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Formation and structure of $[Co\{Ph_2PN(^iBu)PPh_2\text{-}P,P'\}_2(CO)][Co(CO)_4]$ – a cage molecule-pair or an ion-pair complex?

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Abstract

The strong π-acid ligand $Ph_2PN(^iBu)PPh_2$ reacts with $Co_2(CO)_8$ (1:1) to give $Co_2[\mu\text{-}Ph_2PN(^iBu)PPh_2]$ $(\mu\text{-}CO)_2(CO)_4$ (**1**); however, when the ratio is 2:1 a novel species $[Co\{Ph_2PN(^iBu)PPh_2\text{-}P,P'\}_2(CO)][Co(CO)_4]$ (**2**) has been obtained. Crystal data for **2**: $M_r = 1140.83$; triclinic, space group $P\bar{1}$, $a = 12.330(2)$, $b = 13.340(2)$, $c = 18.122(3)$ Å, $\alpha = 86.63(1)$, $\beta = 80.75(1)$, $\gamma = 84.24(1)°$, $V = 2924$ Å^3, $Z = 2$; $R = 0.060$ for 3711 reflections having $I \geqslant 3\sigma(I)$. The results of X-ray diffraction, ESR, variable-temperature magnetic susceptibility, conductivity, and XPS analysis support that the species 2 is a d^9-d^9 cage molecule-pair. The mechanism for the formation of the species **2** has been investigated initially by ^{31}P NMR.

Key words: Cobalt; Cage compound; Phosphazane; Carbonyl

1. Introduction

A variety of organometallic complexes containing diphosphino methane $(X_2PCH_2PX_2)$ has been investigated extensively for more than two decades because of their potential as catalysts and their novel structural and reactive features [1–3]. Interest in the analogous diphosphino amine ligands $[X_2PN(R)PX_2]$ has grown rapidly in recent years [4–11]. It has been found that small structural changes in these ligands produce large effects on aspects of the synthesis of metal complexes.

In the present work, $Co_2(CO)_8$ is found to react with $Ph_2PN(^iBu)PPh_2$ in different ratios to give different products. When the ratio is 1:1, a predicted product, $Co_2[\mu\text{-}Ph_2PN(^iBu)PPh_2](\mu\text{-}CO)_2(CO)_4$ (**1**), is obtained. However, with the ratio 1:2, a novel product, $[Co\{Ph_2PN(^iBu)PPh_2\text{-}P,P'\}_2(CO)][Co(CO)_4]$ (**2**), has been obtained and there is evidence for it being a cage molecule-pair. The mechanism for the formation of **2** has been investigated initially by ^{31}P NMR, and the crystal structure of **2** has been studied by X-ray diffraction.

2. Experimental details

2.1. Reagents and solvents

$Co_2(CO)_8$ (Strem) was used without further purification. All solvents were reagent grade and were purified by general procedures.

2.2. Physical measurements

Microanalyses for C, H and N were carried out with a Perkin-Elmer analyzer model 240. Infrared spectra (KBr disc) were recorded with a WFD-14 spectrophotometer. An AC-P200 NMR spectrometer was used to record ^{31}P spectra at 81.03 Hz ($CDCl_3$, external standard: H_3PO_4). ESR spectrum was measured with a JES-FEIXG apparatus using the X-band. Conductivity was measured in acetonitrile with a DDS-11A conductometer. Variable-temperature magnetic susceptibility was carried out with a Vibrating-Sample Magnetic

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meter model CF. Diamagnetic corrections were made with Pascal's constants. The magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$. The XPS spectra (Mg K$\alpha$) were recorded on the PHI 5300 ESCA system (Perkin-Elmer) at 250 VA (12.5 kV × 20 mA) calibrated by assuming the binding energy of the adventitious carbon to be 284.6 eV, with experimental error ±0.2 eV.

2.3. Synthesis of the compounds

All preparations were carried out under N_2 using Schlenk-type glassware.

2.3.1. Ph$_2$PN(^{i}Bu)PPh$_2$

A solution of Ph$_2$PCl (15 g, 0.067 mmol) in benzene (25 ml) was added to a stirred solution of isobutylamine (12.4 g, 0.17 mmol) in 25 ml of benzene at −5°C, and stirring was continued for 1 h. The amine hydrochloride was filtered off and washed with benzene. The filtrate was passed through a silica column (100–140 mesh), then a solution of triethylamine (6.8 g, 0.067 mol) in 25 ml of benzene was added at 0°C and this was followed by dropwise addition of Ph$_2$PCl (15 g, 0.067 mol) in benzene (25 ml). Stirring was continued for 10 h and the precipitate was removed by filtration. The filtrate was passed through a silica column, then the volume of the solvent was reduced and ethanol was added to give the product (16 g, 54%); M.p. 108–109°C. Anal. Calcd for $C_{28}H_{29}NP_2$: C, 76.20; H, 6.62; N, 3.17. Found: C, 76.18; H, 6.60; N, 3.02%. ^{31}P NMR (CDCl$_3$) δ 62.73 ppm. FD-MS (m/z): 441 (M$^+$, 100%).

