Crystal structure of (η^4-norborna-2,5-dien){2,3-bis[(*S*,*S*)-2,5-dimethylphospholanyl]benzothiophene}rhodium(I) tetrafluoroborate, $[Rh(C_7H_8)(C_{20}H_{28}P_2S)][BF_4]$

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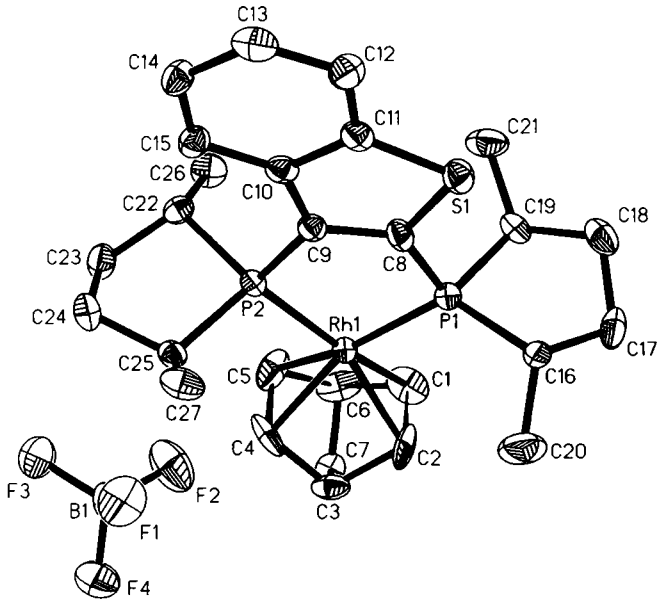

Abstract

$C_{27}H_{36}BF_4P_2RhS$, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.476(2) Å, b = 16.223(3) Å, c = 18.615(4) Å, V = 2861.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.108, T = 200 K.

Source of material

Standard preparation procedure was used according to [1]. The ligand is commercially available from Solvias.

Discussion

Unexpected differences between the title compound and the related compounds with chelating phospholane ligands (like [Rh-MeDuPHOS(NBD)](BF4) in the catalytic hydrogenation of typical hydrogenation substrates motivated us to determine the crystal structure of the title compound. The bite angle P–Rh–P of the title compound with 85.6(1)° is only slightly larger than the average bite angle of (84.8 ± 0.5)° for seven DuPHOS derivates of known structure (see [2]). It is known that the double bonds of the diolefines are not 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) for the title compound is 2.34(1)°. This is clearly smaller than for observed dihedral angles in other bisphosphane rhodium complexes (6.6° – 22.6° [3]).

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Table 1. Data collection and handling.

