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Trivalent Phosphorus Derivatives of Cobalt Carbonyls. I. Infrared and N.M.R. Studies of new Substituted Tetracobaltdodecacarbonyl Complexes

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The syntheses of the first products of the $Co_4(CO)_{12-n}L_n$ series are reported ($L = P(C_2H_5)_3$ $n = 2, 3$; $L = P(OCH_3)_3$ $n = 1, 2, 3, 4$). Infrared analysis, by means of the correlation concept, leads to assignment of the major part of normal modes of vibrations in the CO stretching region of $Co_4(CO)_{12}$. In the case of $Co_4(CO)_{10}(P(C_2H_5)_3)_2$, $Co_4(CO)_9(P(C_2H_5)_3)_3$, $Co_4(CO)_{10}(P(CH_3)_2C_6H_5)_2$ and $Co_4(CO)_9(P(CH_3)_2C_6H_5)_3$ the presence of isomeric species is detected by IR spectra. Temperature dependance of the p.m.r. spectra gives the first experimental evidence in favour of the idea of steric non-rigidity in the clusters.

Introduction

Still present to our mind, the structural determination of tetracobaltdodecacarbonyl remains an intriguing challenge in metal carbonyl cluster chemistry. A major part of the problem has been elucidated by Bor[1] and Haas and Sheline[2] whose I.R. and n.m.r. ^{59}Co studies support Corradini's structure[3] C_{3v} against Smith's structure D_{2d}.[4] To some extent substituted derivatives of $Co_4(CO)_{12}$ by monodentate ligands PR_3 and $P(OR)_3$ may throw new light on the topic. In addition, this would complete the pattern of reactivity of tetranuclear carbonyls $M_4(CO)_{12}$ (M = Co, Rh, Ir) with tertiary phosphines which are already known to give monosubstituted (M = Co, Rh)[5,6,7] disubstituted (M = Rh, Ir)[6,7,8] trisubstituted (M = Rh, Ir)[6,8,9] and tetrasubstituted clusters (M = Co, Rh, Ir).[10]

Experimental Section

To prevent óxydation all preparation and handling were carried out under nitrogen.

Saturated hydrocarbons were dehydrated, distilled and stored over sodium. Aromatic solvents were of reagent grade.

$P(OCH_3)_3$ was purchased from Eastman Organic Chemicals and distilled. $C_6H_5P(CH_3)_2$ and $C_6H_5P(OCH_3)_2$ were prepared by well established procedures.[11,12]

Merck alumina (neutral) was treated before chromatographic separation or purification by heating under vacuum at 300°C for 2 hrs then by cooling under nitrogen. 10% deoxidized water is added to decrease activity.

$Co_4(CO)_{10}(P(C_2H_5)_3)_2$. No selective way of preparing this complex has been found. The ligand is added at room temperature to an hexane solution of $Co_4(CO)_{12}$ to obtain molecular ratio $L/Co_4(CO)_{12} = 2/1$. The reaction is stopped after 1/4 hr. By chromatographic separation, $Co_4(CO)_{10}(P(C_2H_5)_3)_2$ was collected in 10% yield (found: C 35.00%; H 4.06%; Reqd: C 35.14%; H 4.00%.

$Co_4(CO)_9(P(C_2H_5)_3)_3$. This complex was prepared in a similar way with molecular ratio $L/Co_4(CO)_{12} = 4/1$. After removal of the solvent under vacuum the residue was purified by chromatography using hexane-toluene mixture as eluent. Yield around 30% (Found: C 38.56%; H 5.53%; P 10.96%. Reqd: C, 38.52 percent; H 5.34%; P 11.03%).

In the case of $Co_4(CO)_{12-n}(P(OCH_3)_3)_n$ complexed some details have been previously reported[13] so only relevant data on this series are given below.

$Co_4(CO)_{11}P(OCH_3)_3$. ratio $L/Co_4(CO)_{12} = 1$, reaction temperature 0°C, yield 80% (Found: C 25.24%; H 1.47%; P 4.76%; Reqd: C 25.15%; H 1.35%; P 4.64%).

$Co_4(CO)_{10}(P(OCH_3)_3)_2$. ratio $L/Co_4(CO)_{12} = 2$, room temperature, yield 95 % (Found: C 25.13%; H 2.35%; P 8.11%; Reqd: C 25.64%; H 2.48; P 8.11%).

