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Synthesis and molecular structure of a novel binuclear cobalt carbonyl complex with mixed valence $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$ (Ph_2Ppy = diphenylphosphinopyridine)

Zheng-Zhi Zhang *, **Hsu-Kun Wang, Zhen Xi,**

Institute of Elementoorganic Chemistry, Nankai University, Tianjin (China)

Xin-Kan Yao and Ru-Ji Wang

Centre of Measurement and Computation, Nankai University, Tianjin (China)

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Abstract

Under mild conditions reaction of $(Ph_2Ppy)_2CoCl_2$ or Ph_2Ppy (Ph_2Ppy = diphenylphosphinopyridine) and $CoCl_2 \cdot 6H_2O$ with CO in the presence of zinc powder gave a novel binuclear cobalt carbonyl complex with mixed valence $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$. The molecular structure of this compound has been determined by X-ray diffraction. The compound crystallized in the monoclinic space group C_c (No. 9) with the cell parameters *a* 17.327(3), *b* 11.260(2), *c* 18.212(3) Å and β 109.13(1)°. Full matrix least-squares refinement yielded $R = 0.034$. The formation mechanism of this compound is discussed.

Introduction

The study on binuclear transition-metal complexes with bidentate ligands, particularly bis(diphenylphosphino)methane (dppm, $P\frown P$) and diphenylphosphinopyridine (Ph_2Ppy, $P\frown N$), is a considerably interesting topic in organometallic chemistry and plenty of work has been reported [1–3]. The incorporation of two or more bridging bidentate phosphine ligands into a cobalt dimer is not an easy task [4], although a few preparative methods have been presented; for example, Hanson has prepared $Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L\text{–}L)(\mu\text{-}dppm)(\mu\text{-}I)I$ (L–L = dppm, dmpm ($Me_2PCH_2PMe_2$)) from $Co_2(CO)_6(L\text{–}L)$ by an oxidative trapping reaction [4] and Karsch has obtained $[(PMe_3)(\mu\text{-}dmpm)Co]_2PMe_2$ by the reaction of the complex $[(PMe_3)(dmpm)_2Co]X$ with dmpm [5].

In respect to the interest in this field we now describe a very simple synthetic method for obtaining the first novel binuclear cobalt carbonyl complex with mixed valence, $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO(CO)Cl$, and its molecular structure.

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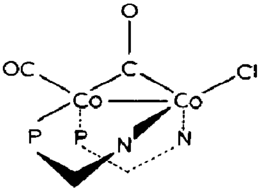
Results and discussion

Synthesis

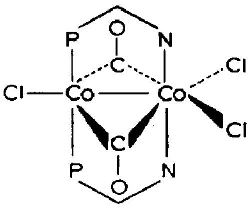
The method previously developed by us [6] was used; under mild conditions (1 atm, room temperature) the reaction of $(Ph_2Ppy)_2CoCl_2$ or $CoCl_2\cdot 6H_2O$ and Ph_2Ppy with carbon monoxide in the presence of zinc powder gave a cobalt dimer with mixed valence, $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$ (**1**), according to eq. 1.



(1)

$$\left.\begin{array}{r}(Ph_2Ppy)_2CoCl\\ CoCl_2\cdot 6H_2O + Ph_2Ppy\end{array}\right] \xrightarrow[\text{1 atm, r.t.}]{\text{CO, THF}} \mathbf{1} \tag{1}$$

We found that this reaction could be promoted by a very small amount of water or alcohol and that the reaction was very slow in absolute tetrahydrofuran. From this reaction we separated an intermediate, $Co^ICo^{II}(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)_2Cl_3$ (**2**) and determined its molecular structure (Jones prepared a $\mu\text{-}R_2P$ bridging $Co^I\text{-}Co^{II}$ complex [7]). This intermediate is also a compound with mixed valence [8]. Besides, we obtained an intermediate, $(Ph_3P)_2Co(CO)_2Cl$ (**3**), in the preparation of the polynuclear complex $(Ph_3P)_mCo_n(CO)_x$ from $(Ph_3P)_2CoCl_2$ using the same method [6b]. This intermediate **3** exhibits trigonal bipyramidal configuration [9]. Also the formation of many compounds with skeleton **4** was seen by Balch and us [2,3] as a process of oxidative addition of a high valence metal complex, such as $(Ph_2Ppy)_2MX_2$, to a low valence one like ML_n or ML_nX. Based on these observations and considerations, we suggest that complex **1** is formed by a reduction-oxidative addition-reduction mechanism as shown in eq. 2.



