacarbonyl dicobalt (0).

(b) If the conditions which we noted in the experimental section and which we shall explain in greater detail later on, are respected, the reaction leads to the formation of derivatives of the $Co_2(CO)_{9-n}L_n$ series.

These compounds could be considered as substituted derivatives of $Co_2(CO)_9$ brought into evidence by Metlin and coll.[10] which would lead to the hypothetical $Co(CO)_5{}^+$ cation by a disproportionation reaction.
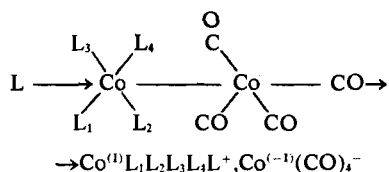
The above complexes of an ionic nature separate out from the reaction mixture by precipitation.

(9) B. L. Booth, M. Gardner, and R. N. Haszeldine, *Chem. Comm.*, 1388 (1969).

(10) S. Metlin, I. Wender, and H. W. Sternberg, *Nature*, *14*, 457 (1959).

(c) Finally, if the ligand is present in great excess in ratio to $Co_2(CO)_8$, we have established that the reaction leads to the formation of acylcobalt carbonyl complexes o the $RCOCo(CO)_{4-n}L_n$ type.[11]

Precipitation of the cations $Co(CO)_{5-n}L_n{}^+$ The method which we developed is derived directly from Hieber's [2] and consists in making a Lewis L base react with $Co_2(CO)_8$ in solution in a slightly polar solvent at temperatures and concentrations varying according to the nature of the ligand. The formation of complexes $Co(CO)_{5-n}L_n{}^+$, $Co(CO_4{}^-$ can be possibly explained by a « heterolytic cleavage » of the Co — Co bond under the influence of an increased charge due to the introduction of a new ligand following for example the scheme

$$L \longrightarrow Co \underset{L_1 \quad L_2}{\overset{L_3 \quad L_4}{|}} Co \underset{CO \quad CO}{\overset{O \atop \| \atop C}{|}} CO \rightarrow$$

$$\rightarrow Co^{(I)}L_1L_2L_3L_4L^+, Co^{(-1)}(CO)_4{}^-$$

in which L_1, L_2, L_3, L_4 can all be both L or CO.

It is interesting to note that the number n of ligands L present in the cation, depends on the nature of L, possibly upon its hardness.

Thus, it can be taken that with B bases such as NH_3 or the primary amines,[12] the formation of $CoB_6{}^{2+}$ complexes passes through the following stage:

$$Co_2(CO)_8 + B \rightarrow CoB(CO)_4{}^+, Co(CO)_4{}^-$$

With alcohols which have a high degree of hardness Tucci [13] has moreover succeded in bringing into evidence at a low temperature the ionic complex:

$$Co(CO)_4ROH^+, Co(CO)_4{}^-$$

With softer bases, such as alkyl or aryl phosphines, Hieber has shown that disubstituted derivatives can be obtained. For our part, we have obtained the same kind of results with PMe_3, PEt_3, and $P[N-(CH_3)_2]_3$.

With even softer bases such as $P(OMe)_3$ [14] $P(OCH_2)_3$ CEt [9] or $Ph_2PCH_2CH_2PPh_2$ [15] it is thus not surprising to find trisubstituted complexes.

To find a reason for these observations, two hypothesis can be considered:

a) the replacement of (n−1) molecules of CO per n ligands on one of the atoms of Co, is necessary in order to promote the cleavage of the Co — Co bond, and thus directly leads to the formation of $Co(CO)_{5-n} L_n{}^+$, $Co(CO)_4{}^-$.

b) the addition of a single ligand L on one of the Co atoms brings about the scission of the Co —Co bond. Then follows a straightfoward substitution

in the cationic part but it is limited to values of n which diminish as L's basicity grows.

According to the results of the experiments performed, immediate separation of the single product $Co(CO)_{5-n}L_n{}^+$, $Co(CO)_4{}^-$ (n = 2 for PR_3; n = 3 for $P(OMe)_3$), through precipitation, would seem to be a serious indication in favour of the first hypothesis.