$Co_4(CO)_9(P(OCH_3)_3)_3$. ratio $L/Co_4(CO)_{12} = 3$, temperature of reaction 60°C, yield 80%, purified by cry-

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(2) H. Haas and R.K. Sheline, *J. Inorg. Nucl. Chem.*, 693 (1966). See also concerning ^{59}Co n.m.r. studies: E.A.C. Lucken, K. Noack, D.F. Williams, *J. Chem. Soc. (A)*, 1967.

(3) P. Corradini, *J. Chem. Phys.*, *31*, 1676 (1959).

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(11) P.R. Bloofield and K. Parvin, *Chim. Ind.*, 541 (1959).

(12) M.I. Kabachnick and E.N. Tsvetkov, *Doklady. Akad. Nauk. S.S.S.R.*, *117*, 817 (1957).

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stallization and/or chromatography (Found: C 25.11%; H 3.13%; P 10.81%; C 25.55%; H 3.47%; P 10.86%).

$Co_4(CO)_8(P(OCH_3)_3)_4$. reaction temperature 60°C until full formation of trisubstituted species with $L/Co_4(CO)_{12} = 3$, then adding L to reach $L/Co_4(CO)_{12} = 4$ at 40°C, yield 50%, isolated by crystallization and/or chromatography. (Found: C 25.10%; H 3.76%; P 12.97%; Reqd: C 25.36%; H 3.88%; P 12.79%.

$Co_4(CO)_{11}P(CH_3)_2C_6H_5$. The careful action of the phosphine at 0°C on $Co_4(CO)_{12}$ gave rise to the formation of the monosubstituted derivative.

$Co_4(CO)_{10}(P(CH_3)_2C_6H_5)_2$. The compound was obtained when the ratio $L/Co_4(CO)_{12}$ reached 2 but the reaction mixture was at that point more complex and chromatography had to be used to isolate the products formed.

A grey solution of $Co_4(CO)_{11}P(CH_3)_2C_6H_5$, an heavy brown solution of $Co_4(CO)_{10}(P(CH_3)_2C_6H_5)_2$ a yellow solution of $Co_2(CO)_6(P(CH_3)_2C_6H_5)_2$ and a brown solution of $Co_4(CO)_9(P(CH_3)_2C_6H_5)_3$ were successively obtained by firstly using as eluent hexane and then hexane-toluene mixture.

$Co_4(CO)_9(P(CH_3)_2C_6H_5)_3$ was present in the preceding reaction mixture and as was shown, it was extracted by chromatography over an alumina column.

$Co_4(CO)_{11}(P(OCH_3)_2C_6H_5)$. The ligand was added in a stoichiometric quantity to the carbonyl solution dissolved in heptane and after an hour at ordinary temperature an infrared spectrum of the reaction mixture rendered the monosubstituted compound observable.

After 12 hours the preceding reaction mixture was essentially composed of the tetracobaltdodecacarbonyl disubstituted and tetrasubstituted derivatives, and recourse to chromatography was found necessary in order to separate the products formed. By adding 3 moles of the ligand to 1 mole of $Co_4(CO)_{12}$ at 20°C a complex reaction mixture was produced from which the disubstituted derivative of $Co_2(CO)_8$ and a black derivative in solution designated as the $Co_4(CO)_9(P(OCH_3)_2C_6H_5)_3$ trisubstituted complex were separated by chromatography.

All these compounds are black crystals, quite similar in aspect to $Co_4(CO)_{12}$.

Owing to the low solubility of $Co_4(CO)_{12}$ in usual solvents (saturated or even aromatic hydrocarbons) all reactions were carried out with small amounts of carbonyl (1 mmole).

Attempts to prepare derivatives of $Co_4(CO)_{12}$ with $L = P(CH_3)_3$ were unsuccessful despite mild experimental conditions (temperature as low as –30°C, ratio $L/Co_4(CO)_{12} = 1/2$); in any case $Co_2(CO)_5(P(CH_3)_3)_3$ was formed.

Attempts to prepare $Co_4(CO)_{10}(P(C_6H_5)_3)_2$ failed resulting in the formation of red $Co_2(CO)_6(P(C_6H_5)_3)_2$. Infrared spectra were run in hexadecane solution, except as otherwise stated, on Perkin Elmer 225 spectrometer in the 1650-2100 cm^{-1} region; they were calibrated with water vapour so that peak positions are accurate within ±1 cm^{-1}.