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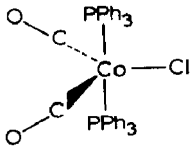

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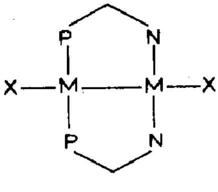


(4)

$$(Ph_2Ppy)_2CoCl_2 \xrightarrow[ZnCl_2]{Zn,\ CO} (Ph_2Ppy)_2Co(CO)_2Cl$$

$$\xrightarrow[Ph_2Ppy]{(Ph_2Ppy)_2CoCl_2} \mathbf{2} \xrightarrow[ZnCl_2,\ CO]{Zn} \mathbf{1} \tag{2}$$

If complex $(Ph_2Ppy)_2CoCl_2$ is partially reduced to Co^+ species two molecules of CO are simultaneously coordinated and the first intermediate, $(Ph_2Ppy)_2Co(CO)_2Cl$, with trigonal bipyramidal configuration is formed. Because of the loss of positive charge, the coordinating ability of Co^+ species toward Ph_2Ppy ligand becomes weaker and two $\mathrm{Ph_2Ppy}$ ligands to $\mathrm{Co^+}$ are lost when $\mathrm{(Ph_2Ppy)_2CoCl_2}$ oxidatively adds to $\mathrm{(Ph_2Pph)_2Co(CO)_2Cl}$. During the formation of the Co–Co bond these two cobalt atoms mutually change the valence states and four μ-bridging bonds are formed giving the second intermediate, $\mathrm{Co^ICo^{II}}(\mu\text{-}\mathrm{Ph_2Ppy})_2(\mu\text{-}\mathrm{CO})_2\mathrm{Cl_3}$ (**2**). The two cobalt atoms in **2** and the P and N atoms in the two $\mathrm{Ph_2Ppy}$ ligands lie in one plane forming an eight-membered heterocycle. Two cobalt atoms, three chlorine atoms and two carbonyl groups lie in another plane. These two planes are perpendicular to each other. $\mathrm{Co^+}$ and $\mathrm{Co^{2+}}$ exhibit five-coordinate trigonal bipyramidal and six-coordinate octahedral configuration, respectively. Further reduction takes place in the presence of zinc powder and the $\mathrm{Co^+}$–$\mathrm{Co^{2+}}$ species is reduced to the $\mathrm{Co^0}$–$\mathrm{Co^I}$ complex **1**. Because of the necessity of a low valence state the skeleton of complex **1** has considerably changed from that of intermediate **2**. Now, both $\mathrm{Co^0}$ and $\mathrm{Co^I}$ have tetrahedral configuration. The formation mechanism and molecular skeleton structure of complex **1** are similar to those of $\mathrm{Ni}(\mu\text{-dppm})_2(\mu\text{-CO})(\mathrm{CO})_2$ (**5**) [10].

Complex **1** is an orange solid, readily soluble in $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$ and THF and very stable to air and moisture. The complex is paramagnetic with a temperature-independent magnetic moment μ_{eff} of 1.1 μ_{B}, which has a delocalized unpaired electron.

Description of molecular structure

The molecular structure of complex **1** is shown in Fig. 1. The two cobalt atoms, two carbonyls and one chlorine atom basically lie in one plane (Plane 1). The two

