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Synthesis and Structure Determination of $[(PEt_3)RhC_2B_9H_{10}]_2$: A Binuclear Rhodacarborane Containing Four Bonds Between Two Icosahedra **

By Paul E. Behnken, Carolyn B. Knobler and M. Frederick Hawthorne *

In the course of our studies on the homogeneous catalysis of olefin hydrogenation by *closo*-3,3-$(PPh_3)_2$-3-(H)-3,1,2-$RhC_2B_9H_{11}$ **1**[1], we characterized and reported the molecular structure of $[(PPh_3)RhC_2B_9H_{11}]_2$ **2**[2], a binuclear phosphinorhodacarborane complex formed by formal loss of dihydrogen and two phosphine ligands from two molecules of **1**. Of interest were the Rh-H-B interactions supporting the Rh-Rh bond and the stereospecificity of their formation. The two terminal B-H bonds involved in the Rh-H-B interactions determine a

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specific stereoisomer and of the six possibilities only **2** is observed with both enantiomers present in the unit cell.

In an attempt to further understand the nature of these interactions, $Rh(COD)(PEt_3)Cl$ was reacted with $Cs_2[7-(7',8'-C_2B_9H_{11})-7,8-C_2B_9H_{11}]$ **3**,[3] to produce a dark blue compound **4**, as depicted in reaction 1.

(1)

The crystal of **4** (figure 1) contains two icosahedral rhodacarborane fragments attached symmetrically at three vertices. Carbon atoms C(1) and C(1′) are covalently bonded as in the carborane precursor. Each C_2B_9 fragment sequesters a rhodium vertex, Rh(3) and Rh(3′), with a Rh-Rh distance of 2.725(1) Å, in the range of a Rh-Rh single bond[4] and comparable to that determined in **2** of 2.763(1) Å.

The Rh-Rh bond is further supported by two Rh-H-B three-center interactions between Rh(3), H(4′), B(4′) and Rh(3′), H(4), B(4) with Rh-B distances of 2.306(7) and 2.323(7) Å, respectively. The Rh-H distances are 1.92(7) Å for Rh(3)-H(4′) and 1.85(7) Å for Rh(3′)-H(4). These distances are comparable to those observed in **2**.

The molecule **4** has C_2 symmetry with the rotation axis bisecting the Rh(3)-Rh(3′) and C(1)-C(1′) bonds. Unlike the asymmetric structure of **2**, the symmetry in **4** is attributed to the C(1)-C(1′) bond which limits the Rh-H-B interactions to the B(4) and B(4′) vertices adjacent to C(1) and C(1′), respectively.

Interestingly, the carborane ligand **3** is diastereomeric by virtue of the asymmetry of the $-C_2B_9H_{11}$ fragment. The mirror plane symmetry of each carborane fragment is destroyed by substitution on one of the carbon vertices and the carborane precursor **3** contains two chemically distinct isomers, verifiable by ^{11}B nmr spectroscopy, which differ by the configuration of one $-C_2B_9H_{11}$ moeity. The ^{31}P nmr spectrum of chromatographed **4** contains resonances attributable to **4** (34.4 ppm, J_{P-Rh}=173 Hz) as well as an unsymmetrical compound (32.3 ppm, J_{P-Rh}=177 Hz; 29.2 ppm, J_{P-Rh}=149 Hz; $^3J_{P-P}$=6.6 Hz) derived from the diastereomeric carborane ligand containing icosahedral fragments of opposite configuration. A hypothetical structure of the unsymmetric isomer structurally analogous to **4** would contain a Rh-H-C as well as a Rh-H-B interaction. Inversion of one $-C_2B_9H_{11}$ fragment maintaining the C(1)-C(1′) and Rh(3)-Rh(3′) bonds would result in an interaction between C(2) and Rh(3′). Interactions of this type have been structurally characterized.[5]