The 60 Mhz p.m.r. spectra were obtained in dichloromethane solutions saturated with the studied complex at –80°C with t.m.s. (tetramethyl silane) as an external standard using Varian Associates model A 60 A n.m.r. spectrometer.

Analyses of carbon, hydrogen, and phosphorus were performed by the Centre National de la Recherche Scientifique Laboratories.

Results and Discussion

$Co_4(CO)_{12}$ is known to react with monodentate ligands $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ to give $Co_4(CO)_{11}P(C_6H_5)_3$[5] and $Co_4(CO)_8(P(OC_6H_5)_3)_4$[10] but no systematic study has been undertaken to synthesize a complete series of derivatives.

Part of our experiment reported herein shows that with a convenient ligand such as $P(OCH_3)_3$ progressive substitution of CO groups can be made from $n = 1$ to $n = 4$. This is not an isolated case and numerous compounds have been isolated[14] and recognized by their I.R. spectra referring to the fully studied series $Co_4(CO)_{12-n}(P(OCH_3)_3)_n$. Characteristic infrared absorption bands for all compounds are listed in Table I.

This aspect of the reactivity of $Co_4(CO)_{12}$ towards $P(OR)_3$ and PR_3 is in contrast with the action of two isolated ligands $P(CH_3)_3$ and $P(C_6H_5)_3$. In both, substitution reactions appear impossible or at least extremely difficult.

$P(CH_3)_3$ being the strongest Lewis base we have tested, we assume that its basicity caused the breaking up the cluster structure.

In the case of $L = P(C_6H_5)_3$ no conclusive evidence of the often noticed steric effect can be advanced because the structure of the tetrahedral cluster allows in other cases, at least four bulky ligands. In our opinion, excessively low solubility of the by-product $Co_2(CO)_6(P(C_6H_5)_3)_2$ might well explain this particular orientation (*vide supra*) of the reaction.

High ratio of $P(OCH_3)_3$ (6 to 10) allows the separation by chromatography of some red crystals whose I.R. spectra is compatible, on account of the filiation of frequencies, with the formular $Co_4(CO)_7(P(OCH_3)_3)_5$

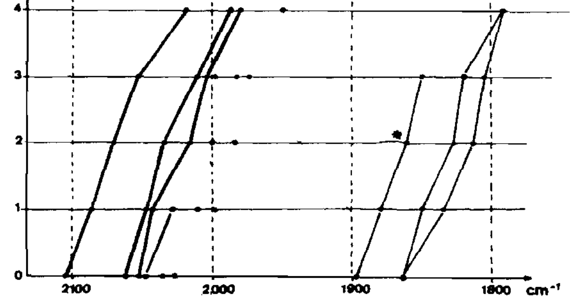

Figure 1. Some experimental filiation of frequencies in the $Co_4(CO)_{12-n}(P(OCH_3)_3)_n$ compounds.

* band arising in solid state spectra (Cs Br pellet).

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[14] D. Labroue, Thèse de spécialité, Toulouse (1971).

Table I. Infrared spectra of the derivatives $Co_4(CO)_{12-n}L_n$.

$Co_4(CO)_{12}$	2104.9vw 2062.5vs 2053.7vs 2047sh 2036w 2026.9w	1897.5vw 1864.4m
$Co_4(CO)_{10}(P(C_2H_5)_3)_2$	2063sh 2059s 2020vs 2016vs 2008vs 1987m 1965m	1820m 1792w
$Co_4(CO)_9(P(C_2H_5)_3)_3$	2036w 2025m 1992m 1978vs 1973sh 1957w 1940w	1780m
$Co_4(CO)_{11}P(C_6H_5)_3$	2082s 2041vs 2036vs 2027s 2003m 1990w	1877w 1851s 1834s
$Co_4(CO)_{11}P(CH_3)_2C_6H_5$	2082s 2042vs 2036vs 2026s 2004m 1988m	1876w 1847m 1830m
$Co_4(CO)_{10}(P(CH_3)_2C_6H_5)_2$	2063sh 2060s 2021vs 2014vs 2005sh 1989m	1820m 1810sh 1800m
$Co_4(CO)_9(P(CH_3)_2C_6H_5)_3$	2037m 2029s 1995vs 1979vs 1960m	1805m 1786s
$Co_4(CO)_{11}P(OCH_3)_3$	2086.5m 2047.5vs 2042vs 2028s 2010w 1998w	1879w 1849m 1834.5m
$Co_4(CO)_{10}(P(OCH_3)_3)_2$	2070s 2035vs 2016vs 2000m 1984m	1828.5m 1814.5m
$Co_4(CO)_9(P(OCH_3)_3)_3$	2052s 2010vs 2003vs 1998sh 1983sh 1974m	1850w 1820m 1805m
$Co_4(CO)_8(P(OCH_3)_3)_4$	2018m 1987sh 1980s 1950vs	1792s
$Co_4(CO)_{10}(P(OCH_3)_2C_6H_5)_2$	2065s 2025vs 2012vs 1980m 1967m	1830m 1814m
$Co_4(CO)_9(P(OCH_3)_2C_6H_5)_3$	2040m 1985vs 1968vs 1930w	1790m
(a) $Co_4(CO)_{10}(P(OCH_2)_3CC_2H_5)_2$	2073w 2035vs 2020vs	1830s
(a) $Co_4(CO)_9(P(OCH_2)_3CC_2H_5)_3$	2052m 2018vs 2000vs	1812s
(a) $Co_4(CO)_8(P(OCH_2)_3CC_2H_5)_4$	2030m 1992vs	1805m