2.3.2. Co$_2$[μ-Ph$_2$PN(^{i}Bu)PPh$_2$](μ-CO)$_2$(CO)$_4$ (1)

A solution of Co$_2$(CO)$_8$ (0.35 g, 1.02 mmol) and Ph$_2$PN(^{i}Bu)PPh$_2$ (0.45 g, 1.02 mmol) in dichloromethane (20 ml) was stirred for 24 h at room temperature. The volume of the solution was reduced to about 5 ml, then ether (15 ml) was added to give an orange precipitate. The crude product was recrystallized from CH$_2$Cl$_2$/hexane. Yield: 0.4 g (52%), M.p. 115°C (dec). Anal. Calcd for $C_{34}H_{29}Co_2NO_6P_2$: C, 56.12; H, 3.99; N, 1.92. Found: C, 56.54; H, 3.53; N, 1.84%. IR: ν(CO), 2040s, 1995s, 1986s, 1976s, 1814w, 1790s cm^{-1}. ^{31}P NMR (CDCl$_3$) δ 79.15 ppm.

2.3.3. [Co{Ph$_2$PN(^{i}Bu)PPh$_2$-P,P'}$_2$(CO)][Co(CO)$_4$] (2)

A solution of Co$_2$(CO)$_8$ (0.33 g, 0.95 mmol) in THF (30 ml) was added dropwise to a solution of Ph$_2$PN(^{i}Bu)PPh$_2$ (0.88 g, 2.00 mmol) in THF (25 ml) at 0°C. Immediately CO gas was evolved, then the solution changed from pale yellow to dark red. After completion of the addition, stirring was continued for 1 h. The solvent was removed by vacuum. The residue was dissolved in CH$_2$Cl$_2$ and diethyl ether. The solution was left overnight at room temperature and red crystals were produced. Yield: 0.46 g (43%), 157–162°C. Anal. Calcd for $C_{61}H_{58}Co_2N_2O_5P_4$: C, 64.22; H, 5.12; N, 2.46. Found: C, 64.18; H, 5.01; N, 2.32%. IR: ν(CO), 1960s, 1870s,br cm^{-1}. ^{31}P NMR (CDCl$_3$) δ 83.72 ppm. ESR (solid, 77 K): $g_{iso} = 2.132$ and 2.357. Conductivity (CH$_3$CN): 62.8 Ω^{-1} cm^2 mol^{-1}. XPS (Co, 2p$_{3/2}$): 778.9 (FWHM = 1.71) and 780.0 (FWHM = 1.92) eV.

TABLE 1. Experimental details of the X-ray diffraction study of [Co{Ph$_2$PN(^{i}Bu)PPh$_2$-P,P'}$_2$(CO)][Co(CO)$_4$] (2)

Formula	$C_{61}H_{58}Co_2N_2O_5P_4$
Molecular weight	1140.83
Colour	red
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	12.330(2)
b, Å	13.340(2)
c, Å	18.122(3)
α, °	86.63(1)
β, °	80.75(1)
γ, °	84.24(1)
V, Å^a	2924.3
Z	2
D_{calcd}, g cm^{-3}	1.30
D_{exp} (flotation in ClCH$_2$CH$_2$Cl/CHCl$_3$), g cm^{-3}	1.29
Radiation	Mo Kα (0.71073 Å)
Temperature, °C	23
μ, cm^{-1}	7.20
Scan mode	$\omega-2\theta$
Data collected	$4° \leq 2\theta \leq 40°$ $\pm h \pm k \pm l$
Unique data measured	5470
Obs. data [$I > 3\sigma(I)$]	3711
Weighting scheme	unit weights
No. of variables	667
R factor	0.060
R_w factor	0.068
F(000)	1184
Residual extreme in final difference map, e A^{-3}	0.73

2.4. X-ray crystallography

A crystal of **2** was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. The corrections for LP factors and for empirical absorptions were applied to the intensity data. The experimental details of X-ray diffraction study of **2** are listed in Table 1.

The crystal structure of **2** was solved by the direct phase determination method (MULTAN 82). Two independent Co atoms were located on an E-map, and the coordinates of the other non-hydrogen atoms were found by successive difference Fourier syntheses. The hydrogen atoms were not included in the refinements and the calculations of structure factors. In the final refinement by full-matrix least-squares, anisotropic thermal parameters were refined for all non-hydrogen atoms, where all carbon atoms were refined isotropically in order to reduce the number of variables. The final reliability indices are given in Table 1. The fractional coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2.

All calculations were performed on a PDP11/44 computer using SDP-PLUS programs.