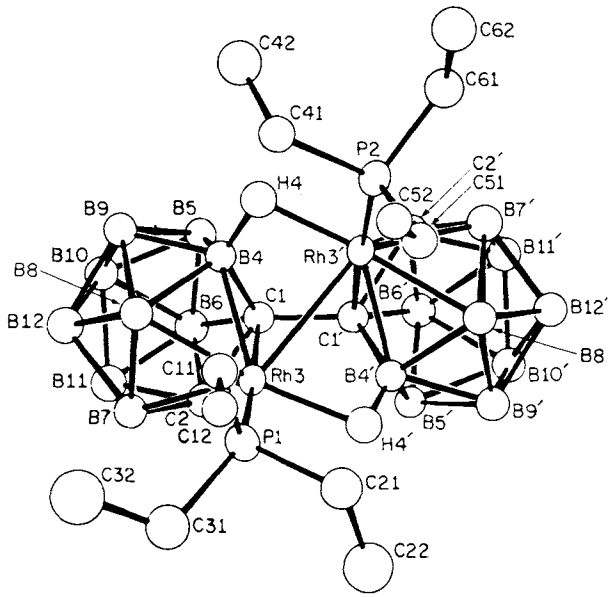

Fig. 1. ORTEP projection of the title compound. Hydrogen atoms, other tha those involved in bridging, are omitted for clarity. Hydrogen atoms have been numbered to correspond to the number of the attached atom.

Table 1

Crystal and Intensity Collection Data for $[(PEt_3)RhC_2B_9H_{10}]_2$, 4

Formula	$C_{16}H_{50}B_{18}Rh_2$
Formula wt.	704.93
a/Å	11.153(6)
b/Å	15.228(9)
c/Å	18.844(10)
β/deg	91.83(2)
V/Å^3	3198.8
density(calcd)/g·cm^{-3}	1.46
density(obsd)/g·cm^{-3}	1.47
Space Group	$P2_1/c$
Boundary Faces[c]	(100),(-100),(00-1),(001)
	(1-1-1),(11-1),(-111),(-1-11)
	(0-11),(011),(01-1),(0-1-1)
Radiation Source (lambda/Å)	MoKalpha (Zr filter), 0.71069
Absorption coefficient μ /cm^{-1}	11.255
Scan rate /deg min^{-1}	2.0
Scan range	2.2(1 + 0.692 tan theta)
2 θ limit /deg	45.
Observations	h,k,±l
Total measured data	4119
No. unique observed data (I>3σ(I))	3003
Total no. of variables	353
R[a]	0.031

Rw[b]	0.036
Error in observation of unit weight	1.29

[a] $R = \sum||Fo|-|Fc||/\sum|Fo|$

[b] $Rw = [\sum w(|Fo|-|Fc|)^2/\sum wFo^2]^{1/2}$

$w = 1/(\sigma^2|Fo|)$

[c] at distances (cm) perpendicular to these faces of 0.0079, 0.0088, 0., 0.038, 0., 0., 0.024, 0.021, 0.027, 0.030, 0.0031, and 0.0031, respectively, from a common point.