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder
(a) Spectra in dichloromethane.

(*vide infra*: Figure 1). Further experiments were performed in this way. In any other case n = 4 appears as the upper limit of the degree of substitution.

Infrared Study. Monosubstituted derivatives of $Co_4(CO)_{12}$ do have C_s symmetry so that the number of the infrared active CO stretching bands is expected to be equal to the number of CO groups. Indeed, this remark is not of great benefit in the terminal CO region which is too complex (8 bands) but is of some interest in the much simpler bridging CO region (3 bands in a Corradini's structure) and may dispose of the problem of the structure of derivatives $Co_4(CO)_{12-n}L_n$.

In fact monosubstituted derivatives described therein exhibit three bands. This is compatible with the structure deriving directly from Corradini's structure. Thus we shall assume that Corradini's structure remains valid in these derivatives, being an opposite case to the previously reported $Co_4(CO)_{10}RC_2R$ structure.[15]

Experimental filiation[16] of CO stretching frequencies is of current interest in the metal carbonyl series of derivatives $M_x(CO)_{y-n}L_n$ because a regular graph usually joins plotted bands having correlated normal modes of vibrations.

The case of $Co_4(CO)_{12-n}(P(OCH)_3)_n$ is presented in figure 1. Infrared spectra of $Co_4(CO)_{12}$ has been reinvestigated and the frequencies plotted in the n=0 line are consequent in the limit of solvent effect, with Bor's earlier observation.[1]

The highest frequency band (2104.9 cm^{-1}) had been previously recognized(1) as the totally symmetric CO stretching vibration (ν_1 CO) and indicates from this example an obvious filiation on each step of the substitution. This would strongly support if it was necessary, Bor's determination of the ν_1 CO band. In figure 1 other experimental filiations have been presented allowing several determinations of stretching modes of vibrations.

Groupe theoretical method readily yield infrared active CO stretching modes for Corradini's model eight bands are predicted.

Terminal CO : $3A_1+3E$

Bridging CO : A_1+E

Dealing first with CO bridges it is worth that unambiguous filiation arising from 1897.5 cm^{-1} band of $Co_4(CO)_{12}$ is simple whereas filiation arising from 1864 cm^{-1} exhibits a splitting on substituted derivatives. This is consequent with the lifting of the degeneracy of an E mode. Thence full assignment of bridging CO vibration modes is proposed: 1897.5 cm^{-1} appears to be A_1 mode(17) and 1864.4 cm^{1-} E mode. Turning our attention now to the bands arising from terminal CO groups we notice first a conspicuous experimental filiation of the strongest bands (2062.5 cm^{-1} and 2053.7 cm^{-1}) for $Co_4(CO)_{12}$. No conclusive evidence can be advanced in this case but with reference to a general observation in the metal carbonyl IR studies we may assign these intense bands to E mode. Relationship between decreasing symmetry of the molecule and rising intensity of correlated bands is well illustrated in the case of the ν_1 CO band as well as the band situated at 1897.5 cm^{-1} (see Figure 2).

