Crystal structure of (η^4-cycloocta-1,5-dien)-((+)-1,1′-bis((2*R*,4*R*)-2,4-diethyl-phosphotano)-ferrocene)-rhodium(I) tetrafluoroborate, $[Rh(C_8H_{12})Fe(C_{12}H_{18}FeP)_2][BF_4]$

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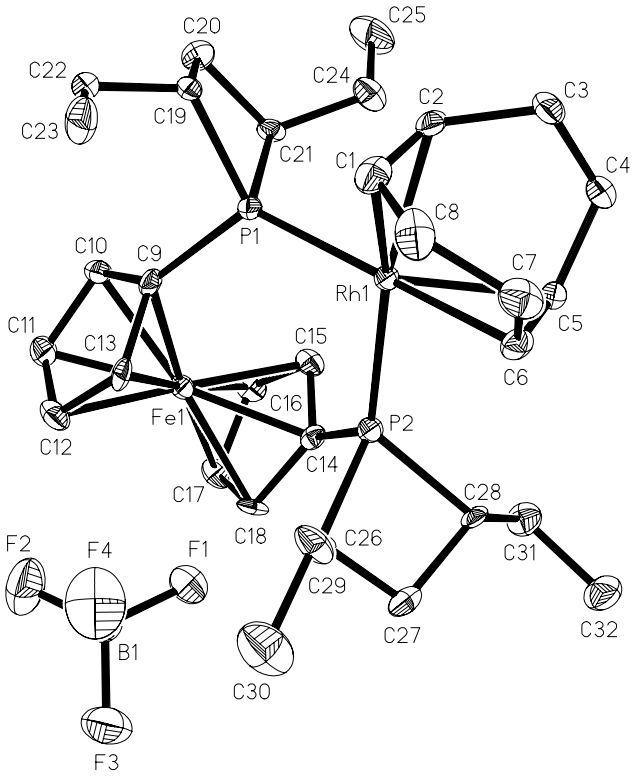

Abstract

$C_{32}H_{48}BF_4FeP_2Rh$, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.640(2) Å, b = 16.007(3) Å, c = 19.460(4) Å, V = 3314.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.089, T = 200 K.

Source of material

Standard procedure was performed according to [1]. The ligand was obtained commercially.

Discussion

Rhodium catalysts with Et-FerroTANE lead to unexpected high enantioselectivities of ≥ 99 % in the hydrogenation of β-arylsubstituted β-aminoacrylates [2]. A comparison between the title compound and the related norborna-2,5-diene complex [2] in the catalytic hydrogenation of the diolefines norborna-2,5-diene and (*Z*,*Z*)-cycloocta-1,5-diene motivated us to determine the crystal structure of the title compound. The ratio of the rate constants for the hydrogenation of the diolefine complexes is approximately 97 [3].

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It is well known that the double bonds of the diolefines are not coordinated perpendicular to the P–Rh–P plane. The dihedral angle between the planes P–Rh–P and *X*–Rh–*X* (*X* = centroid of the double bond) is in the case of the (*R*,*R*)-COD-complex 15.5° (clockwise twist) and for the (*R*,*R*)-NBD-complex 5.3° (clockwise twist).

Table 1. Data collection and handling.

