

METAL-ORGANIC COMPOUNDS

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Dichloro[ferrocene-1,1'-diylbis(diphenylphosphine-*P*)]cobalt(II)

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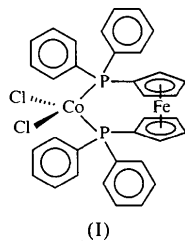
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Abstract

The crystal structure of the title compound, $[\text{CoCl}_2(\text{C}_{34}\text{H}_{28}\text{FeP}_2)]$, has been determined. The molecule is a discrete monomeric complex which has two chloride ions and a *cisoid*-arranged 1,1'-bis(diphenylphosphino)ferrocene molecule as ligands. The geometry about the Co^{II} atom is distorted tetrahedral.

Comment

Due to the versatile bonding modes and chemical reactivities of transition metal complexes of 1,1'-bis(diphenylphosphino)ferrocene (dppf), several efforts have been made to prepare and study metal complexes of this ligand (Hayashi & Kumata, 1982; Corain *et al.*, 1989). In earlier studies, a series of simple four-coordinate metal complexes of dppf, $[\text{MX}_2(\text{dppf})]$, where *M* is Co, Ni, Pd, Pt, Zn or Cd, and *X* is Cl or Br, was prepared. However, only five of these complexes have been crystallographically studied. We describe here the crystal structure of the title compound, $[\text{CoCl}_2(\text{dppf})]$, (I).



The complexes $[\text{PdCl}_2(\text{dppf})]$ (Hayashi *et al.*, 1984) and $[\text{PtCl}_2(\text{dppf})]$ (Clemente *et al.*, 1986) both have square-planar geometry, while $[\text{NiBr}_2(\text{dppf})]$ (Butler *et al.*, 1985), $[\text{NiCl}_2(\text{dppf})]$ (Casellato *et al.*, 1988) and $[\text{HgCl}_2(\text{dppf})]$ (McGinley *et al.*, 1998) are distorted tetrahedral. The main differences between square-planar and tetrahedral arrangements are the staggered geometry of the two Cp (cyclopentadienyl) rings and the smaller P—M—P angles in square-planar complexes. Strictly

speaking, however, these values are delicately dependent upon the kinds of metals and halides present in the complexes.

The molecular structure of (I) is very similar to those of $[\text{NiBr}_2(\text{dppf})]$ and $[\text{NiCl}_2(\text{dppf})]$. The geometry about the Co^{II} atom is best described as distorted tetrahedral. The Cl1—Co—Cl2 and Cl2—Co—P2 angles [$115.92(4)$ and $113.05(4)^\circ$, respectively] deviate from the ideal tetrahedral angle of 109.75° . The P1—Co—P2 and Cl1—Co—P2 angles [$107.87(3)$ and $98.89(4)^\circ$, respectively] are smaller than the ideal value. This distortion of the P_2Cl_2 coordination sphere may be attributed to the dppf ligand, and this is closely related to the geometry of the two Cp rings of dppf. Moreover, the position of the ferrocenyl moiety is not symmetric relative to the two Cl atoms; the two different values of the Fe—P1—Co—Cl1 [$73.49(4)^\circ$] and Fe—P1—Co—Cl2 [$-157.40(4)^\circ$] torsion angles clearly demonstrate the leaning of the ferrocenyl moiety towards the Cl1 atom rather than the Cl2 atom.

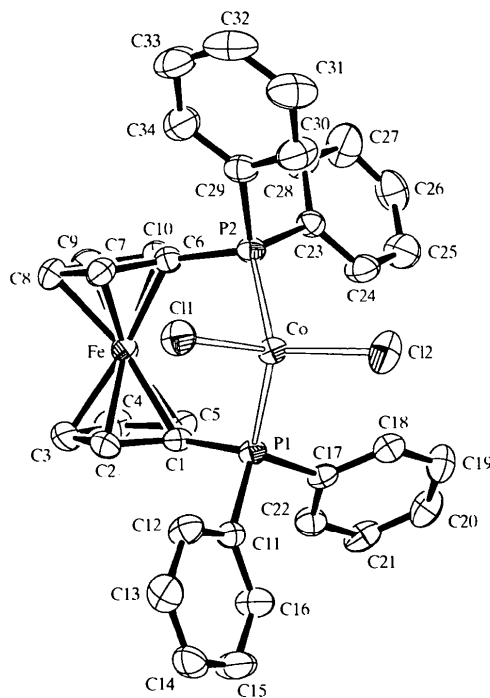


Fig. 1. A molecular view of compound (I). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms have been omitted for clarity.

