Table 2. *Selected interatomic distances (Å)*

Mo(1)—Mo(6)	2.5968 (6)	Mo(6)—O(4)	1.981 (4)
Mo(1)—O(1)	1.676 (4)	Mo(6)—O(14)	2.071 (4)
Mo(1)—O(2)	2.082 (4)	Mo(6)—O(15)	1.675 (4)
Mo(1)—O(3)	1.945 (4)	Mo(6)—O(16)	2.267 (4)
Mo(1)—O(4)	1.985 (4)	Mo(6)—O(30)	2.065 (4)
Mo(1)—O(18)	2.274 (4)	Co(1)—O(4)	2.128 (4)
Mo(1)—O(20)	2.049 (4)	Co(1)—O(6)	2.161 (4)
Mo(2)—Mo(3)	2.5961 (7)	Co(1)—O(12)	2.187 (4)
Mo(2)—O(2)	2.087 (4)	Co(2)—O(19)	2.085 (4)
Mo(2)—O(5)	1.666 (4)	Co(2)—O(28)	2.124 (4)
Mo(2)—O(6)	1.985 (4)	Co(2)—O(34)	2.139 (4)
Mo(2)—O(7)	1.940 (4)	Co(3)—O(19)	2.114 (4)
Mo(2)—O(18)	2.339 (4)	Co(3)—O(24)	1.988 (4)
Mo(2)—O(22)	2.066 (4)	Co(3)—O(28^i)	2.337 (4)
Mo(3)—O(6)	1.991 (4)	Co(3)—O(32)	2.068 (4)
Mo(3)—O(7)	1.936 (4)	Co(3)—O(33)	2.086 (4)
Mo(3)—O(8)	1.675 (4)	Co(3)—O(34)	2.185 (4)
Mo(3)—O(9)	2.118 (4)	P(1)—O(16)	1.540 (4)
Mo(3)—O(17)	2.293 (4)	P(1)—O(17)	1.532 (4)
Mo(3)—O(25)	2.062 (4)	P(1)—O(18)	1.538 (4)
Mo(4)—Mo(5)	2.5849 (7)	P(1)—O(19)	1.533 (4)
Mo(4)—O(9)	2.082 (4)	P(2)—O(20)	1.536 (4)
Mo(4)—O(10)	1.677 (4)	P(2)—O(21)	1.581 (5)
Mo(4)—O(11)	1.923 (4)	P(2)—O(22)	1.518 (4)
Mo(4)—O(12)	1.987 (4)	P(2)—O(23)	1.504 (4)
Mo(4)—O(17)	2.333 (4)	P(3)—O(24)	1.494 (4)
Mo(4)—O(26)	2.031 (4)	P(3)—O(25)	1.527 (4)
Mo(5)—O(11)	1.940 (4)	P(3)—O(26)	1.542 (4)
Mo(5)—O(12)	1.986 (4)	P(3)—O(27)	1.570 (5)
Mo(5)—O(13)	1.674 (4)	P(4)—O(28)	1.508 (4)
Mo(5)—O(14)	2.106 (4)	P(4)—O(29)	1.529 (4)
Mo(5)—O(16)	2.287 (4)	P(4)—O(30)	1.548 (4)
Mo(5)—O(29)	2.095 (4)	P(4)—O(31)	1.565 (4)
Mo(6)—O(3)	1.945 (4)		

Symmetry code: (i) $-x, -y, 2 - z$.

H atoms on the tetramethylammonium cations were placed geometrically and treated as riding atoms. Hydroxy and water molecule H atoms were not located.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corpration, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1218). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[1,1′-Bis(methylphenylphosphino)ferrocene-*P*,*P*′](pentane-2,4-dionato-*O*,*O*′)palladium Tetrafluoroborate†

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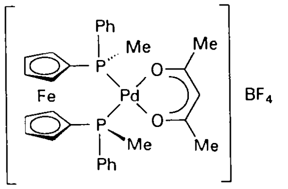
Abstract

The C_2 symmetric bisphosphine *rac*-$Fe(C_5H_4PMePh)_2$ (*rac*-mppf) forms a Pd^{II} complex [(*rac*-mppf)Pd(acac)]BF_4 (acac = pentane-2,4-dionate, $C_5H_7O_2$). The coordination geometry of the Pd centre is square planar while the ring–ring conformation of the *rac*-mppf ligand is intermediate between synperiplanar and synclinal eclipsed, with a torsion angle of 16.4°.