It would be unlikely that the substitution of the hypothetical cation $Co(CO)_3[P(OMe)_3]_2{}^+$ could take place instantaneously to give $Co(CO)_2[P(OMe)_3]_3{}^+$ which in our case was obtained, when the substitution in this latter cation demands drastic conditions.

This statement, however, does not constitute a definitive proof in favour of mecanism (a); in fact the solvent and the *formation of ion pairs or "outer sphere" complexes*, could also possibly have a determining role to play.

The cleavage could also, finally, be observed with ligands which decrease in number, according to their hardness.

It is known [16] concerning the reactivity of the ionic compounds obtained, that a loss of CO can occur through heating, and a return to a dinuclear form takes place, the ligands being divided among the two Co atoms.

On replacing the anion $Co(CO)_4{}^-$ by a stable anion such as $BPh_4{}^-$, the reactivity of simply the cations $Co(CO)_{5-n}L_n{}^+$ can be studied without involving the anion $Co(CO)_4{}^-$.

Substitution in cationic complexes obtained by precipitation. In order to replace progressively the molecules of CO existing in the original cations $Co(CO)_{5-n}L_n{}^+$ by molecules of the ligand L or another ligand L' (mixed compounds), the classical methods of metal carbonyl chemistry, essentially those of thermic or photochemical activation, can be used.

Total substitution could only be reached in the case of phosphites for which tri, tetra, and penta substituted derivatives were obtained.[16] The other ligands cannot lead to high substitution levels; only the di and tri substituted complexes were able to be isolated in the case of phosphines.

Unlike other cases,[17] the replacement of two CO molecules by bidentate ligands such as the dienes was not found to be possible.

The structure of pentacoordinated cationic compounds in solution. Several discrepancies between the results of the I.R. and N.M.R. spectroscopies, prevent a rigid structure from being attributed to the compounds $Co(CO)_{5-n}L_n{}^+$ and the possibility of intramolecular exchange[18,19] can be admitted in some cases.

1) n=2, L=PMe_3.

The existence of a single CO stretching frequency is compatible with a D_{3h} symmetry. In protonic resonance, the protons of the methyl groups, give rise to a single triplet compatible with two ligands occupy-

(11) R. F. Heck, *J. Chem. Soc.*, 85, 1220 (1962).
(12) I. Wender, H. W. Sternberg, and N. Orchin, *J. Amer. Chem. Soc.*, 74, 1216 (1951); W. Hieber and J. Sedlmeier, *Chem. Ber.*, 87, 25 (1953).
(13) E. R. Tucci and B. H. Gwynn, *J. Amer. Chem. Soc.*, 86, 4838 (1964).
(14) S. Attali and R. Poilblanc, *C. R. Acad. Sci. Ser. C*, 718 (1968).
(15) A. Sacco, *Gazz. Chim. Ital.*, 93, 698 (1963).
(16) J. A. McCleverty, A. Davison, and G. Wilkinson, *J. Chem. Soc.*, 3890 (1965).
(17) R. Mathieu, *Thèse 3ème cycle*, Toulouse (1968).
(18) E.L. Muetterties and R.A. Schunn, *Quart Review*, 20, 245 (1966).
(19) S. Berry, *J. Chem. Phys.*, 32, 933 (1969).

ing equivalent positions. The particular aspect of the triplet, is due, under the second order effect, to a significant. J_{P-P} coupling,[20] an argument in favour of apical positions of the two Phosphorus atoms.[2] In this case, the D_{3h} symmetry could possibly be retained.