Crystal:	red prism fragment, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.75 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS 1, φ
$2\theta_{max}$:	44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14132, 4067
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3575
$N(param)_{refined}$:	370
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*a*	0.1613	–0.4619	–0.2259	0.047
H(2A)	4*a*	0.2107	–0.3798	–0.1436	0.044
H(3A)	4*a*	0.1969	–0.2412	–0.1446	0.048
H(3B)	4*a*	0.1368	–0.2443	–0.2181	0.048
H(4A)	4*a*	0.0131	–0.2300	–0.0925	0.046
H(4B)	4*a*	–0.0125	–0.1792	–0.1597	0.046
H(5A)	4*a*	–0.1807	–0.2759	–0.1311	0.032
H(6A)	4*a*	–0.2192	–0.3370	–0.2295	0.038
H(7A)	4*a*	–0.0101	–0.2649	–0.2837	0.055
H(7B)	4*a*	–0.1052	–0.3213	–0.3241	0.055
H(8A)	4*a*	0.0125	–0.4372	–0.3107	0.061
H(8B)	4*a*	0.1159	–0.3687	–0.3210	0.061
H(10A)	4*a*	0.0541	–0.6686	0.0272	0.034
H(11A)	4*a*	–0.1086	–0.7840	0.0172	0.040
H(12A)	4*a*	–0.2245	–0.7682	–0.0966	0.039
H(13A)	4*a*	–0.1348	–0.6402	–0.1596	0.032
H(15A)	4*a*	–0.1317	–0.4715	0.0302	0.031
H(16A)	4*a*	–0.1976	–0.5858	0.1164	0.037
H(17A)	4*a*	–0.3760	–0.6698	0.0596	0.039
H(18A)	4*a*	–0.4235	–0.6077	–0.0580	0.030
H(19A)	4*a*	0.2713	–0.5042	–0.1241	0.028
H(20A)	4*a*	0.2587	–0.6011	–0.0020	0.045
H(20B)	4*a*	0.3282	–0.5144	–0.0122	0.045
H(21A)	4*a*	0.0883	–0.5299	0.0353	0.028
H(22A)	4*a*	0.2216	–0.6773	–0.1184	0.039
H(22B)	4*a*	0.3565	–0.6408	–0.1303	0.039
H(23A)	4*a*	0.2693	–0.6813	–0.2347	0.073
H(23B)	4*a*	0.2915	–0.5845	–0.2352	0.073
H(23C)	4*a*	0.1560	–0.6202	–0.2232	0.073
H(24A)	4*a*	0.1960	–0.3805	–0.0172	0.046

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(24B)	4*a*	0.0645	–0.3823	0.0191	0.046
H(25A)	4*a*	0.2166	–0.3387	0.0966	0.099
H(25B)	4*a*	0.2921	–0.4217	0.0850	0.099
H(25C)	4*a*	0.1607	–0.4242	0.1214	0.099
H(26A)	4*a*	–0.3616	–0.5784	–0.1614	0.034
H(27A)	4*a*	–0.5036	–0.4443	–0.1967	0.040
H(27B)	4*a*	–0.5140	–0.4904	–0.1248	0.040
H(28A)	4*a*	–0.3662	–0.3484	–0.1568	0.030
H(29A)	4*a*	–0.3074	–0.4617	–0.2692	0.048

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(29B)	4*a*	–0.2239	–0.5414	–0.2579	0.048
H(30A)	4*a*	–0.3727	–0.5683	–0.3445	0.120
H(30B)	4*a*	–0.4823	–0.5479	–0.2933	0.120
H(30C)	4*a*	–0.3989	–0.6275	–0.2820	0.120
H(31A)	4*a*	–0.4590	–0.3934	–0.0248	0.048
H(31B)	4*a*	–0.3696	–0.3168	–0.0366	0.048
H(32A)	4*a*	–0.5781	–0.2708	–0.0316	0.079
H(32B)	4*a*	–0.6133	–0.3293	–0.0932	0.079
H(32C)	4*a*	–0.5240	–0.2528	–0.1050	0.079

