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Reductive carbonylation route to Co(0) and Co(I) carbonyl complexes containing bridging, chelating and cleaved diphosphazanes. Structures of $[Co(CO)\{P(OR)_2(NHMe)\}_2\{P(O)(OR)_2\}\{P(H)(OR')_2\}]$ ($R = CH_2CF_3$, $R' = CH_2CH_3$), $[Co_2(CO)_2\{\mu\text{-}MeN\{P(OR)_2\}_2\}_3]$ ($R = CH_2CF_3$), and $[Co(CO)\{\eta^2\text{-}MeN\{P(OR)_2\}_2\}_2][CoCl_3(OC_4H_8)]$ ($R = Ph$)[1]

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Abstract

Reduction of $CoCl_2$ by $NaBH_4$ in ethanol in the presence of $MeN\{P(OR)_2\}_2$ ($R = CH_2CF_3$ $\mathbf{L^1}$) and carbon monoxide at one atmospheric pressure gives an unusual mononuclear complex, $[Co(CO)\{P(OR)_2(NHMe)\}_2\{P(O)(OR)_2\}\{P(H)(OR')_2\}]$, ($R = CH_2CF_3$, $R' = CH_2CH_3$) **1** formed by cleavage of a P–N bond and by *trans* esterification. When the reductive carbonylation is carried out by using Zn as the reducing agent in the presence of the diphosphazanes, $MeN\{P(OR)_2\}_2$ ($R = CH_2CF_3$ $\mathbf{L^1}$; Ph $\mathbf{L^2}$), the complexes $[Co_2(CO)_2(\mu\text{-}\mathbf{L^1})_3]$ **2**, $[Co_2(CO)_4(\mu\text{-}\mathbf{L^2})_2]$ **3**, and $[Co(CO)(\eta^2\text{-}\mathbf{L^2})_2][CoCl_3(thf)]$ **4** are isolated. All the complexes have been characterised by elemental analyses and IR, ^1H- and ^{31}P-NMR spectroscopic data. The structures of the complexes **1**, **2** and **4** are confirmed by single-crystal X-ray diffraction studies.

Keywords: Cobalt-diphosphazne-carbonyl complexes; Unusual P–N cleavage; Reductive carbonylation; NMR spectra; X-ray structures

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1. Introduction

Transition metal clusters containing carbon monoxide and phosphane ligands have attracted considerable attention in recent years in view of their interesting structural features and catalytic applications. Reduction of metal halides with reducing agents such as $NaBH_4$ or Zn in the presence of a phosphane ligand and CO offers a convenient method to prepare a variety of novel metal-phosphane-carbonyl complexes [2–9]. This method provides an alternative procedure for the synthesis of metal-phosphane-carbonyl complexes obviating the use of metal carbonyls as the starting materials [10]. Recently, Zhang et. al. have reported that the carbonylation of iron(III) halides in the presence of the diphosphazanes $RN(PPh_2)_2$ ($R = Pr^i$ or Bu^i), (L–L) gives the carbonyl halide complexes *trans*-$[Fe(CO)_2X_2(L–L)]$ ($X = Cl$, Br or I) [11]. In continuation of our work on organometallic chemistry of diphosphazane ligands [1,12,13], we report in this paper the reductive carbonylation of $CoCl_2$ in the presence of the strong π-acceptor bidentate phosphorus ligands, $MeN\{P(OR)_2\}_2$ ($R = CH_2CF_3$ $\mathbf{L^1}$, Ph $\mathbf{L^2}$). The mono- and dimetallic cobalt complexes $[Co(CO)\{P(OR)_2(NHMe)\}_2\{P(O)(OR)_2\}\{P(H)(OR')_2\}]$ ($R = CH_2CF_3$, $R' = CH_2CH_3$) **1**, $[Co_2(CO)_2(\mu\text{-}\mathbf{L^1})_3]$ **2**, $[Co_2(CO)_4(\mu\text{-}\mathbf{L^2})_2]$ **3**, and $[Co(CO)(\eta^2\text{-}\mathbf{L^2})_2][CoCl_3(thf)]$ (thf = tetrahydrofuran) **4** have been isolated and their structures elucidated by NMR and X-ray crystallographic studies.

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[1] This is part 14 of the series 'Organometallic Chemistry of Diphosphazanes'; for part 13 see Ref. [1].

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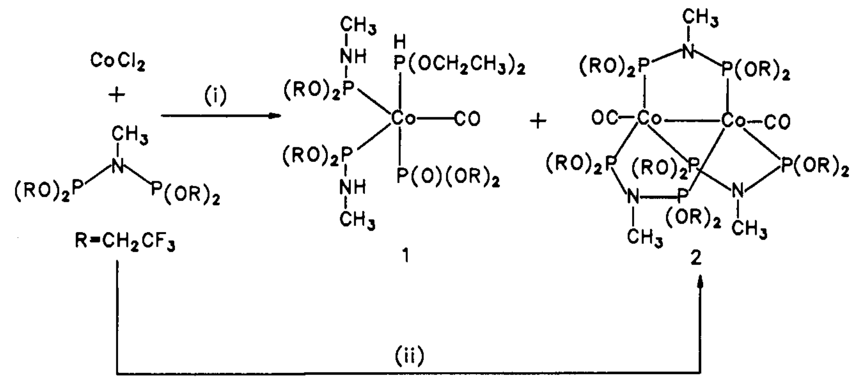


Scheme 1. (i) $NaBH_4$/CO/EtOH/25°C/10 h. (ii) Zn/CO/thf/25°C/10 h.

