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SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND REACTIONS OF (CLOSO-1,3---ETC(U)
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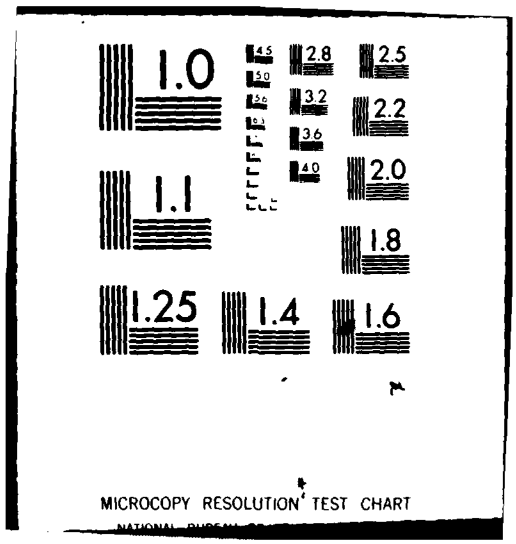
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TR-114

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SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND REACTIONS OF [*closo*-1,3-μ-2,3-μ-(1,2-μ-(η^2-3,4-$CH_2CH_2C(CH_3)=CHCH_2CH_2CH_2$))-3-H-3-$PPh_3$-3,1,2-$RhC_2B_9H_9$], A METALLOCARBABORANE CATALYST.

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SUMMARY

The synthesis, X-ray crystal structure of the title compound (1) and the initial rates of some alkene hydrogenations catalysed by (1) are reported.

In addition to our studies of alkene reduction catalysed by [closo-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$][1] (2) we have modified the parent catalyst through synthesis by replacing one triphenylphosphine ligand with a chelating alkene attached to the dicarbollide ligand. We have previously reported the synthesis, structure and reactions of [closo-1,3-μ-(η^2-3,4-CH_2=$CHCH_2CH_2$)-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$][2](3) and now report the synthesis, structure and reactions of [closo-1,3-μ-(1,2-μ-(η^2-3,4-$CH_2CH_2C(CH_3)$=$CHCH_2CH_2CH_2$))-3-H-$RhC_2B_9H_9$], (1). Complex (1) is a member of the relatively rare hydrido-alkene class of complexes[2,3] and, to our knowledge, only the second such rhodium complex isolated and structurally characterized[2].

When an ethanol solution of [$RhCl(PPh_3)_3$] and a 20% molar excess of Cs^+[7,8-bis(butenyl)-7,8-$C_2B_9H_{10}$]$^{-}$[4] were heated to reflux under nitrogen for 3 hrs. a yellow microcrystalline precipitate was obtained in a 90% yield†. This product was recrystallized from $CHCl_3$-heptane or 1,2-dichloroethane-heptane under an inert atmosphere (m.p. 195-197°C, decomposition). Elemental analysis, n.m.r., and i.r. spectra supported the propsed formula for (1).

Crystal data: (1), monoclinic, space group $P2_1/c$; a = 9.834 (3), b = 9.615(4), c = 39.291(12) Å, β = 98.72(2)°, U = 2825(1) Å^3, D_c = 1.431 g cm^{-3}, D_m = 1.361 g cm^{-3} (flotation in aqueous KI)[5]. X-ray intensity data were collected by the θ-2θ scan technique with MO-Kα radiation (zirconium filter) on a Picker FACS 1 automated diffractometer equipped with a scintallation counter and pulse height analyser. Of a total of 3403 reflections examined, 1942 had $I>3\sigma(I)$ and were used in the structure determination. The data were corrected for absorption, Lorentz, and polarization effects. The structure was solved by using heavy-atom methods and refined by full matrix least squares techniques, converging at R=0.082 and R_w= 0.096‡. The molecular structure of (1) is shown in the Figure together with significant bond distances and angles. The two butenyl side chains attached to the dicarbollide ligand have dimerized in a "head to tail" manner and the resulting chelating alkene is bound to the rhodium in such a fashion that C=C bond is nearly parallel to the dicarbollide ligand similar to the bonding in (3)[2]. Such a "head to tail" dimerization of alkenes around a rhodium center has previously been observed by Bennet[6].

