Crystal structure of (η^4-cycloocta-1,5-dien)-*N*-(2-(diphenylphosphinooxy)-3-(naphthalen-1-yloxy)propyl)-*N*-(pentan-3-yl)-1,1-diphenylphosphinamine-rhodium(I) tetrafluoroborate, $[Rh(C_8H_{12})(C_{42}H_{43}NO_2P_2)][BF_4]$

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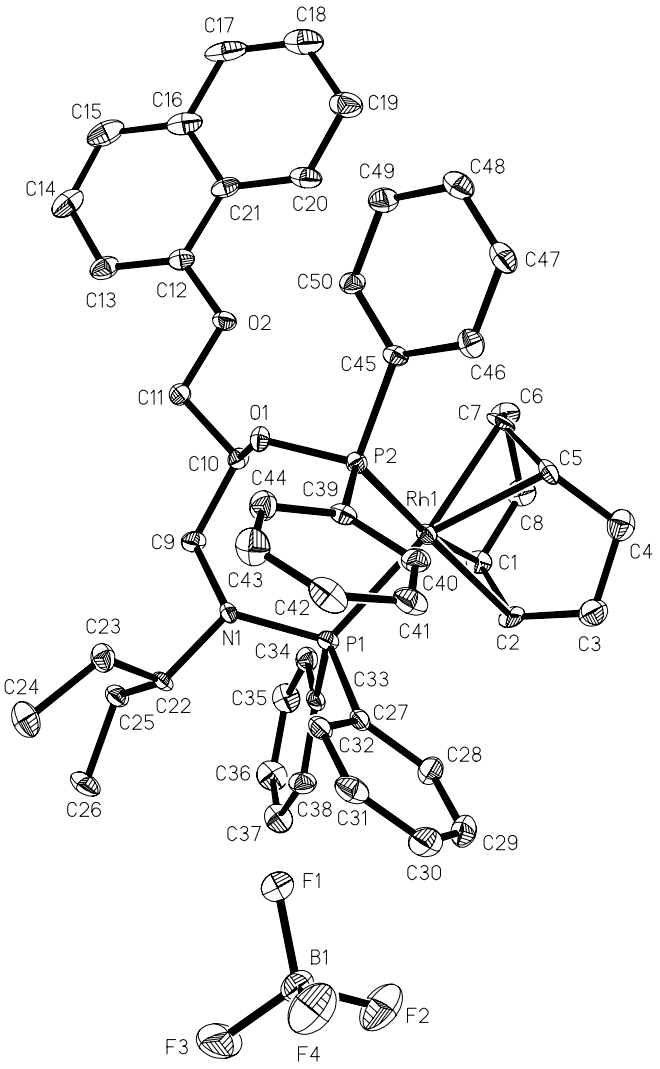

Abstract

$C_{50}H_{55}BF_4NO_2P_2Rh$, monoclinic, $P12_11$ (no. 4), a = 12.722(3) Å, b = 15.248(3) Å, c = 12.818(3) Å, β = 115.80(3)°, V = 2238.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.079, T = 200 K.

Source of material

The synthesis is described in [1].

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Discussion

Unexpected differences between the title compound and the related norborna-2,5-diene complex in the catalytic hydrogenation of the diolefines norborna-2,5-diene and (*Z*,*Z*)-cycloocta-1,5-diene [2] 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 5.3 [3].

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 5.6° (clockwise twist) and for the (*R*,*R*)-NBD-complex 5.3° (clockwise twist).

Table 1. Data collection and handling.