2. Results and discussion

2.1. Synthesis and spectroscopic data

The reduction of anhydrous $CoCl_2$ by $NaBH_4$ in the presence of 2.5 equivalents of **L**^{1} and a stream of CO in ethanol at 25°C gives the pentacoordinated mononuclear cobalt complex, **1** in low yield ($< 10\%$). When the metal to ligand ratio is changed to 1:1 or 1:2, the dinuclear complex **2** is also formed in small amounts ($< 5\%$) along with complex **1**. When the reductive carbonylation is carried out using 1:3 stoichiometric ratio of the metal and the ligand in the presence of Zn dust as the reducing agent, the yield of the complex **2** is improved (15%) (Scheme 1). Complex **1** is not formed in this reaction. This indicates that the ligand is susceptible to cleavage in the presence of $NaBH_4$ in ethanol medium. Complex **1** is a pale yellow crystalline solid, soluble in CH_2Cl_2, $CHCl_3$, acetone and thf. It slowly decomposes in solution. Complex **2** is an air-stable purple solid. It is readily soluble in acetone or thf but sparingly soluble in CH_2Cl_2 or $CHCl_3$. Pyrolysis of **2** in boiling heptane for 24 h does not give any high nuclearity clusters and the starting material is recovered. The stability of the metal core can be attributed to the strong π-acceptor capability of the ligand **L**^{1}.

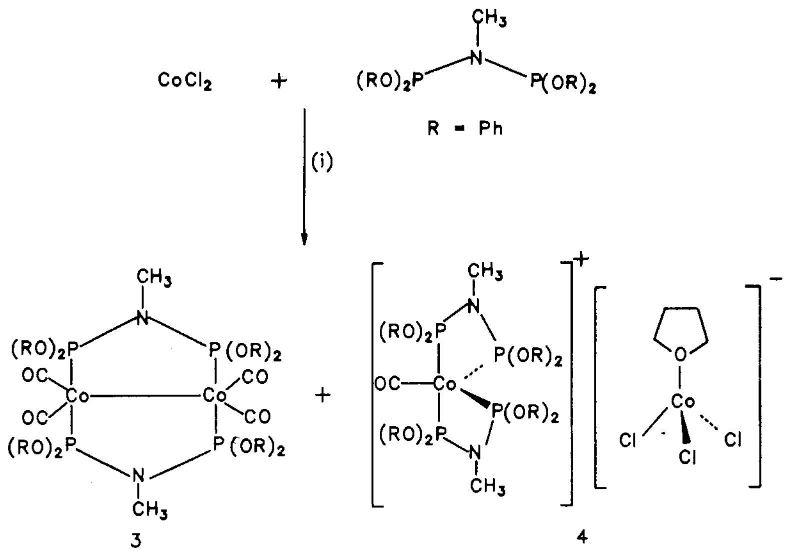
When the reductive carbonylation of $CoCl_2$ is carried out in thf at 25°C in the presence of the phenoxy derivative **L**^{2} using Zn dust as a reducing agent, complexes **3** and **4** are formed (Scheme 2). Complexes **3** and **4** can be isolated by fractional crystallization. Complex **3** is a black solid, moderately stable to air. Complex **4** is yellow air-sensitive solid. Both are soluble in CH_2Cl_2, $CHCl_3$, acetone and thf.

The IR spectrum of **1** shows a peak at 1955 cm^{-1} for the terminal CO group. This value is comparable with the C–O stretching frequencies observed for other pentacoordinated cobalt carbonyl complexes [14–19]. The ^{31}P-{^{1}H}- and ^{1}H-NMR spectra of **1** are illustrated in Fig. 1. The ^{1}H-NMR spectrum shows the presence of OCH_2CF_3, OCH_2CH_3 and NMe groups. The resonance for the PH proton is observed at 6.96 ppm as a doublet of doublet of triplets owing to coupling with three different phosphorus nuclei. The observed one-bond P–H coupling constant (430.3 Hz) is considerably higher than that reported for other cobalt carbonyl complexes of secondary phosphanes such as PMe_2H or PPh_2H [20–22]. The ^{31}P-{^{1}H}-NMR spectrum of **1** displays an AM_2X spin pattern; the assignment of the chemical shifts are shown in Fig. 1. The magnitude of ^2J(AX) *(trans* coupling) is higher than that of ^2J(AM) or ^2J(MX) *(cis* coupling). The assignment of the resonances is further confirmed by the proton coupled ^{31}P-NMR spectrum. The multiplet at 180.0 ppm can be assigned to P_x as it shows a large coupling ($^1J(PH) = 430.3$ Hz) to the proton directly bonded to P_x.

The IR spectrum of **2** shows a peak at 1938 cm^{-1} due to the terminal CO group which is shifted to a lower value compared to that for $[CO_2(CO)_2\{\mu\text{-}MeN(PF_2)_2\}_3]$ [23]. The ^{31}P-{^{1}H}-NMR spectrum of **2** shows a single peak at 153.0 ppm indicating that all phosphorus nuclei are equivalent.

The ^{31}P-{^{1}H}-NMR spectrum of the reaction mixture resulting from $NaBH_4$ reduction (Scheme 1 (i)) shows that besides complexes **1** and **2**, there are several other products, of which the one giving rise to a singlet at 160.0 ppm is present in appreciable quantities. The ^{31}P-{^{1}H}-NMR spectrum of the reaction mixture obtained by Zn reduction in thf medium at 0°C (Scheme 1 (ii)), after isolation of complex **2**, also shows a singlet at 160.0 ppm but resonances corresponding to **1** are absent. The singlet may be attributed to the dinuclear cobalt complex, $[Co_2\ (\mathbf{L}^1)_2(CO)_4]$ based on the chemical shift value for the corresponding complex with ligand **L**^{2} (see below).