Table 2

Positional Parameters for $[(PEt_3)RhC_2B_9H_{10}]_2$ 4

Atom	x	y	z
Rh(3′)	0.06957(4)	0.10124(3)	0.15058(2)
Rh(3)	0.27258(4)	0.02164(3)	0.20297(2)
P(1)	0.2841(1)	0.4848(1)	-0.17589(8)
P(2)	-0.0956(1)	0.0864(1)	0.21845(8)
B(04′)	0.2380(6)	0.1655(4)	0.1701(4)
B(04)	0.1455(6)	-0.0380(4)	0.1291(3)
B(05′)	0.3265(6)	0.2006(4)	0.0960(4)
B(05)	0.1851(6)	-0.0541(5)	0.0374(4)
B(06′)	0.2408(6)	0.1933(5)	0.0149(4)
B(06)	0.3391(6)	-0.0350(5)	0.0268(4)
B(07′)	0.0246(7)	0.2259(5)	0.0949(4)
B(07)	0.3858(7)	-0.0920(5)	0.1744(4)
B(08′)	0.1111(6)	0.2379(5)	0.1793(4)
B(08)	0.2245(6)	-0.1163(5)	0.1859(4)
B(09′)	0.2576(6)	0.2783(5)	0.1537(4)
B(09)	0.1657(6)	-0.1447(5)	0.0971(4)
B(10′)	0.2581(6)	0.2949(5)	0.0604(4)
B(10)	0.2849(6)	-0.1440(5)	0.0351(4)
B(11′)	0.1176(6)	0.2630(5)	0.0230(4)
B(11)	0.4191(6)	-0.1114(5)	0.0817(4)
B(12′)	0.1253(6)	0.3158(5)	0.1076(4)
B(12)	0.3138(6)	-0.1783(5)	0.1256(4)

C(01′)	0.2246(5)	0.1197(4)	0.0846(3)
C(01)	0.2579(5)	0.0239(4)	0.0860(3)
C(02′)	0.1034(5)	0.1562(4)	0.0424(3)
C(02)	0.3910(5)	-0.0097(4)	0.1114(3)
C(11)	0.1537(6)	0.5343(5)	-0.1356(4)
C(12)	0.1513(9)	0.5351(7)	-0.0552(4)
C(21)	0.2904(7)	0.3752(5)	-0.1352(4)
C(22)	0.4075(8)	0.3251(7)	-0.1446(5)
C(31)	0.4127(7)	0.5419(5)	-0.1354(4)
C(32)	0.4019(9)	0.6424(7)	-0.1375(5)
C(41)	-0.1387(6)	-0.0279(4)	0.2336(3)
C(42)	-0.1865(7)	-0.0778(5)	0.1680(4)
C(51)	-0.0801(6)	0.1381(5)	0.3064(4)
C(52)	-0.1472(7)	0.1001(6)	0.3683(4)
C(61)	-0.2292(6)	0.1364(5)	0.1775(4)
C(62)	-0.3481(7)	0.1249(6)	0.2142(4)
H(002′)	0.0665(62)	0.1216(45)	0.0069(36)
H(002)	0.4510(62)	0.0370(46)	0.1122(36)
H(004′)	0.2961(59)	0.1461(46)	0.2100(35)
H(004)	0.0434(60)	-0.0165(45)	0.1311(35)
H(005′)	0.4262(60)	0.1848(45)	0.0956(35)
H(005)	0.1191(60)	-0.0318(44)	-0.0035(36)
H(006′)	0.2726(59)	0.1655(46)	-0.0338(36)
H(006)	0.3790(60)	-0.0061(45)	-0.0120(37)
H(007′)	-0.0739(59)	0.2318(44)	0.0840(34)
H(007)	0.4548(62)	-0.0999(44)	0.2103(36)

H(008´)	0.0831(59)	0.2570(45)	0.2276(36)
H(008)	0.1815(60)	-0.1570(45)	0.2284(35)
H(009´)	0.3183(60)	0.3204(46)	0.1899(35)
H(009)	0.0874(61)	-0.1914(45)	0.0919(35)
H(010´)	0.3164(61)	0.3429(47)	0.0396(35)
H(010)	0.2867(58)	-0.1870(47)	-0.0098(34)
H(011´)	0.0745(59)	0.2907(45)	-0.0259(35)
H(011)	0.5169(62)	-0.1333(44)	0.0641(35)
H(012´)	0.0960(60)	0.3831(46)	0.1154(36)
H(012)	0.3384(58)	-0.2447(48)	0.1327(35)
H(111)	0.1622(66)	0.5860(53)	-0.1494(40)
H(112)	0.0880(68)	0.5037(49)	-0.1559(39)
H(121)	0.0959(83)	0.5705(61)	-0.0458(49)
H(122)	0.1498(83)	0.4780(61)	-0.0409(49)
H(123)	0.2211(83)	0.5678(63)	-0.0411(49)
H(211)	0.2803(68)	0.3900(49)	-0.0881(43)
H(212)	0.2296(70)	0.3413(51)	-0.1533(40)
H(221)	0.3952(75)	0.2544(62)	-0.1199(45)
H(222)	0.4295(81)	0.3140(62)	-0.1927(48)
H(223)	0.4641(88)	0.3526(69)	-0.1211(52)
H(311)	0.4427(68)	0.5226(49)	-0.0761(43)
H(312)	0.4877(71)	0.5088(53)	-0.1599(42)
H(321)	0.4656(82)	0.6636(61)	-0.0808(50)
H(322)	0.3940(84)	0.6819(65)	-0.1875(52)
H(323)	0.3256(91)	0.6606(64)	-0.1057(52)
H(411)	-0.1962(65)	-0.0241(45)	0.2658(38)