3. Results and discussion

Dicobalt complexes of the type $Co_2(CO)_{8-2n}(L-L)_n$ ($n = 1$–3) are normally obtained from reaction of bidentate ligands R_2PXPR_2 ($X = CH_2$ or NR′) with $Co_2(CO)_8$ [12–15]. The ligand $Ph_2PN(^iBu)PPh_2$ thus reacts with $Co_2(CO)_8$ (1 : 1) to give a complex of the type $Co_2(CO)_6(L-L)$, $Co_2(CO)_6[\mu\text{-}Ph_2PN(^iBu)PPh_2]$ (**1**). However, reaction of $Ph_2PN(^iBu)PPh_2/Co_2(CO)_8$ in a 2 : 1 mole ratio does not give $Co_2[\mu\text{-}Ph_2PN(^iBu)PPh_2]_2(CO)_4$, but instead a novel species, [Co{$Ph_2PN(^iBu)PPh_2$-*P*,*P*′}$_2$(CO)][Co(CO)$_4$] (**2**), has been obtained. The perspective drawing of complex **2** based on X-ray diffraction analysis is shown in Fig. 1. Selected bond distances and angles for **2** are given in Table 3.

The structure of **2** suggests formulation as an ion-pair complex, since phosphines or phosphites are well known to cause disproportionation of $Co_2(CO)_8$ to form ion-pair complexes, $[Co(PR_8)_n(CO)_{5-n}][Co(CO)_4]$ [16–18]. However, X-ray diffraction, ESR, variable-temperature magnetic susceptibility, conductivity and XPS measurement appear to show formation of **2** as a d^9–d^9 cage molecule-pair instead of as an ion-pair complex. The structure determination by X-ray diffraction analysis has shown distinct differences between the structural data of the neutral species $[Co(CO)_4]$ and those reported for anionic $[Co(CO)_4]^-$ [19,20]. The average Co–C and C–O distances are 1.81 and 1.09 Å, respectively, in the neutral $Co(CO)_4$ unit, but 1.77 and 1.14 Å in the $Co(CO)_4^-$ anion, which show that the cobalt atom exhibits a weaker d_π–p_π^* property in the former than in the latter. The latter shows the ν(CO) stretching vibration at 1870vs cm^{-1}, and the former has three absorption peaks at 2015w, 1931s and 1895vs cm^{-1}.