The structure of complex **3** is deduced from elemental analysis, IR and NMR spectra. The IR spectrum shows peaks at 1940 and 1978 cm^{-1} attributable to the terminal CO groups; these frequencies are shifted to higher wave numbers compared to those observed for the complexes $[Co_2(CO)_4\{\mu\text{-}MeN\{P(OCH_3)_2\}_2\}_2]$ [24], $[Co_2(CO)_4\{\mu\text{-}EtN\{P(OCH_2)_2\}_2\}_2]$ [17] and



Scheme 2. (i) Zn/CO/thf/25°C/10 h.

$[Co_2(CO)_4(\mu\text{-dppm})_2]$ [4]. The $^{31}P\text{-}\{^1H\}$-NMR spectrum of **3** shows a singlet at 150.5 ppm indicating the equivalence of all phosphorus nuclei. The ^1H-NMR spectrum of **4** shows a quintet for the methyl group attached to nitrogen indicating the presence of two diphosphazane ligands attached to the metal. The $^{31}P\text{-}\{^1H\}$-NMR spectrum shows a singlet at 109.5 ppm indicating the equivalence of all phosphorus nuclei at room temperature. The ^{31}P chemical shift for **4** is considerably shifted upfield ($\delta_{complex} - \delta_{ligand} = -25.6$ ppm) compared to the value for the ligand which is in contrast to the downfield shift observed for $[Co(\eta^2\text{-dppa})_2(CO)]^+$ compared to the corresponding value for dppa, $HN(PPh_2)_2$ [10]. It may also be noted that for complex **3** containing bridging diphosphazane ligands, the ^{31}P chemical shift lies downfield to that for the free ligand in contrast to the upfield shift observed for chelate complex **4**. Futhermore, $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) value for the three dibridged dicobalt complexes,$[Co_2(CO)_4(\mu\text{-dppa})_2]$, $[Co_2(CO)_4\{\mu\text{-MeN}\{P(OCH_3)_2\}_2\}_2]$, and $[Co_2(CO)_4\{\mu\text{-MeN}\{P(OPh)_2\}_2\}_2]$ are 45.0, 17.8 and 15.4 ppm, respectively. This trend correlates with the increasing π-acceptor ability of the three ligands. The $^{31}P\text{-}\{^1H\}$-NMR spectrum of the reaction mixture obtained by the treatment of $CoCl_2$ with $\mathbf{L}^2$ shows the formation of **3** and **4** as the major products. There is no signal corresponding to a tribridged complex $[Co_2\mathbf{L}^2_3(CO)_2]$ analogous to **2**.

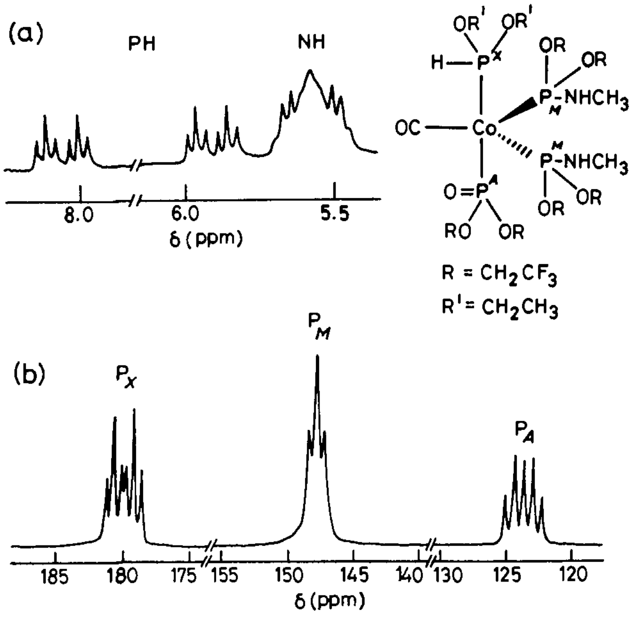


Fig. 1. (a) The ^1H-NMR spectrum (200 MHz) of **1**. Only the NH and the PH resonances are shown. (b) The $^{31}P\text{-}\{^1H\}$-NMR spectrum (162 MHz) of **1**.

2.2. Single-crystal X-ray diffraction studies

2.2.1. Molecular structure of 1

The structure of **1** has been confirmed by X-ray diffraction studies. A perspective view of the molecule is shown in Fig. 2. Selected bond lengths and bond angles are listed in Table 1. The complex is formed by an unusual P–N bond cleavage and also *trans*-esterification giving rise to a phosphonite ligand coordinated to cobalt. The complex also contains a phosphoranyl ligand so that the metal has a formal oxidation state of +1. The geometry around cobalt is distorted trigonal bipyramidal. The Co(1), P(1), P(2) and C(1) atoms define the equatorial plane and P(3) and P(4) atoms occupy axial positions. The *trans* P(3)–Co(l)–P(4) angle is 173.79(6)° compared to the ideal value of 180°. The three *cis*-angles P(1)–Co(1)–P(2), P(2)–Co(1)–C(1), and C(1)–Co(1)–P(1) are 112.5(1), 124.7(2) and 122.8(2)°, respectively compared to the ideal value of

