Crystal structure of (2,3-bis((2*R*,5*R*)-2,5-dimethylphosphonalyl)maleic anhydride)-(η^4-norbornadiene)-rhodium(I) tetrafluoroborate, $[Rh(C_7H_8)(C_{16}H_{24}O_3P_2)][BF_4]$

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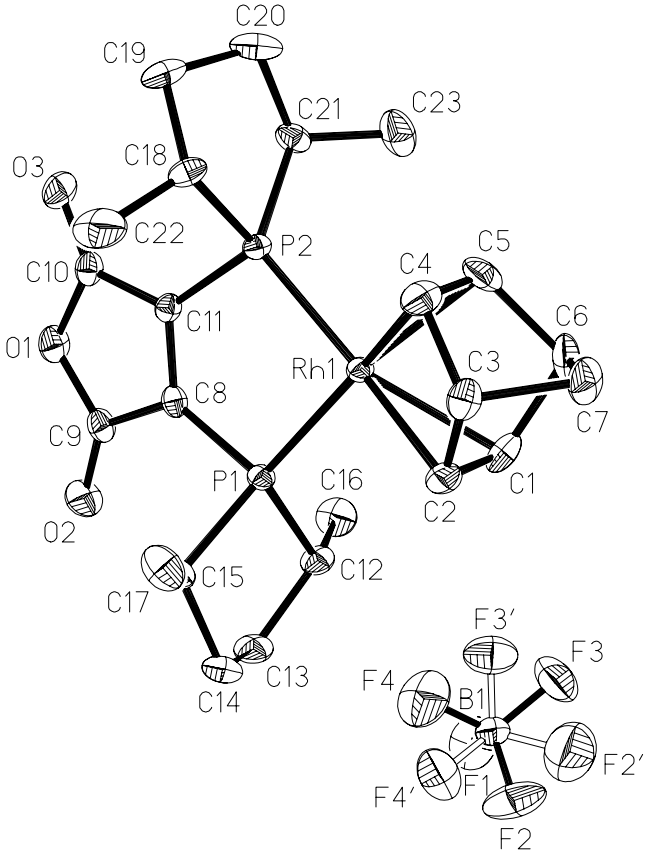

Abstract

$C_{23}H_{32}BF_4O_3P_2Rh$, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.147(2) Å, b = 13.246(3) Å, c = 18.827(4) Å, V = 2530.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.067, T = 200 K.

Source of material

The synthesis is described in [1].

Discussion

Unexpected differences between the title compound and the related cycloocta-1,5-diene (COD) complex [2] in the catalytic hydrogenation of the diolefines norborna-2,5-diene (NBD) and (*Z*,*Z*)-cycloocta-1,5-diene motivated us to determine the crystal structure of the title compound.

The double bonds of the diolefines are not coordinated perpendicular to the P,Rh,P plane which is well-known. 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 COD complex 25.4° [2] and for the title NBD complex 8.8°.

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Table 1. Data collection and handling.

Crystal:	red block, size 0.3 × 0.4 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.54 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	53.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	38897, 5344
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5037
$N(param)_{refined}$:	330
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*a*	0.6424	0.5377	0.1485	0.049
H(2A)	4*a*	0.5630	0.6919	0.0958	0.044
H(3A)	4*a*	0.5189	0.6653	–0.0342	0.044
H(4A)	4*a*	0.3403	0.5349	–0.0407	0.052
H(5A)	4*a*	0.4175	0.3789	0.0104	0.058
H(6A)	4*a*	0.6518	0.4018	0.0541	0.057
H(7A)	4*a*	0.6378	0.4996	–0.0618	0.058
H(7B)	4*a*	0.7263	0.5627	–0.0078	0.058
H(12A)	4*a*	0.5142	0.6036	0.2728	0.040
H(13A)	4*a*	0.4842	0.7199	0.3597	0.051
H(13B)	4*a*	0.3297	0.7079	0.3580	0.051
H(14A)	4*a*	0.3791	0.8535	0.2913	0.055
H(14B)	4*a*	0.4841	0.7940	0.2461	0.055
H(15A)	4*a*	0.2086	0.7682	0.2430	0.039
H(16A)	4*a*	0.4651	0.5137	0.3757	0.077
H(16B)	4*a*	0.4192	0.4531	0.3086	0.077
H(16C)	4*a*	0.3156	0.5114	0.3548	0.077
H(17A)	4*a*	0.2785	0.8823	0.1578	0.079
H(17B)	4*a*	0.2181	0.7867	0.1211	0.079
H(17C)	4*a*	0.3714	0.8005	0.1245	0.079
H(18A)	4*a*	0.1139	0.4946	–0.0070	0.039
H(19A)	4*a*	–0.1108	0.4272	0.0659	0.052
H(19B)	4*a*	–0.0835	0.4175	–0.0162	0.052
H(20A)	4*a*	0.0838	0.3044	0.0020	0.063
H(20B)	4*a*	–0.0327	0.2661	0.0500	0.063
H(21A)	4*a*	0.0628	0.3174	0.1509	0.041
H(22A)	4*a*	–0.0432	0.6204	–0.0069	0.114
H(22B)	4*a*	0.0837	0.6543	0.0341	0.114
H(22C)	4*a*	–0.0424	0.6215	0.0763	0.114
H(23A)	4*a*	0.1981	0.1896	0.1106	0.086
H(23B)	4*a*	0.2804	0.2674	0.1550	0.086
H(23C)	4*a*	0.2881	0.2685	0.0718	0.086