Crystal:	red prism, size 0.2 × 0.4 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.11 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS 2, ω/φ
$2\theta_{max}$:	46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10753, 6202
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5557
$N(param)_{refined}$:	550
Programs:	SHELXS-97 [4], SHELXS-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*a*	–0.3981	–0.2615	–0.2900	0.08
H(2A)	2*a*	–0.4115	–0.3785	–0.3896	0.08
H(3A)	2*a*	–0.2625	–0.3660	–0.4563	0.08
H(3B)	2*a*	–0.2579	–0.4545	–0.3951	0.08
H(4A)	2*a*	–0.0976	–0.3185	–0.3085	0.08
H(4B)	2*a*	–0.0688	–0.4165	–0.3161	0.08
H(5A)	2*a*	–0.0397	–0.4344	–0.1325	0.08
H(6A)	2*a*	–0.0446	–0.3322	–0.0199	0.08
H(7A)	2*a*	–0.0632	–0.1982	–0.1272	0.08
H(7B)	2*a*	–0.1509	–0.2028	–0.0731	0.08
H(8A)	2*a*	–0.2649	–0.1590	–0.2545	0.08
H(8B)	2*a*	–0.2009	–0.2178	–0.3073	0.08
H(9A)	2*a*	–0.4585	–0.4378	0.0788	0.08
H(9B)	2*a*	–0.4896	–0.3663	–0.0157	0.08
H(10A)	2*a*	–0.2996	–0.3425	0.0251	0.08
H(11A)	2*a*	–0.3613	–0.2975	0.1707	0.08
H(11B)	2*a*	–0.2923	–0.3776	0.2435	0.08
H(13A)	2*a*	–0.3134	–0.2567	0.3435	0.08
H(14A)	2*a*	–0.2627	–0.1607	0.5054	0.08
H(15A)	2*a*	–0.0831	–0.0909	0.5869	0.08
H(17A)	2*a*	0.1066	–0.0557	0.5821	0.08

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(18A)	2*a*	0.2340	–0.0737	0.4976	0.08
H(19A)	2*a*	0.1811	–0.1598	0.3288	0.08
H(20A)	2*a*	–0.0042	–0.2272	0.2455	0.08
H(22A)	2*a*	–0.6034	–0.5645	–0.1581	0.08
H(23A)	2*a*	–0.5012	–0.5710	0.0853	0.08
H(23B)	2*a*	–0.4882	–0.6417	0.0047	0.08
H(24A)	2*a*	–0.6166	–0.6922	0.0768	0.08
H(24B)	2*a*	–0.6967	–0.6103	0.0233	0.08
H(24C)	2*a*	–0.6836	–0.6818	–0.0581	0.08
H(25A)	2*a*	–0.6669	–0.4168	–0.1280	0.08
H(25B)	2*a*	–0.6678	–0.4594	–0.0187	0.08
H(26A)	2*a*	–0.8568	–0.4635	–0.1707	0.08
H(26B)	2*a*	–0.8108	–0.5166	–0.2471	0.08
H(26C)	2*a*	–0.8117	–0.5598	–0.1365	0.08
H(28A)	2*a*	–0.4868	–0.5117	–0.4188	0.08
H(29A)	2*a*	–0.4878	–0.6446	–0.5140	0.08
H(30A)	2*a*	–0.4653	–0.7784	–0.4167	0.08

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(31A)	2*a*	–0.4363	–0.7811	–0.2237	0.08
H(32A)	2*a*	–0.4337	–0.6486	–0.1281	0.08
H(34A)	2*a*	–0.5148	–0.2839	–0.2049	0.08
H(35A)	2*a*	–0.6892	–0.2049	–0.3049	0.08
H(36A)	2*a*	–0.8568	–0.2775	–0.4335	0.08
H(37A)	2*a*	–0.8507	–0.4249	–0.4677	0.08
H(38A)	2*a*	–0.6715	–0.5050	–0.3795	0.08
H(40A)	2*a*	–0.1555	–0.6071	–0.1340	0.08
H(41A)	2*a*	–0.1545	–0.7614	–0.1396	0.08
H(42A)	2*a*	–0.1927	–0.8419	–0.0056	0.08
H(43A)	2*a*	–0.2171	–0.7713	0.1447	0.08
H(44A)	2*a*	–0.2150	–0.6159	0.1526	0.08
H(46A)	2*a*	0.0403	–0.5407	0.0147	0.08
H(47A)	2*a*	0.2394	–0.5158	0.1323	0.08
H(48A)	2*a*	0.2985	–0.4304	0.3003	0.08
H(49A)	2*a*	0.1579	–0.3709	0.3498	0.08
H(50A)	2*a*	–0.0414	–0.3903	0.2325	0.08