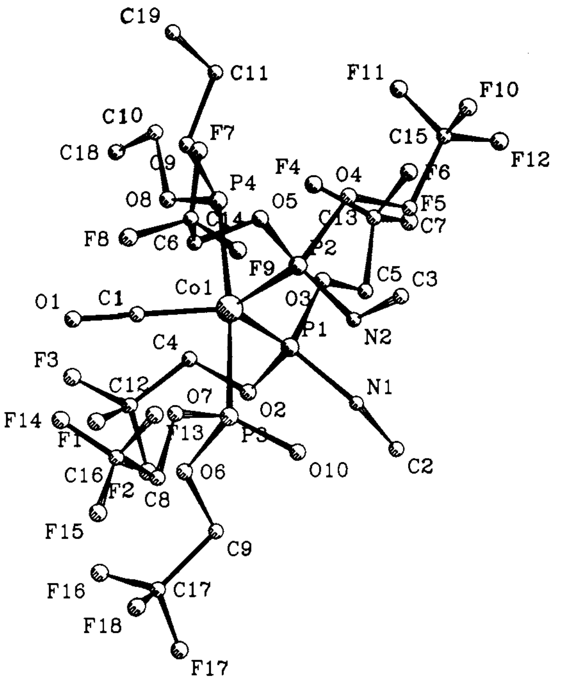


Fig. 2. Molecular structure of complex **1**. Disordered C17′, C12′ and fluorines attached to them have been omitted for clarity.

120°. The Co(1)–P(3) distance [2.184(2) Å] is longer than the Co(1)–P(4) [2.147(2) Å], Co(1)–P(1) [2.151(2) Å] or Co(1)–P(2) [2.160(2) Å] distances. Two intramolecular bifurcated hydrogen bonds are observed between N(1) or N(2) and O(10); also an intramolecular H-bond is observed between P(4) and F(11). There are numerous other C–H···O and C–H···F inter and intramolecular short contacts, some of which can be regarded as weak to moderately strong hydrogen bonds (see supplementary material).

2.2.2. Molecular structure of 2

The molecular structure of **2** is shown in Fig. 3. Selected bond lengths and bond angles are listed in Table 2. The molecule consists of two cobalt centres bridged by three $\mathbf{L^1}$ ligands and two CO groups occupying the axial positions. The molecule adopts a partially staggered configuration; the torsion angles of P(1)–Co(1)–Co(2)–P(2), P(3)–Co(1)–Co(2)–P(4) and P(5)–Co(1)–Co(2)–P(6) are 30.64(6), 28.89(7) and 24.18(7)°, respectively. The structural features are very similar to those of the dicobalt complexes $[Co_2L_2\{MeN(PF_2)_2\}_3]$ [L = CO, F_2PNHMe] but the Co(1)–Co(2) distance [2.782(1) Å] in **2** is slightly longer than that [2.71–2.77 Å] found for $[Co_2L_2\{MeN(PF_2)_2\}_3]$ [L = CO, F_2PNHMe] [23]. The average Co–P distance (2.122 Å) is 0.08 Å shorter than average Co–P distance found in $[Co_2(CO)_4(\mu\text{-dppm})_2]$ complex [4]. This trend is an indication of the better π-acceptor ability of ligand $\mathbf{L^1}$ compared to dppm. The structure is stabilised by numerous C–H···F, CH···O and C–H···N short contacts (see supplementary material).

Table 1
Selected bond lengths [Å] and angles [°] for **1**

Co(1)–C(1)	1.739(6)	C(1)–Co(1)–P(4)	88.1(2)
Co(1)–P(4)	2.147(2)	C(1)–Co(1)–P(1)	122.8(2)
Co(1)–P(1)	2.151(2)	P(4)–Co(1)–P(1)	94.25(6)
Co(1)–P(2)	2.160(2)	C(1)–Co(1)–P(2)	124.7(2)
Co(1)–P(3)	2.184(2)	P(4)–Co(1)–P(2)	89.31(7)
P(1)–N(1)	1.633(6)	P(1)–Co(1)–P(2)	112.54(7)
P(2)–N(2)	1.618(5)	C(1)–Co(1)–P(3)	85.8(2)
P(3)–O(10)	1.484(4)	P(4)–Co(1)–P(3)	173.79(6)
		P(1)–Co(1)–P(3)	90.31(6)
		P(2)–Co(1)–P(3)	92.84(7)
		O(1)–C(1)–Co(1)	179.5(6)

2.2.3. Molecular strucutre of 4

The structure of **4** as determined by X-ray diffraction is shown in Fig. 4. Selected bond distances and bond angles are listed in Table 3. The formal oxidation states of cobalt in the cationic and the anionic moieties are +1 and +2, respectively. The coordination geometry of cobalt in the cationic moiety is distorted trigonal bipyramidal and that in the anionic moiety is distorted tetrahedral. The Co(1), P(2), P(3) and C(1) atoms lie in the equatorial plane and the P(4) and P(1) atoms occupy the axial positions. The angle between the two axial phosphorus atoms P(4)–Co(1)–P(1) [163.85(9)°] is slightly smaller than that [165.1(1)°] found in $[Co(CO)\{\eta^2\text{-EtN}\{P(OPr^i)_2\}_2\}_2]^+$ [17] probably due to steric requirement of the phenyl groups. One of the axial Co–P bond lengths [Co(1)–P(1) = 2.138(2) Å] is shorter than the other axial and the equatorial cobalt-phosphorus lengths [2.146–2.150(2) Å]. These distances are comparable to Co–P distances observed in the related species, $[Co(CO)(dppm)_2]^+$ [18,19] and $[Co(CO)\{EtN\{P(OPr^i)_2\}_2\}_2]^+$ [17]. However, the average Co–P distance [2.146 Å] in **4** is shorter than the average Co–P distance [2.16 Å] found in a closely related species $[Co(CO)\{EtN\{P(OPr^i)_2\}_2\}_2]$ [17].

