SYNTHESIS AND ^{31}P NMR CHARACTERIZATION OF SUBSTITUTED CARBONYLCOBALT(I) COMPLEXES

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Summary

Reactions of $(C_6F_5)Co(CO)_4$ (I) with equimolar amounts of different phosphorus donors give monosubstituted complexes $(C_6F_5)Co(CO)_3L$ being L = PEt_3·(II), P-n-But$_3$ (III), PPh_3 (IV), PMe_2Ph (V), $PMePh_2$ (VI), $P(OMe)_3$ (VII), $P(OEt)_3$ (VIII), and $P(OPh)_3$ (IX). Complexes II–IV as well as the dimer $(C_6F_5)Co(CO)_3PPh_2$-$(CH_2)_2PPh_2(CO)_3Co(C_6F_5)$ (X) have been previously described.

When the same reactions are made using an excess of the ligand, the disubstituted species $(C_6F_5)Co(CO)_2L_2$ are isolated, being L = PEt_3 (XI), P-n-But$_3$ (XII), PPh_3 (XIII), PMe_2Ph (XIV), $PMePh_2$ (XV), $P(OMe)_3$ (XVI), $P(OEt)_3$ (XVII) and $P(OPh_3)$ (XVIII). The mononuclear compound XIX with the bidentate ligand $PPh_2(CH_2)_2PPh_2$ only could be obtained by reducing $(C_6F_5)_2Co(PPh_2(CH_2)_2PPh_2)$ with $NaBH_4$ under CO.

The IR and ^{31}P NMR spectra of all these compounds permit to make a structural assignment.

Introduction

The isolation of phosphine substituted carbonylcobalt(I) complexes $(C_6F_5)Co(CO)_3L$ has been achieved [1] by reaction of $(C_6F_5)Co(CO)_4$ with various ligands L = PEt_3, P-n-But$_3$, PPh_3, dppe. In order to establish the limits of this type of substitution we have extended our previous experiments to reactions with different amounts of various phosphine and phosphite ligands.

Results and discussion

Preparative results

The addition of equimolar amounts of different monodentate ligands L = PEt_3, P-n-But$_3$, PPh_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, and $P(OPh)_3$ to solutions of $(C_6F_5)Co(CO)_4$ gives the monosubstituted complexes $(C_6F_5)Co(CO)_3L$ (II–IX),

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR PHOSPHINE CARBONYLCOBALT(I) COMPLEXES

Complex		Analyses (Found (calcd.) (%))		Colour	M.p. (°C)
		C	H		
(V)	$(C_6F_5)Co(CO)_3(PMe_2Ph)$	46.13 (45.56)	2.64 (2.47)	yellow	96–102 (d)
(VI)	$(C_6F_5)Co(CO)_3(PMePh_2)$	51.70 (51.79)	2.75 (2.57)	yellow	105–130 (d)
(VII)	$(C_6F_5)Co(CO)_3P(OMe)_3$	33.95 (33.20)	2.29 (2.09)	pale yellow	38–39 (d)
(VIII)	$(C_6F_5)Co(CO)_3P(OEt)_3$	–	–	pale yellow	–
(IX)	$(C_6F_5)Co(CO)_3P(OPh)_3$	52.49 (52.28)	2.56 (2.44)	pale yellow	85–92 (d)
(XI)	$(C_6F_5)Co(CO)_2(PEt_3)_2$	(45.98) (46.35)	(5.00) (5.83)	dark yellow	20
(XII)	$(C_6F_5)Co(CO)_2(P-n-Bu^t_3)_2$	56.30 (55.98)	7.41 (7.93)	dark yellow	20
(XIII)	$(C_6F_5)Co(CO)_2(PPh_3)_2$	66.01 (65.52)	3.90 (3.75)	orange	100–115
(XIV)	$(C_6F_5)Co(CO)_2(PMe_2Ph)_2$	51.65 (51.63)	4.22 (3.97)	pale orange	130–136
(XV)	$(C_6F_5)Co(CO)_2(PMePh_2)_2$	59.97 (59.84)	3.86 (3.84)	orange yellow	117–127
(XVI)	$(C_6F_5)Co(CO)_2(P(OMe)_3)_2$	32.04 (31.72)	3.64 (3.42)	yellow lemon	88–94
(XVII)	$(C_6F_5)Co(CO)_2(P(OEt)_3)_2$	–		pale yellow	
(XVIII)	$(C_6F_5)Co(CO)_2(P(OPh)_3)_2$	58.65 (58.55)	3.58 (3.35)	yellow	130–36
(XIX)	$(C_6F_5)Co(CO)_2(dppe)$	60.85 (60.02)	4.32 (3.58)	orange	110–115