TABLE 2. Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms for **2**

	x	y	z	B_{eq} (Å^2)
Co(1)	0.1118(1)	0.26129(9)	0.28761(7)	2.73(3)
P(1)	−0.0251(2)	0.3507(2)	0.2458(2)	3.05(6)
P(2)	0.1601(2)	0.4127(2)	0.2590(2)	3.06(6)
P(3)	0.2694(2)	0.1710(2)	0.2872(2)	3.07(6)
P(4)	0.0931(2)	0.1107(2)	0.2548(2)	3.07(6)
O	0.0267(6)	0.2581(6)	0.4485(4)	5.8(2)
N(1)	0.0289(6)	0.4617(5)	0.2498(4)	3.1(2)
N(2)	0.2149(6)	0.0600(5)	0.2828(4)	3.3(2)
C	0.0605(8)	0.2585(7)	0.3861(6)	4.0(2)
C(5)	−0.0077(8)	0.5639(6)	0.2190(6)	3.9(2)
C(6)	−0.0208(9)	0.6429(7)	0.2772(7)	5.0(3)
C(7)	−0.123(1)	0.631(1)	0.3394(8)	7.2(4)
C(8)	−0.033(1)	0.7494(8)	0.2351(9)	8.1(4)
C(9)	0.2726(9)	−0.0428(7)	0.2666(6)	4.4(3)
C(10)	0.2240(9)	−0.1231(7)	0.3243(6)	4.8(3)
C(11)	0.258(1)	−0.114(1)	0.4011(7)	7.3(4)
C(12)	0.266(1)	−0.2294(8)	0.2914(9)	7.1(4)
C(21)	−0.0514(8)	0.3411(7)	0.1509(6)	3.7(2)
C(22)	0.0121(8)	0.3887(7)	0.0907(6)	4.3(3)
C(23)	−0.004(1)	0.3729(8)	0.0169(6)	5.5(3)
C(24)	−0.082(1)	0.3097(9)	0.0047(7)	6.7(3)
C(25)	−0.146(1)	0.2605(9)	0.0660(7)	5.9(3)
C(26)	−0.1317(8)	0.2761(7)	0.1383(6)	4.9(3)
C(31)	−0.1656(7)	0.3560(7)	0.2965(5)	3.6(2)
C(32)	−0.2475(8)	0.4249(8)	0.2741(7)	4.9(3)
C(33)	−0.3560(9)	0.4236(8)	0.3103(7)	5.7(3)
C(34)	−0.3837(9)	0.3526(8)	0.3663(7)	5.7(3)
C(35)	−0.3021(9)	0.2821(8)	0.3891(7)	5.2(3)
C(36)	−0.1928(7)	0.2819(7)	0.3538(6)	3.9(2)
C(41)	0.2483(7)	0.4535(7)	0.1740(5)	3.3(2)
C(42)	0.2713(8)	0.5571(8)	0.1641(7)	5.0(3)
C(43)	0.327(1)	0.5901(9)	0.0946(8)	6.7(3)
C(44)	0.356(1)	0.524(1)	0.0359(8)	6.9(4)
C(45)	0.3341(9)	0.4216(9)	0.0480(7)	6.0(3)
C(46)	0.2791(8)	0.3885(8)	0.1175(6)	4.0(2)
C(51)	0.2043(8)	0.4764(7)	0.3334(5)	3.7(2)
C(52)	0.3177(8)	0.4898(7)	0.3307(6)	4.5(3)
C(53)	0.3531(9)	0.5288(8)	0.3936(7)	6.1(3)
C(54)	0.215(1)	0.5512(9)	0.4575(7)	7.0(3)
C(55)	0.165(1)	0.5383(9)	0.4589(7)	5.9(3)
C(56)	0.1290(9)	0.4975(7)	0.3982(6)	4.7(3)
C(61)	0.3423(7)	0.1650(7)	0.3668(5)	3.4(2)
C(62)	0.4366(8)	0.0966(7)	0.3692(6)	4.7(3)
C(63)	0.4936(8)	0.0949(8)	0.4293(7)	5.3(3)
C(64)	0.4611(8)	0.1602(9)	0.4868(6)	5.4(3)
C(65)	0.3688(9)	0.2298(9)	0.4843(6)	5.6(3)
C(66)	0.3080(8)	0.2329(8)	0.4237(6)	4.4(2)
C(71)	0.3821(7)	0.1792(6)	0.2102(5)	3.4(2)
C(72)	0.3853(9)	0.1250(8)	0.1458(6)	4.6(3)
C(73)	0.469(1)	0.1381(9)	0.0839(7)	6.2(3)
C(74)	0.548(1)	0.208(1)	0.0880(8)	7.0(4)
C(75)	0.5455(9)	0.2617(9)	0.1516(7)	5.8(3)
C(76)	0.4618(8)	0.2474(8)	0.2146(7)	5.0(3)
C(81)	−0.0194(8)	0.0467(6)	0.3086(6)	3.7(2)
C(82)	−0.0131(9)	0.0155(7)	0.3829(6)	4.3(3)
C(83)	−0.103(1)	−0.0281(9)	0.4265(7)	6.2(3)
C(84)	−0.195(1)	−0.0414(9)	0.3954(8)	6.7(3)
C(85)	−0.204(1)	−0.0078(9)	0.3223(8)	6.7(3)
C(86)	−0.1134(8)	0.0357(8)	0.2756(7)	5.1(3)

TABLE 2 (continued)

	x	y	z	B_{eq} Å^2)
C(91)	0.0997(8)	0.0719(7)	0.1614(6)	3.9(2)
C(92)	0.1332(8)	0.1399(7)	0.1001(6)	4.1(2)
C(93)	0.151(1)	0.1090(9)	0.0281(7)	6.4(3)
C(94)	0.138(2)	0.009(1)	0.0149(8)	11.0(5)
C(95)	0.101(2)	−0.059(1)	0.0744(9)	11.5(6)
C(96)	0.085(1)	−0.0284(8)	0.1489(7)	6.8(3)
Co(2)	0.6132(2)	−0.1963(2)	0.1799(1)	9.65(7)
O(1)	0.4217(8)	−0.1635(8)	0.1065(6)	9.4(3)
O(2)	0.564(1)	−0.242(1)	0.3365(7)	17.6(6)
O(3)	0.717(1)	−0.007(1)	0.1561(8)	15.9(5)
O(4)	0.756(1)	−0.364(1)	0.1224(8)	14.6(4)
C(1)	0.496(1)	−0.178(1)	0.1355(8)	7.8(4)
C(2)	0.583(1)	−0.223(2)	0.2729(7)	13.4(7)
C(3)	0.679(2)	−0.081(1)	0.165(1)	15.8(6)
C(4)	0.699(2)	−0.296(1)	0.1449(9)	12.4(5)

$B_{eq} = (4/3)\cdot[a^2\cdot B_{1,1}) + b^2\cdot B_{2,2} + c^2\cdot B_{3,3} + ab(\cos\gamma)\cdot B_{1,2} + ac(\cos\beta)\cdot B_{1,3} + bc(\cos\alpha)\cdot B_{2,3}]$.

