Supplementary Information

for

Synthesis and reactivity of boryloxorhodium complexes. relevance to intermolecular transmetalation from boron to rhodium in Rh-catalyzed reactions

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1. Crystallographic data and details of structure refinement of 1

Experimental

Data Collection

A pale yellow prismatic crystal of $C_{28}H_{48}B_2O_6Rh_2$ having approximate dimensions of 0.450 x 0.300 x 0.200 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer using graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 18 carefully centered reflections in the range $18.93 < 2q < 21.09^o$ corresponded to a C-centered monoclinic cell with dimensions:

a = 22.997(5) Å

b = 6.3442(13) Å β = 95.25100°

c = 20.881(6) Å

V = 3033.6(12) Å^3

For Z = 4 and F.W. = 708.11, the calculated density is 1.550 g/cm^3. Based on the reflection conditions of:

hkl: h+k = 2n

h0l: l = 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2/c (#15)

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 6.0°. Scans of $(1.63 + 0.30 \tan \theta)^o$ were made at speeds ranging from 16.0 to 8.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 6.0 x 6.0 mm (horizontal x vertical).

Data Reduction

Of the 2764 reflections were collected, where 2696 were unique (R_{int} = 0.0221); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards increased by 3.3%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient, μ, for Mo-Kα radiation is 11.236 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by heavy-atom Patterson methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 2744 observed reflections and 196 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; | \; |Fo| - |Fc| \; | \; / \Sigma \; |Fo| = 0.0310$$

$$wR2 = [\Sigma \; (w \; (Fo^2 - Fc^2)^2) / \Sigma \; w(Fo^2)^2]^{1/2} = 0.0939$$

The goodness of fit[3] was 1.03. A Sheldrick weighting scheme was used. Plots of S w $(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.52 and -0.74 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography (IT), Vol. IV, Table 2.2B [4]. Anomalous dispersion effects were included in Fcalc[5]; the values for Δf' and Δf" were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8,9] crystallographic software package.

References

(1) PATTY: Beurskens, P.T., Admiraal, G., Behm, H., Beurskens, G., Smits, J.M.M. and Smykalla, C. (1991). Z. f. Kristallogr. Suppl.4, p.99.

(2) Least Squares function minimized:

$$\Sigma \; w(F_o^2 - F_c^2)^2 \qquad \text{where w = Least Squares weights.}$$

(3) Goodness of fit is defined as:

$$[\Sigma \; w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(4) International Tables for X-ray Crystallography, Vol. IV (1974). Ed. J.A. Ibers and W.C. Hamilton, The Kynoch Press, Birmingham, England, Table 2.2B, pp. 99.

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W.J; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.

(9) CRYSTALS Issue 11: Carruthers, J.R., Rollett,J.S., Betteridge, P.W., Kinna, D., Pearce, L., Larsen, A., and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{28}H_{48}B_2O_6Rh_2$
Formula Weight	708.11
Crystal Color, Habit	pale yellow, prismatic
Crystal Dimensions	0.450 X 0.300 X 0.200 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	18 (18.9 - 21.1°)
Omega Scan Peak Width at Half-height	0.32°
Lattice Parameters	a = 22.997(5) Å b = 6.3442(13) Å c = 20.881(6) Å β = 95.25100 ° V = 3033.6(12) Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.550 g/cm^3
F_{000}	1456.00
μ(MoKα)	11.236 cm^{-1}

B. Intensity Measurements

Diffractometer	AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.52, 11.54, 41.93)
Take-off Angle	6.0°
Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	258 mm
Voltage, Current	50kV, 180mA
Temperature	23.0°C

Scan Type	ω-2θ
Scan Rate	16.0 - 8.0°/min (in ω) (up to 3 scans)
Scan Width	(1.63 + 0.30 tan θ)°
$2\theta_{max}$	50.0°
No. of Reflections Measured	Total: 2744 Unique: 2676 (R_{int} = 0.0221)
Corrections	Lorentz-polarization Decay (3.27% increase)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	$1/[0.0010Fo^2+1.0000s(Fo^2)]/(4Fo^2)$
$2q_{max}$ cutoff	52.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2744
No. Variables	196
Reflection/Parameter Ratio	14.00
Residuals: R1 (I>2.00s(I))	0.0310
Residuals: R (All reflections)	0.0399
Residuals: wR2 (All reflections)	0.0939
Goodness of Fit Indicator	1.029
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.52 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.74 $e^-/Å^3$