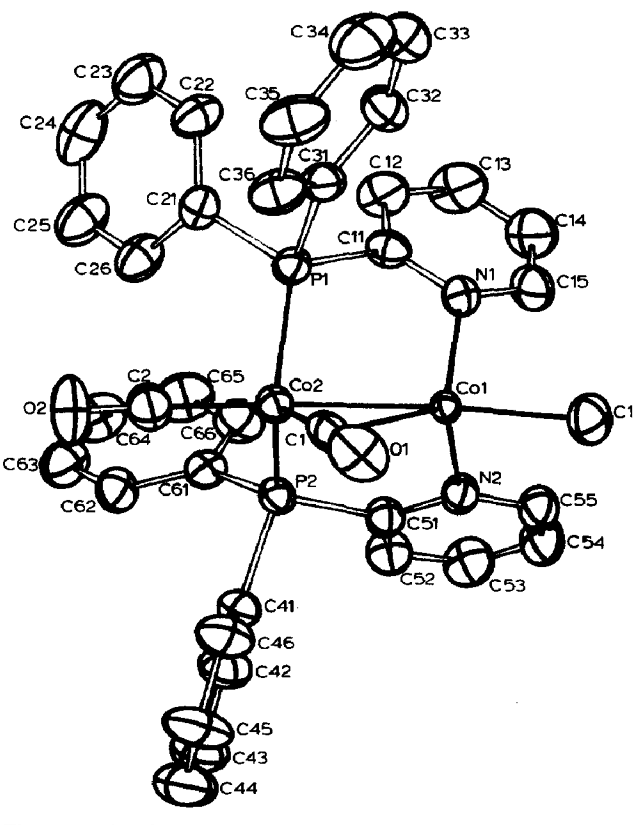


Fig. 1. Molecular structure of complex 1.

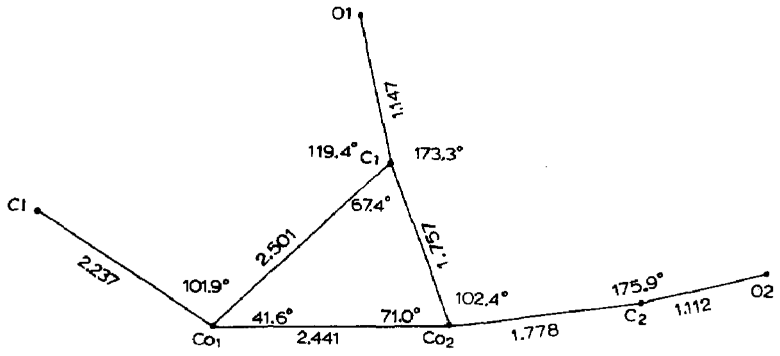
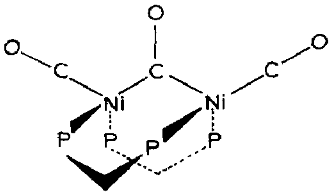
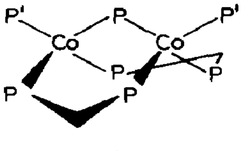


Fig. 2. Atomic arrangement in plane 1.

cobalt atoms and P(1), C(11), N(1) or P(2), C(51), N(2) lie in two other planes (Plane 2 and Plane 3), respectively. The dihedral angles between Plane 1 and Plane 2 or 3 are 127.1° and −131.0°, respectively. Therefore, the molecule is nearly symmetric with respect to Plane 1. Both cobalt atoms possess pseudotetrahedral configurations. The atomic arrangement in Plane 1 is shown in Fig. 2. The distances of the bridging carbonyl to Co(1) and Co(2) are different (2.501 and 1.757 Å) and this may be related to the steric repulsive interaction of a chlorine atom or the semibridging character of carbonyl to Co(1). The Co–Co distance is 2.441 Å, which is much shorter than the Co–Co bond (2.685 Å) in intermediate **2** [8]. The distance in complex **1** is also shorter than in Karsch's “Co$_2^+$” complex (6) (2.603Å) [5], but similar to Co–Co distances in “Co$_2^{2+}$” complexes **7** (2.43 Å) [11] and **8** (2.4 Å) [12], which are considered to be double bond compounds). The molecular of **1** has

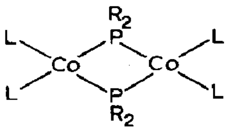


(5)



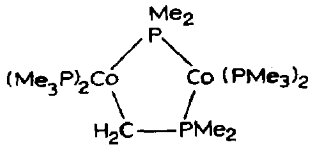
P=PMe$_2$, P'=PMe$_3$

(6)



L=Co, PMe$_3$; R=PMe$_2$

(7)



(8)

W-frame structure. In this type of structure two central six-membered rings usually have chair–boat (as complex **6**) or chair–chair (as complex **5**) configurations, but both six-membered rings in complex **1** (Co(1)–C(1)–Co(2)–P(1)–C(11)–N(1) and Co(1)–C(1)–Co(2)–P(2)–C(51)–N(2)) have envelope conformations and this can be attributed to the rigidity of the Ph$_2$Ppy ligand.