according to analytical data shown in Table 1 whereas the same reaction with dppe gives the dinuclear complex $[(C_6F_5)Co(CO)_3]_2(\mu\text{-dppe})$ (X). Reactions of complexes II–IX containing monodentate ligands with an additional mole of the ligand produce the substitution of the second CO group to give the disubstituted complexes XI–XVIII, $(C_6F_5)Co(CO)_2L_2$. Complexes VIII and XVII with $P(OEt)_3$ are detected in solution but can not be isolated in the solid. These compounds can also be obtained directly by treating $(C_6F_5)Co(CO)_4$ with an excess of the ligand, although the excess must be avoided in order to facilitate the crystallization of the final product. The same reaction with dppe only gives the insoluble monosubstituted dinuclear complex X as the reaction does not go further. However we have also isolated the mononuclear disubstituted dppe complex $(C_6F_5)Co(CO)_2dppe$ (XIX) by reducing $(C_6F_5)_2Co(dppe)$ [2] with $NaBH_4$ under CO, according to the following equation

$$(C_6F_5)_2Co(dppe) + CO + NaBH_4 \rightarrow (C_6F_5)Co(dppe)(CO)_2$$

Complexes XI–XIX do not react further with an excess of the ligand as the

increasing substitution of CO by phosphines increases the back donation and reinforces the Co–CO bonds of the remaining CO groups, so that the monocarbonyl complexes $(C_6F_5)Co(CO)L_3$ cannot be obtained by this method, even by heating or under UV irradiation.

All the complexes are diamagnetic pentacoordinate d^8 species at room temperature.

Infrared and ^{31}P NMR spectra

Characteristic C_6F_5 absorptions at 1500, 1055 and 955 cm^{-1} [3] as well as the characteristic absorptions of the different ligands are observed.

The energy difference between the two possible trigonal bipyramid and square pyramid structures is low. A single crystal X-ray analysis has shown the similar pentacoordinate cobalt(I) complex $[Co(CH_3NC)_5]^+$ [4] to be a trigonal bipyramid. By analogy we assume that all the phosphine carbonylcobalt(I) complexes will also have the same geometry.

The four different configurations shown in Scheme 1 can be proposed for the tricarbonyl complexes II–IX.
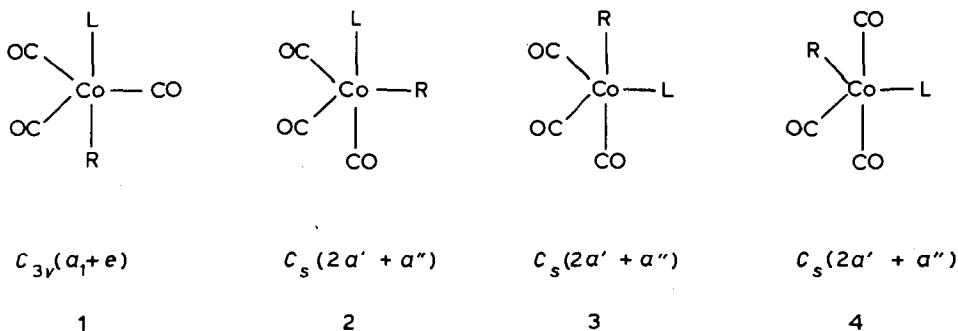
SCHEME 1

According to the $\nu(CO)$ stretching frequencies given in Table 2, we assign the configuration 1 to complexes IV, V, VI and IX as they show only two absorption bands. Complexes II, III and VII show three $\nu(CO)$ absorptions so that any of the configurations 2–4 could be assigned and we can not make a definitive assignment. We feel that 2 or 3 are the most reasonable as 4 contains two mutually *trans* CO groups. We have the same uncertainty for complex X containing the bridge dppe ligand.

It must be noted that complexes with smaller ligands adopt a structure with the ligand *cis* to C_6F_5 whereas the bigger ligands prefer the less sterically hindered configuration with the ligand *trans* to C_6F_5.

The chemical shifts due to the coordination of phosphine measured by the difference between δ(coordinated ligand) and δ(free ligand) increase between 61.8 and 79.3 ppm as the π acceptor capacity of the phosphine decreases (Table 2).

Phosphite complexes show lower chemical shifts and complex VII with $P(OMe)_3$ presents an unexpectedly low value. This behavior suggests that probably VII adopts a different configuration.

All the carbonyl complexes XI–XIX may present any of the configurations shown in Scheme 2 as all they show two $\nu(CO)$ absorptions.