H(412)	-0.0698(66)	-0.0524(48)	0.2495(38)
H(421)	-0.2158(70)	-0.1434(57)	0.1790(41)
H(422)	-0.1479(73)	-0.0683(54)	0.1209(45)
H(423)	-0.2451(78)	-0.0533(62)	0.1530(49)
H(511)	-0.1082(61)	0.1949(49)	0.2934(36)
H(512)	-0.0059(68)	0.1374(48)	0.3130(36)
H(521)	-0.1315(68)	0.1393(53)	0.4072(43)
H(522)	-0.1311(71)	0.0396(57)	0.3772(42)
H(523)	-0.2228(77)	0.0920(57)	0.3595(45)
H(611)	-0.2372(63)	0.1111(49)	0.1329(41)
H(612)	-0.2115(64)	0.1922(51)	0.1702(39)
H(621)	-0.4231(73)	0.1665(54)	0.1873(42)
H(622)	-0.3503(81)	0.1516(59)	0.2529(46)
H(623)	-0.3715(79)	0.0717(59)	0.2270(47)

Table 3

Selected Distances and Angles

Rh(3´)	H(004)	1.85 (7)	Rh(3)	H(004´)	1.92 (7)
Rh(3´)	B(04´)	2.139(7)	Rh(3)	B(04)	2.155(6)
Rh(3´)	C(01´)	2.180(5)	Rh(3)	C(01)	2.205(5)
Rh(3´)	B(08´)	2.196(7)	Rh(3)	B(08)	2.189(7)
Rh(3´)	B(07´)	2.219(7)	Rh(3)	B(07)	2.219(7)
Rh(3´)	C(02´)	2.247(6)	Rh(3)	C(02)	2.258(6)
Rh(3´)	P(2)	2.287(2)	Rh(3)	P(1)	2.284(2)
Rh(3´)	B(04)	2.323(7)	Rh(3)	B(04´)	2.306(7)
Rh(3´)	Rh(3)	2.725(1)			
P(1)	C(31)	1.823(8)	P(2)	C(41)	1.831(7)
P(1)	C(11)	1.825(7)	P(2)	C(51)	1.838(7)
P(1)	C(21)	1.837(8)	P(2)	C(61)	1.823(7)
B(04´)	H(004´)	1.02 (7)	B(04)	H(004)	1.19 (7)
B(04´)	C(01´)	1.759(8)	B(04)	C(01)	1.784(8)
B(04´)	B(09´)	1.759(10)	B(04)	B(09)	1.751(9)
B(04´)	B(08´)	1.806(9)	B(04)	B(08)	1.812(9)
B(04´)	B(05´)	1.816(9)	B(04)	B(05)	1.813(9)
B(05´)	C(01´)	1.685(8)	B(05)	C(01)	1.691(9)
B(05´)	B(10´)	1.750(10)	B(05)	B(10)	1.767(10)
B(05´)	B(06´)	1.780(9)	B(05)	B(06)	1.760(10)
B(05´)	B(09´)	1.796(10)	B(05)	B(09)	1.798(10)
B(06´)	C(02´)	1.728(9)	B(06)	C(02)	1.722(9)
B(06´)	C(01´)	1.739(9)	B(06)	C(01)	1.714(9)