2) n=3, L=P(OMe)₃ (fig. 1-a) L=PMe₃ (fig. 1-b)

The Co(CO)₂L₃⁺ cation gives rise to two CO stretching bands incompatible with a D_{3h} symmetry, while the single signal (a triplet for P(OMe)₃, a doublet for PMe₃) observed in N.M.R. spectra seems to indicate that the three ligands are magnetically equivalent.
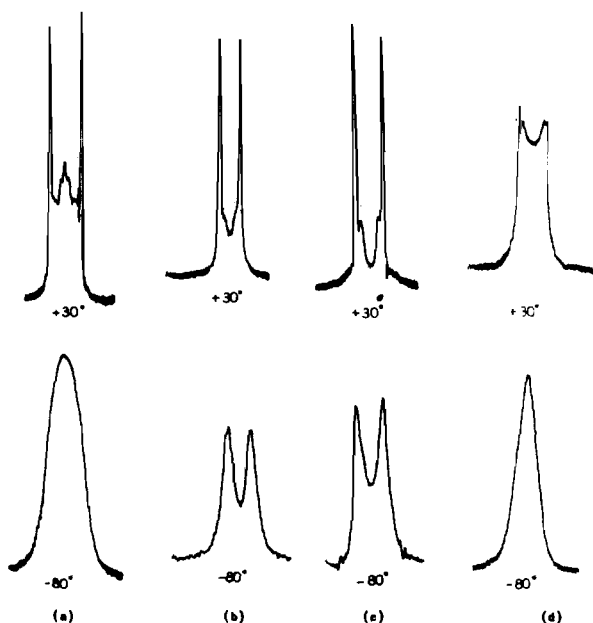

Figure 1. P.M.R. Spectra of the compounds: (a) Co(CO)₂-[P(OMe)₃]₃⁺; (b) Co(CO)₂[PMe₃]₃⁺; (c) Co(CO)[P-(OMe)₃]₄⁺; (d) Co[P(OMe)₃]₅⁺.

This equivalence could only appear in a bipyramidale structure with phosphorus atoms in equatorial positions. This structure should not give rise to two infrared CO absorption bands.

In both cases L = P(OMe)₃ and P(Me)₃, therefore

(20) R.K. Harris, Can J. of Chem., 42, 2275 (1964).

the phenomenon of stereochemical non-rigidity can be brought into consideration.

3) n=4, L=P(OMe)₃ (fig. 1-c)

The single absorption band observed on the infrared spectrum evidently does not permit the structure of the complex to be clearly described.

The N.M.R. spectrum shows a simple doublet. Therefore the four ligands appear to be equivalent. This would be possible in a tetragonal pyramid with the four phosphorus atoms arranged in the base. However the spectrum's aspect seems to indicate a slight J_{P-P} coupling, at first sight difficult to admit in the rigid structure envisaged.

4) n=5, L=P(OMe)₃ (fig. 1-d)

The cation Co[P(OMe)₃]₅⁺ offers a single type of protonic signal, which would seem to correspond to five equivalent ligands. This similarity of the five coordination sites is impossible in all rigid structures derived from the tetragonal pyramid or trigonal bipyramid. In this case, the phenomenon of interconversion must also be considered.

A study of the diverse incompatibilities found has been attempted by studying the P(OMe)₃ compounds at variable temperature. (Figure 1)

The trisubstituted derivative Co(CO)₂ [P(OMe₃]₃⁺ presents a triplet at ordinary temperature; from +30°C to —60°C an increase in the central band is observed which at —70°C leads to coalescence. The spectrum obtained at –80°C presents a single, relatively sharp band which grows larger towards –90°C.

The tetrasubstituted derivative Co(CO) [P(OMe)₃]₄⁺ shows a rather simple doublet at +30°C which until –80°C gives no coalescence. However, the peaks tend to grow larger while a central band seems to appear and to indicate the beginning of coalescence.

The pentasubstituted compound presents a wide peak poorly defined on which nevertheless the J_{P-H} coupling can be distinguished. Coalescence takes place at —60°C and gives rise to a single relatively sharp peak which afterwards grows wider at —90°C.

The widenings observed after coalescence, probably announce the transformation at lower temperature, towards spectra corresponding to slow exchanges. In these conditions the necessity of a lower temperature for reaching this expected behaviour, precludes a definitive demonstration of the postulated stereochemical non rigidity to be effective.