Table S1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Rh1	0.030070(10)	0.16806(4)	0.191150(10)	2.230(7)
O1	-0.10134(11)	0.4896(5)	0.13323(13)	3.80(6)
O2	-0.05077(10)	0.2834(4)	0.21538(11)	2.96(5)
O3	-0.15491(12)	0.2636(5)	0.18852(13)	4.05(6)
C1	0.0289(2)	-0.2380(8)	0.1148(3)	5.77(13)
C2	-0.2481(2)	0.2636(9)	0.1270(2)	5.09(11)
C3	0.00767(17)	0.1521(6)	0.09174(17)	3.13(8)
C4	0.11475(15)	0.1330(6)	0.16286(18)	3.21(8)

C5	-0.1585(3)	0.3513(9)	0.0413(2)	5.60(13)
C6	-0.19680(17)	0.3988(7)	0.15234(19)	3.58(9)
C7	-0.15999(16)	0.4900(7)	0.10029(18)	3.50(8)
C8	-0.00599(16)	-0.0400(6)	0.11972(19)	3.55(9)
C9	0.0598(2)	0.1862(9)	0.0543(2)	4.99(12)
C10	-0.1746(3)	0.7149(8)	0.0805(3)	5.67(13)
C11	0.09905(17)	-0.0480(6)	0.1948(2)	3.61(9)
C12	0.1168(2)	0.1463(10)	0.0911(2)	5.34(13)
C13	-0.2170(2)	0.5648(10)	0.1979(2)	5.86(14)
C14	0.0798(3)	-0.2520(9)	0.1628(3)	6.73(15)
B1	-0.10027(17)	0.3420(7)	0.18101(18)	2.55(8)

B_{eq} = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\square + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh1	0.02174(18)	0.03554(19)	0.02741(18)	0.00103(10)	0.00195(11)	-0.00083(10)
O1	0.0299(13)	0.0606(18)	0.0532(15)	-0.0001(13)	-0.0001(11)	0.0178(14)
O2	0.0268(12)	0.0556(17)	0.0302(12)	0.0070(12)	0.0036(10)	0.0014(11)
O3	0.0335(14)	0.0680(19)	0.0512(16)	0.0016(14)	-0.0021(13)	0.0215(15)
C1	0.071(3)	0.044(3)	0.101(4)	-0.001(3)	-0.007(3)	-0.023(3)
C2	0.037(2)	0.080(3)	0.075(3)	-0.004(2)	-0.007(2)	0.004(3)
C3	0.0339(19)	0.055(2)	0.0293(18)	0.0080(17)	-0.0016(15)	-0.0045(16)
C4	0.0233(17)	0.060(3)	0.039(2)	0.0054(17)	0.0053(15)	-0.0076(17)
C5	0.070(3)	0.103(4)	0.039(2)	0.012(3)	0.003(2)	-0.006(2)
C6	0.0303(19)	0.063(3)	0.042(2)	0.0065(19)	-0.0014(17)	0.0063(19)
C7	0.0328(18)	0.055(2)	0.044(2)	0.0080(19)	-0.0012(15)	0.0099(19)
C8	0.0305(18)	0.052(3)	0.051(2)	-0.0055(17)	-0.0037(16)	-0.0168(18)
C9	0.053(3)	0.098(4)	0.040(2)	0.002(3)	0.011(2)	0.002(2)
C10	0.067(3)	0.068(3)	0.080(4)	0.013(3)	0.002(3)	0.033(3)
C11	0.036(2)	0.047(2)	0.053(2)	0.0115(17)	-0.0034(17)	0.0003(18)
C12	0.040(2)	0.123(5)	0.041(2)	0.007(3)	0.0133(19)	0.001(3)
C13	0.054(3)	0.104(5)	0.066(3)	0.014(3)	0.013(2)	-0.022(3)
C14	0.081(4)	0.044(3)	0.127(5)	0.016(3)	-0.009(4)	-0.014(3)
B1	0.0252(19)	0.044(2)	0.0272(18)	0.0053(16)	0.0003(15)	-0.0028(16)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk$

+ 2a*c*U_{13}hl + 2b*c*U_{23}kl))