Experimental

Synthesis

The infrared spectrum was recorded on a WDF-14 infrared spectrometer. The electronic spectrum was recorded on a Shimadzu UV-spectrometer. Solid-state susceptibility measurements were with a PAR-155 magnetometer between 1.5–300 K.

Preparation of $(Ph_2Ppy)_2CoCl_2$. A solution of 1.2 g (5.0 mmol) of $CoCl_2 \cdot 6H_2O$ in absolute ethanol (20 ml) under nitrogen was added to a solution of 2.63 g (10.0 mmol) of Ph_2Ppy in absolute ethanol (20 ml). After 0.5 h stirring the volume of the solution was reduced to 20 ml, and a blue crystal precipitated overnight at room temperature. The precipitate was filtered, then washed with 3 × 10 ml of acetone and dried in vacuum, yield 2.7 g (82%), m.p. 192–193 °C (dec.). Elemental analysis: Found: C, 61.87; H, 4.22; N, 4.71. $C_{34}H_{28}CoCl_2N_2P_2$ calcd.: C, 62.20; H, 4.27; N, 4.27%.

Preparation of $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$. (A) A flask containing 1.0 g (1.5 mmol) of $(Ph_2Ppy)_2CoCl_2$ and 40 ml of absolute tetrahydrofuran was purged with nitrogen, then 1.0 g of zinc powder was added and carbon monoxide bubbled into the mixture with stirring for 7 h at room temperature. The solution changed in color from green to orange. After reaction had stopped the mixture was filtered and the volume of the solution was reduced to 15 ml, then 20 ml of absolute methanol were added and the volume of the solution was further reduced to 15 ml. An orange precipitate was obtained. After filtration the precipitate was crystallized from CH_2Cl_2/CH_3OH, yield 0.1 g (21%), m.p. 201–202 °C (dec.). Elemental analysis: Found: C, 58.33; H, 3.76; N, 4.02. $C_{32}H_{28}Co_2ClN_2P_2$ calcd.: C, 58.74; H, 3.81; N, 3.01%. IR (ν(CO), KBr disc): 1930, 1855 cm^{-1}. UV (CH_2Cl_2): 300 nm ($\sigma \rightarrow \sigma^*$).

(B) A flask containing 0.6 g (2.5 mmol) of $CoCl_2 \cdot 6H_2O$, 1.3 g (5.0 mmol) of Ph_2Ppy and 40 ml of tetrahydrofuran was purged with nitrogen and 1.0 g of zinc

Table 1

Crystal and structural data for $Co^0Co^I(\mu\text{-}Ph_2Pph)_2(\mu\text{-}CO)(CO)Cl$

formula	$C_{36}H_{28}Co_2ClN_2O_2P_2$
MW	735.9
space group	monoclinic; C_c (No. 9)
cell dimens	
a(Å)	17.327(3)
b(Å)	11.260(2)
c(Å)	18.212(3)
β(deg)	109.13(1)
V(Å^3)	1667.8
Z	4
d_{calcd} (g cm^{-3})	1.46
radiation	Mo-K_α
scan mode	$\omega-2\theta$
no. of unique reflections	3329
no. of obsd reflections	2917
R	0.034
R_w	0.043

powder was added. Carbon monoxide was bubbled into the mixture at room temperature with stirring for 4 h. The reaction mixture was treated as in method A, yield 0.31 g (34%).

Table 2

Fractional atomic coordinates and thermal factors for $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$