A tetrohydrofuran(THF) solution (1) (2.72×10^{-3}M) displayed the following initial rates of the hydrogenation of the following terminal alkenes (9.84×10^{-2}M) at 25°C [$p(H_2)$=585mm Hg]: 1.1×10^{-3} mol sec^{-1}/(mol Rh), 3,3-dimethylbut-1-ene; 2.4×10^{-3} mol sec^{-1}/(mol Rh), trimethylvinylsilane; and 9.1×10^{-4} mol sec^{-1}/(mol Rh), n-butyl acrylate. Under the same conditions (2) exhibited comparable rates[8] while a THF solution of (3) (1.8×10^{-4}), one of the most reactive homogeneous hydrogenation catalysts reported to date, and the following alkenes (0.13M) displayed the following initial rates: 2.3×10^{-1} mol sec^{-1}/(mol Rh), trimethylvinylsilane; and 8.9 mol sec^{-1}/(mol Rh), 3,3-dimethyl but-1-ene at 0°C [$p(H_2)$ = 705 mm Hg][2]. Complex (1) unlike (3) may be recovered unchanged from THF solutions exposed to hydrogen at 25° or 40°C indicating that the chelating alkenyl moiety is not hydrogenated as in (3)[2]. Complex (1) shows no enhancement in the rate of hydrogenation of alkenes over the rates displayed by (2). Complex (1) was also found to catalyse the isomerisation of alkenes but was not active for the hydrogenation of alkynes or for hydroformylation of alkenes.

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† Yield based on Rhodium consumed.

‡ Crystallographic details are available on request.

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4. Bis (butenyl)-*o*-carborane may be prepared in a method similar to the method preparation of 4-(o-carboranyl) butene by D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, W. Schwartz, M.S. Cohen and M. Fein Inorg. Chem., 1963, 2, 1120, and degraded by the method of M.F. Hawthorne, D.C. Young, P.M. Garrett, D.A. Owen and P.A. Wegner, J. Am. Chem. Soc., 1968, 90, 862.

5. Unit cell dimensions were measured at -153°C. Dm was measured at 25°C.

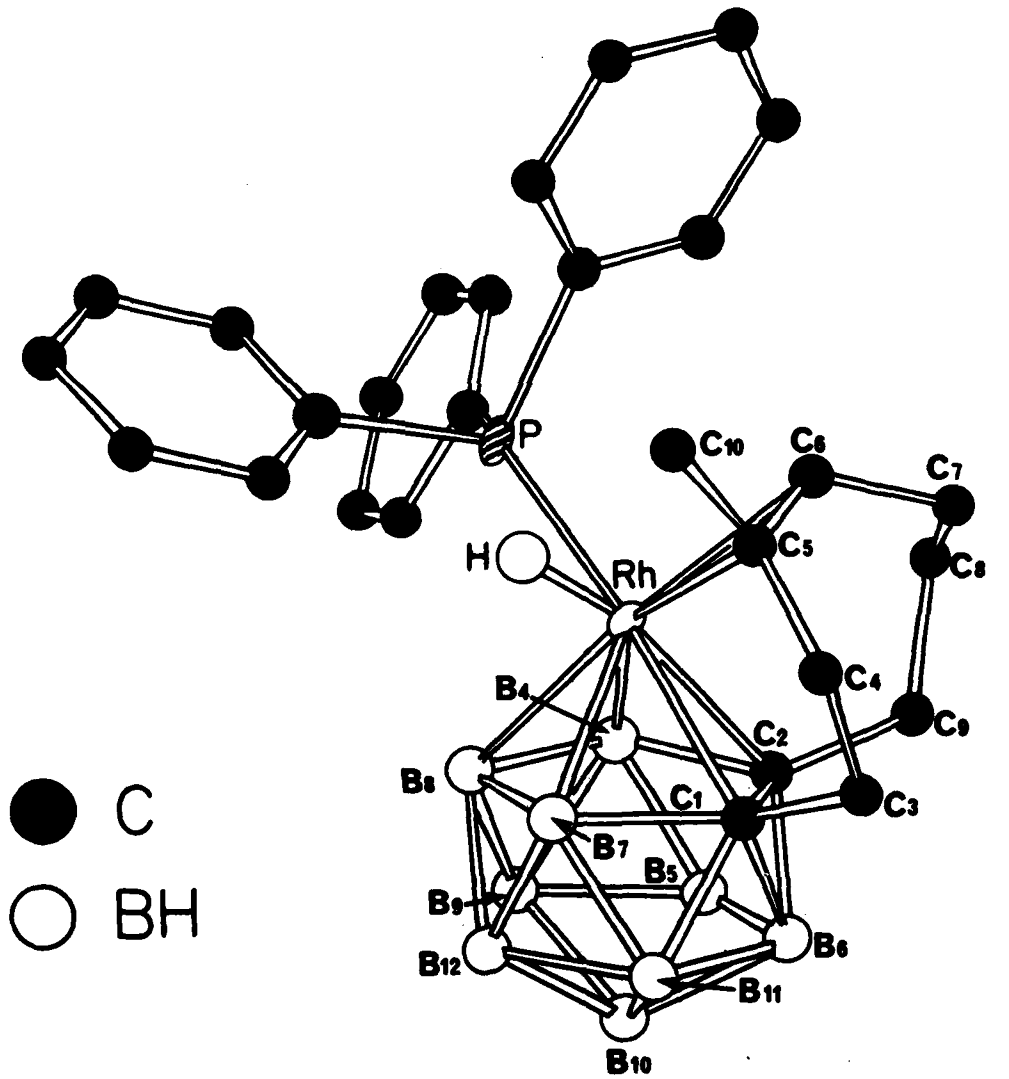
6. M.A. Bennet, R.N. Johnson and B. Tomkins, J. Organometal. Chem., 1973, 54, C48.

7. This atomic position was not refined.

8. R.T. Baker, UCLA doctoral dissertation, 1980.

FIGURE

Molecular structure of (1). (all hydrogen atoms except the rhodium hydride have been omitted for clarity). Distances from Rh to the attached atoms are H 1.4[7], P 2.342(5), C_2, 2.239(17), C_1 2.318(14), B_4 2.235(20), B_7 2.205(22), B_8 2.201(21), C_5 2.260(15), C_6 2.317(15) Å and C_5-C_6 1.459(24), C_5-C_{10} 1.515(23) Å. Some significant angles are C_5-Rh-C_6 37.2(6), C_2-Rh-C_5 82.2(6), C_1-Rh-C_6 93.3(6), H-Rh-C_5 79[7], H-Rh-C_6 92[7], H-Rh-P 52[7], C_5-Rh-P 109.8(4), C_6-Rh-P 93.1(5), C_4-C_5-C_6 123(2), C_4-C_5-C_{10} 113(1), C_{10}-C_5-C_6 117(2), C_5-C_6-C_7 130(2), H_2C_6-C_5 116(2)°.



P
H
Rh
C10
C6
C7
C5
C8
C4
C9
B4
C2
B8
C1
C3
B7
B5
B9
B12
B6
B11
B10
C
BH

TABLE I

ATOMIC POSITIONS AND TEMPERATURE FACTORS.

ATOM	x	y	z	B
HRh	0.0850	0.3100	0.3600	2.00
HC31	0.3095	0.2236	0.2438	2.00
HC32	0.2734	0.3947	0.2290	2.00
HC41	0.0710	0.2327	0.2215	2.00
HC42	0.0513	0.3789	0.2474	2.00
HC6	0.1034	0.0448	0.3349	2.00
HC71	0.2131	-0.0986	0.2822	2.00
HC72	0.2609	0.0435	0.2591	2.00
HC81	0.3729	-0.0053	0.3520	2.00
HC82	0.4407	-0.0921	0.3143	2.00
HC91	0.5742	0.1083	0.3295	2.00
HC92	0.4863	0.1286	0.2798	2.00
H4	0.5000	0.2710	0.4080	2.00
H5	0.6600	0.3100	0.3750	2.00
H6	0.5210	0.3540	0.2750	2.00
H7	0.1530	0.5340	0.3140	2.00
H8	0.2710	0.4690	0.4150	2.00
H9	0.5410	0.5260	0.4250	2.00
H10	0.604	0.625	0.3420	2.00
H11	0.3540	0.6140	0.2720	2.00
H12	0.363	0.695	0.375	2.00

Table II

ATOMIC POSITIONS AND TEMPERATURE FACTORS[a].

ATOM	x	y	z	B
C2	0.3231(16)	0.3714(19)	0.2978(6)	1.54(35)
C1	0.4278(14)	0.2674(19)	0.3257(5)	1.11(30)
B4	0.4299(21)	0.2986(24)	0.3839(7)	1.89(44)
B5	0.5664(21)	0.3632(25)	0.3571(7)	2.00(44)
B6	0.4951(23)	0.4019(25)	0.3022(8)	2.30(50)
B7	0.2406(20)	0.4891(22)	0.3293(7)	1.51(41)
B8	0.3096(19)	0.4520(23)	0.3867(6)	1.29(40)
B9	0.4879(20)	0.4749(24)	0.3937(7)	1.80(43)
B10	0.5324(22)	0.5356(26)	0.3398(8)	2.51(48)
B11	0.3801(21)	0.5389(23)	0.3031(7)	1.70(44)
B12	0.3770(21)	0.5890(24)	0.3587(7)	1.83(43)

[a] Estimated standard deviations, shown in parentheses, refer to the last digit or digits of the preceding number.

Table III

ATOMIC POSITIONS AND TEMPERATURE FACTORS[a] ($X10^5$)

ATOM	x	y	z	$\beta 11$[b]	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
Rh	0.2412(1)	0.2712(1)	0.34949(4)	376(14)	259(19)	19(1)	10(17)	44(3)	2(6)
P	0.1430(4)	0.1781(5)	0.4138(1)	321(50)	363(70)	17(5)	54(43)	16(13)	3(14)
C3	0.2594(16)	0.3204(18)	0.2518(5)	443(200)	659(291)	23(20)	311(183)	106(54)	6(60)
C4	0.1042(15)	0.2866(21)	0.2492(6)	330(184)	909(306)	53(22)	-48(204)	6(54)	32(74)
C5	0.0647(16)	0.2085(21)	0.2887(5)	499(199)	738(305)	20(19)	-164(210)	-40(52)	70(66)
C6	0.1341(16)	0.0811(19)	0.3061(5)	293(193)	431(271)	32(22)	-305(183)	20(55)	-88(64)
C7	0.2476(19)	-0.0014(18)	0.2891(5)	1085(260)	275(254)	6(20)	143(208)	124(60)	89(58)
C8	0.3881(20)	-0.0036(19)	0.3196(6)	1031(275)	148(262)	57(26)	143(219)	47(71)	13(66)
C9	0.4768(18)	0.1251(20)	0.3130(6)	551(229	519(291)	47(26)	-12(214)	65(60)	-65(68)
C10	-0.0869(18)	0.2210(24)	0.2926(6)	883(241)	1365(373)	45(22)	-122(258)	75(61)	-159(85)

[a] Estimated standard deviations, shown in parentheses, refer to the last digit or digits of the preceding number.

[b] The anisotropic temperature factor <u>T</u> is defined as $T=\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]\}$

Table IV

GROUP PARAMETERS[a]

GROUP	X	Y	Z	ϕ	Θ	ρ	GROUP B
PHENYL 1	0.0204(9)	0.2896(11)	0.4395(3)	0.079(9)	2.224(6)	2.358(10)	1.60(14)
PHENYL 2	0.2669(10)	0.1365(12)	0.4648(3)	-0.404(6)	3.113(6)	1.067(7)	1.75(15)
PHENYL 3	0.0435(10)	0.0155(9)	0.4027(4)	-2.077(6)	3.122(7)	-0.333(7)	1.83(15)

[a] ϕ, Θ and ρ are given in radians. For the definition of these terms see C. Scheringer, Acta Cryst., 16, 546 (1963).

Table IV (continued)

GROUP ATOMS - DERIVED POSITIONAL PARAMETERS

Group	Atom	x	y	z
1	1	0.020429	0.289633	0.439509
1	2	-0.007741	0.250022	0.481368
1	3	-0.104953	0.323001	0.501314
1	4	-0.173855	0.435487	0.479372
1	5	-0.145685	0.475098	0.437512
1	6	-0.048473	0.402119	0.417566
1	7	0.041822	0.169122	0.497144
1	8	-0.125086	0.294424	0.531390
1	9	-0.243551	0.487809	0.493672
1	10	-0.195108	0.555893	0.421708
1	11	-0.028200	0.430591	0.387462
2	1	0.266855	0.136490	0.464815
2	2	0.260533	0.009080	0.486253
2	3	0.343266	-0.015134	0.526931
2	4	0.432203	0.088097	0.546112
2	5	0.438524	0.215506	0.524674
2	6	0.355791	0.239720	0.483997
2	7	0.196565	-0.065149	0.472453
2	8	0.338615	-0.106723	0.542295
2	9	0.491519	0.070736	0.575277
2	10	0.502373	0.289770	0.538416
2	11	0.360324	0.331344	0.468574
3	1	0.043532	0.015530	0.402686
3	2	-0.099552	0.016698	0.395896
3	3	-0.172174	-0.102759	0.380727
3	4	-0.101609	-0.223213	0.372371
3	5	0.041475	-0.224381	0.379162
3	6	0.114098	-0.104924	0.394330
3	7	-0.150284	0.103336	0.401907
3	8	-0.274974	-0.101766	0.375863
3	9	-0.153676	-0.308858	0.361496
3	10	0.092312	-0.310848	0.373172
3	11	0.217002	-0.105745	0.399216

Table V

INTER ATOMIC DISTANCES

Bond Distance	Å	Bond Distance	Å
Rh-H	(1.43)[a]	B5-B9	1.797(30)
Rh-P	2.342(5)	B5-B10	1.753(34)
Rh-C2	2.239(17)	B6-B10	1.720(33)
Rh-C1	2.317(14)	B6-B11	1.737(32)
Rh-C5	2.260(15)	B7-B8	1.805(28)
Rh-C6	2.317(16)	B7-B11	1.748(29)
Rh-B4	2.235(20)	B7-B12	1.775(28)
Rh-B7	2.205(22)	B8-B9	1.747(26)
Rh-B8	2.201(21)	B8-B12	1.748(30)
C2-C3	1.521(23)	B9-B10	1.846(30)
C1-C2	1.584(22)	B9-B12	1.782(29)
C2-B6	1.701(26)	B10-B11	1.728(29)
C2-B7	1.754(27)	B10-B12	1.782(30)
C2-B11	1.703(28)	B11-B12	1.754(29)
C1-B9	1.517(24)	C3-C4	1.549(21)
C1-B4	1.787(26)	C4-C5	1.512(24)
C1-B5	1.795(26)	C5-C6	1.459(24)
C1-B6	1.657(29)	C5-C10	1.515(23)
B4-B5	1.780(30)	C6-C7	1.517(23)
B4-B8	1.897(30)	C7-C8	1.542(25)
B4-B9	1.796(32)	C8-C9	1.542(25)
B5-B6	1.746(31)		
P-Phenyl group(Ave)	1.85(8)		

[a]This atomic position (HRh) was not refined.

Table VI

ANGLES	(°)	ANGLES	(°)	ANGLES	(°)
H-Rh-P	(52)[a]	C1-Rh-C2	40.6(6)	Rh-C1-C9	115.4(11)
H-Rh-C5	(79)	C2-Rh-B4	76.0(7)	Rh-C1-C2	67.0(8)
H-Rh-C6	(92)	C2-Rh-B7	46.5(7)	Rh-C1-B4	64.5(8)
H-Rh-C2	(136)	C2-Rh-B8	79.0(7)	Rh-C1-B5	118.6(10)
H-Rh-C1	(174)	C1-Rh-B4	46.2(6)	Rh-C1-B6	123.9(12)
H-Rh-B4	(130)	C1-Rh-B7	77.3(7)	B4-C1-B5	59.6(11)
H-Rh-B7	(96)	C1-Rh-B8	80.5(6)	B4-C1-B6	110.2(15)
H-Rh-B8	(93)	B4-Rh-B7	82.9(7)	B5-C1-B6	60.6(12)
P-Rh-C2	167.8(4)	B4-Rh-B8	50.6(8)	Rh-B4-C1	69.3(8)
P-Rh-C1	130.4(4)	B7-Rh-B8	48.4(7)	Rh-B4-B5	123.7(13)
P-Rh-B4	92.0(6)	Rh-C2-C1	72.3(8)	Rh-B4-B8	63.8(9)
P-Rh-B7	130.8(6)	Rh-C2-C3	109.2(11)	Rh-B4-B9	116.3(12)
P-Rh-B8	91.8(5)	Rh-C2-B6	126.2(12)	C1-B4-B5	60.4(11)
P-Rh-C5	109.8(4)	Rh-C2-B7	65.7(9)	C1-B4-B8	104.9(14)
P-Rh-C6	93.1(5)	Rh-C2-B11	121.6(12)	C1-B4-B9	106.1(15)
C5-Rh-C6	37.2(6)	C1-C2-C3	115.6(15)	B5-B4-B8	105.4(15)
C5-Rh-C2	82.2(6)	C1-C2-B6	60.4(11)	B5-B4-B9	60.3(12)
C5-Rh-C1	104.6(6)	C1-C2-B7	115.5(14)	B8-B4-B9	56.4(11)
C5-Rh-B4	150.3(7)	C1-C2-B11	111.4(13)	C1-B5-B4	60.0(10)
C5-Rh-B7	96.7(7)	B6-C2-B7	112.2(14)	C1-B5-B6	55.8(11)
C5-Rh-B8	143.4(7)	B6-C2-B11	61.4(12)	C1-B5-B9	105.8(13)
C6-Rh-C2	95.6(6)	B7-C2-B11	60.8(12)	C1-B5-B10	103.2(14)
C6-Rh-C1	93.3(6)	C2-C1-C9	129.6(14)	B4-B5-B6	106.6(14)
C6-Rh-B4	125.2(7)	C2-C1-B4	109.5(14)	B4-B5-B9	60.3(12)
C6-Rh-B7	129.3(7)	C2-C1-B5	110.0(14)	B4-B5-B10	110.0(16)
C6-Rh-B8	173.7(6)	C2-C1-B6	63.3(12)	B6-B5-B9	108.2(15)