TABLE 2

IR AND ^{31}P NMR SPECTRA OF PHOSPHINE CARBONYLCOBALT(I) COMPLEXES

Complex		ν(CO)[a] (cm^{-1})	Δ^{31}P[b]
(II)	$(C_6F_5)Co(CO)_3(PEt_3)$	(N) 2060m 1990–1960vs, 1900vs	–
		(h) 2055m, 2000–1970vs, 1900vs	
(III)	$(C_6F_5)Co(CO)_3(Pn\text{-}But_3)$	(N) 2050m, 1990–1970vs, 1900s	–
		(h) 2065m, 1990–1970vs, 1900s	
(IV)	$(C_6F_5)Co(CO)_3(PPh_3)$	(N) 1990–1970vs	61.8
		(t) 1995m, 1980s	
(V)	$(C_6F_5)Co(CO)_3(PMe_2Ph)$	(KBr) 2055m, 1980vs	79.3
		(D) 2060w, 1980–1970vs	
(VI)	$(C_6F_5)Co(CO)_3(PMePh_2)$	(KBr) 2055m, 1990–1965vs	72.6
		(D) 2060w, 1990–1980vs	
(VII)	$(C_6F_5)Co(CO)_3P(OMe)_3$	(P) 2075m, 2020–1990vs, 1945s	19.0
		(KBr) 2070m, 2000–1980vs, 1940–1930s	
(VIII)	$(C_6F_5)Co(CO)_3P(OEt)_3$	(h) 2070w, 2010–1990vs, 1935s	–
(IX)	$(C_6F_5)Co(CO)_3P(OPh)_3$	(h) 2075, 2000–2020vs	28.9
(X)	$((C_6F_5)Co(CO)_3)_2(dppe)$	(N) 2060m, 2000vs, 1970vs	71.0
		(t) 2060w, 1995s, 1975s	
(XI)	$(C_6F_5)Co(CO)_2(PEt_3)_2$	(N) 1970vs, 1905vs	76.0
		(h) 1965vs, 1905vs	
(XII)	$(C_6F_5)Co(CO)_2(Pn\text{-}But_3)_2$	(N) 1970vs, 1900vs	65.9
		(h) 1960vs, 1900vs	
(XIII)	$(C_6F_5)Co(CO)_2(PPh_3)_2$	(N) 1980vs, 1900vs	31.4
		(h) 1960vs, 1915vs	
(XIV)	$(C_6F_5)Co(CO)_2(PMe_2Ph)_2$	(KBr) 1955vs, 1900vs	82.3
		(D) 1970vs, 1905vs	
(XV)	$(C_6F_5)Co(CO)_2(PMePh_2)_2$	(KBr) 1965vs, 1900vs	79.3
		(D) 1970vs, 1910vs	
(XVI)	$(C_6F_5)Co(CO)_2(P(OMe)_3)_2$	(KBr) 2000–1995vs, 1940–1920b	19.0
		(h) 2000vs, 1945vs	
(XVII)	$(C_6F_5)Co(CO)_2(P(OEt)_3)_2$	(h) 2000–1990vs, 1945s	–
(XVIII)	$(C_6F_5)Co(CO)_2(P(OPh)_3)_2$	(KBr) 2020vs, 1960vs	16.2
		(D) 2020vs, 1955vs	
(XIX)	$(C_6F_5)Co(CO)_2(dppe)$	(KBr) 1995vs, 1940vs	42.4
	$ClCo(CO)_2(PPh_3)_2$	(Cl) 1984s, 1919vs	63.4
	$BrCo(CO)_2(PPh_3)_2$	(Cl) 1988s, 1922vs	62.5
	$ICo(CO)_2(PPh_3)_2$	(Cl) 1992s, 1928vs	61.4

[a] N = Nujol, h = hexane, t = toluene, Cl = Chloroform, KBr = KBr pellets, P = pentane, D = dichloromethane. [b] Δ^{31}P = δ(coordinated ligand) $- \delta$(free ligand) in C_6D_6 ref. H_3PO_4.