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)	2*a*	–0.26122(3)	–0.40252(2)	–0.15335(3)	0.0174(2)	0.0194(2)	0.0206(2)	–0.0012(2)	0.0080(1)	0.0020(2)
P(2)	2*a*	–0.1776(1)	–0.47961(8)	0.0161(1)	0.0174(7)	0.0193(7)	0.0206(6)	0.0011(5)	0.0083(6)	0.0014(5)
P(1)	2*a*	–0.4436(1)	–0.46178(8)	–0.1884(1)	0.0165(7)	0.0211(7)	0.0208(6)	–0.0016(5)	0.0067(6)	–0.0011(5)
O(1)	2*a*	–0.2306(3)	–0.4543(2)	0.1070(3)	0.023(2)	0.025(2)	0.021(2)	0.005(2)	0.013(2)	0.004(1)
O(2)	2*a*	–0.1905(3)	–0.2851(2)	0.2273(3)	0.022(2)	0.031(2)	0.027(2)	–0.008(2)	0.010(2)	–0.011(2)
N(1)	2*a*	–0.4661(3)	–0.4845(2)	–0.0699(3)	0.017(2)	0.023(2)	0.023(2)	–0.004(2)	0.012(2)	–0.003(2)
C(1)	2*a*	–0.3239(5)	–0.2845(3)	–0.2795(4)	0.027(3)	0.019(3)	0.021(3)	0.001(2)	0.004(2)	0.012(2)
C(2)	2*a*	–0.3327(5)	–0.3598(3)	–0.3432(4)	0.030(3)	0.032(3)	0.009(2)	0.000(2)	0.000(2)	0.009(2)
C(3)	2*a*	–0.2465(4)	–0.3924(5)	–0.3829(4)	0.043(3)	0.039(4)	0.033(3)	–0.004(3)	0.016(3)	–0.005(3)
C(4)	2*a*	–0.1177(5)	–0.3774(3)	–0.2980(4)	0.040(3)	0.039(4)	0.038(3)	0.007(2)	0.019(3)	0.004(2)
C(5)	2*a*	–0.0957(4)	–0.3894(4)	–0.1719(4)	0.017(2)	0.032(4)	0.033(2)	–0.002(3)	0.014(2)	0.004(3)
C(6)	2*a*	–0.0982(4)	–0.3236(4)	–0.0997(4)	0.015(3)	0.031(3)	0.032(3)	–0.015(2)	0.002(2)	0.005(2)
C(7)	2*a*	–0.1303(5)	–0.2287(3)	–0.1298(4)	0.039(4)	0.030(3)	0.030(3)	–0.003(3)	0.009(3)	0.000(2)
C(8)	2*a*	–0.2308(5)	–0.2158(4)	–0.2503(5)	0.041(4)	0.029(3)	0.037(3)	–0.001(3)	0.014(3)	0.002(2)
C(9)	2*a*	–0.4394(4)	–0.4155(4)	0.0191(4)	0.021(2)	0.023(3)	0.026(2)	0.002(2)	0.010(2)	–0.010(2)
C(10)	2*a*	–0.3127(4)	–0.3823(3)	0.0762(4)	0.018(3)	0.021(3)	0.019(2)	0.005(2)	0.008(2)	–0.001(2)
C(11)	2*a*	–0.2963(4)	–0.3358(3)	0.1859(4)	0.026(3)	0.028(3)	0.025(3)	–0.006(2)	0.014(2)	–0.010(2)
C(12)	2*a*	–0.1671(5)	–0.2326(3)	0.3235(4)	0.025(3)	0.020(3)	0.022(3)	0.003(2)	0.005(2)	0.002(2)
C(13)	2*a*	–0.2413(5)	–0.2247(4)	0.3732(4)	0.029(3)	0.039(3)	0.025(3)	0.010(3)	0.006(3)	–0.004(2)
C(14)	2*a*	–0.2094(6)	–0.1690(4)	0.4716(5)	0.049(4)	0.044(4)	0.026(3)	0.019(3)	0.012(3)	–0.001(3)