Atom	x	y	z	$B_{eq.}$ (Å^2) [a]
Co(1)	0.500	0.04910(7)	0.694	1.58(1)
Co(2)	0.36622(6)	0.14364(8)	0.66048(6)	2.17(2)
P(1)	0.4385(1)	0.2965(2)	0.7168(1)	2.41(3)
P(2)	0.3620(1)	0.1126(2)	0.5410(1)	2.36(3)
Cl	0.5800(1)	−0.0892(2)	0.7695(1)	3.76(4)
C(11)	0.5428(4)	0.3063(7)	0.7075(4)	2.8(1)
C(12)	0.5814(5)	0.4131(8)	0.6979(5)	4.1(2)
C(13)	0.6621(5)	0.4041(9)	0.6960(6)	5.1(2)
C(14)	0.6990(5)	0.294(1)	0.7020(6)	4.7(2)
C(15)	0.6551(4)	0.1938(8)	0.7087(5)	3.7(2)
N(1)	0.5780(3)	0.2009(6)	0.7109(4)	2.9(1)
C(21)	0.4025(4)	0.4509(7)	0.6902(4)	3.1(2)
C(22)	0.4336(6)	0.5451(8)	0.7423(6)	4.4(2)
C(23)	0.4155(6)	0.6608(8)	0.7164(7)	5.3(3)
C(24)	0.3633(6)	0.6824(9)	0.6371(6)	5.8(2)
C(25)	0.3297(6)	0.5871(9)	0.5876(6)	4.9(2)
C(26)	0.3499(5)	0.4726(8)	0.6134(5)	4.0(2)
C(31)	0.4639(4)	0.2990(7)	0.8233(4)	2.8(2)
C(32)	0.5383(5)	0.3425(8)	0.8738(5)	3.7(2)
C(33)	0.5521(6)	0.3476(9)	0.9548(5)	4.9(2)
C(34)	0.4923(6)	0.3067(9)	0.9862(5)	5.0(2)
C(35)	0.4176(6)	0.2648(9)	0.9342(5)	4.6(2)
C(36)	0.4033(5)	0.2589(8)	0.8535(4)	3.6(2)
C(41)	0.2848(4)	0.0033(7)	0.4864(4)	2.9(2)
C(42)	0.2657(5)	−0.0164(9)	0.4052(5)	4.2(2)
C(43)	0.2091(6)	−0.1024(9)	0.3675(5)	5.0(2)
C(44)	0.1700(6)	−0.1704(9)	0.4082(6)	5.6(3)
C(45)	0.1881(6)	−0.1522(9)	0.4900(6)	5.3(2)
C(46)	0.2451(5)	−0.0633(8)	0.5280(5)	3.9(2)
C(51)	0.4547(4)	0.0534(7)	0.4508(4)	2.8(2)
C(52)	0.4676(5)	0.0548(8)	0.4508(4)	3.6(2)
C(53)	0.5406(5)	0.008(1)	0.4450(5)	4.6(2)
C(54)	0.5962(5)	−0.0400(9)	0.5110(5)	4.2(2)
C(55)	0.5794(5)	−0.0410(8)	0.5789(5)	3.5(2)
N(2)	0.5111(3)	0.0067(6)	0.5851(3)	2.8(1)
C(61)	0.3372(4)	0.2408(7)	0.4753(4)	2.7(1)
C(62)	0.2557(5)	0.2735(8)	0.4399(5)	3.6(2)
C(63)	0.2360(6)	0.3780(9)	0.3961(5)	4.6(2)
C(64)	0.2954(6)	0.4529(9)	0.3876(5)	4.9(2)
C(65)	0.3789(7)	0.4209(9)	0.4221(6)	5.4(2)
C(66)	0.4002(5)	0.3160(8)	0.4667(5)	4.1(2)
C(1)	0.3698(4)	0.0234(7)	0.7230(4)	3.0(2)
C(2)	0.2652(5)	0.1981(8)	0.6418(5)	3.5(2)
O(1)	0.3646(3)	−0.0519(5)	0.7635(3)	4.0(1)
O(2)	0.2016(3)	0.2275(7)	0.6331(5)	6.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)^*B_{1,2}+ac(\cos\beta)\times B_{1,3}+bc(\cos\alpha)\times B_{2,3}]$.

X-ray diffraction analysis

A single crystal was grown by slow diffusion of methanol into a dichloromethane solution of $\mathrm{Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl}$. The intensity data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo-K_α radiation. From the systematic absence of hkl: $h+k=2n+1$, $h0l$: $l=2n+1$ and subsequent least-squares refinement the space group C_c was determined. A total of 3329 unique reflections in the range of $2° < \theta < 25°$ were collected using the ω–2θ scan technique, from which 2917 reflections with $I > 3\sigma(I)$ were considered to be observed. LP and absorption corrections were applied. The structure was solved by direct method (MULTAN 82). Two cobalt atoms were located from the E-map. The remaining non-hydrogen atoms were found in the succeeding difference Fourier syntheses. The refinement was converged with unweighted and weighted R factors of 0.034 and 0.043, respectively, using the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The highest peak on the final difference Fourier map is 0.7 e/Å^3. All calculations were performed on a PDP 11/44 computer using SDP-PLUS program system. The crystal structure data and processing parameters are given in Table 1, positional and thermal parameters for non-hydrogen atoms in Table 2, bond distances and angles in Tables 3 and 4, respectively. The least squares planes and deviation of atoms are listed in Table 5.