B(06´)	B(11´)	1.747(10)	B(06)	B(11)	1.778(10)
B(06´)	B(10´)	1.777(10)	B(06)	B(10)	1.775(10)
B(07´)	C(02´)	1.713(9)	B(07)	C(02)	1.728(9)
B(07´)	B(12´)	1.782(10)	B(07)	B(12)	1.781(10)
B(07´)	B(11´)	1.823(10)	B(07)	B(11)	1.822(10)
B(07´)	B(08´)	1.842(10)	B(07)	B(08)	1.856(10)
B(08´)	B(12´)	1.809(10)	B(08)	B(12)	1.802(10)
B(08´)	B(09´)	1.825(10)	B(08)	B(09)	1.830(10)
B(09´)	B(10´)	1.777(10)	B(09)	B(10)	1.798(10)
B(09´)	B(12´)	1.784(10)	B(09)	B(12)	1.795(10)
B(10´)	B(11´)	1.766(10)	B(10)	B(11)	1.781(10)
B(10´)	B(12´)	1.780(10)	B(10)	B(12)	1.803(10)
B(11´)	C(02´)	1.676(9)	B(11)	C(02)	1.679(9)
B(11´)	B(12´)	1.786(10)	B(11)	B(12)	1.779(10)
C(01´)	C(01)	1.506(8)			
C(01´)	C(02´)	1.642(8)	C(01)	C(02)	1.627(8)

H(004)	Rh(3´)	P(2)	84. (2)	H(004´	Rh(3)	P(1)	88. (2)
H(004)	Rh(3´)	Rh(3)	76. (2)	H(004´	Rh(3)	Rh(3´)	72. (2)
B(04´)	Rh(3´)	C(01´)	48.03(22)	B(04)	Rh(3)	C(01)	48.30(22)
B(04´)	Rh(3´)	B(08´)	49.21(25)	B(04)	Rh(3)	B(08)	49.31(25)
B(04´)	Rh(3´)	B(07´)	82.75(27)	B(04)	Rh(3)	B(07)	83.23(26)
B(04´)	Rh(3´)	C(02´)	79.24(24)	B(04)	Rh(3)	C(02)	78.79(23)
B(04´)	Rh(3´)	B(04)	97.16(24)	B(04)	Rh(3)	B(04´)	97.23(25)
B(04´)	Rh(3´)	P(2)	131.86(19)	B(04)	Rh(3)	P(1)	129.94(18)