C(15)	2*a*	–0.1040(6)	–0.1267(4)	0.5191(5)	0.059(5)	0.032(3)	0.029(3)	0.011(3)	0.006(3)	–0.008(3)
C(16)	2*a*	–0.0268(5)	–0.1346(3)	0.4674(4)	0.041(4)	0.020(3)	0.030(3)	0.002(3)	–0.002(3)	0.002(2)
C(17)	2*a*	0.0840(6)	–0.0914(4)	0.5140(5)	0.058(5)	0.026(3)	0.028(3)	–0.012(3)	–0.013(3)	0.006(3)
C(18)	2*a*	0.1594(7)	–0.1025(4)	0.4641(5)	0.054(5)	0.041(4)	0.042(4)	–0.022(3)	–0.002(4)	0.016(3)
C(19)	2*a*	0.1278(6)	–0.1529(4)	0.3631(5)	0.040(4)	0.046(4)	0.040(3)	–0.014(3)	0.006(3)	0.009(3)
C(20)	2*a*	0.0189(5)	–0.1941(4)	0.3157(5)	0.027(3)	0.034(3)	0.031(3)	–0.005(3)	–0.001(3)	0.005(2)
C(21)	2*a*	–0.0577(5)	–0.1878(3)	0.3664(4)	0.031(3)	0.020(3)	0.018(2)	0.003(2)	0.002(2)	0.001(2)
C(22)	2*a*	–0.5768(4)	–0.5326(3)	–0.0866(4)	0.013(2)	0.024(3)	0.023(2)	–0.005(2)	0.007(2)	–0.001(2)
C(23)	2*a*	–0.5416(5)	–0.6007(3)	0.0125(4)	0.031(3)	0.030(3)	0.030(3)	0.000(3)	0.016(2)	0.007(2)
C(24)	2*a*	–0.6439(5)	–0.6510(4)	0.0139(5)	0.049(4)	0.029(3)	0.052(4)	–0.005(3)	0.028(3)	0.014(3)
C(25)	2*a*	–0.6759(4)	–0.4713(3)	–0.0954(4)	0.019(3)	0.030(3)	0.030(3)	–0.004(2)	0.012(2)	–0.005(2)
C(26)	2*a*	–0.8006(5)	–0.5060(4)	–0.1695(5)	0.017(3)	0.047(4)	0.045(3)	–0.007(3)	0.008(3)	–0.001(3)
C(27)	2*a*	–0.4577(4)	–0.5678(3)	–0.2629(4)	0.019(3)	0.022(3)	0.027(3)	–0.005(2)	0.014(2)	–0.005(2)
C(28)	2*a*	–0.4745(5)	–0.5665(4)	–0.3783(4)	0.039(3)	0.030(3)	0.029(3)	–0.002(3)	0.018(3)	–0.002(2)
C(29)	2*a*	–0.4770(5)	–0.6453(4)	–0.4350(5)	0.046(4)	0.044(4)	0.041(3)	–0.004(3)	0.029(3)	–0.009(3)
C(30)	2*a*	–0.4631(5)	–0.7242(4)	–0.3776(5)	0.039(4)	0.029(3)	0.053(4)	–0.001(3)	0.022(3)	–0.018(3)
C(31)	2*a*	–0.4465(5)	–0.7261(4)	–0.2635(6)	0.022(3)	0.031(4)	0.048(4)	0.000(3)	0.012(3)	–0.004(3)
C(32)	2*a*	–0.4438(4)	–0.6474(3)	–0.2068(4)	0.021(3)	0.026(3)	0.032(3)	–0.006(2)	0.014(2)	–0.005(2)
C(33)	2*a*	–0.5754(3)	–0.4012(5)	–0.2834(3)	0.019(2)	0.029(2)	0.020(2)	–0.005(3)	0.009(2)	0.005(3)
C(34)	2*a*	–0.5823(5)	–0.3130(3)	–0.2619(4)	0.034(3)	0.028(3)	0.029(3)	–0.004(3)	0.017(3)	0.001(2)
C(35)	2*a*	–0.6866(5)	–0.2665(4)	–0.3187(5)	0.040(4)	0.030(3)	0.042(3)	0.005(3)	0.018(3)	0.008(3)