In contrast with the reported trigonal bipyramidal configurations of $[Co(dppm)_2(CO)]^+$ [21] and $[Co(dppe)_2(CO)]^+$ [22,23] the species [Co{$Ph_2PN(^iBu)PPh_2$-*P*,*P'*}$_2$(CO)] exhibits a square pyramidal geometry and its structure is similar to a five-coordinate cobalt(0) complex with stronger π-acid diphosphine ligand, namely [2,3-bis(diphenylphosphino) maleic anhydride tricarbonyl cobalt(0) [24]. Four P atoms lie in the same plane and the Co atom is located over the plane about 0.4 Å towards the carbonyl in this species. The average Co–P distance (2.17 Å) is shorter than those in $[Co(dppm)_2(CO)]^+$ (2.217 Å) and $[Co(dppe)_2(CO)]^+$ (2.231 Å). Orpen [25] has recently described that the σ^* orbitals of P–R bonds have been recognized as playing the role of acceptor in PR_3. The order of increasing π-acid character is:

$$PMe_3 < PAr_3 < P(OMe)_3 < P(OAr)_3 < P(NR_2)_3 < PCl_3 < CO$$

Therefore, the ligand $Ph_2PN(^iBu)PPh_2$ is expected to be a stronger π-acid than dppm and dppe, and a stronger back-donating d_π–σ^* bond could be formed with the Co atom, which may be an important reason for the formation of the neutral species **2**.

The ESR spectrum of the powdered sample of the species **2** at 77 K shows two broad signals centred at $g_{iso} = 2.132$ and 2.357. The former is close to $g_\perp = 2.128$ of species $Co(CO)_4$ in the matrix ESR spectrum at 6 K [26]. The magnetic moment μ_{eff} is calculated as 3.75 BM based on the determination of variable-temperature magnetic susceptibility (1.4–295 K) (Fig. 2), which suggests that there are two unpaired electrons in **2**. The conductivity of **2** in CH_3CN is 62.8 Ω^{-1} cm^2 mol^{-1} at room temperature, which falls within the range for a non-electrolyte [27]. In contrast $[Co(dppm)_2(CO)]^+$ complexes are diamagnetic solids which give conducting solutions [28]. The photoelectron spectrum of **2** shows that the Co $2p_{3/2}$ lines locate at 778.9 eV (FWHM = 1.71 eV) and 780.0 eV (FWHM = 1.92 eV). The latter is close to that (780.2 eV) of $Co_2(CO)_8$ determined at the same conditions. The

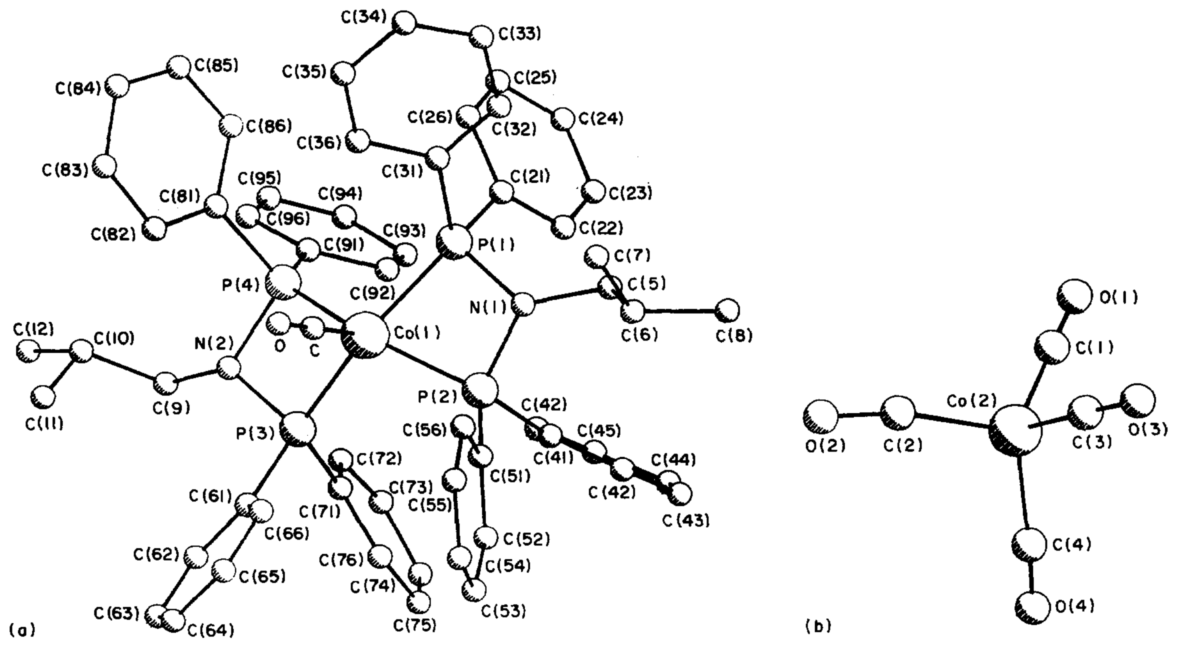


Fig. 1. A perspective view of **2** showing the atomic labelling scheme.