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	4*a*		0.36893(2)	0.53493(2)	0.10989(1)	0.0211(1)	0.0273(1)	0.0205(1)	–0.0032(1)	0.0017(1)	–0.0046(1)
P(1)	4*a*		0.31391(8)	0.61606(6)	0.21303(4)	0.0255(4)	0.0257(4)	0.0186(4)	–0.0006(3)	–0.0005(3)	–0.0031(3)
P(2)	4*a*		0.16274(7)	0.46721(6)	0.11131(4)	0.0228(4)	0.0259(3)	0.0210(3)	–0.0035(3)	–0.0006(3)	–0.0010(4)
O(1)	4*a*		–0.0533(2)	0.5406(2)	0.2886(1)	0.035(1)	0.046(1)	0.037(1)	0.001(1)	0.014(1)	0.002(1)
O(2)	4*a*		0.0860(3)	0.6367(3)	0.3523(2)	0.054(2)	0.060(2)	0.031(2)	0.000(2)	0.013(1)	–0.014(1)
O(3)	4*a*		–0.1393(3)	0.4460(2)	0.2011(2)	0.029(1)	0.050(2)	0.056(2)	–0.009(1)	0.009(1)	0.002(1)
C(1)	4*a*		0.5866(3)	0.5393(3)	0.1060(2)	0.021(1)	0.058(2)	0.044(2)	–0.007(2)	–0.001(2)	0.011(2)
C(2)	4*a*		0.5431(4)	0.6250(3)	0.0762(2)	0.030(2)	0.035(2)	0.045(2)	–0.011(2)	0.004(2)	–0.002(2)
C(3)	4*a*		0.5245(4)	0.6061(3)	–0.0031(2)	0.033(2)	0.044(2)	0.035(2)	–0.001(2)	0.008(2)	0.010(2)
C(4)	4*a*		0.4100(4)	0.5322(4)	–0.0047(2)	0.037(2)	0.070(3)	0.023(2)	–0.013(2)	0.006(1)	–0.011(2)
C(5)	4*a*		0.4525(5)	0.4451(3)	0.0242(3)	0.054(3)	0.038(2)	0.054(3)	–0.016(2)	0.030(2)	–0.023(2)
C(6)	4*a*		0.5979(4)	0.4620(4)	0.0453(3)	0.037(2)	0.038(2)	0.069(3)	0.011(2)	0.025(2)	0.011(2)
C(7)	4*a*		0.6408(4)	0.5320(4)	–0.0156(2)	0.036(2)	0.055(2)	0.053(2)	–0.002(2)	0.022(2)	0.006(2)
C(8)	4*a*		0.1505(3)	0.5701(3)	0.2368(2)	0.029(2)	0.028(2)	0.023(2)	0.006(1)	0.004(1)	0.003(1)
C(9)	4*a*		0.0648(4)	0.5894(3)	0.2996(2)	0.033(2)	0.034(2)	0.032(2)	0.004(2)	0.010(2)	–0.000(2)
C(10)	4*a*		–0.0496(4)	0.4926(3)	0.2234(2)	0.028(2)	0.033(2)	0.035(2)	0.002(1)	0.006(1)	0.007(2)
C(11)	4*a*		0.0840(3)	0.5132(2)	0.1918(2)	0.023(2)	0.025(2)	0.028(2)	–0.001(1)	0.002(1)	0.003(1)
C(12)	4*a*		0.4238(4)	0.6063(3)	0.2910(2)	0.034(2)	0.043(2)	0.023(2)	–0.003(2)	–0.008(1)	–0.003(2)
C(13)	4*a*		0.4090(4)	0.7075(3)	0.3291(2)	0.047(2)	0.052(2)	0.028(2)	–0.008(2)	–0.008(2)	–0.012(2)
C(14)	4*a*		0.4005(5)	0.7884(3)	0.2707(2)	0.052(3)	0.032(2)	0.053(2)	–0.009(2)	–0.005(2)	–0.013(2)
C(15)	4*a*		0.2932(4)	0.7558(3)	0.2195(2)	0.038(2)	0.024(2)	0.034(2)	0.003(1)	–0.000(2)	–0.002(2)
C(16)	4*a*		0.4041(5)	0.5124(3)	0.3368(2)	0.062(3)	0.052(3)	0.039(2)	0.004(2)	–0.014(2)	0.010(2)