The mean P–N bond distances in **1** and **4** are 1.670(5) and 1.673(6) Å, respectively which are shorter than the accepted value for a P–N single bond distance. The P–N–P angle of the bridging diphosphazanes in **2** varies from 112.9(3)–115.9(3)°; in the chelate complex **4**, the P–N–P angles are 96.9(3) and 96.4(3)°. In spite of this large variation in the P–N–P angles, the planarity around the nitrogen is maintained in all cases as observed in numerous other diphosphazane complexes [12].

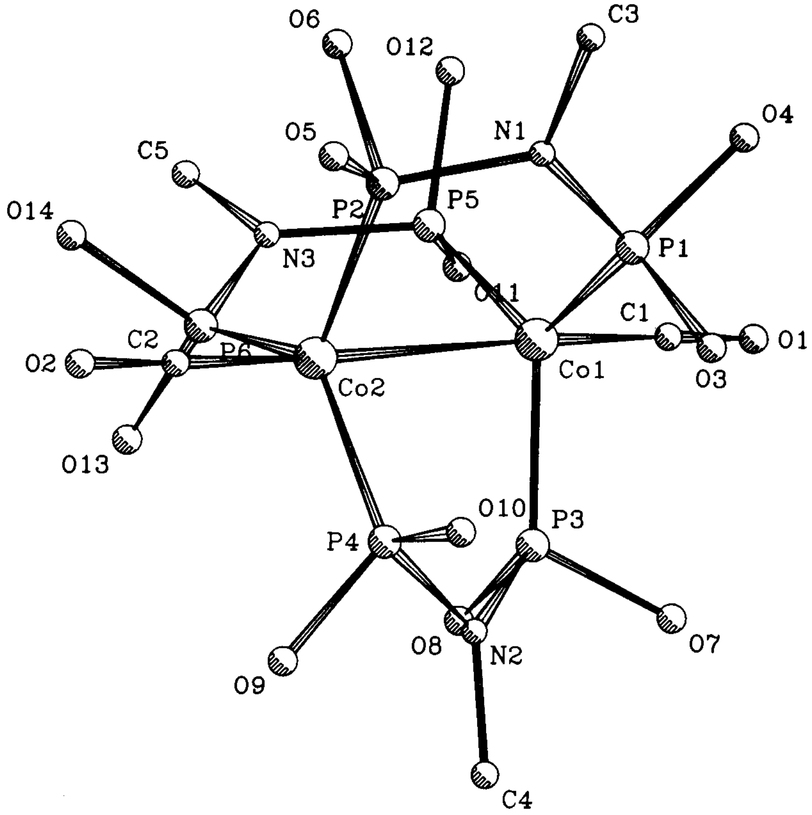


Fig. 3. Molecular structure of complex **2**. The CH_2CF_3 groups have been omitted for clarity.

3. Conclusion

Reductive carbonylation of transition metal halides in the presence of diphosphazane ligands provides a convenient method for metal-phosphane-carbonyl complexes of known structural types (e.g. **2** and **3**). Besides it can give rise to unusual products (e.g. **1** and **4**) although the yields are low. Fluorine substituted diphosphazane ligands $MeN(PX_2)_2$ [X = F [23] or OCH_2CF_3] are strong π-acceptors comparable to CO and give tribridged derivatives of the type $[Co_2(L-L)_3(CO)_2]$. On the other hand, diphosphazane ligands with less electronegative substituents, viz, $RN(PX_2)_2$(R-Me, X-Ome [24] or OPh; R-Et, X-OPr^i [17] or $X_2 =$

Table 2
Selected bond lengths [Å] and angles [°] for **2**

Co(1)–C(1)	1.722(7)	Co(2)–P(6)	2.127(2)
Co(1)–P(3)	2.117(2)	P(2)–N(1)	1.674(5)
Co(1)–P(1)	2.123(2)	P(1)–N(1)	1.669(5)
Co(1)–P(5)	2.126(2)	P(3)–N(2)	1.675(5)
Co(1)–Co(2)	2.7820(12)	P(4)–N(2)	1.675(5)
Co(2)–C(2)	1.710(7)	P(5)–N(3)	1.657(6)
Co(2)–P(2)	2.116(2)	P(6)–N(3)	1.670(5)
Co(2)–P(4)	2.124(2)		
C(1)–Co(1)–P(3)	90.5(2)	C(2)–Co(2)–Co(1)	177.6(2)
C(1)–Co(1)–P(1)	97.5(2)	P(3)–Co(1)–Co(2)	86.58(5)
C(1)–Co(1)–P(5)	88.9(3)	P(1)–Co(1)–Co(2)	87.49(6)
C(2)–Co(2)–P(2)	92.5(2)	P(5)–Co(1)–Co(2)	89.14(6)
C(2)–Co(2)–P(4)	94.3(2)	P(2)–Co(2)–Co(1)	86.27(5)
C(2)–Co(2)–P(6)	90.6(2)	P(4)–Co(2)–Co(1)	88.14(5)
P(3)–Co(1)–P(1)	118.18(7)	P(6)–Co(2)–Co(1)	87.99(6)
P(3)–Co(1)–P(5)	120.82(7)	P(1)–N(1)–P(2)	112.9(3)
P(1)–Co(1)–P(5)	120.54(7)	P(3)–N(2)–P(4)	113.0(3)
C(1)–Co(1)–Co(2)	175.0(2)	P(6)–N(3)–P(5)	115.9(3)
P(2)–Co(2)–P(4)	119.96(7)	O(1)–C(1)–Co(1)	177.0(7)
P(2)–Co(2)–P(6)	113.95(7)	O(2)–C(2)–Co(2)	178.4(6)
P(4)–Co(2)–P(6)	125.53(7)		