Comment

We have recently described *rac*-$Fe(C_5H_4PMePh)_2$ (*rac*-mppf), a new C_2-symmetric chiral bisphosphine (Herberich & Moss, 1995). We report here the crystal structure of the complex [(*rac*-mppf)Pd(acac)]BF_4, (I), as part of an ongoing study of the preferential conformations and the flexibility of complexes of the ligand *rac*-mppf.



[(*rac*-mppf)Pd(acac)][BF_4]

The cation of the title compound (Fig. 1) possesses a square planar Pd^{II} centre. The phosphine ligand is closely related to the well known complex 1,1′-bis(diphenylphosphino)ferrocene, $Fe(C_5H_4PPh_2)_2$ (dppf), for which much structural data are available (Gan & Hor, 1995). The ferrocene skeleton of the *rac*-mppf ligand exhibits slight distortions from idealized geometry, as is commonly observed for complexes of dppf. The cyclopentadienyl rings are planar with mean deviations of the C atoms from the best cyclopentadienyl (Cp) planes

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† Systematic name: bis[μ-methylphenylphosphino-$2\kappa P$:$1(\eta^5)$-cyclopentadienyl](pentane-2,4-dionato-$2\kappa^2O.O'$)ironpalladium tetrafluoroborate.

of 0.0026 and 0.0028 Å, respectively. They are nearly parallel with an interplanar angle of 4 (2)° and a ring tilt angle *X*1—Fe—*X*2 of 176.6°, where *X*1 and *X*2 are the centroids of the two Cp rings. Their rotational position corresponds to a conformation intermediate between synperiplanar and synclinal eclipsed, with a torsion angle C10—*X*1—*X*2—C20 of 16.4° and a P1—Fe—P2 angle of 57.9°. The P atoms are slightly tilted out of the Cp planes and away from the Fe atom with vertical displacements of 0.021 (1) and 0.089 (1) Å, respectively. This situation adjusts the mppf bite to the size of the Pd$^{\text{II}}$ atom, resulting in a P1···P2 distance of 3.264 (2) Å and a P1—Pd—P2 bite angle of 92.70 (4)°.

We also note that the P_2PdO_2 plane is folded towards the ferrocene moiety, thereby reducing the molecular symmetry to C_1. However, solution NMR spectra (measured on a Varian Unity 500 spectrometer at ambient temperature and down to 180 K) show effective C_2 symmetry; even at low temperatures, only one signal for each symmetry-related pair of methyl groups and P atoms is observed (Schultz, 1994). Thus, the conformation is highly flexible in solution.

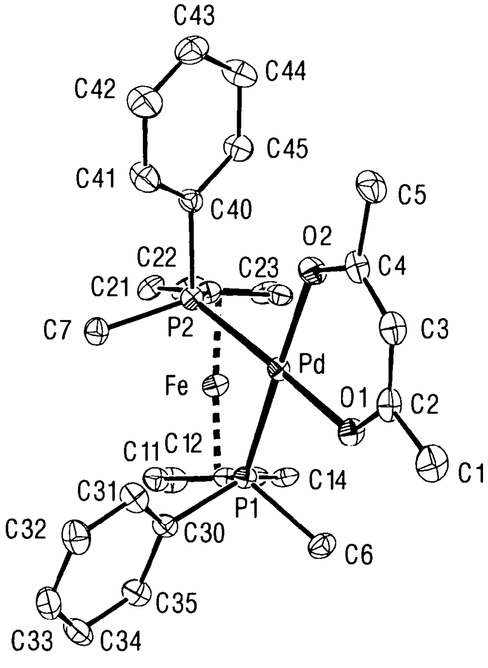

Fig. 1. *PLATON* (Spek, 1994) plot of the [(*rac*-mppf)Pd(acac)]$^+$ cation in the title compound with 30% probability ellipsoids. H atoms are omitted for clarity.

Experimental

The reaction of *trans*-$PdCl_2(NCPh)_2$ with *rac*-mppf in toluene and subsequent dehalogenation in CH_2Cl_2/PhCN with $AgBF_4$ in $MeNO_2$ afforded [(*rac*-mppf)Pd(NCPh)]$(BF_4)_2$ (Schultz, 1994). This complex was treated with pentane-2,4-dione and powdered Na_2CO_3 in CH_2Cl_2 to give the title compound, [(*rac*-mppf)Pd(acac)]BF_4 (Schultz, 1994). Recrystallization from CH_2Cl_2 provided orange–red crystals suitable for X-ray crystallographic study; m.p. 483–487 K (dec.); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, *versus*. 85% aqueous H_3PO_4): δ = 28.6p.p.m.

