Crystal structure of (η^4-norborna-2,5-dien)-(1,2-bis((*R*,*R*)-2,5-bis-(methoxymethyl)phospholanyl)benzene)rhodium(I) tetrafluoroborate, $[Rh(C_{22}H_{36}O_4P_2)(C_7H_8)](BF_4)$

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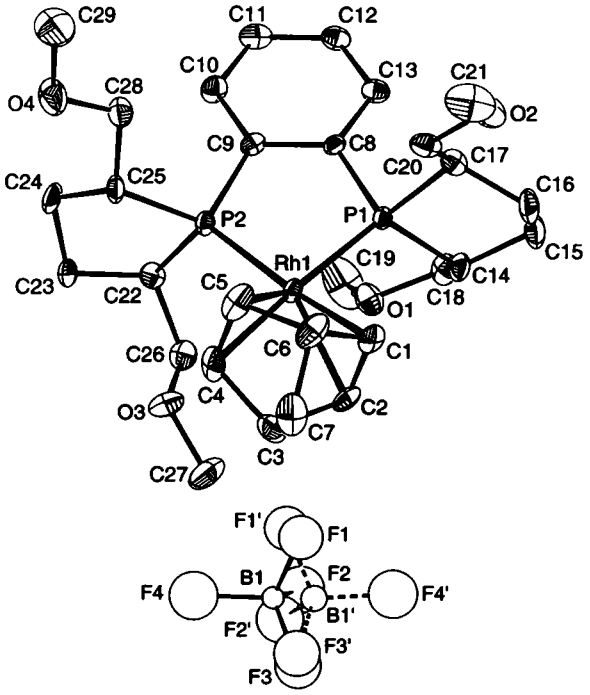

Abstract

$C_{29}H_{44}BF_4O_4P_2Rh$, monoclinic, $P2_1$ (no. 4),
$a = 10.119(2)$ Å, $b = 14.125(3)$ Å, $c = 11.542(2)$ Å,
$\beta = 106.87(3)°$, $V = 1578.7$ Å^3, $Z = 2$,
$R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.090$, $T = 200$ K.

Source of material

Standard preparation according to [1]. The synthesis of the ligand is described in [2].

Experimental details

The hydrogen atoms were placed in theoretical positions and refined using a riding model. The disorder of the BF_4^- anion was resolved in two tetrahedra, whereas all F and B atoms were split into two positions and treated as isotropic in the structure refinement resulting in an occupational ratio of 0.60(1)/0.40.

Discussion

Unexpected differences between the title compound and the related (*Z*,*Z*)-cycloocta-1,5-diene complex [2] in the catalytic hydrogenation of the diolefines norborna-2,5-diene and (*Z*,*Z*)-cycloocta-1,5-diene [3] 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 750. 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 21.8° (clockwise twist) and for the (*R*,*R*)-NBD-complex 22.2° (clockwise twist).

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Table 1. Data collection and handling.

Crystal:	red prism, size 0.30 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.98 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7171, 4083
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3876
$N(param)_{refined}$:	361
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1A)	2*a*		0.6959	0.0304	0.7967	0.08
H(2A)	2*a*		0.5513	−0.0512	0.6232	0.08
H(3A)	2*a*		0.4763	−0.2046	0.6878	0.08
H(4A)	2*a*		0.3333	−0.1648	0.8253	0.08
H(5A)	2*a*		0.4767	−0.0819	1.0022	0.08
H(6A)	2*a*		0.7170	−0.0678	0.9796	0.08
H(7A)	2*a*		0.7229	−0.1847	0.8194	0.08
H(7B)	2*a*		0.6364	−0.2277	0.9003	0.08
H(10A)	2*a*		0.0060	0.2031	0.8640	0.08
H(11A)	2*a*		−0.0192	0.3679	0.8389	0.08
H(12A)	2*a*		0.1401	0.4544	0.7722	0.08
H(13A)	2*a*		0.3290	0.3794	0.7341	0.08
H(14A)	2*a*		0.4774	0.1611	0.5665	0.08
H(15A)	2*a*		0.5300	0.3493	0.6318	0.08
H(15B)	2*a*		0.6093	0.2853	0.5642	0.08
H(16A)	2*a*		0.7345	0.3089	0.7764	0.08
H(16B)	2*a*		0.7118	0.2029	0.7389	0.08
H(17A)	2*a*		0.5522	0.3071	0.8539	0.08
H(18A)	2*a*		0.2854	0.3092	0.5334	0.08
H(18B)	2*a*		0.3295	0.2585	0.4307	0.08
H(19A)	2*a*		0.0118	0.1689	0.4387	0.08
H(19B)	2*a*		0.0609	0.2702	0.4885	0.08
H(19C)	2*a*		0.0735	0.2385	0.3620	0.08
H(20A)	2*a*		0.5959	0.2013	1.0101	0.08
H(20B)	2*a*		0.6748	0.1342	0.9460	0.08
H(21A)	2*a*		0.9488	0.2381	1.1498	0.08
H(21B)	2*a*		0.8167	0.1960	1.1754	0.08
H(21C)	2*a*		0.8894	0.1405	1.0934	0.08