Table S3. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Rh1	Rh1[1]	2.9283(7)	Rh1	O2	2.102(2)
Rh1	O2[1]	2.098(2)	Rh1	C3	2.095(4)
Rh1	C4	2.098(4)	Rh1	C8	2.104(4)
Rh1	C11	2.092(4)	O1	C7	1.457(4)
O1	B1	1.367(5)	O2	B1	1.342(4)
O3	C6	1.450(5)	O3	B1	1.374(5)
C1	C8	1.499(7)	C1	C14	1.473(8)
C2	C6	1.514(6)	C3	C8	1.400(6)
C3	C9	1.505(6)	C4	C11	1.392(6)
C4	C12	1.506(6)	C5	C7	1.516(6)
C6	C7	1.549(6)	C6	C13	1.520(7)
C7	C10	1.515(7)	C9	C12	1.480(6)
C11	C14	1.505(7)			

Symmetry Operators:
(1) -X,Y,-Z+1/2

Table S4. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Rh1[1]	Rh1	O2	45.74(6)	Rh1[1]	Rh1	O2[1]	45.86(7)
Rh1[1]	Rh1	C3	137.68(11)	Rh1[1]	Rh1	C4	139.31(10)
Rh1[1]	Rh1	C8	114.15(11)	Rh1[1]	Rh1	C11	112.59(12)
O2	Rh1	O2[1]	77.59(9)	O2	Rh1	C3	96.46(12)
O2	Rh1	C4	165.64(13)	O2	Rh1	C8	95.11(12)
O2	Rh1	C11	154.60(13)	O2[1]	Rh1	C3	162.35(13)
O2[1]	Rh1	C4	99.29(12)	O2[1]	Rh1	C8	156.82(13)
O2[1]	Rh1	C11	95.04(13)	C3	Rh1	C4	82.32(15)
C3	Rh1	C8	38.95(15)	C3	Rh1	C11	96.97(16)
C4	Rh1	C8	92.85(15)	C4	Rh1	C11	38.80(16)
C8	Rh1	C11	82.14(15)	C7	O1	B1	107.4(3)
Rh1	O2	Rh1[1]	88.40(9)	Rh1	O2	B1	133.9(2)
Rh1[1]	O2	B1	134.7(2)	C6	O3	B1	107.3(3)
C8	C1	C14	113.7(4)	Rh1	C3	C8	70.9(2)
Rh1	C3	C9	111.9(3)	C8	C3	C9	124.2(4)
Rh1	C4	C11	70.4(2)	Rh1	C4	C12	112.9(3)

C11	C4	C12	123.8(4)	O3	C6	C2	107.8(4)
O3	C6	C7	101.9(3)	O3	C6	C13	108.1(3)
C2	C6	C7	115.1(3)	C2	C6	C13	109.8(4)
C7	C6	C13	113.5(4)	O1	C7	C5	107.1(3)
O1	C7	C6	102.1(3)	O1	C7	C10	107.6(4)
C5	C7	C6	114.0(4)	C5	C7	C10	110.2(4)
C6	C7	C10	115.0(4)	Rh1	C8	C1	113.3(3)
Rh1	C8	C3	70.2(2)	C1	C8	C3	124.0(4)
C3	C9	C12	114.6(4)	Rh1	C11	C4	70.8(2)
Rh1	C11	C14	110.9(3)	C4	C11	C14	125.1(4)
C4	C12	C9	114.8(4)	C1	C14	C11	115.7(4)
O1	B1	O2	122.6(3)	O1	B1	O3	112.1(3)
O2	B1	O3	125.4(3)				

Symmetry Operators:
(1) -X,Y,-Z+1/2

2. Crystallographic data and details of structure refinement of 2

Experimental

Data Collection

A dark yellow prismatic crystal of $C_{32}H_{39}BO_3PRh$ having approximate dimensions of 0.650 x 0.530 x 0.300 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer using graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range $18.87 < 2q < 21.62^o$ corresponded to a primitive triclinic cell with dimensions:

a =	10.519(2) Å	α =	102.334(17)°
b =	15.348(3) Å	β =	96.79140°
c =	9.920(2) Å	γ =	102.86550°
V =	1502.1(6) Å^3		

For Z = 2 and F.W. = 616.35, the calculated density is 1.363 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 6.0°. Scans of (1.68 + 0.30 tan θ)° were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 250 mm, and the detector aperture was 6.0 x 6.0 mm (horizontal x vertical).