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	4*a*	–0.04412(5)	–0.42151(3)	–0.14667(3)	0.0186(3)	0.0190(2)	0.0244(3)	–0.0011(2)	0.0014(2)	0.0057(2)
Fe(1)	4*a*	–0.17739(9)	–0.62581(6)	–0.02189(4)	0.0229(6)	0.0198(5)	0.0206(5)	–0.0032(4)	0.0006(4)	0.0013(4)
P(1)	4*a*	0.0609(2)	–0.5253(1)	–0.08671(8)	0.018(1)	0.0192(9)	0.0250(9)	0.0000(8)	0.0011(8)	0.0016(7)
P(2)	4*a*	–0.2451(2)	–0.4635(1)	–0.11624(9)	0.021(1)	0.0212(9)	0.0253(9)	–0.0007(8)	0.0008(8)	0.0037(8)
C(1)	4*a*	0.1084(7)	–0.4119(5)	–0.2233(4)	0.032(4)	0.041(5)	0.046(5)	0.006(4)	0.013(4)	0.013(4)
C(2)	4*a*	0.1405(7)	–0.3593(4)	–0.1715(4)	0.016(4)	0.030(4)	0.065(6)	0.001(3)	0.002(4)	0.020(4)
C(3)	4*a*	0.1286(7)	–0.2647(4)	–0.1714(4)	0.036(5)	0.028(4)	0.057(5)	–0.011(4)	–0.009(4)	0.012(4)
C(4)	4*a*	0.0047(6)	–0.2347(4)	–0.1419(4)	0.035(5)	0.024(4)	0.055(5)	–0.004(3)	–0.005(4)	–0.006(4)
C(5)	4*a*	–0.1050(6)	–0.2896(4)	–0.1575(4)	0.022(4)	0.021(3)	0.039(5)	0.001(3)	0.000(3)	0.002(3)
C(6)	4*a*	–0.1297(7)	–0.3279(4)	–0.2204(4)	0.029(5)	0.034(4)	0.033(5)	0.003(4)	–0.007(3)	0.010(3)
C(7)	4*a*	–0.0509(8)	–0.3191(5)	–0.2841(4)	0.048(5)	0.051(5)	0.039(5)	–0.011(5)	0.000(4)	0.011(4)
C(8)	4*a*	0.0503(9)	–0.3880(5)	–0.2903(4)	0.064(6)	0.041(4)	0.048(5)	0.001(5)	0.025(5)	0.003(4)
C(9)	4*a*	–0.0122(6)	–0.6250(4)	–0.0721(3)	0.023(4)	0.019(4)	0.027(4)	0.006(3)	–0.003(3)	0.006(3)
C(10)	4*a*	–0.0034(6)	–0.6771(4)	–0.0116(4)	0.022(4)	0.024(4)	0.038(4)	–0.004(3)	–0.006(3)	0.005(3)
C(11)	4*a*	–0.0920(7)	–0.7409(4)	–0.0175(4)	0.032(4)	0.022(4)	0.046(5)	–0.003(3)	0.004(4)	0.008(4)
C(12)	4*a*	–0.1564(7)	–0.7322(4)	–0.0801(4)	0.034(5)	0.025(4)	0.039(5)	–0.011(4)	0.004(4)	–0.003(3)
C(13)	4*a*	–0.1075(7)	–0.6612(4)	–0.1147(4)	0.032(4)	0.020(4)	0.028(4)	0.013(3)	0.003(3)	–0.006(3)
C(14)	4*a*	–0.2756(6)	–0.5196(4)	–0.0373(3)	0.020(4)	0.025(4)	0.019(4)	0.005(3)	0.001(3)	–0.004(3)
C(15)	4*a*	–0.1987(6)	–0.5126(4)	0.0232(3)	0.026(4)	0.027(4)	0.024(4)	–0.007(3)	0.009(3)	–0.001(3)
C(16)	4*a*	–0.2348(6)	–0.5754(5)	0.0712(3)	0.037(4)	0.035(4)	0.021(4)	–0.004(4)	0.003(3)	–0.002(3)