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(22A)	2a		–0.0136	0.0782	0.6767	0.08
H(23A)	2a		0.0074	–0.1050	0.7678	0.08
H(23B)	2a		–0.1257	–0.0432	0.7272	0.08
H(24A)	2a		–0.0273	–0.0536	0.9461	0.08
H(24B)	2a		–0.0478	0.0502	0.8977	0.08
H(25A)	2a		0.2009	–0.0508	0.9583	0.08
H(26A)	2a		–0.0214	–0.0272	0.5262	0.08
H(26B)	2a		0.1204	0.0245	0.5541	0.08
H(27A)	2a		0.2302	–0.1991	0.5455	0.08
H(27B)	2a		0.1076	–0.1488	0.4505	0.08
H(27C)	2a		0.2479	–0.0953	0.5041	0.08
H(28A)	2a		0.3044	0.0740	1.0833	0.08
H(28B)	2a		0.1595	0.1214	1.0547	0.08

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(29A)	2a		0.2039	0.0110	1.3270	0.08
H(29B)	2a		0.3255	0.0578	1.2890	0.08
H(29C)	2a		0.1857	0.1122	1.2688	0.08
B(1)	2a	0.6	0.6775(7)	0.0762(5)	0.4334(6)	0.025(2)
F(1)	2a	0.6	0.584(1)	0.1444(6)	0.3742(9)	0.101(2)
F(2)	2a	0.6	0.6058(9)	–0.0063(6)	0.4336(9)	0.116(3)
F(3)	2a	0.6	0.7754(9)	0.0624(6)	0.3740(8)	0.110(3)
F(4)	2a	0.6	0.740(1)	0.1063(7)	0.5495(8)	0.123(3)
B(1')	2a	0.4	0.647(1)	0.0655(7)	0.3710(9)	0.035(4)
F(1')	2a	0.4	0.574(1)	0.138(1)	0.405(1)	0.101(2)
F(2')	2a	0.4	0.672(2)	–0.0060(9)	0.457(1)	0.116(3)
F(3')	2a	0.4	0.772(1)	0.099(1)	0.361(1)	0.110(3)
F(4')	2a	0.4	0.571(1)	0.031(1)	0.260(1)	0.123(3)