Crystal data

$[FePd(C_5H_7O_2)(C_{12}H_{12}P)_2]$-$BF_4$
M_r = 722.57
Triclinic
$P\overline{1}$
a = 10.719 (7) Å
b = 14.198 (5) Å
c = 9.773 (3) Å
α = 90.05 (3)°
β = 96.31 (4)°
γ = 89.32 (4)°
V = 1478 (2) Å^3
Z = 2
D_x = 1.61 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–15°
μ = 1.239 mm^{-1}
T = 263 K
Parallelepiped
0.3 × 0.2 × 0.2 mm
Orange–red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
6307 measured reflections
5015 independent reflections
4429 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.026
θ_{max} = 26.97°
$h = -6 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.040
wR = 0.049
S = 1.366
4429 reflections
361 parameters
H atoms were refined with a riding model

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\text{max}}$ = 0.001
$\Delta\rho_{\text{max}}$ = 0.937 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −0.586 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0.20902 (3)	0.15941 (2)	0.47382 (3)	0.02499 (7)
Fe	0.16565 (6)	0.36979 (5)	0.17077 (6)	0.0279 (2)
P1	0.1825 (1)	0.31530 (8)	0.5129 (1)	0.0264 (3)
P2	0.3307 (1)	0.18586 (8)	0.3053 (1)	0.0263 (3)
F1	0.7862 (4)	0.3624 (3)	0.0624 (4)	0.091 (1)
F2	0.7705 (4)	0.2948 (3)	0.2640 (4)	0.093 (1)
F3	0.6275 (3)	0.2630 (3)	0.0854 (3)	0.066 (1)
F4	0.8273 (4)	0.2072 (3)	0.0952 (6)	0.109 (2)
O1	0.1134 (3)	0.1305 (2)	0.6395 (3)	0.0380 (9)
O2	0.2260 (3)	0.0195 (2)	0.4355 (4)	0.0395 (9)
C1	0.0372 (6)	0.0457 (4)	0.8178 (5)	0.058 (2)
C2	0.0993 (5)	0.0471 (4)	0.6874 (5)	0.040 (1)
C3	0.1358 (5)	−0.0366 (4)	0.6307 (5)	0.042 (1)
C4	0.1922 (5)	−0.0466 (3)	0.5101 (5)	0.038 (1)

C5	0.2192 (6)	−0.1444 (4)	0.4572 (6)	0.053 (2)
C6	0.0437 (5)	0.3313 (3)	0.6014 (5)	0.037 (1)
C7	0.4685 (5)	0.2546 (4)	0.3574 (5)	0.037 (1)
C10	0.1520 (4)	0.3969 (3)	0.3719 (4)	0.027 (1)
C11	0.2351 (5)	0.4619 (3)	0.3180 (5)	0.032 (1)
C12	0.1670 (5)	0.5119 (3)	0.2087 (5)	0.041 (1)
C13	0.0426 (5)	0.4780 (3)	0.1932 (5)	0.042 (1)
C14	0.0317 (5)	0.4075 (3)	0.2939 (5)	0.032 (1)
C20	0.2518 (4)	0.2441 (3)	0.1591 (4)	0.029 (1)
C21	0.3066 (5)	0.3102 (3)	0.0726 (5)	0.035 (1)
C22	0.2084 (5)	0.3432 (4)	−0.0254 (5)	0.041 (1)
C23	0.0959 (5)	0.2988 (4)	−0.0029 (5)	0.038 (1)
C24	0.1216 (4)	0.2376 (3)	0.1109 (5)	0.032 (1)
C30	0.3085 (5)	0.3664 (3)	0.6270 (4)	0.031 (1)
C31	0.4046 (5)	0.3096 (4)	0.6890 (5)	0.039 (1)
C32	0.4974 (5)	0.3468 (4)	0.7836 (5)	0.049 (2)
C33	0.4956 (5)	0.4406 (4)	0.8158 (5)	0.050 (2)
C34	0.4010 (6)	0.4993 (4)	0.7532 (6)	0.050 (2)
C35	0.3079 (5)	0.4617 (3)	0.6594 (5)	0.038 (1)
C40	0.3901 (4)	0.0772 (3)	0.2384 (5)	0.030 (1)
C41	0.5018 (5)	0.0375 (4)	0.2940 (6)	0.051 (2)
C42	0.5453 (6)	−0.0454 (4)	0.2404 (7)	0.062 (2)
C43	0.4754 (6)	−0.0905 (4)	0.1346 (6)	0.051 (2)
C44	0.3617 (6)	−0.0535 (4)	0.0829 (6)	0.053 (2)
C45	0.3197 (5)	0.0305 (4)	0.1325 (5)	0.042 (1)
B	0.7528 (6)	0.2818 (5)	0.1201 (7)	0.048 (2)