Data Reduction

Of the 7269 reflections were collected, where 6894 were unique (R_{int} = 0.0145); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 0.9%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient, μ, for Mo-Kα radiation is 6.507 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by heavy-atom Patterson methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 6894

observed reflections and 382 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; | \; |Fo| - |Fc| \; | \; / \Sigma \; |Fo| = 0.0372$$

$$wR2 = [\Sigma \; (w(Fo^2 - Fc^2)^2) / \Sigma \; w(Fo^2)^2]^{1/2} = 0.1021$$

The goodness of fit[3] was 1.08. A Chebychev polynomial weighting scheme was used[4]. Plots of S w $(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.85 and -1.15 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography (IT), Vol. IV, Table 2.2B [5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) PATTY: Beurskens, P.T., Admiraal, G., Behm, H., Beurskens, G., Smits, J.M.M. and Smykalla, C. (1991). Z. f. Kristallogr. Suppl.4, p.99.

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$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Goodness of fit is defined as:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

(4) Carruthers, J.R. and Watkin, D.J. (1979), Acta Cryst, A35, 698-699

(5) International Tables for X-ray Crystallography, Vol. IV (1974). Ed. J.A. Ibers and W.C. Hamilton, The Kynoch Press, Birmingham, England, Table 2.2B, pp. 99.

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{32}H_{39}BO_3PRh$
Formula Weight	616.35
Crystal Color, Habit	dark yellow, prismatic
Crystal Dimensions	0.650 X 0.530 X 0.300 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20 (18.9 - 21.6°)
Omega Scan Peak Width at Half-height	0.32°
Lattice Parameters	a = 10.519(2) Å b = 15.348(3) Å c = 9.920(2) Å α = 102.334(17) ° β = 96.79140 ° γ = 102.86550 ° V = 1502.1(6) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.363 g/cm^3
F_{000}	640.00
μ(MoKα)	6.507 cm^{-1}

B. Intensity Measurements

Diffractometer	AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.63, 11.97, 42.77)
Take-off Angle	6.0°
Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	250 mm
Voltage, Current	50kV, 180mA
Temperature	23.0°C
Scan Type	ω-2θ

Scan Rate	16.0°/min (in ω) (up to 3 scans)
Scan Width	(1.68 + 0.30 tan θ)°
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 7269 Unique: 6894 (R_{int} = 0.0145)
Corrections	Lorentz-polarization Decay (0.93% decline)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	Chebychev polynomial with 3 parameters 68800.7000,68778.3000,0.0000,
$2q_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6894
No. Variables	382
Reflection/Parameter Ratio	18.05
Residuals: R1 (I>2.00s(I))	0.0372
Residuals: R (All reflections)	0.0440
Residuals: wR2 (All reflections)	0.1021
Goodness of Fit Indicator	1.084
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.85 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.15 $e^-/Å^3$

Table S5. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Rh1	0.20638(3)	0.34814(2)	0.28340(3)	2.463(5)
P1	0.13413(9)	0.21553(6)	0.35910(9)	2.587(17)
O1	0.3913(3)	0.2213(2)	-0.0506(3)	4.08(7)
O2	0.5076(3)	0.3092(2)	0.1647(3)	4.13(7)
O3	0.2674(3)	0.26761(18)	0.1245(3)	3.29(6)
C1	-0.0805(5)	0.0558(3)	0.2697(5)	4.43(10)
C2	0.5279(5)	0.2211(4)	-0.0529(6)	5.16(12)
C3	-0.0262(6)	0.2492(4)	0.7759(5)	5.17(13)