Crystal:	red prism, size 0.3 x 0.4 x 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.23 cm^{-1}
Diffractometer, scan mode:	STOE IPDS I, φ
$2\theta_{max}$:	45.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12742, 3706
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2850
$N(param)_{refined}$:	325
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*	0.3832	1.0575	0.6513	0.080
H(2A)	4*a*	0.1302	1.0543	0.6536	0.078
H(3A)	4*a*	0.0498	1.1030	0.7739	0.064
H(4A)	4*a*	0.1400	1.0061	0.8628	0.076
H(5A)	4*a*	0.3964	1.0022	0.8612	0.084
H(6A)	4*a*	0.4755	1.1068	0.7679	0.078
H(7A)	4*a*	0.2592	1.1934	0.7456	0.055
H(7B)	4*a*	0.2638	1.1709	0.8290	0.055
H(12A)	4*a*	0.2284	0.4772	0.6394	0.051
H(13A)	4*a*	0.2282	0.4072	0.7457	0.060
H(14A)	4*a*	0.2514	0.4741	0.8549	0.050
H(15A)	4*a*	0.2489	0.6162	0.8591	0.047
H(16A)	4*a*	0.1084	0.7974	0.5524	0.050
H(17A)	4*a*	0.2301	0.9441	0.5014	0.069
H(17B)	4*a*	0.1775	0.8687	0.4554	0.069
H(18A)	4*a*	0.3611	0.7860	0.4973	0.067
H(18B)	4*a*	0.4319	0.8689	0.4721	0.067
H(19A)	4*a*	0.4491	0.9172	0.5837	0.053
H(20A)	4*a*	–0.0596	0.8990	0.5382	0.134
H(20B)	4*a*	0.0223	0.9564	0.5916	0.134
H(20C)	4*a*	–0.0465	0.8745	0.6193	0.134
H(21A)	4*a*	0.6212	0.8189	0.5697	0.101
H(21B)	4*a*	0.5205	0.7513	0.6012	0.101
H(21C)	4*a*	0.5739	0.8234	0.6503	0.101
H(22A)	4*a*	0.4089	0.7232	0.8701	0.044
H(23A)	4*a*	0.3769	0.7833	0.9809	0.062
H(23B)	4*a*	0.3297	0.8675	0.9464	0.062
H(24A)	4*a*	0.1227	0.8009	0.9773	0.055
H(24B)	4*a*	0.1740	0.7181	0.9420	0.055
H(25A)	4*a*	0.0781	0.8611	0.8723	0.042
H(26A)	4*a*	0.6074	0.8036	0.8920	0.081
H(26B)	4*a*	0.5353	0.8798	0.8555	0.081
H(26C)	4*a*	0.5762	0.8026	0.8093	0.081
H(27A)	4*a*	–0.0851	0.7561	0.8791	0.079
H(27B)	4*a*	0.0146	0.6983	0.8346	0.079
H(27C)	4*a*	–0.0513	0.7767	0.7987	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*	0.26364(6)	0.93060(4)	0.73871(3)	0.0359(3)	0.0375(3)	0.0290(3)	0.0020(4)	0.0012(3)	0.0015(3)
S(1)	4*a*	0.2432(3)	0.6578(1)	0.61241(9)	0.053(1)	0.044(1)	0.0356(9)	0.000(2)	–0.003(1)	–0.0073(8)
P(1)	4*a*	0.2627(3)	0.8490(1)	0.63867(9)	0.039(1)	0.042(1)	0.0309(9)	0.007(1)	–0.000(1)	–0.0004(8)
P(2)	4*a*	0.2610(2)	0.8091(1)	0.80250(9)	0.031(1)	0.034(1)	0.0292(9)	–0.000(1)	0.003(1)	–0.0023(7)
C(1)	4*a*	0.329(1)	1.0516(7)	0.6959(8)	0.079(8)	0.021(8)	0.10(1)	–0.020(7)	0.038(8)	0.015(7)
C(2)	4*a*	0.189(1)	1.0491(8)	0.6968(5)	0.11(1)	0.06(1)	0.025(6)	–0.013(8)	–0.032(6)	0.001(5)
C(3)	4*a*	0.1476(8)	1.0843(6)	0.7689(7)	0.030(4)	0.044(7)	0.085(8)	0.003(4)	0.011(5)	0.014(7)
C(4)	4*a*	0.196(1)	1.0217(8)	0.8206(6)	0.086(9)	0.052(8)	0.052(8)	–0.022(6)	0.046(6)	–0.022(6)
C(5)	4*a*	0.339(2)	1.0177(8)	0.8196(6)	0.12(1)	0.041(9)	0.049(8)	0.002(7)	–0.040(7)	–0.012(6)