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)	2a	0.40941(3)	0.02366(3)	0.78636(3)	0.0198(2)	0.0257(2)	0.0298(2)	0.0033(2)	0.0123(1)	0.0054(2)
P(1)	2a	0.4244(1)	0.1800(1)	0.7476(1)	0.0198(7)	0.0253(7)	0.0275(8)	–0.0019(6)	0.0105(6)	0.0008(7)
P(2)	2a	0.2056(1)	0.0633(1)	0.8162(1)	0.0190(7)	0.0267(6)	0.0327(8)	–0.0004(5)	0.0108(6)	0.0037(5)
O(1)	2a	0.2119(4)	0.1800(3)	0.4994(4)	0.037(2)	0.041(2)	0.045(3)	–0.005(2)	0.002(2)	0.005(2)
O(2)	2a	0.7789(5)	0.2490(4)	1.0104(5)	0.046(3)	0.061(3)	0.070(3)	–0.007(2)	–0.008(3)	–0.014(3)
O(3)	2a	0.1363(5)	–0.1066(3)	0.6161(4)	0.054(3)	0.055(3)	0.045(3)	0.015(2)	0.022(2)	–0.008(2)
O(4)	2a	0.1760(5)	0.0099(4)	1.1531(4)	0.094(3)	0.077(4)	0.040(3)	–0.042(3)	0.024(2)	–0.002(3)
C(1)	2a	0.6276(5)	–0.0152(4)	0.8020(6)	0.020(3)	0.040(3)	0.050(4)	0.014(2)	0.016(3)	0.005(3)
C(2)	2a	0.5464(6)	–0.0617(4)	0.7041(6)	0.028(3)	0.049(4)	0.041(4)	0.011(3)	0.021(3)	–0.004(3)
C(3)	2a	0.5080(7)	–0.1565(4)	0.7483(7)	0.047(4)	0.029(3)	0.084(5)	–0.005(3)	0.028(4)	–0.011(3)
C(4)	2a	0.4144(7)	–0.1293(4)	0.8257(8)	0.054(4)	0.023(3)	0.083(5)	0.010(3)	0.039(4)	0.025(4)
C(5)	2a	0.4947(7)	–0.0813(5)	0.9250(6)	0.048(4)	0.062(4)	0.046(4)	0.025(3)	0.021(3)	0.028(4)
C(6)	2a	0.6417(6)	–0.0803(6)	0.9085(6)	0.032(4)	0.082(5)	0.042(4)	0.015(3)	0.012(3)	0.008(4)
C(7)	2a	0.6447(8)	–0.1756(5)	0.8494(9)	0.044(4)	0.048(5)	0.113(7)	0.025(4)	0.034(5)	0.033(5)
C(8)	2a	0.2807(5)	0.2447(3)	0.7768(4)	0.027(3)	0.025(3)	0.020(3)	0.001(2)	0.010(2)	–0.001(2)
C(9)	2a	0.1837(5)	0.1923(4)	0.8147(4)	0.016(3)	0.033(3)	0.023(3)	0.007(2)	0.003(2)	0.000(2)
C(10)	2a	0.0727(6)	0.2391(4)	0.8380(5)	0.028(3)	0.036(3)	0.042(3)	0.007(2)	0.012(3)	0.003(3)
C(11)	2a	0.0573(6)	0.3365(4)	0.8220(5)	0.027(3)	0.044(4)	0.037(4)	0.009(3)	–0.001(3)	–0.008(3)
C(12)	2a	0.1522(6)	0.3873(4)	0.7834(5)	0.035(3)	0.028(3)	0.037(3)	0.006(3)	0.006(3)	–0.002(2)
C(13)	2a	0.2640(6)	0.3429(4)	0.7617(5)	0.035(3)	0.027(3)	0.032(3)	0.005(2)	0.007(3)	0.000(2)
C(14)	2a	0.4467(6)	0.2160(4)	0.6002(5)	0.039(3)	0.040(3)	0.029(3)	–0.006(3)	0.016(3)	0.007(2)
C(15)	2a	0.5643(7)	0.2865(5)	0.6269(6)	0.051(4)	0.051(4)	0.057(4)	–0.021(3)	0.025(3)	0.007(3)
C(16)	2a	0.6659(6)	0.2607(5)	0.7479(7)	0.034(4)	0.052(4)	0.066(5)	–0.018(3)	0.022(3)	0.003(3)
C(17)	2a	0.5819(6)	0.2455(4)	0.8366(6)	0.022(3)	0.033(3)	0.038(3)	0.000(2)	0.001(3)	–0.002(2)
C(18)	2a	0.3141(6)	0.2498(4)	0.5083(6)	0.051(4)	0.039(3)	0.038(4)	0.004(3)	0.016(3)	0.016(3)
C(19)	2a	0.0790(8)	0.2177(7)	0.443(1)	0.051(5)	0.075(6)	0.128(8)	0.004(4)	–0.015(5)	0.030(6)
C(20)	2a	0.6543(6)	0.1992(4)	0.9579(6)	0.031(3)	0.041(4)	0.050(4)	0.001(3)	0.006(3)	–0.016(3)
C(21)	2a	0.8659(8)	0.2022(7)	1.1162(8)	0.050(5)	0.092(6)	0.080(6)	0.020(4)	–0.025(4)	–0.018(5)
C(22)	2a	0.0445(4)	0.0236(6)	0.7000(4)	0.014(2)	0.038(3)	0.044(3)	0.000(4)	0.005(2)	–0.006(4)
C(23)	2a	–0.0282(6)	–0.0419(5)	0.7671(6)	0.031(3)	0.051(4)	0.058(4)	–0.020(3)	0.027(3)	–0.015(3)
C(24)	2a	0.0011(6)	–0.0079(5)	0.8965(6)	0.029(3)	0.062(5)	0.050(4)	–0.014(3)	0.027(3)	–0.006(3)
C(25)	2a	0.1582(5)	0.0104(4)	0.9445(5)	0.032(3)	0.030(4)	0.044(3)	–0.006(3)	0.021(2)	0.007(3)
C(26)	2a	0.0659(6)	–0.0181(4)	0.5863(5)	0.037(3)	0.044(3)	0.034(3)	0.001(3)	0.009(3)	0.006(3)
C(27)	2a	0.1843(9)	–0.1397(7)	0.5215(8)	0.075(6)	0.079(6)	0.070(6)	0.009(5)	0.050(5)	–0.009(5)
C(28)	2a	0.2069(6)	0.0618(4)	1.0621(5)	0.036(3)	0.045(3)	0.037(4)	–0.009(2)	0.010(3)	0.002(3)
C(29)	2a	0.227(1)	0.0511(6)	1.2686(6)	0.132(8)	0.093(8)	0.035(4)	–0.030(6)	0.019(4)	–0.004(4)

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