C4	-0.0179(4)	0.1355(3)	0.0949(4)	3.40(8)
C5	0.4784(7)	0.0773(5)	0.3898(6)	6.84(18)
C6	0.2073(4)	0.4472(3)	0.1547(4)	3.65(9)
C7	-0.1912(5)	-0.0031(3)	0.0310(6)	4.97(11)
C8	0.1503(5)	0.2285(3)	0.6495(4)	4.02(10)
C9	0.0710(4)	0.2246(3)	0.5239(4)	3.07(8)
C10	0.0870(5)	0.4842(4)	0.1684(5)	4.71(12)
C11	0.1017(6)	0.2409(4)	0.7743(5)	5.08(12)
C12	0.7291(6)	0.2897(5)	0.1545(8)	7.91(19)
C13	0.3969(4)	0.2101(4)	0.3960(5)	4.39(11)
C14	0.0493(5)	0.4942(3)	0.3134(5)	4.56(11)
C15	0.3262(5)	0.4763(3)	0.2490(5)	3.96(10)
C16	-0.1139(4)	0.0687(3)	-0.0048(5)	4.26(10)
C17	0.6394(9)	0.3949(5)	0.0381(10)	10.8(3)
C18	-0.0587(4)	0.2334(3)	0.5263(5)	3.76(9)
C19	0.6041(5)	0.3035(4)	0.0741(6)	4.77(11)
C20	0.0000(4)	0.1289(3)	0.2327(4)	3.03(7)
C21	0.5013(5)	0.1687(5)	0.4009(6)	6.07(16)
C22	-0.1056(5)	0.2458(4)	0.6513(5)	4.77(12)
C23	0.5570(8)	0.2232(7)	-0.1953(7)	10.2(3)
C24	0.3538(5)	0.5560(3)	0.3795(6)	5.12(12)
C25	0.2061(5)	0.4382(3)	0.4770(4)	4.00(9)
C26	0.0838(5)	0.4231(3)	0.3869(4)	3.65(9)
C27	0.3188(6)	0.5237(4)	0.5090(6)	5.80(13)
C28	-0.1752(5)	-0.0108(3)	0.1682(6)	5.21(12)
C29	0.2436(6)	0.0642(3)	0.3717(5)	4.90(12)
C30	0.2670(4)	0.1578(3)	0.3795(4)	3.21(8)
C31	0.3517(8)	0.0238(4)	0.3765(6)	6.87(17)
C32	0.5427(6)	0.1286(4)	-0.0237(9)	8.2(2)
B1	0.3808(4)	0.2671(3)	0.0845(5)	3.03(8)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\square + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S6. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh1	0.03324(14)	0.03178(14)	0.02963(13)	0.01131(10)	0.00740(10)	0.00572(10)
P1	0.0341(4)	0.0348(5)	0.0313(4)	0.0120(4)	0.0056(4)	0.0088(4)
O1	0.0389(15)	0.071(2)	0.0439(16)	0.0206(14)	0.0142(12)	0.0001(14)