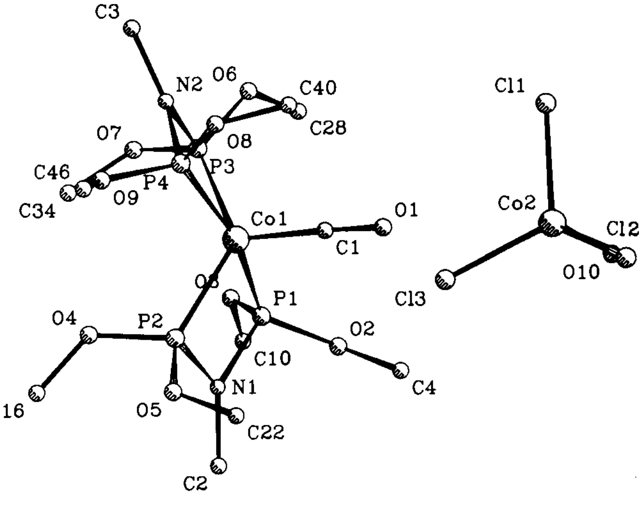


Fig. 4. Molecular structure of complex **4**. Phenyl rings and thf ring have been omitted for clarity.

Table 3
Selected bond lengths [Å] and angles [°] for 4

Co(1)–C(1)	1.771(9)	P(3)–N(2)	1.676(6)
Co(1)–P(1)	2.138(2)	P(4)–N(2)	1.660(7)
Co(1)–P(2)	2.146(2)	Co(2)–O(10)	2.069(7)
Co(1)–P(3)	2.149(2)	Co(2)–Cl(3)	2.217(3)
Co(1)–P(4)	2.150(2)	Co(2)–Cl(2)	2.222(3)
P(1)–N(1)	1.666(7)	Co(2)–Cl(1)	2.224(3)
P(2)–N(1)	1.691(7)		
C(1)–Co(1)–P(1)	97.3(3)	P(4)–N(2)–P(3)	96.9(3)
C(1)–Co(1)–P(2)	119.3(3)	P(1)–N(1)–P(2)	96.4(3)
P(1)–Co(1)–P(2)	71.50(9)	O(1)–C(1)–Co(1)	177.9(7)
C(1)–Co(1)–P(3)	116.4(3)	O(10)–Co(2)–Cl(3)	105.3(3)
P(1)–Co(1)–P(3)	100.70(9)	O(10)–Co(2)–Cl(2)	100.7(2)
P(2)–Co(1)–P(3)	124.30(10)	Cl(3)–Co(2)–Cl(2)	118.2(2)
C(1)–Co(1)–P(4)	98.9(3)	O(10)–Co(2)–Cl(1)	100.6(3)
P(1)–Co(1)–P(4)	163.85(9)	Cl(3)–Co(2)–Cl(1)	113.39(12)
P(2)–Co(1)–P(4)	101.25(9)	Cl(2)–Co(2)–Cl(1)	115.36(13)
P(3)–Co(1)–P(4)	70.98(9)		

$(OCH_2)_2$ [25]) form preferably dibridged derivatives of the type $[CO_2\ (L-L)_2(CO)_4]$. The absence of a tribridged dicobalt derivative of ligand $\mathbf{L}^2$ may also be due to steric factors. Thus the nature of products formed with diphosphazane ligands appear to depend on a subtle balance of steric and electronic factores. The mechanism of the cleavage of the P–N bond and *trans*-esterification to yield complex **1** is not clear and requires further investigations. Furthermore, complex **1** containing a P–H group can be a potential source for preparing water-soluble cobalt-phosphane complex by conversion of the P–H into $P(CH_2OH)$ group [26].

4. Experimental

4.1. Instrumentation

The ^1H- and ^{31}P-NMR spectra were recorded using a Bruker ACF-200 or a Bruker AMX-400 spectrometer with $(CH_3)_4Si$ as an internal standard for ^1H-NMR measurements and 85% H_3PO_4 as an external standard for ^{31}P-$\{^1H\}$-NMR measurements. Chemical shifts downfield from the standard were assigned positive values. Infrared spectra were recorded using a BIO-RAD FTIR Model FTS-7 or a Perkin-Elmer Model 457 spectrometer.

4.2. Materials and procedures

All manipulations were carried out under dry dinitrogen by using standard Schlenk-line techniques. Solvents were distilled under nitrogen prior to use. The diphosphazanes $MeN\{P(OR)_2\}_2$ [$R = CH_2CF_3$ $\mathbf{L}^1$; Ph $\mathbf{L}^2$] were prepared as reported previously [27]. Anhydrous $CoCl_2$ was prepared from $CoCl_2 \cdot 6H_20$ by a literature method [28].