Table 3

Bond distances (Å) in $\mathrm{Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl}$ [a]

Co(1)–Co(2)	2.441(2)	C(24)–C(25)	1.40(1)
Co(1)–Cl	2.238(3)	C(25)–C(26)	1.38(1)
Co(1)–N(1)	2.137(7)	C(31)–C(32)	1.40(1)
Co(1)–N(2)	2.100(6)	C(31)–C(36)	1.41(1)
Co(1)–C(1)	2.501(8)	C(32)–C(33)	1.42(1)
Co(2)–P(1)	2.177(3)	C(33)–C(34)	1.41(2)
Co(2)–P(2)	2.182(2)	C(34)–C(35)	1.41(1)
Co(2)–C(1)	1.757(9)	C(35)–C(36)	1.41(1)
Co(2)–C(2)	1.778(8)	C(41)–C(42)	1.42(1)
P(1)–C(11)	1.873(8)	C(41)–C(46)	1.40(1)
P(1)–C(21)	1.857(9)	C(42)–C(43)	1.39(1)
P(1)–C(31)	1.844(8)	C(43)–C(44)	1.39(2)
P(2)–C(41)	1.850(7)	C(44)–C(45)	1.43(2)
P(2)–C(51)	1.867(8)	C(45)–C(46)	1.42(1)
P(2)–C(61)	1.833(8)	C(51)–C(52)	1.40(1)
C(11)–C(12)	1.41(1)	C(51)–N(2)	1.339(8)
C(11)–N(1)	1.33(1)	C(52)–C(53)	1.41(1)
C(12)–C(13)	1.41(1)	C(53)–C(54)	1.38(1)
C(13)–C(14)	1.39(1)	C(54)–C(55)	1.36(1)
C(14)–C(15)	1.39(1)	C(55)–N(2)	1.34(2)
C(15)–N(1)	1.35(2)	C(61)–C(62)	1.40(2)
C(21)–C(22)	1.41(1)	C(61)–C(66)	1.43(1)
C(21)–C(26)	1.42(2)	C(62)–C(63)	1.41(1)
C(22)–C(23)	1.39(1)	C(63)–C(64)	1.38(2)
C(23)–C(24)	1.45(1)	C(64)–C(65)	1.42(1)
C(65)–C(66)	1.41(1)	C(2)–O(2)	1.11(1)
C(1)–O(1)	1.15(2)		

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

Table 4

Bond angles (deg.) in $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$ [a]