B(04′)	Rh(3′)	Rh(3)	55.02(19)	B(04)	Rh(3)	Rh(3′)	55.37(18)
C(01′)	Rh(3′)	B(08′)	81.55(23)	B(08)	Rh(3)	C(01)	81.84(23)
C(01′)	Rh(3′)	B(07′)	77.94(24)	C(01)	Rh(3)	B(07)	78.11(24)
C(01′)	Rh(3′)	C(02′)	43.51(20)	C(01)	Rh(3)	C(02)	42.74(20)
C(01′)	Rh(3′)	P(2)	177.99(15)	C(01)	Rh(3)	P(1)	178.11(15)
C(01′)	Rh(3′)	B(04)	73.64(21)	C(01)	Rh(3)	B(04′)	73.16(22)
C(01′)	Rh(3′)	Rh(3)	66.39(14)	C(01)	Rh(3)	Rh(3′)	66.22(14)
B(08′)	Rh(3′)	B(07′)	49.33(26)	B(08)	Rh(3)	B(07)	49.78(25)
B(08′)	Rh(3′)	C(02′)	80.20(24)	B(08)	Rh(3)	C(02)	80.26(24)
B(08′)	Rh(3′)	P(2)	97.07(19)	B(08)	Rh(3)	P(1)	96.38(19)
B(08′)	Rh(3′)	B(04)	146.35(25)	B(08)	Rh(3)	B(04′)	146.53(25)
B(08′)	Rh(3′)	Rh(3)	99.56(18)	B(08)	Rh(3)	Rh(3′)	100.19(18)
B(07′)	Rh(3′)	C(02′)	45.09(23)	B(07)	Rh(3)	C(02)	45.41(23)
B(07′)	Rh(3′)	P(2)	100.06(19)	B(07)	Rh(3)	P(1)	101.23(20)
B(07′)	Rh(3′)	B(04)	140.95(24)	B(07)	Rh(3)	B(04′)	140.14(25)
B(07′)	Rh(3′)	Rh(3)	136.43(19)	B(07)	Rh(3)	Rh(3′)	137.02(20)
C(02′)	Rh(3′)	P(2)	134.89(15)	C(02)	Rh(3)	P(1)	137.68(15)
C(02′)	Rh(3′)	B(04)	96.28(22)	C(02)	Rh(3)	B(04′)	95.33(23)
C(02′)	Rh(3′)	Rh(3)	109.43(15)	C(02)	Rh(3)	Rh(3′)	108.46(15)
P(2)	Rh(3′)	B(04)	108.19(17)	P(1)	Rh(3)	B(04′)	108.23(18)
P(2)	Rh(3′)	Rh(3)	115.37(5)	P(1)	Rh(3)	Rh(3′)	113.62(5)
B(04)	Rh(3′)	Rh(3)	49.75(16)	B(04′)	Rh(3)	Rh(3′)	49.47(17)
C(01)	C(01′)	C(02′)	122.39(45)	C(01′)	C(01)	C(02)	122.20(45)
C(01)	C(01′)	B(05′)	122.71(46)	C(01′)	C(01)	B(05)	123.79(46)
C(01)	C(01′)	B(06′)	127.32(46)	C(01′)	C(01)	B(06)	129.10(46)
C(01)	C(01′)	B(04′)	110.72(43)	C(01′)	C(01)	B(04)	110.09(41)

C(01)	C(01′)	Rh(3′)	93.67(32)	C(01′)	C(01)	Rh(3)	92.52(32)
B(04′)	H(004′)	Rh(3)	99. (5)	B(04)	H(004)	Rh(3′)	97. (4)

Experimental

Triethylphosphine (150 µl, 1.0 mmol) is transferred via syringe to a stirred solution of $[Rh(COD)Cl]_2$ (0.25 g, 0.51 mmol) in CH_2Cl_2 (20 mL). The solvent is removed under vacuum, yielding a yellow precipitate to which 3 (0.27 g, 0.51 mmol) is added as a solid. THF (25 ml) is added and the reaction is heated to reflux 15 hr. The solvent is removed under vacuum and the resultant dark green residue is separated on silica gel. The blue band eluting with 25% heptane/toluene is collected and recrystallized from toluene by layering with heptane yielding 57 mg 4 as a black microcrystalline solid (16%).

^1H nmr (d_8-toluene): 4.15 (s, 2H, carborane C-H), 1.78-1.46 (m, 12H, CH_2), 1.05-0.60 (m, 18H, CH_3), -5.90 (s, broad, 2H, Rh-H-B).

^{31}P nmr (10% C_6D_6/THF): 34.4 (d, J_{P-Rh} = 173 Hz)

Analysis: Calculated for $C_{16}H_{50}B_{18}P_2Rh$: C, 27.26; H, 7.15; B, 27.61; P, 8.79; Rh, 29.20. Found: C, 28.38; H, 7.63; B, 25.65; P, 9.00; Rh, 29.40.

Dark blue/black crystals of 4 were grown by layering a toluene solution of 4 with heptane. Crystallographic data is summarized in Table 1.

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