C(6)	4*a*	0.3782(9)	1.0865(7)	0.7661(8)	0.026(4)	0.053(8)	0.12(1)	–0.017(4)	–0.022(6)	0.000(9)
C(7)	4*a*	0.2620(9)	1.1490(5)	0.7805(4)	0.052(5)	0.037(4)	0.049(4)	–0.009(6)	–0.006(6)	0.000(4)
C(8)	4*a*	0.253(1)	0.7436(4)	0.6685(3)	0.041(4)	0.046(5)	0.028(4)	–0.002(6)	0.001(5)	–0.009(3)
C(9)	4*a*	0.2517(8)	0.7232(4)	0.7392(3)	0.028(3)	0.037(4)	0.033(4)	0.001(4)	–0.001(6)	–0.004(3)
C(10)	4*a*	0.2460(8)	0.6338(4)	0.7513(3)	0.025(3)	0.041(4)	0.040(4)	0.002(4)	–0.003(6)	–0.006(3)
C(11)	4*a*	0.239(1)	0.5917(5)	0.6855(3)	0.025(4)	0.048(5)	0.038(4)	0.001(6)	–0.003(4)	–0.009(3)
C(12)	4*a*	0.233(1)	0.5052(5)	0.6829(4)	0.049(6)	0.037(5)	0.041(4)	0.000(6)	–0.009(5)	–0.006(3)
C(13)	4*a*	0.2346(8)	0.4644(5)	0.7463(4)	0.040(4)	0.031(4)	0.078(6)	–0.006(4)	0.017(7)	0.004(4)
C(14)	4*a*	0.245(1)	0.5045(5)	0.8127(4)	0.049(5)	0.041(5)	0.035(4)	0.001(7)	–0.011(5)	0.001(3)
C(15)	4*a*	0.247(1)	0.5890(4)	0.8151(3)	0.036(4)	0.043(5)	0.038(4)	0.000(6)	–0.004(5)	0.003(3)
C(16)	4*a*	0.1355(9)	0.8543(6)	0.5634(5)	0.049(6)	0.044(6)	0.033(6)	0.016(5)	–0.005(4)	–0.005(5)
C(17)	4*a*	0.222(1)	0.8845(6)	0.5002(4)	0.091(8)	0.054(6)	0.028(4)	–0.001(6)	–0.010(6)	0.006(4)
C(18)	4*a*	0.368(1)	0.8447(7)	0.5067(5)	0.069(7)	0.052(7)	0.048(6)	–0.002(5)	0.024(5)	0.000(5)
C(19)	4*a*	0.4198(9)	0.8593(7)	0.5813(5)	0.047(5)	0.046(7)	0.040(6)	0.001(5)	0.011(4)	–0.010(5)
C(20)	4*a*	0.001(1)	0.9002(8)	0.5796(6)	0.053(7)	0.12(1)	0.095(9)	0.035(7)	–0.027(6)	–0.032(8)
C(21)	4*a*	0.545(1)	0.8087(7)	0.6025(6)	0.048(6)	0.063(8)	0.091(8)	0.017(5)	0.021(5)	0.016(6)
C(22)	4*a*	0.3979(8)	0.7833(6)	0.8698(5)	0.037(5)	0.030(6)	0.044(6)	–0.002(4)	–0.004(4)	0.003(5)
C(23)	4*a*	0.3276(9)	0.8081(7)	0.9407(5)	0.053(6)	0.065(8)	0.037(6)	–0.004(5)	–0.004(4)	0.007(5)
C(24)	4*a*	0.1763(9)	0.7777(6)	0.9378(5)	0.051(5)	0.055(7)	0.032(5)	–0.011(5)	0.006(4)	0.000(5)
C(25)	4*a*	0.1115(8)	0.8044(6)	0.8659(5)	0.038(5)	0.031(6)	0.037(5)	0.001(4)	0.008(4)	0.001(4)
C(26)	4*a*	0.5426(9)	0.8208(7)	0.8553(5)	0.036(5)	0.063(7)	0.064(6)	–0.009(5)	–0.004(4)	–0.001(5)
C(27)	4*a*	–0.0139(8)	0.7544(6)	0.8425(5)	0.028(5)	0.052(6)	0.078(7)	–0.008(4)	0.011(4)	–0.007(5)
B(1)	4*a*	–0.0960(7)	0.9477(4)	0.9980(3)	0.061(7)	0.060(9)	0.033(6)	–0.010(6)	0.005(5)	0.002(5)
F(1)	4*a*	–0.1651(6)	0.8838(4)	0.9652(3)	0.093(4)	0.069(4)	0.091(4)	–0.024(4)	–0.020(4)	–0.008(3)
F(2)	4*a*	0.0034(7)	0.9775(4)	0.9515(3)	0.119(6)	0.079(5)	0.103(5)	–0.030(4)	0.049(5)	–0.008(4)
F(3)	4*a*	–0.0329(6)	0.9191(5)	1.0591(3)	0.087(4)	0.131(6)	0.053(4)	0.021(4)	–0.014(3)	0.001(4)
F(4)	4*a*	–0.1881(6)	1.0102(4)	1.0144(3)	0.093(5)	0.095(5)	0.088(4)	0.034(4)	0.015(3)	–0.013(4)

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