4.3. Synthesis of $[Co(CO)\{P(OCH_2CF_3)_2(NHMe)\}_2 \{P(O)(OCH_2CF_3)2\}\{P(H)(OCH_2CH_3)_2\}]$ (1) and $[Co_2(CO)_2\{\mu\text{-}MeN\{P(OCH_2CF_3)_2\}_2\}_3]$ (2)

A solution of anhydrous $CoCl_2$ (0.051 g, 0.39 mmol) and $\mathbf{L}^1$ (0.477 g, 0.98 mmol) in absolute ethanol (50 ml) was saturated with CO for 20 min. A suspension of $NaBH_4$ (0.045 g, 1.19 mmol) in ethanol (10 ml) was added dropwise over a period of 30 min while CO was bubbled through the solution rapidly. The color of the solution changed to orange. The mixture was stirred for 6 h while CO was passed through the solution. The solvent was removed under reduced pressure and the residue was dissolved in CH_2C1_2 (8 ml). The extract was filtered and petroleum ether (b.p 60–80°C) (3 ml) was added to the filtrate. The solution was cooled at -15°C for 7 days to obtain 31 mg (8%) crystals of **1**. M.p. 176°C. Anal. Found: C, 22.03; H, 3.25; N, 2.59. $C_{19}H_{31}CoF_{18}N_2O_{10}P_4$ (971.94). Anal. Calc.: C, 23.45; H, 3.18; N, 2.88. IR (Nujol, cm^{-1}): ν(C=O) 1956 s, ν(P–O) 1265 s, ν(P–H) 2310 w, ν(N–H) 3240 m br. ^1H-NMR ($CDCl_3$, 25°C): $\delta = 1.34$ (t, 3H, OCH_2CH_3), 3.9–4.28 (m, 16 H, OCH_2CF_3 and OCH_2CH_3), 2.65 (dd, $^3J(PH) = 9.9$ Hz, $^3J(HH) = 5.1$ Hz) (6 H, NMe), 5.56 (br m, 2 H, NH), 6.96 (ddt, $^1J(P_xH) = 430.3$ Hz, $^3J(P_AH) = 21.5$ Hz, $^3J(P_MH) = 6.30$ Hz, 1 H, PH,). ^{31}P-$\{^1H\}$-NMR: $\delta = 123.7$ (dt, P_A), 147.3 (br t, P_M), 180.0 (dt, P_x); $^2J(P_AP_M) = 112.8$ Hz, $^2J(P_AP_X) = 230.4$ Hz, $^2J(P_XP_M) = 92.6$ Hz. Suitable single crystals for X-ray crystallography were grown from CH_2Cl_2/petrol (v/v; 1/1).

When the above reaction was carried out with a 1:2 stoichiometric ratio of anhydrous $CoCl_2$ and $\mathbf{L}^1$, both compounds **1** and **2** were formed. Crystallization of the crude product from CH_2Cl_2 at -15°C for 5 days gave crystals of **1** (light yellow) and **2** (dark violet) (m.p. > 120°C) which were separated by hand picking. The yield of complex **2** was very low (< 5%). Anal. Found: C, 20.59; H, 2.21; N, 2.30. $C_{29}H_{33}Co_2F_{36}N_3O_{14}P_6$ (1634.88). Anal. Calc.: C, 21.28; H, 2.01; N, 2.56. IR (Neat, cm^{-1}): ν(C=O) 1938 s. ^1H-NMR ($CDCl_3$, 25°C): $\delta = 2.78$ (brt, 9 H, NMe), 4.2 (br, 24 H, OCH_2CF_3).^{13}C-$\{^1H\}$-MR(acetone $-$ d_6, 25°C): $\delta = 35.3$ (s, 3 C, NMe), 67.31 (q, $^2J(CF) = 36.9$ Hz, 12 C, CH_2), 128.75 (q, $^1J(CF) = 277.0$ Hz, 12 C, CF_3), 215.4 (s, 2 C, CO). ^{31}P-$\{^1H\}$-NMR: $\delta = 152.8$ s.

4.4. Alternative method for $[Co_2(CO)_2\{\mu\text{-}MeN\{P(OCH_2CF_3)_2\}_2\}_3$ (2)

Granular zinc powder (0.28 g, 4.3 mmol) was suspended in a solution of anhydrous $CoCl_2$ (0.06 g, 0.43 mmol) in dry thf (50 ml) placed in a 100 ml round bottom flask fitted with an air condenser. The solution

Table 4
Details of the X-ray data collections and refinements for compounds **1**, **2** and **4**