$C_s(2a)$ $C_{2v}(a_1 + b_1)$ $C_{2v}(a_1 + b_2)$ $C_s(a' + a'')$ $C_1(2a)$

1   2   3   4   5
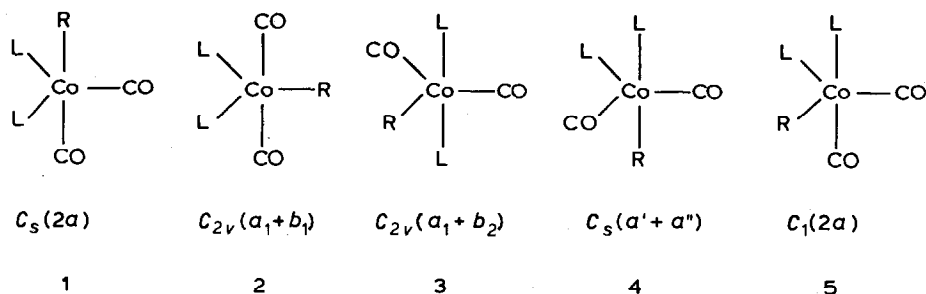
SCHEME 2

All these complexes show a single ^{31}P resonance indicating that both phosphorus atoms are magnetically equivalent. This is only possible for configurations 1–3, so that configurations 4 and 5 must be discharged on the basis of the NMR data. The same behaviour was observed at −80°C.

Only configurations 1 and 2 must be considered for complex XIX with the bidentate dppe ligand as both phosphorus atoms must occupy *cis* positions.

The ratio of intensities I(*as*)/I(*s*) of the antisymmetric and symmetric ν(CO) frequencies in complex XIX is 0.657. From this value a CO–Co–CO bond angle of 101° can be calculated according to the procedure given by Bigorgne [5] so that configuration 1 must be assigned to complex XIX.

Values for CO–Co–CO bond angles between 107–112° are found for complexes XI–XVIII so that configuration 2 must also be discharged for these complexes.

We tentatively assign the same configuration 1 found for complex XIX, to all these complexes although 3 cannot be excluded.

Chemical shifts increase with decreasing electronegativity of the phosphorus substituents indicating a decreasing π acceptor capacity of the ligand, although values observed for methyl phenylphosphine complexes are unexpectedly high [6].

It is not possible to correlate the chemical shifts observed for dicarbonyl and tricarbonyl complexes in order to distinguish between axial and equatorial phosphines as these differences can not be easily compared if the coordination sphere and the π acceptor capacity vary simultaneously [7].

We have also included for comparison the ^{31}P NMR spectra of the halo-carbonylcobalt(I) complexes, for which discrepancies were previously known [8,9].

The differences observed for these compounds are higher as shown in Table 2 suggesting probably a structure containing both phosphine ligands on the axial positions in agreement with proposals made by Klein and Karch [10] and Bordignon [11] for similar compounds with PMe_3 and $P(OEt)_2Ph$. On the other hand a displacement to lower fields is observed for the ^{31}P resonances in these halocomplexes as a result of the higher electronegativity of the halogen.

Experimental

All experiments were performed under vacuum in an inert atmosphere using Schlenk type glassware, with solvents previously distilled and dried before use. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls or solutions. NMR spectra were recorded using a Varian FT 80A spectrometer. C, H analyses were made with a Perkin–Elmer 240B microanalyzer. Melting points were determined with a Reichert Thermopan microscope. $(C_6F_5)Co(CO)_4$ was prepared as described in [1].

$(C_6F_5)Co(CO)_3L$ (L = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ (V–IX))

The method is similar to that described previously [1] for complexes II–III. The ligand (5.0 mmol) was added to a solution of I (1.69 g, 5.0 mmol) in hexane (50 ml). The solvent was removed under vacuum at 0°C to give yellow crystals of corresponding complexes. Yield 45–65%.

$(C_6F_5)Co(CO)_2L_2$ (L = PEt_3, P-n-But_3, PPh_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ (XI–XVIII))

PEt_3 (0.7 ml, 5.0 mmol) was carefully added to a solution recently prepared of I

(0.845 g, 2.5 mmol) in hexane (40 ml). The original pale yellow solution became dark. After stirring at room temperature for 30 min when solution was dark red, the solvent was evaporated and dark yellow crystals were formed on cooling at $-78°C$. The solid was filtered off and recrystallized from hexane by cooling. Yield 60%.

Compound XII and XIV–XVIII were prepared similarly.

Compound XIII was prepared using benzene as solvent instead of hexane. The final solution was evaporated under vacuum at dryness and the residue was repeatedly washed with hexane and recrystallized from benzene/hexane to give orange crystals. Yield 40–60%.

(C₆F₅)Co(CO)₂(dppe) (XIX)

A suspension of $(C_6F_5)_2Co(dppe)$ (0.8 g, 1.0 mmol) was treated with a freshly prepared solution of $NaBH_4$ (0.019 g, 0.50 mmol) in ethanol with simultaneous bubbling of CO at room temperature.

After 30 min of stirring, the solution was filtered and concentrated under vacuum. The resulting residue was extracted with toluene, concentrated and hexane added giving orange crystals. Yield 30%.

Acknowledgements

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