TABLE 3. Selected bond distances (Å) and angles (°) for **2**

Co(1)–P(1)	2.179(2)	Co(1)–P(4)	2.173(2)
Co(1)–P(2)	2.174(2)	Co(1)–C	1.796(9)
Co(1)–P(3)	2.180(2)	O–C	1.140(7)
P(1)–Co(1)–P(2)	71.94(6)	P(2)–Co(1)–P(4)	150.29(7)
P(1)–Co(1)–P(3)	159.74(7)	P(2)–Co(1)–C	105.9(2)
P(1)–Co(1)–P(4)	102.24(6)	P(3)–Co(1)–P(4)	71.94(6)
P(1)–Co(1)–C	100.0(2)	P(3)–Co(1)–C	100.3(2)
P(2)–Co(1)–P(3)	103.17(6)	P(4)–Co(1)–C	103.8(2)
Co(1)–C–O	178.8(6)		
Co(2)–C(1)	1.75(2)	Co(2)–C(3)	1.80(1)
Co(2)–C(2)	1.70(1)	Co(2)–C(4)	1.70(1)
O(1)–C(1)	1.128(9)	O(3)–C(3)	1.13(1)
O(2)–C(2)	1.16(1)	O(4)–C(4)	1.14(1)
C(1)–Co(2)–C(2)	113.3(5)	C(2)–Co(2)–C(3)	108.7(7)
C(1)–Co(2)–C(3)	106.9(6)	C(2)–Co(2)–C(4)	105.6(6)
C(1)–Co(2)–C(4)	110.7(5)	C(3)–Co(2)–C(4)	111.7(8)
Co(2)–C(1)–O(1)	177.9(9)	Co(2)–C(3)–O(3)	177(2)
Co(2)–C(2)–O(2)	179(1)	Co(2)–C(4)–O(4)	180(1)
P(1)–N(1)	1.694(4)	P(3)–N(2)	1.698(4)
P(1)–C(21)	1.814(7)	P(3)–C(61)	1.812(7)
P(1)–C(31)	1.823(6)	P(3)–C(71)	1.811(7)
P(2)–N(1)	1.712(5)	P(4)–N(2)	1.724(5)
P(2)–C(41)	1.826(6)	P(4)–C(81)	1.819(7)
P(2)–C(51)	1.816(7)	P(4)–C(91)	1.785(6)
N(1)–C(5)	1.498(7)	N(2)–C(9)	1.504(7)
Co(1)–P(1)–N(1)	93.9(2)	Co(1)–P(3)–N(2)	93.9(2)
Co(1)–P(1)–C(21)	121.6(2)	Co(1)–P(3)–C(61)	121.3(2)
Co(1)–P(1)–C(31)	122.2(2)	Co(1)–P(3)–C(71)	122.0(2)
N(1)–P(1)–C(21)	107.6(3)	N(2)–P(3)–C(61)	109.4(2)
N(1)–P(1)–C(31)	110.4(2)	N(2)–P(3)–C(71)	107.9(3)
C(21)–P(1)–C(31)	100.3(3)	C(61)–P(3)–C(71)	101.2(3)
Co(1)–P(2)–N(1)	93.7(2)	Co(1)–P(4)–N(2)	93.4(2)
Co(1)–P(2)–C(41)	126.5(2)	Co(1)–P(4)–C(31)	116.5(2)
Co(1)–P(2)–C(51)	115.8(2)	Co(1)–P(4)–C(91)	126.4(2)
N(1)–P(2)–C(41)	105.9(2)	N(2)–P(4)–C(31)	108.4(3)
N(1)–P(2)–C(51)	108.3(3)	N(2)–P(4)–C(91)	105.5(3)
C(41)–P(2)–C(51)	104.5(3)	C(81)–P(4)–C(91)	104.5(3)
P(1)–N(1)–P(2)	97.3(2)	P(3)–N(2)–P(4)	96.8(2)
P(1)–N(1)–C(5)	128.9(4)	P(3)–N(2)–C(9)	129.3(4)
P(2)–N(1)–C(5)	128.2(4)	P(4)–N(2)–C(9)	126.7(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

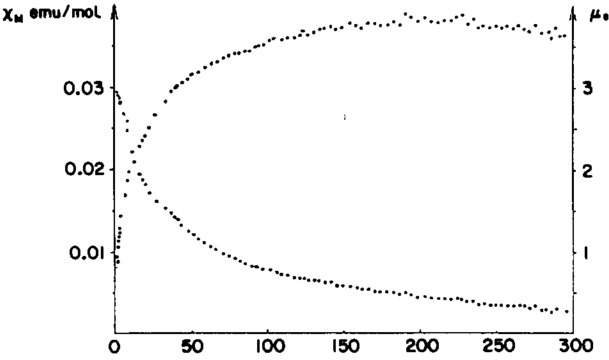
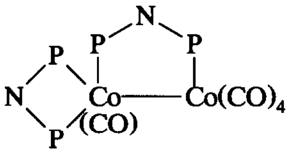
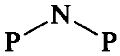


Fig. 2. Plot of molar susceptibility, χ_m, and effective moment, μ_{eff} for **2**.

crystal structural analysis indicated that the species $Co(CO)_4$ is enclosed in the cage consisted of species [Co{$Ph_2PN(^iBu)PPh_2$-*P*,*P*'}$_2$(CO)] (Fig. 3) and the Co(1)–Co(2) distance is 8.320 Å.