C(17)	4*a*		0.2900(5)	0.8114(4)	0.1493(3)	0.072(3)	0.037(2)	0.049(3)	0.010(2)	0.002(2)	0.009(2)
C(18)	4*a*		0.0580(4)	0.5017(3)	0.0352(2)	0.033(2)	0.040(2)	0.026(2)	–0.009(2)	–0.009(2)	0.005(1)
C(19)	4*a*		–0.0426(4)	0.4179(3)	0.0303(2)	0.038(2)	0.060(3)	0.033(2)	–0.023(2)	–0.008(2)	–0.001(2)
C(20)	4*a*		0.0300(6)	0.3205(4)	0.0431(2)	0.076(3)	0.043(2)	0.039(2)	–0.025(2)	–0.008(2)	–0.008(2)
C(21)	4*a*		0.1183(4)	0.3307(2)	0.1093(2)	0.042(2)	0.025(1)	0.035(2)	–0.008(1)	0.008(2)	–0.003(2)
C(22)	4*a*		0.0096(7)	0.6092(4)	0.0346(4)	0.092(4)	0.045(3)	0.089(4)	0.009(3)	–0.060(4)	0.004(3)
C(23)	4*a*		0.2315(5)	0.2574(3)	0.1119(4)	0.060(3)	0.032(2)	0.080(4)	0.004(2)	0.024(3)	0.006(2)
B(1)	4*a*		0.3251(5)	0.7234(3)	0.8209(3)	0.049(3)	0.045(3)	0.070(4)	–0.008(2)	–0.005(3)	–0.005(3)
F(1)	4*a*		0.2951(4)	0.7098(3)	0.8900(2)	0.108(3)	0.122(3)	0.086(3)	0.007(3)	0.004(3)	0.035(3)
F(2)	4*a*	0.633(6)	0.4161(7)	0.7923(5)	0.8113(4)	0.117(2)	0.100(4)	0.116(5)	–0.071(3)	–0.025(4)	0.041(4)
F(3)	4*a*	0.633	0.3693(9)	0.6322(5)	0.8012(5)	0.117(2)	0.083(4)	0.203(6)	0.003(4)	0.053(5)	–0.059(4)
F(4)	4*a*	0.633	0.2109(8)	0.7511(7)	0.7897(4)	0.117(2)	0.170(6)	0.082(4)	0.015(5)	–0.039(4)	0.012(4)
F(2′)	4*a*	0.367	0.450(1)	0.7036(8)	0.8051(8)	0.117(2)	0.190(9)	0.175(9)	0.006(7)	0.009(6)	–0.024(7)
F(3′)	4*a*	0.367	0.265(1)	0.6673(7)	0.7720(4)	0.117(2)	0.082(6)	0.076(5)	–0.035(5)	0.003(5)	0.003(5)
F(4′)	4*a*	0.367	0.294(1)	0.8179(6)	0.8032(6)	0.117(2)	0.086(6)	0.118(7)	0.021(5)	0.018(6)	–0.002(5)

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References

1. Holz, J.; Monsees, A.; Jiao, H.; You, J.; Komarov, I. V.; Fischer, C.; Drauz, K.; Börner, A.: Synthesis of a New Chiral Bisphospholane Ligand for the Rh(I) Catalyzed Enantioselective Hydrogenation of Isomeric β-Acylamido Acrylates. J. Org. Chem. (2003) 1701-1707.
2. Holz, J.; Zayas, O.; Jiao, H.; Baumann, W.; Spannenberg, A.; Monsees, A.; Riermeier, T. H.; Almena, J.; Kadyrov, R.; Börner, A.: A Highly Tunable Family of Chiral Bisphospholanes for Rh-Catalyzed Enantioselective Hydrogenation Reactions. Chem. Eur. J. **12** (2006) 5001-5013.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen.