A Homogeneous Metallocarborane Catalyst: 3,3-[PPh₃]₂-3-H-3,1,2-RhC₂B₉H₁₁

BY GORDON E. HARDY, KENNETH P. CALLAHAN, CHARLES E. STROUSE AND M. FREDERICK HAWTHORNE

Department of Chemistry,* University of California, Los Angeles, California 90024, *U.S.A.*

Abstract. $C_{38}H_{42}B_9P_2Rh$, monoclinic, $P2_1/n$, $a=12\cdot669$ (6), $b=18\cdot587$ (4), $c=16\cdot041$ (7) Å, $\beta=97\cdot08$ (4)°, $Z=4$, $D_m=1\cdot29$ (2) (flotation), $D_x=1\cdot294$ g cm⁻³. The Rh(III) ion is complexed by one terminal hydride, one π-$B_9C_2H_{11}^{2-}$ and two triphenylphosphine ligands.

Introduction. In a recent investigation by Paxson & Hawthorne (1974), it was demonstrated that the rhodium carborane hydride complex, RhH(PPh₃)₂ (B₉C₂H₁₁), can act as a homogeneous hydrogenation, isomerization, hydrosilylation and hydrogen–deuterium exchange catalyst. In view of the potential utility of this catalyst, a single-crystal X-ray diffraction study of the complex was undertaken in an effort to identify any unique structural features associated with its catalytic activity. Of particular interest was the nature of the rhodium–hydride interaction. While spectroscopic evidence suggested the presence of a terminal metal hydride, possible existence of a bridging interaction of the M–H–B type, as recently documented for several metallocarboranes (Callahan, Lo, Strouse, Sims & Hawthorne, 1974), could not be dismissed.

The title compound was prepared by the reaction of Rh(PPh₃)₃⁺ and (CH₃)₃NH⁺[7,8-C₂B₉H₁₂]⁻ in methanol solution. An irregularly shaped crystal (average diameter 0·20 mm) was mounted on a Syntex P1̄ automated diffractometer. A series of axial photographs showed monoclinic Laue symmetry, and 15 automatically centered reflections were used to calcu-

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late lattice parameters. Two octants of intensity data were collected to a maximum 2θ of 45°. These data exhibited systematic absences characteristic of the space group $P2_1/n$ (nonstandard setting of $P2_1/c$, C_{2h}^5, No. 14). 2362 reflections with intensities greater than 3σ were used in the structure determination. Because of the irregular but roughly equidimensional shape of the crystal, no absorption correction was applied ($\mu=6\cdot63$ cm⁻¹). Experimental and computational procedures utilized in this investigation were similar to those used by Callahan *et al.* (1974).

Standard Patterson and difference Fourier techniques were used to locate all the non-hydrogen atoms. Full matrix least-squares refinement of these positions, with all the cage atoms assigned boron scattering factors, led to the identification of the carbon atoms. On the basis of temperature factors and bond lengths, one of the atoms in the five-membered face (Fig. 1) coordinated to the rhodium atom was identified as a carbon and the two adjacent atoms in this face were assigned scattering factors of statistically disordered carbon and boron atoms. A second difference Fourier was used to locate the hydrogen atoms. Chemically reasonable positions were found for the hydride hydrogen atom and for all but one of the cage hydrogen atoms. Chemically reasonable coordinates were calculated for this atom and the hydrogen positions were included in subsequent least-squares refinement. In the final refinement, phenyl groups were refined as rigid bodies (C–C 1·39, C–H 1·0 Å). Positions of all other atoms, including hydrogen, were refined, along with

Table 1. *Final atomic parameters*

Estimated standard deviations (in parentheses) refer to the last digit of the preceding number. The anisotropic temperature factor T is defined as $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Thermal ellipsoids are depicted in Fig. 1.

(*a*) Atomic parameters × 10⁴.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	304 (1)	2137 (1)	864 (1)	33·7 (6)	18·2 (3)	24·1 (4)	−0·8 (5)	7·2 (3)	0·1 (4)
P(1)	−1025 (2)	2847 (2)	193 (2)	35 (2)	20 (1)	29 (1)	2 (2)	7 (1)	−1 (1)
P(2)	1677 (2)	2374 (2)	35 (2)	42 (2)	19 (1)	27 (1)	−3 (1)	8 (1)	−2 (1)
CB(1)	1193 (9)	1409 (7)	1793 (8)	36 (9)	32 (6)	34 (6)	−8 (6)	5 (6)	6 (4)
C(2)	661 (9)	942 (6)	961 (7)	68 (12)	19 (4)	28 (6)	0 (1)	16 (7)	6 (4)
CB(3)	−613 (11)	1077 (7)	780 (8)	75 (12)	27 (5)	26 (6)	−4 (6)	12 (7)	3 (5)
B(4)	−956 (10)	1669 (7)	1545 (8)	34 (10)	28 (6)	32 (7)	1 (6)	0 (7)	6 (5)
B(5)	232 (11)	1855 (8)	2239 (8)	57 (11)	31 (6)	27 (7)	−4 (7)	8 (7)	−1 (5)
B(6)	1009 (12)	467 (8)	1844 (9)	66 (12)	25 (6)	43 (8)	0 (7)	2 (8)	13 (5)
B(7)	−147 (12)	257 (8)	1212 (9)	73 (12)	25 (5)	28 (7)	−16 (7)	0 (7)	5 (5)
B(8)	−1199 (11)	734 (7)	1587 (9)	48 (11)	26 (5)	35 (7)	−13 (6)	15 (7)	5 (5)
B(9)	−659 (11)	1206 (8)	2522 (8)	51 (12)	37 (6)	25 (6)	−9 (7)	11 (7)	1 (5)
B(10)	704 (12)	1029 (8)	2667 (9)	58 (12)	38 (6)	32 (7)	−7 (7)	−2 (8)	12 (6)
B(11)	−148 (11)	348 (8)	2295 (9)	66 (13)	24 (6)	42 (8)	−1 (7)	11 (8)	13 (5)

Table 1 (cont.)

(b) Fractional coordinates × 10³.

	x	y	z	B(Å²)
HA	65 (6)	288 (5)	123 (5)	3·0
H(1)	191 (7)	160 (5)	189 (6)	3·0
H(2)	95 (8)	84 (5)	50 (6)	3·0
H(3)	−93 (7)	104 (5)	14 (6)	3·0
H(4)	−159 (7)	192 (5)	145 (5)	3·0
H(5)	33 (7)	231 (5)	256 (6)	3·0
H(6)	175 (7)	25 (5)	195 (5)	3·0
H(7)	−35 (5)	−23 (5)	81 (6)	3·0
H(8)	−202 (7)	50 (5)	152 (5)	3·0
H(9)	−115 (7)	129 (5)	304 (6)	3·0
H(10)	126 (7)	105 (5)	320 (6)	3·0
H(11)	−30 (7)	−10 (5)	270 (5)	3·0
C(11)	−163	347	89	3·4 (2)
C(12)	−128	349	175	4·1 (3)
C(13)	−171	399	225	5·7 (3)
C(14)	−249	447	190	5·3 (3)
C(15)	−284	444	105	5·2 (3)
C(16)	−241	394	54	4·8 (3)
H(12)	−72	315	200	4·0
H(13)	−146	401	287	4·0
H(14)	−280	483	227	4·0
H(15)	−340	478	79	4·0
H(16)	−266	392	−7	4·0
C(21)	−72	351	−59	2·7 (2)
C(22)	−135	360	−136	4·3 (3)
C(23)	−113	416	−189	4·9 (3)
C(24)	−29	462	−165	5·0 (3)
C(25)	33	454	−89	4·6 (3)
C(26)	12	398	−36	3·8 (3)
H(22)	−195	326	−153	4·0
H(23)	−158	422	−244	4·0
H(24)	−14	503	−204	4·0
H(25)	94	487	−72	4·0
H(26)	57	391	19	4·0
C(31)	−217	234	−34	3·1 (2)
C(32)	−202	195	−106	4·5 (3)
C(33)	−285	153	−144	5·7 (3)
C(34)	−381	150	−112	5·4 (3)
C(35)	−396	189	−40	6·1 (3)
C(36)	−313	231	−1	4·2 (3)
H(32)	−133	197	−129	4·0
H(33)	−275	124	−196	4·0
H(34)	−441	119	−140	4·0
H(35)	−465	187	−17	4·0
H(36)	−324	259	50	4·0
C(41)	269	165	17	2·9 (2)
C(42)	345	169	87	3·1 (2)
C(43)	417	113	105	3·7 (3)
C(44)	412	52	53	4·3 (3)
C(45)	335	48	−17	4·7 (3)
C(46)	264	105	−35	3·5 (2)
H(42)	349	212	124	4·0
H(43)	472	116	155	4·0
H(44)	463	12	66	4·0
H(45)	331	5	−54	4·0
H(46)	209	102	−85	4·0
C(51)	260	314	30	2·8 (2)
C(52)	244	363	93	3·5 (3)
C(53)	315	419	112	4·2 (3)
C(54)	403	426	69	4·0 (3)
C(55)	420	377	6	4·1 (3)
C(56)	348	321	−13	3·7 (3)
H(52)	180	358	124	4·0
H(53)	303	454	157	4·0
H(54)	455	466	82	4·0
H(55)	483	382	−25	4·0
H(56)	360	285	−58	4·0
C(61)	128	242	−111	2·5 (2)
C(62)	162	295	−163	3·3 (2)

Table 1 (cont.)

	x	y	z	B(Å²)
C(63)	132	291	−249	4·6 (3)
C(64)	69	235	−284	4·6 (3)
C(65)	35	182	−231	3·9 (3)
C(66)	65	185	−145	3·5 (2)
H(62)	92	245	−241	4·0
H(63)	188	354	−259	4·0
H(64)	280	413	−139	4·0
H(65)	276	364	−2	4·0
H(66)	180	256	16	4·0

isotropic temperature factors for the phenyl carbons, and anisotropic thermal parameters for all other non-hydrogen atoms, to a conventional R value of 0·053. Final atomic parameters are tabulated in Table 1.*

Discussion. The rhodium atom in this complex (Fig. 1) exhibits pseudo-octahedral coordination with the carborane cage occupying three coordination sites, and two phosphine ligands, and the hydride ligand occupying the remaining sites. The bonding of the metal atoms to the carborane cage is highly symmetric with distances from the rhodium atom to the five nearest cage atoms in the range 2·22 (1) to 2·28 (1) Å. Bond distances within the carborane polyhedron reflect the positions of the heteroatoms. In the five-membered face, the average C–CB distance is 1·64 (2), the average B–CB distance 1·72 (2) and the unique B–B distance 1·79 (2) Å. Similarly, the average distances from C, CB and B in the coordinated face to adjacent boron atoms in the lower ring are 1·72 (2), 1·74 (2) and 1·77 (2) Å respectively.

A puzzling asymmetry is observed in the rhodium–phosphorus bonding. While the Rh–P(2) distance of 2·357 (3) Å is quite similar to that observed in other triphenylphosphine complexes of rhodium (Baker & Pauling, 1969), the chemically equivalent Rh–P(1) distance is significantly shorter, 2·301 (1) Å. This short distance is probably best attributed to a strong packing interaction.

The hydride ligand in this complex occupies a pseudo-octahedral coordination site on the rhodium atom with no evidence of interaction with the carborane ligand. The Rh–H distance of 1·54 (9) Å, obtained by least-squares refinement, is not significantly different from the 1·72 (15) Å distance obtained by La Placa & Ibers (1963) from the electron density map of RhH(CO) (PPH₃)₃.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31339 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
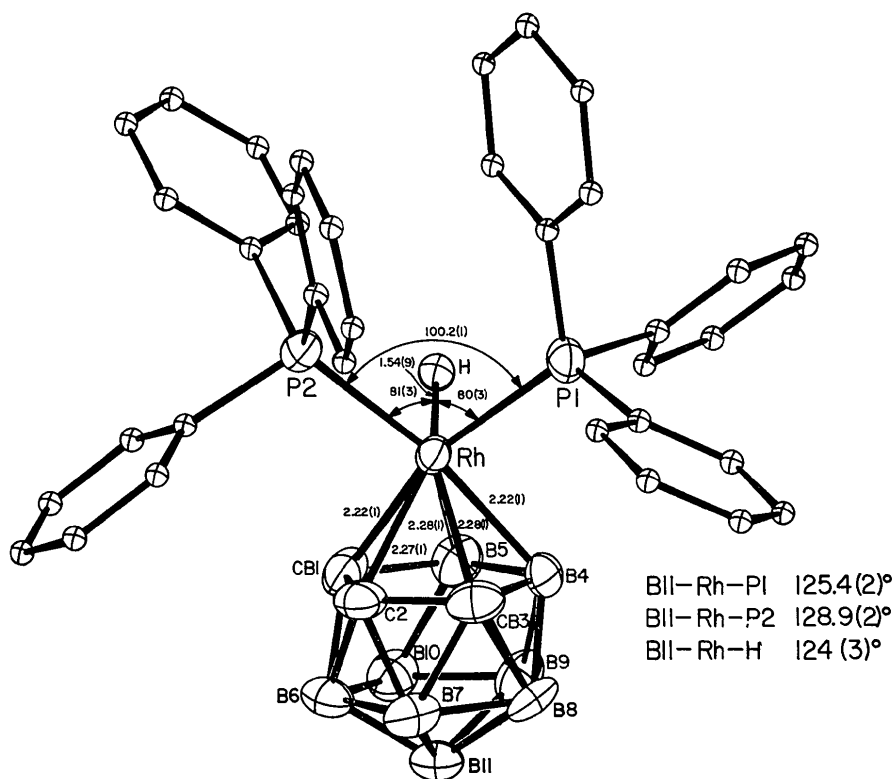
Fig. 1. The molecular structure of $RhH(PPh_3)_2(C_2B_9H_{11})$. All hydrogen atcms except the hydride are omitted for clarity. A atoms except the phenyl carbon atoms are depicted as 50% probability ellipsoids.

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An Efficient Laser Material, Lithium Neodymium Phosphate LiNdP4O12

BY H. KOIZUMI

Musashino Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Musashino-shi, Tokyo 180, Japan

Abstract. Monoclinic, $I2/c$ (C_{2h}^6), $a = 9.844$ (2), $b = 7.008$ (3), $c = 13.25$ (2) Å, $\beta = 90.1$ (2)°, $Z = 4$, $D_c = 3.39$, $D_o = 3.38$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 62.0$ cm^{-1}. Structural framework is helical chains of $(PO_3)_\infty$ along the b axis. Both Nd^{3+} and Li^+ ions alternate on twofold axes in the middle of four such chains. NdO_8 dodecahedra and considerably distorted LiO_4 tetrahedra form linear chains sharing their edges. The refinement converged to $R = 0.035$ for 1095 independent observed reflexions.

Introduction. Recently a phosphate laser material with high Nd concentration, $LiNdP_4O_{12}$, was produced in our laboratory and ·is reported to have a high laser performance (Yamada, Otsuka & Nakano, 1974), comparable to or better than that of NdP_5O_{14}.

Specimens were selected from the crystals grown from the melt of $Li_2O–Nd_2O_3–P_2O_5$ by the Kyropolous technique (Yamada et al., 1974). Precession and Weissenberg photographs exhibited $2/m$ Laue symme-