Table VI (continued)

ANGLES	(°)	ANGLES	(°)	ANGLES	(°)
B6-B5-B10	58.9(13)	B4-B8-B12	106.2(14)	B6-B11-B7	110.8(16)
B9-B5-B10	62.6(13)	B7-B8-B9	108.7(14)	B6-B11-B10	59.5(13)
C1-B6-C2	56.2(11)	B7-B8-B12	59.9(12)	B6-B11-B12	109.1(16)
C2-B6-B5	107.0(16)	B9-B8-B12	61.3(12)	B7-B11-B10	111.5(16)
C2-B6-B10	107.0(16)	B4-B9-B5	59.4(12)	B7-B11-B12	60.9 (12)
C2-B6-B11	59.4(12)	B4-B9-B8	64.7(12)	B10-B11-B12	61.6(13)
C1-B6-B5	63.6(12)	B4-B9-B10	105.2(15)	B7-B12-B8	61.6(12)
C1-B6-B10	110.9(17)	B4-B9-B12	109.2(14)	B7-B12-B9	108.5(16)
C1-B6-B11	106.3(16)	B5-B9-B8	111.3(15)	B7-B12-B10	107.7(15)
B5-B6-B10	60.8(14)	B5-B9-B10	57.5(12)	B7-B12-B11	59.4(12)
B5-B6-B11	108.4(17)	B5-B9-B12	106.2(15)	B8-B12-B9	59.3(11)
B10-B6-B11	60.0(13)	B8-B9-B10	107.2(14)	B8-B12-B10	110.0(16)
Rh-B7-C2	67.8(9)	B8-B9-B12	59.4(11)	B8-B12-B11	108.7(16)
Rh-B7-B8	65.7(9)	B10-B9-B12	58.8(12)	B9-B12-B10	62.4(12)
Rh-B7-B11	121.1(13)	B5-B10-B6	60.3(13)	B9-B12-B11	107.9(15)
Rh-B7-B12	119.0(13)	B5-B10-B9	59.9(12)	B10-B12-B11	58.5(12)
C2-B7-B8	105.0(14)	B5-B10-B11	108.5(16)	C2-C3-C4	112.5(13)
C2-B7-B11	58.2(11)	B5-B10-B12	108.1(16)	C3-C4-C5	115.5(14)
C2-B7-B12	104.2(13)	B6-B10-B9	107.2(17)	C4-C5-C6	122.6(16)
B8-B7-B11	106.4(13)	B6-B10-B11	60.5(13)	C4-C5-C10	113.1(15)
B8-B7-B12	58.4(11)	B6-B10-B12	108.5(16)	C10-C5-C6	116.8(16)
B11-B7-B12	59.7(11)	B9-B10-B11	106.2(15)	C5-C6-C7	130.0(15)
Rh-B8-B4	65.6(9)	B9-B10-B12	58.8(12)	C6-C7-C8	116.3(14)
Rh-B8-B7	65.9(9)	B11-B10-B12	59.9(12)	C7-C8-C9	112.6(15)
Rh-B8-B9	120.4(13)	C2-B11-B6	59.2(12)	C8-C9-C1	118.8(14)
Rh-B8-B12	120.5(13)	C2-B11-B7	61.1(11)		
B4-B8-B7	105.0(14)	C2-B11-B10	106.6(15)		
B4-B8-B9	58.9(11)	C2-B11-B12	107.4(15)		

[a]This atomic position (HRh) was not refined.

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The synthesis, X-ray crystal structure of the title compound (1) and the initial rates of some alkene hydrogenations catalysed by (1) are reported.

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