According to this rough principle, any A_1 vibration mode can be predicted to behave in a similar way

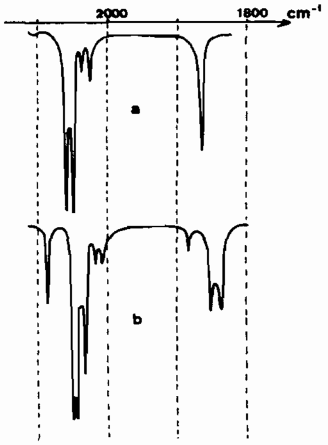

Figure 2. (a) spectrum of $Co_4(CO)_{12}$; (b) spectrum of $Co_4(CO)_{11}P(OCH_3)_3$.

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(15) L.F. Dahl and D.L. Smith, *J. Am. Chem. Soc.*, *84*, 2450 (1962).
(16) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962).
(17) In so far as another experimental proof to Bor's proposition based on intensity argument.

and consequently the 2047 cm^{-1} band of $Co_4(CO)_{12}$ (shoulder) might well be found reinforced at 2028 cm^{-1} in the monosubstituted derivative. No assignment can be stated for the two weak bands situated respectively at 2036 cm^{-1} and 2026 cm^{-1}. It is important that the presence at these frequencies, of $^{13}C-O$ stretching vibrations must not be in either case neglected. Proposed assignments are given below. Terminal $C-O$: 2104.9 cm^{-1} A_1; 2062.5 cm^1 E; 2053.7 cm^{-1} E; 2047 cm^{-1} A_1; 2036 cm^{-1}; 2026.9.
Bridging CO: 1897.5 cm^{-1} A_1; 1864.4 cm^{-1} E.
Owing to the intense color of $Co_4(CO)_{12}$ we were unable to record Raman Spectra in order to make this assignment sufficiently rigorous.

Another point of interest which appears in the infrared spectra of the derivatives is the probable existence of the first isomeric species of $Co_4(CO)_{12}$ derivatives ever mentioned. The derivatives $Co_4(CO)_{10}(P(C_2H_5)_3)_2$, $Co_4(CO)_{10}(P(CH_3))_2C_6H_5)_2$ and $Co_4(CO)_9(P(CH_3)_2C_6H_5)_3$ *purified by chromatography,* exhibit a splitting of the high frequency band. *Knowing that this band is* A_1 and taking advantage of its isolation (40 cm^{-1}) we can conclude that in the four cases there is a mixture of isomers. For $Co_4(CO)_9(P(C_2H_5)_3)_3$, further evidence is contained in the excessive number of terminal CO bands. In the four cases subsequent crystallization or column chromatography did not bring about separation of the isomers.

P.m.r. Study. Preliminary p.m.r. study of substituted derivatives reveals interesting properties of the molecule. Owing to the simplicity of the $P(OCH_3)_3$ signal we have focused our attention on the series $Co_4(CO)_{12-n}(P(OCH_3)_3)_n$. Chemical shift and coupling constants at room temperature are listed in Table II.

Table II. Coupling constants and chemical shifts at 60 Mhz in CH_2Cl_2.

	J cps	δ p.p.m.
$Co_4(CO)_{11}P(OCH_3)_3$	11.0	–4.23
$Co_4(CO)_{10}(P(OCH_3)_3)_2$	11.3	–4.20
$Co_4(CO)_9(P(OCH_3)_3)_3$	10.4	–4.23
$Co_4(CO)_8(P(OCH_3)_3)_4$	10.3	–4.21

As for a general behaviour of all these compounds is concerned, we can notice first that the signals of the p.m.r. spectra are *temperature dependent.* Starting with an initial doublet, the spectra progressively progress towards a single line while temperature decreases. This effect is reversible with the temperature and may be taken as an evidence of an exchange phenomenon. Addition at room temperature of extra free ligand allows the observation of two separate doublets so, the nature of the exchange seems to be rather intramolecular than intermolecular. Unfortunately at a temperature as low as –90°C in CH_2Cl_2 the exchange is still too fast to record the limiting spectra; thus we cannot predict the possible form of the isomers corresponding to limiting forms. Studies are in progress to clarify this interesting point. Nevertheless our observation could possibly contribute to the idea of steric non rigidity in the cluster, as developped by Cotton[18] in the case of $Co_4(CO)_{12}$, as a first experimental support. In the same connection, it would be of great interest now to run high temperature n.m.r. ^{59}Co on $Co_4(CO)_{12}$ to examine whether CO groups can exchange or not and to compare the behaviour of $Co_4(CO)_{12}$ and of its derivatives.

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(18) F.A. Cotton, *Inorg. Chem.*, 5, 1083 (1966).