Table 2. *Selected bond lengths (Å) and bond angles (°)*

Pd—P1	2.266 (1)	P2—C(Cp)	1.778 (4)
Pd—P2	2.245 (1)	P2—C(Ph)	1.811 (4)
Pd—O1	2.054 (3)	C—C(Cp)$_{av}$	1.421
Pd—O2	2.031 (3)	C—C(Cp)$_{min}$	1.406 (7)
Fe—C(Cp)$_{av}$	2.035	C—C(Cp)$_{max}$	1.437 (6)
Fe—C(Cp)$_{min}$	2.009 (4)	O1—C2	1.290 (5)
Fe—C(Cp)$_{max}$	2.053 (4)	O2—C4	1.269 (5)
P1—C(Me)	1.813 (4)	C1—C2	1.502 (6)
P1—C(Cp)	1.801 (4)	C2—C3	1.382 (7)
P1—C(Ph)	1.812 (4)	C3—C4	1.388 (7)
P2—C(Me)	1.805 (4)	C4—C5	1.517 (6)
P1—Pd—P2	92.70 (4)	C(Me)—P1—C(Ph)	104.7 (2)
P1—Pd—O1	89.17 (9)	C(Cp)—P1—C(Ph)	105.6 (2)
P1—Pd—O2	177.8 (1)	Pd—P2—C(Me)	114.4 (1)
P2—Pd—O1	174.34 (9)	Pd—P2—C(Cp)	114.0 (1)
P2—Pd—O2	87.97 (9)	Pd—P2—C(Ph)	111.8 (1)
O1—Pd—O2	90.4 (1)	C(Me)—P2—C(Cp)	106.0 (2)
Pd—P1—C(Me)	108.5 (1)	C(Me)—P2—C(Ph)	105.0 (2)
Pd—P1—C(Cp)	120.8 (1)	C(Cp)—P2—C(Ph)	104.8 (2)
Pd—P1—C(Ph)	113.8 (1)	Pd—O1—C2	124.4 (3)
C(Me)—P1—C(Cp)	101.7 (2)	Pd—O2—C4	125.7 (3)

The structure was solved by Patterson and difference Fourier methods. All non-H atoms were refined anisotropically. In the final full-matrix refinement H atoms were included as riding in standard positions (C—H = 0.98 Å).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Software*. Data reduction: *BEGIN* in *SDP* (Frenz, 1978). Program(s) used to solve structure: *FOUR* in *SDP*. Program(s) used to refine structure: *LSFM* in *SDP*. Molecular graphics: *PLATON* (Spek, 1994). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:4 Adduct of Tetrachlorobis(μ-phenylimido)dizirconium(IV) and Tetrahydrofuran

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Abstract

The title complex, bis(μ-phenylimido)bis[dichlorobis(tetrahydrofuran)zinc], $[Zr_2Cl_4(C_6H_5N)_2(C_4H_8O)_4]$, contains two octahedral Zr^{IV} ions which are connected by two bridging phenylimido ligands. The Zr coordination polyhedra have significantly different geometries. In one, the chloro ligands are *cis*, while in the other they take up *trans* positions. Both Zr^{IV} ions are situated on a twofold axis.

Comment

Complexes containing Zr—N bonds are predominantly octahedral $[ZrX_nL_m]$ adducts formed by the reaction between a monodentate or polydentate amine and a zirconium halide (Fay, 1987). Various homoleptic dialkylamido complexes involving zirconium and other early transition metals are also known (Bradley & Chisholm, 1976).

The title compound, (I), is a dimer in which two phenylimido ligands bridge two Zr^{IV} ions *via* N atoms (Fig. 1). The N1—Zr1 and N1—Zr2 distances [2.068 (2)

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