C(36)	2*a*	–0.7850(5)	–0.3093(4)	–0.3947(5)	0.031(3)	0.038(4)	0.043(3)	0.014(3)	0.009(3)	0.014(3)
C(37)	2*a*	–0.7804(4)	–0.3957(5)	–0.4158(4)	0.030(3)	0.044(3)	0.033(3)	0.005(4)	0.007(2)	0.018(4)
C(38)	2*a*	–0.6745(5)	–0.4440(4)	–0.3624(4)	0.027(3)	0.033(3)	0.023(3)	–0.003(2)	0.004(2)	0.002(2)
C(39)	2*a*	–0.1865(4)	–0.5978(3)	0.0091(4)	0.016(3)	0.016(3)	0.023(2)	0.000(2)	0.002(2)	0.005(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(40)	2*a*	–0.1689(4)	–0.6407(3)	–0.0776(4)	0.021(3)	0.036(3)	0.026(3)	0.000(2)	0.005(2)	–0.003(2)
C(41)	2*a*	–0.1695(5)	–0.7317(3)	–0.0814(5)	0.021(3)	0.031(3)	0.046(3)	–0.001(2)	0.011(3)	–0.006(3)
C(42)	2*a*	–0.1885(5)	–0.7791(4)	–0.0001(6)	0.029(3)	0.027(3)	0.062(4)	0.004(3)	0.017(3)	0.006(3)
C(43)	2*a*	–0.2060(6)	–0.7378(3)	0.0870(5)	0.055(4)	0.022(3)	0.053(4)	–0.003(3)	0.029(3)	0.003(3)
C(44)	2*a*	–0.2040(5)	–0.6457(3)	0.0921(4)	0.037(3)	0.032(3)	0.032(3)	–0.002(2)	0.017(3)	0.002(2)
C(45)	2*a*	–0.0219(4)	–0.4657(3)	0.1094(4)	0.016(3)	0.019(3)	0.020(2)	0.000(2)	0.003(2)	0.006(2)
C(46)	2*a*	0.0636(5)	–0.5044(3)	0.0823(4)	0.031(3)	0.023(3)	0.035(3)	–0.001(2)	0.017(3)	0.003(2)
C(47)	2*a*	0.1817(5)	–0.4903(4)	0.1524(5)	0.023(3)	0.038(3)	0.043(3)	0.003(2)	0.016(3)	0.008(3)
C(48)	2*a*	0.2171(5)	–0.4402(4)	0.2516(5)	0.023(3)	0.037(3)	0.041(3)	0.000(2)	0.010(3)	0.004(2)
C(49)	2*a*	0.1336(4)	–0.4048(5)	0.2800(4)	0.027(3)	0.042(3)	0.027(2)	0.001(4)	0.005(2)	0.004(4)
C(50)	2*a*	0.0149(4)	–0.4162(4)	0.2107(4)	0.020(2)	0.029(4)	0.020(2)	0.004(2)	0.004(2)	0.001(2)
B(1)	2*a*	–0.5214(6)	–0.9973(5)	–0.3050(5)	0.031(4)	0.051(5)	0.026(3)	0.003(3)	0.010(3)	–0.007(3)
F(1)	2*a*	–0.4560(3)	–0.9449(2)	–0.2114(2)	0.041(2)	0.058(2)	0.031(2)	–0.014(2)	0.016(2)	–0.011(1)
F(2)	2*a*	–0.5234(4)	–0.9591(3)	–0.4048(3)	0.077(3)	0.080(3)	0.031(2)	0.019(2)	0.019(2)	0.008(2)
F(3)	2*a*	–0.6335(3)	–1.0058(3)	–0.3139(4)	0.030(2)	0.114(4)	0.083(3)	–0.016(2)	0.026(2)	–0.048(3)
F(4)	2*a*	–0.4708(4)	–1.0790(3)	–0.2894(3)	0.087(3)	0.048(3)	0.061(3)	0.023(2)	0.036(2)	–0.002(2)

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