The mechanism for the formation of **2** has initially been investigated by ^{31}P NMR. The ^{31}P NMR species shows that an intermediate is present during the reaction, in which there might be three different environmental phosphorus atoms and the coupling interaction is complicated. It has been established [18] that $Co_2(CO)_8$ reacts with dppm rapidly (a few minutes) to give a salt [Co(dppm)(CO)$_3$][Co(CO)$_4$], which loses CO to form $Co_2(\mu\text{-dppm})(\mu\text{-CO})_2(CO)_4$. Following the above considerations and in view of the ^{31}P NMR spectrum we consider the intermediate probably has the following structure:




$= Ph_2PN(^iBu)PPh_2$

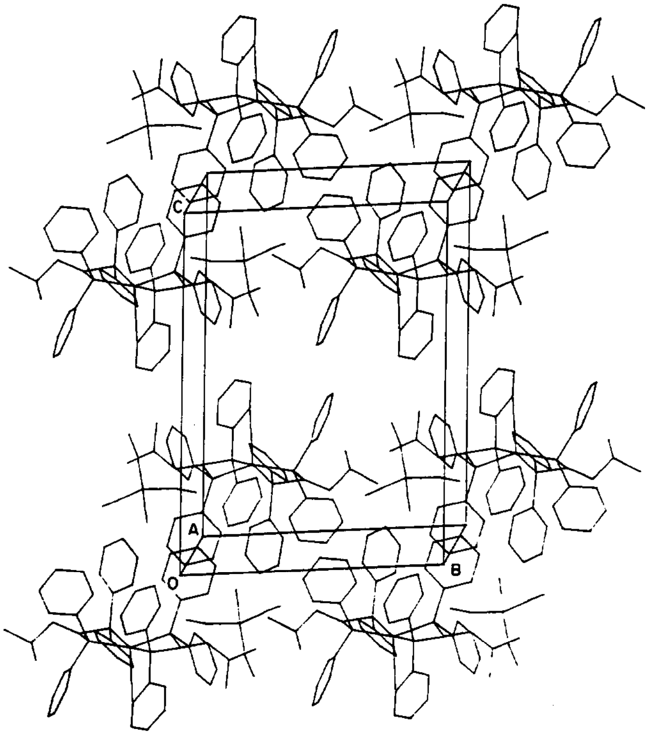


Fig. 3. A view of the packing arrangement in a cell of crystal **2**.