Previous ^{57}Fe Mössbauer spectroscopic data have shown that there is an approximate linear correlation between the isomer shift (δ) and the quadruple splitting (Δ) (Houlton *et al.*, 1990; Corain *et al.*, 1989). Moreover, there is a linear correlation between the iron-

to-ring distances and the observed change in δ and Δ , with decreases in both with decreasing distance. Thus, the ring tilt can change these distances and the resultant δ and Δ values. Compared with the data given in the previously cited work, (I) shows almost the same δ and Δ values as [NiCl₂(dppf)] or [HgCl₂(dppf)], in which the two Cp rings are tilted by 4.5 and 2.8 (4)^o, respectively. In (I), the Cp rings are tilted by 6.1 (3)^o. The inter-ring spacing in (I) increases gradually from the far side of the rings towards the phosphine substituent. The respective distances from Fe to the two Cp rings are 1.6597 (18) and 1.6607 (16) Å. The two Cp rings of (I) are rotated by only 9.55 (2)^o from an exact eclipsed conformation, based on the P1—C1—C6—P2 torsion angle. Therefore, compound (I) possesses two eclipsed Cp rings. This is in contrast to [CoCl₂(L)], where L represents 1,1'-bis(diphenylphosphino)-3,3'-bis(trimethylsilyl)ferrocene (Ahmet *et al.*, 1993), despite the fact that (I) shows comparable Co—P and Co—Cl distances to those in [CoCl₂(L)]. Thus, from this consideration, the 3,3'-substituents of the dppf ligand in [CoCl₂(L)] do affect the coordination environment of the dppf ligand. In [HgCl₂(dppf)], the large Hg^{II} ion enables the Cp rings of dppf to be rotated by -37.8 (3)^o, which is greater than in (I) or [NiCl₂(dppf)], to accommodate a tetrahedral geometry, whereas the smaller Co^{II} and Ni^{II} ions can adopt a tetrahedral structure with an almost eclipsed conformation of the two Cp rings.

Experimental

The title compound was prepared using an adaptation of the literature method of Hermes & Girolami (1988) for the preparation of [CoCl₂(dippe)] [dippe is 1,2-bis(diisopropylphosphino)ethane]. Recrystallization of the product from CH₂Cl₂ by slow evaporation produced X-ray quality dark-green crystals of (I).

Crystal data

[CoCl₂(C₃₄H₂₈FeP₂)]

$M_r = 684.18$

Triclinic

$P\bar{1}$

$a = 9.6615 (10) \text{ \AA}$

$b = 9.7829 (10) \text{ \AA}$

$c = 18.4857 (10) \text{ \AA}$

$\alpha = 101.784 (10)^\circ$

$\beta = 96.993 (10)^\circ$

$\gamma = 115.568 (10)^\circ$

$V = 1498.7 (2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.516 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9.32\text{--}12.17^\circ$

$\mu = 1.346 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block

$0.3 \times 0.2 \times 0.2 \text{ mm}$

Dark green

Data collection

Enraf-Nonius CAD-4

MACH3 diffractometer

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 24.97^\circ$

$2\theta/\omega$ scans

Absorption correction: none

5617 measured reflections

5273 independent reflections

3787 reflections with

$I > 2\sigma(I)$

$h = 0 \rightarrow 11$

$k = -11 \rightarrow 10$

$l = -21 \rightarrow 21$

3 standard reflections

frequency: 60 min

intensity decay: negligible

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.095$

$S = 1.034$

5273 reflections

352 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.6270P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.025$

$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Co—C11	2.2358 (10)	Fe—C6	2.054 (3)
Co—C12	2.2184 (11)	Fe—C7	2.039 (4)
Co—P1	2.3699 (10)	Fe—C8	2.043 (4)
Co—P2	2.3570 (10)	Fe—C9	2.051 (4)
Fe—C1	2.074 (3)	Fe—C10	2.0584 (9)
Fe—C2	2.041 (4)	P1—C11	1.826 (4)
Fe—C3	2.043 (4)	P1—C17	1.817 (3)
Fe—C4	2.043 (4)	P2—C23	1.810 (3)
Fe—C5	2.049 (4)	P2—C29	1.829 (4)
Cl2—Co—C11	115.92 (4)	Cl2—Co—P1	110.83 (4)
Cl1—Co—P1	109.50 (4)	Cl2—Co—P2	113.05 (4)
Cl1—Co—P2	98.89 (4)	P2—Co—P1	107.87 (3)

Except for some residual electron density in the region of Fe (highest peak 0.43 e \AA^{-3} at 0.98 \AA from Fe), the final difference map showed no significant features.