C(17)	4*a*	–0.3338(7)	–0.6211(4)	0.0396(3)	0.036(5)	0.029(4)	0.032(4)	–0.012(4)	0.007(3)	0.003(3)
C(18)	4*a*	–0.3595(6)	–0.5875(4)	–0.0258(3)	0.015(4)	0.032(4)	0.027(4)	–0.013(3)	–0.005(3)	0.002(3)
C(19)	4*a*	0.2301(6)	–0.5517(4)	–0.1017(3)	0.018(4)	0.019(4)	0.033(4)	–0.004(3)	0.001(3)	0.004(3)
C(20)	4*a*	0.2532(7)	–0.5462(5)	–0.0229(4)	0.032(5)	0.038(4)	0.042(5)	0.004(4)	–0.010(4)	0.003(4)
C(21)	4*a*	0.1316(6)	–0.4994(4)	–0.0014(3)	0.022(4)	0.026(4)	0.022(4)	–0.006(3)	–0.010(3)	0.006(3)
C(22)	4*a*	0.2677(6)	–0.6309(4)	–0.1382(4)	0.023(4)	0.024(4)	0.051(5)	0.001(3)	–0.003(4)	–0.006(4)
C(23)	4*a*	0.2440(9)	–0.6290(5)	–0.2148(4)	0.062(6)	0.037(5)	0.048(5)	0.013(4)	0.002(4)	–0.014(4)
C(24)	4*a*	0.1466(8)	–0.4085(5)	0.0178(4)	0.047(5)	0.033(4)	0.034(4)	–0.011(4)	–0.005(4)	–0.002(4)
C(25)	4*a*	0.2097(9)	–0.3972(6)	0.0864(5)	0.069(7)	0.065(7)	0.065(6)	–0.023(5)	–0.016(5)	–0.023(5)
C(26)	4*a*	–0.3469(6)	–0.5211(4)	–0.1771(3)	0.024(4)	0.027(4)	0.033(4)	–0.013(3)	–0.010(3)	0.004(3)
C(27)	4*a*	–0.4571(7)	–0.4633(4)	–0.1568(4)	0.024(4)	0.040(4)	0.037(4)	0.009(4)	–0.002(4)	0.009(3)
C(28)	4*a*	–0.3837(6)	–0.3917(4)	–0.1225(3)	0.010(4)	0.027(4)	0.038(4)	0.004(3)	0.002(3)	0.008(3)
C(29)	4*a*	–0.3082(8)	–0.5191(5)	–0.2531(3)	0.061(6)	0.034(5)	0.025(4)	–0.018(4)	–0.013(4)	0.001(3)
C(30)	4*a*	–0.399(1)	–0.5705(7)	–0.2974(5)	0.104(8)	0.076(7)	0.060(6)	–0.026(7)	–0.014(6)	0.008(6)
C(31)	4*a*	–0.4350(7)	–0.3505(5)	–0.0575(4)	0.033(5)	0.044(5)	0.044(5)	0.005(4)	0.008(4)	–0.002(4)
C(32)	4*a*	–0.5480(8)	–0.2958(5)	–0.0733(4)	0.038(5)	0.054(5)	0.067(6)	0.014(5)	–0.005(5)	–0.016(4)
B(1)	4*a*	–0.457(1)	–0.8050(5)	–0.1877(4)	0.033(6)	0.044(5)	0.033(5)	0.005(5)	0.007(5)	–0.003(4)
F(1)	4*a*	–0.4494(5)	–0.7355(3)	–0.1466(3)	0.064(3)	0.052(3)	0.083(3)	0.002(3)	–0.024(4)	–0.026(3)
F(2)	4*a*	–0.4050(6)	–0.8724(3)	–0.1535(3)	0.106(5)	0.058(3)	0.086(4)	0.028(3)	–0.008(4)	0.009(3)
F(3)	4*a*	–0.5801(5)	–0.8210(4)	–0.2027(3)	0.056(4)	0.084(4)	0.082(4)	–0.012(3)	–0.014(3)	–0.017(3)
F(4)	4*a*	–0.3918(7)	–0.7933(4)	–0.2472(3)	0.126(6)	0.106(5)	0.081(4)	–0.001(4)	0.053(4)	0.015(4)

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