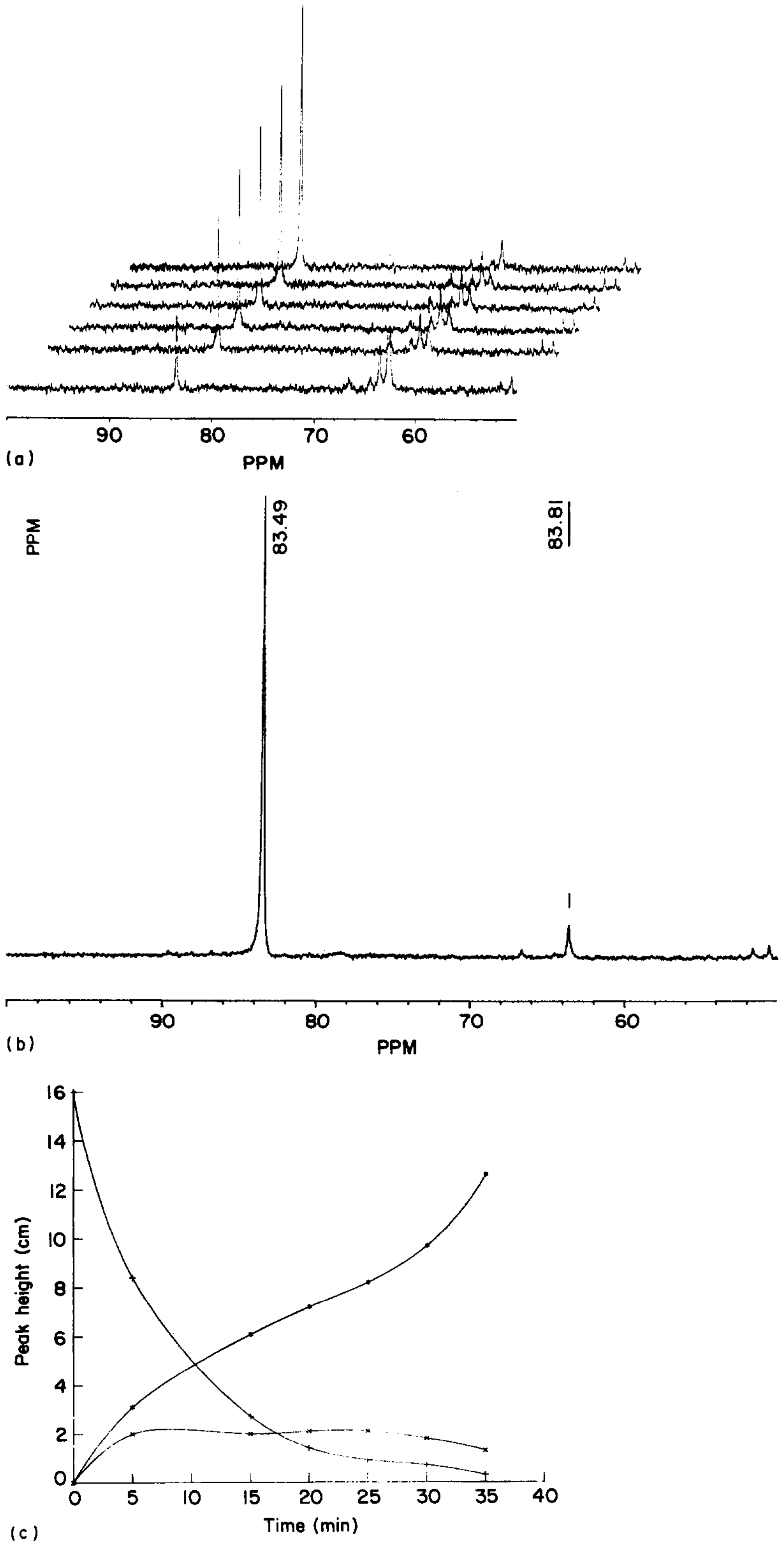


Fig. 4. $^{13}P\{^1H\}$ NMR monitoring of the reaction between ligand $Ph_2PN(^iBu)PPh_2$ and $Co_2(CO)_8$ (solvent: $CDCl_3$, room temperature). (a) t = 5–35 min; (b) t = 60 min; (c) peak height of chemical shift as a function of reaction time. +, ligand $Ph_2PN(^iBu)PPh_2$, δ: 62.73 ppm. *, species **2**, δ: 83.52 ppm. ×, species **3**, δ: 63.81 ppm.

We have isolated a minor orange species (**3**) by fractional crystallization, which gives three CO absorption bands at 2000s, 1962s and 1888s,br cm^{-1}, and this seems to support our hypothesis. The relation of the amount of phosphazane, intermediate **3** and product **2**, *vs.* the reaction time detected by ^{31}P NMR is given in Fig. 4.

Here the ^{31}P signal of **1** ($\delta = 79.13$ ppm) is not observed. It is possible that **1** reacts rapidly with $Ph_2PN(^iBu)PPh_2$ to form the stable intermediate **3**, and the latter changes slowly to **2** by homolytic Co–Co bond cleavage and heterolytic P–Co bond cleavage. After reacting for 35 min the peak height for the ligand, $Ph_2PN(^iBu)PPh_2$, disappeared (Fig. 4(a)), however the peak height for species **2** continued to increase (Fig. 4(b) and (c)) which shows that the intermediate **3** continues to transfer to product **2**. Therefore, the total process of the reaction of $Co_2(CO)_8$ with $Ph_2PN(^iBu)PPh_2$ (1:2) is probably as follows:

$$Co_2(CO)_8 + Ph_2PN(^iBu)PPh_2 \xrightarrow{\text{fast}}$$

$$[Co\{Ph_2PN(^iBu)PPh_2\text{-}P,P'\}(CO)_3][Co(CO)_4] \xrightarrow{\text{fast}}$$

$$Co_2[\mu\text{-}Ph_2PN(^iBu)PPh_2](\mu\text{-}CO)_2(CO)_4 \xrightarrow[\text{fast}]{Ph_2PN(^iBu)PPh_2}$$

$$Co_2[\mu\text{-}Ph_2PN(^iBu)PPh_2][Ph_2PN(^iBu)PPh_2\text{-}P,P'](CO)_5 \xrightarrow{\text{slow}}$$

$$[Co\{Ph_2PN(^iBu)PPh_2\text{-}P,P'\}_2(CO)][Co(CO)_4]$$

2 probably has different structures in the solid state and in solution, and a strong interaction between [Co{$Ph_2PN(^iBu)PPh_2$-*P*,*P'*}$_2$(CO)] and [Co(CO)$_4$] might be present when in solution [29].

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