Co(2)–Co(1)–Cl	143.33(7)	C(21)–P(1)–C(31)	101.8(4)
Co(2)–Co(1)–N(1)	101.0(2)	Co(2)–P(2)–C(41)	115.2(3)
Co(2)–Co(1)–N(2)	103.8(1)	Co(2)–P(2)–C(51)	119.1(2)
Co(2)–Co(1)–C(1)	41.6(2)	Co(2)–P(2)–C(61)	116.7(3)
Cl–Co(1)–N(1)	103.4(2)	C(41)–P(2)–C(51)	100.4(4)
Cl–Co(1)–N(2)	101.2(2)	C(41)–P(2)–C(61)	101.5(3)
Cl–Co(1)–C(1)	102.0(2)	C(51)–P(2)–C(61)	101.3(4)
N(1)–Co(1)–N(2)	94.3(2)	P(1)–C(11)–C(12)	124.8(6)
N(1)–Co(1)–C(1)	129.2(3)	P(1)–C(11)–N(1)	112.7(5)
N(2)–Co(1)–C(1)	122.8(2)	C(12)–C(11)–N(1)	122.5(7)
Co(1)–Co(2)–P(1)	82.85(7)	C(11)–C(12)–C(13)	117.0(8)
Co(1)–Co(2)–P(2)	83.96(7)	C(12)–C(13)–C(14)	120 (1)
Co(1)–Co(2)–C(1)	71.0(2)	C(13)–C(14)–C(15)	118.9(8)
Co(1)–Co(2)–C(2)	173.3(3)	C(14)–C(15)–N(1)	122.1(9)
P(1)–Co(2)–P(2)	115.0(7)	Co(1)–N(1)–C(11)	116.7(5)
P(1)–Co(2)–C(1)	114.3(2)	Co(1)–N(1)–C(15)	122.1(5)
P(1)–Co(2)–C(2)	101.3(3)	C(11)–N(1)–C(15)	119.6(7)
P(2)–Co(2)–C(1)	120.4(3)	P(1)–C(21)–C(22)	120.6(5)
P(2)–Co(2)–C(2)	99.0(3)	P(1)–C(21)–C(26)	118.1(6)
C(1)–Co(2)–C(2)	102.4(4)	C(22)–C(21)–C(26)	121.1(7)
Co(2)–P(1)–C(11)	115.3(2)	C(21)–C(22)–C(23)	119.0(9)
Co(2)–P(1)–C(21)	121.7(2)	C(22)–C(23)–C(24)	119.6(9)
Co(2)–P(1)–C(31)	114.2(3)	C(23)–C(24)–C(25)	120.2(9)
C(11)–P(1)–C(21)	100.0(4)	C(24)–C(25)–C(26)	119.6(8)
C(11)–P(1)–C(31)	100.9(3)	C(21)–C(26)–C(25)	120.4(8)
P(1)–C(31)–C(32)	123.1(7)	C(51)–C(52)–C(53)	119.3(7)
P(1)–C(31)–C(36)	117.0(5)	C(52)–C(53)–C(54)	118.0(9)
C(32)–C(31)–C(36)	119.8(7)	C(53)–C(54)–C(55)	119.9(8)
C(31)–C(32)–C(33)	120.1(9)	C(54)–C(55)–N(2)	122.2(7)
C(32)–C(33)–C(34)	120.7(8)	Co(1)–N(2)–C(51)	116.2(5)
C(33)–C(34)–C(35)	118.1(9)	Co(1)–N(2)–C(55)	121.8(4)
C(34)–C(35)–C(36)	122 (1)	C(51)–N(2)–C(55)	120.4(7)
C(31)–C(36)–C(35)	119.5(7)	P(2)–C(61)–C(62)	119.6(6)
P(2)–C(41)–C(42)	122.9(7)	P(2)–C(61)–C(66)	120.9(5)
P(2)–C(41)–C(46)	117.6(6)	C(62)–C(61)–C(66)	119.1(7)
C(42)–C(41)–C(46)	119.5(7)	C(61)–C(62)–C(63)	120.4(8)
C(41)–C(42)–C(43)	121 (1)	C(62)–C(63)–C(64)	121.8(8)
C(42)–C(43)–C(44)	121 (1)	C(63)–C(64)–C(65)	119.0(9)
C(43)–C(44)–C(45)	119.9(9)	C(64)–C(65)–C(66)	121 (1)
C(44)–C(45)–C(46)	119 (1)	C(61)–C(66)–C(65)	119.6(8)
C(41)–C(46)–C(45)	120.2(8)	Co(1)–C(1)–CO(2)	67.4(3)
P(2)–C(51)–C(52)	124.9(5)	Co(1)–C(1)–O(1)	119.4(5)
P(2)–C(51)–N(2)	114.9(6)	Co(2)–C(1)–O(1)	173.3(7)
C(52)–C(51)–N(2)	120.2(7)	Co(2)–C(2)–O(2)	175.9(8)

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

Table 5

Least squares planes and deviation of atoms for $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$

Plane I		Plane II		Plane III	
Co(1)	0.0602	Co(1)	−0.1559	Co(1)	−0.0209
Co(2)	−0.0020	Co(2)	0.2259	Co(2)	−0.0173
Cl	−0.0637	P(1)	−0.2889	P(2)	0.0592
C(1)	0.0191	C(11)	0.1869	C(51)	−0.0988
C(2)	−0.0123	N(1)	0.0319	N(2)	0.0778
O(1)	0.0235				
O(2)	−0.0249				

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