Empirical formula	$C_{19}H_{31}CoF_{18}N_2O_{10}P_4$	$C_{29}H_{33}Co_2F_{36}N_3O_{14}P_6$	$C_{55}H_{54}Cl_3Co_2N_2O_{10}P_4$
Formula weight	972.27	1635.26	1251.09
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	8.744(2)	12.399(3)	12.372(6)
b (Å)	12.415(6)	12.777(2)	36.872(3)
c (Å)°	18.108(8)	19.550(2)	12.848(2)
α (°)	92.43(4)	80.177(10)	90.00
β (°)	93.50(3)	89.372(10)	96.24(2)
γ (°)	104.91(3)	70.011(10)	90.00
Volume (Å^3)	1892.6(13)	2864.1(9)	5826(3)
Z	2	2	4
$D_{calc.}$ (M gm^{-3})	1.706	1.896	1.426
μ(Mo–K$_\alpha$) (mm^{-1})	0.759	0.922	0.874
F(000)	976	1616	2572
Crystal size (mm)	$0.14\times0.18\times0.12$	$0.3\times0.375\times0.2$	$0.25\times0.35\times0.075$
Θ Ranges (°)	1.13–26.96	1.06–25.00	1.10–24.02
h, k, l ranges	−0 to 11	0 to 14	0 to 14
	−15 to 15	−14 to 15	0 to 43
	−23 to 23	−23 to 23	−15 to 15
Reflections collected	8904	10670	10844
Independent reflections	8224 [$R_{int}=0.0273$]	10074 [$R_{int}=0.0481$]	10261 [$R_{int}=0.0274$]
Data/restraints/parameters	8220/96/485	10067/117/805	10251/38/681
Goodness-of-fit on F^2	0.997	1.077	1.061
Final R indices [$I>2\sigma(I)$][a]	$R_1=0.0738$, $wR_2=0.2025$	$R_1=0.064$, $wR_2=0.1630$	$R_1=0.0806$, $wR_2=0.1852$
R indices (all data)[b]	$R_1=0.1050$, $wR_2=0.2434$	$R_1=0.1010$, $wR_2=0.1995$	$R_1=0.1589$, $wR_2=0.2511$
Largest difference Peak and hole (e Å^{-3})	1.145 and −0.817	0.809 and −0.653	1.019 and −0.704

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_c|$.

[b] $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ $w=1/[\sigma^2(F_o^2)+(0.0600\times p)^2+0.15\times p]$where $p=(\max(F_o^2,0)+2\times F_o^2)/3$.

was saturated with CO for 30 min at 25°C. To this solution was added $\mathbf{L^1}$ (0.63 g, 1.3 mmol) in thf (10 ml). The reaction mixture was stirred for 10 h while CO was bubbled through the solution. The color changed from blue to dark violet. The solvent was removed under reduced pressure; the residue was dissolved in diethyl ether (15 ml) and the solution filtered. The filtrate was cooled at −15°C for 4 days to obtain crystals of **2**. The crystals were washed with diethyl ether and dried in air. (Yield 53 mg; 15%).

4.5. Synthesis of [$Co_2(CO)_4\{\mu$-MeN$\{P(OPh)_2\}_2\}_2$] (3) and [Co(CO)$\{\eta^2$-MeN$\{P(OPh)_2\}_2\}_2$][$CoCl_3$(thf) (4)

Anhydrous $CoCl_2$ (0.070 g, 0.52 mmol), $\mathbf{L^2}$ (0.73 g, 1.58 mmol) and dry thf (60 ml) were taken in a 100 ml round bottom flask fitted with an air condenser. Zinc powder (0.38 g, 5.74 mmol) was added and CO was bubbled through the solution for 10 h with stirring at 25°C. The solvent was removed under reduced pressure; the residue was extracted with diethyl ether (20 ml) and the extract filtered. The filtrate was cooled at −15°C for 4 days to obtain black crystals of **3** and a small quantity of yellow precipitate of complex **4**. The two compounds were separated by hand-picking. The black crystals of **3** were washed with diethyl ether and dried in vacuum. A substantial quantity of complex **4** was present in the mother liquor. Addition of petrol (30 ml) resulted in its precipitation as an yellow solid. An analytically pure sample of **4** was obtained by recrystallizing it from acetone:petrol (1:1) at −15°C.

[$Co_2(CO)_4\{\mu$-MeN$\{P(OPh)_2\}_2\}_2$] (**3**). M.p. 110–115°C. 80 mg (25.5%). Anal. Found: C, 56.11; H, 3.85; N, 2.44. $C_{54}H_{46}Co_2N_2O_{12}P_4$ (1155.86). Anal. Calc.: C, 56.06; H, 3.97; N, 2.42. IR (Nujol, cm^{-1}) ν(C=O) 1940 s, 1978 s. ^{1}H-NMR (CDCl$_3$, 25°C): $\delta=2.6$ (q, 6 H, NMe), 7.0–7.3 (m, 40 H, Ph). ^{31}P-{^{1}H}-NMR: $\delta=$ 150.5 (s).

[Co(CO)$\{\eta^2$-MeN$\{P(OPh)_2\}_2\}_2$][$CoCl_3$(thf)] (**4**): m.p. > 120°C. 210 mg (63%). Anal. Found: C, 50.26; H, 3.89; N, 2.29. $C_{55}H_{54}Cl_3Co_2N_2O_{10}P_4$ (1250.21). Anal. Calc.: C, 52.79; H. 4.31; N, 2.23. IR (Nujol, cm^{-1}): ν(C=O) 1998 s. ^{1}H-NMR (CDCl$_3$, 25°C): $\delta=2.5$ (q, 6 H, NMe), 1.85 and 3.8 (m, 8 H, thf), 7.0–7.4 (m, 40 H, Ph). ^{31}P-{^{1}H}-NMR: $\delta=109.5$ (s).

4.6. X-ray crystallography

The diffraction data for complexes **1**, **2** and **4** were collected using a Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda=$ 0.7107 Å). Details of data collection and refinements are given in Table 4. The structures were solved by conventional Patterson method using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93 [29]. All hydrogen atoms were included in the calculated positions [C–H = 0.96–0.97 Å] with a fixed isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically except disordered atoms. Absorption correction was not applied as μ values were low.

In the structures **1** and **2**, disorder of two of the CF_3 carbon atoms and the fluorine atoms attached to them was observed. In structure **4**, disorder of the phenyl and furan ring carbon atoms was observed. The refinements of these atoms were carried out using SADI option available in SHELXL-93. The site occupancy factors are given in the Supplementary Material.

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