Data collection: *CAD-4-PC Software* (Enraf-Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1001). Services for accessing these data are described at the back of the journal.

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***trans*-Carbonyl[η^2 -dihydrobis(pyrazol-1-yl-*N*²)borato]hydridobis(triphenylarsine)-ruthenium(II) monohydrate**

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Abstract

The molecule of the title compound, [RuH(C₆H₈BN₄)-(C₁₈H₁₅As)₂(CO)]·H₂O, is a discrete monomeric complex which has the hydride, carbonyl and dihydrobis(pyrazol-1-yl)borate ligands in equatorial positions, and two *trans*-positioned AsPh₃ ligands. The geometry around the Ru^{II} atom is distorted octahedral. In addition to the water dimer formed by strong intermolecular hydrogen bonds, two possible weak intramolecular hydrogen bonds have been observed within the complex.

Comment

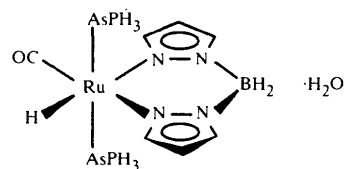
A variety of poly(pyrazol-1-yl)borates have been prepared and used in transition metal or main-group chemistry for three decades because of their versatile electronic and steric properties (Trofimenko, 1993). Most

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effort has been focused on the possible tridentate ligands [HB(pz*)₃][−] (pz* is pyrazol-1-yl with various substituents at the 3, 4 or 5 positions). However, the study of Ru^{II} complexes with these ligands has been initiated only very recently. Furthermore, compounds of Ru^{II} with bidentate dihydrobis(pyrazol-1-yl)borates are very scarce.

We have been studying the reaction of bidentate dihydrobis(pyrazol-1-yl)borates with [RuHCl(CO)(PPh₃)₃]. Hydridocarbonyl–Ru^{II} complexes bearing several bidentate dihydrobis(pyrazol-1-yl)borates have been prepared by our group (Huh *et al.*, 1999); they are indefinitely air stable in the solid state. The crystal structures of two of them, namely [RuH(CO)(PPh₃)₂(η^2 -H₂Bpz₂)] and [RuH(CO)(PPh₃)₂{ η^2 -H₂B(4-Brpz₂)}] (pz is pyrazol-1-yl), have been solved. Unlike the latter compound, the former shows a high degree of hydrogen-bond interaction, in which four intramolecular and one intermolecular hydrogen bond can be accounted for. The two PPh₃ ligands adopt a staggered conformation based on the *ipso*-C atoms, while the latter compound shows an eclipsed conformation.

Stimulated by this interesting difference, we have synthesized one of the AsPh₃ analogues, [RuH(CO)-(AsPh₃)₂(η^2 -H₂Bpz₂)], (1), to compare its structure with the corresponding PPh₃ analogues. The title compound cocrystallizes with one solvent water molecule. Basically, the geometrical structures around the Ru^{II} metal centres are the same. However, we have observed only two probable hydrogen-bond interactions in (1) apart from the hydrogen bonds between two adjacent solvent water molecules. There are two possible weak hydrogen-bond interactions, C3—H3···N1 and C25—H25···N4; their respective donor–acceptor distances and angles at hydrogen are 3.413(9)/3.469(9) Å and 145/157°. Adjacent water molecules form a dimer by way of intermolecular hydrogen bonds, which must be disordered across an inversion centre. The title compound shows a staggered conformation of the two AsPh₃ ligands relative to the *ipso*-C atoms, similar to [RuH(CO)(PPh₃)₂(η^2 -H₂Bpz₂)].



(1)

The coordination geometry of (1) is distorted octahedral with two *trans*-positioned AsPh₃ in axial positions and the remaining ligands in equatorial positions. The Ru—As bond distances are almost the same, 2.4393(8) and 2.4485(7) Å. These bond lengths are longer than those of the PPh₃ analogue, which has Ru—P distances of 2.3576(12) and 2.3482(12) Å. These longer