O2	0.0360(14)	0.0628(19)	0.0492(17)	0.0055(13)	0.0125(13)	-0.0006(14)
O3	0.0390(14)	0.0439(15)	0.0427(14)	0.0141(12)	0.0157(12)	0.0042(12)
C1	0.052(3)	0.050(2)	0.061(3)	0.003(2)	0.001(2)	0.019(2)
C2	0.042(2)	0.088(4)	0.063(3)	0.019(2)	0.024(2)	0.001(3)
C3	0.086(4)	0.079(3)	0.053(3)	0.039(3)	0.036(3)	0.030(3)
C4	0.040(2)	0.044(2)	0.042(2)	0.0103(17)	0.0044(16)	0.0061(17)
C5	0.089(4)	0.130(6)	0.067(3)	0.081(4)	0.008(3)	0.029(4)
C6	0.059(3)	0.045(2)	0.042(2)	0.0167(19)	0.0171(19)	0.0180(18)
C7	0.045(2)	0.056(3)	0.069(3)	0.006(2)	-0.008(2)	-0.008(2)
C8	0.054(2)	0.064(3)	0.040(2)	0.023(2)	0.0081(18)	0.0143(19)
C9	0.043(2)	0.043(2)	0.0374(19)	0.0180(16)	0.0129(16)	0.0143(16)
C10	0.070(3)	0.063(3)	0.060(3)	0.034(3)	0.009(2)	0.027(2)
C11	0.081(4)	0.083(4)	0.038(2)	0.034(3)	0.011(2)	0.018(2)
C12	0.046(3)	0.131(6)	0.107(5)	0.023(4)	0.008(3)	-0.003(4)
C13	0.043(2)	0.078(3)	0.056(3)	0.025(2)	0.007(2)	0.029(2)
C14	0.058(3)	0.055(3)	0.077(3)	0.034(2)	0.024(2)	0.023(2)
C15	0.052(2)	0.041(2)	0.062(3)	0.0101(18)	0.022(2)	0.019(2)
C16	0.045(2)	0.060(3)	0.047(2)	0.013(2)	-0.0058(19)	-0.001(2)
C17	0.140(7)	0.089(5)	0.209(10)	0.015(5)	0.113(7)	0.064(6)
C18	0.047(2)	0.059(3)	0.047(2)	0.023(2)	0.0149(18)	0.021(2)
C19	0.041(2)	0.067(3)	0.071(3)	0.009(2)	0.024(2)	0.011(2)
C20	0.0352(18)	0.0363(19)	0.042(2)	0.0098(15)	0.0029(15)	0.0068(15)
C21	0.054(3)	0.126(5)	0.074(4)	0.047(3)	0.013(3)	0.048(4)
C22	0.062(3)	0.073(3)	0.068(3)	0.036(3)	0.032(2)	0.032(3)
C23	0.092(5)	0.227(10)	0.071(4)	0.047(6)	0.048(4)	0.018(5)
C24	0.061(3)	0.039(2)	0.080(4)	0.001(2)	0.002(3)	0.002(2)
C25	0.075(3)	0.044(2)	0.0310(19)	0.020(2)	0.0105(19)	-0.0004(16)
C26	0.059(3)	0.042(2)	0.047(2)	0.0240(19)	0.0266(19)	0.0093(17)
C27	0.085(4)	0.055(3)	0.057(3)	0.004(3)	-0.007(3)	-0.010(2)
C28	0.053(3)	0.046(3)	0.088(4)	-0.003(2)	0.007(3)	0.012(2)
C29	0.073(3)	0.053(3)	0.061(3)	0.032(2)	-0.006(2)	0.009(2)
C30	0.050(2)	0.045(2)	0.0324(18)	0.0227(18)	0.0058(16)	0.0106(16)
C31	0.123(6)	0.070(4)	0.077(4)	0.067(4)	-0.010(4)	0.008(3)
C32	0.067(4)	0.078(4)	0.164(7)	0.041(3)	0.025(4)	-0.001(4)
B1	0.043(2)	0.036(2)	0.036(2)	0.0103(17)	0.0144(18)	0.0067(17)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S7. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Rh1	P1	2.3202(11)	Rh1	O3	2.046(3)
Rh1	C6	2.183(5)	Rh1	C15	2.203(5)
Rh1	C25	2.114(4)	Rh1	C26	2.124(5)
P1	C9	1.826(4)	P1	C20	1.834(3)
P1	C30	1.828(5)	O1	C2	1.440(6)
O1	B1	1.404(5)	O2	C19	1.439(6)
O2	B1	1.405(5)	O3	B1	1.302(6)
C1	C20	1.392(6)	C1	C28	1.386(6)
C2	C19	1.567(6)	C2	C23	1.486(9)
C2	C32	1.546(10)	C3	C11	1.382(9)
C3	C22	1.392(7)	C4	C16	1.385(5)
C4	C20	1.386(6)	C5	C21	1.347(11)
C5	C31	1.376(10)	C6	C10	1.507(8)
C6	C15	1.391(6)	C7	C16	1.355(7)
C7	C28	1.385(9)	C8	C9	1.398(6)
C8	C11	1.387(7)	C9	C18	1.403(6)
C10	C14	1.522(8)	C12	C19	1.536(9)
C13	C21	1.387(9)	C13	C30	1.393(6)
C14	C26	1.519(8)	C15	C24	1.527(6)
C17	C19	1.500(11)	C18	C22	1.380(7)
C24	C27	1.528(8)	C25	C26	1.420(6)
C25	C27	1.506(7)	C29	C30	1.385(7)
C29	C31	1.412(10)			

Table S8. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
P1	Rh1	O3	87.10(9)	P1	Rh1	C6	158.50(10)
P1	Rh1	C15	164.16(13)	P1	Rh1	C25	94.08(13)
P1	Rh1	C26	95.97(13)	O3	Rh1	C6	87.45(15)
O3	Rh1	C15	92.36(15)	O3	Rh1	C25	161.89(16)
O3	Rh1	C26	158.69(13)	C6	Rh1	C15	36.97(16)
C6	Rh1	C25	97.50(17)	C6	Rh1	C26	82.00(18)
C15	Rh1	C25	81.60(17)	C15	Rh1	C26	90.28(17)
C25	Rh1	C26	39.15(18)	Rh1	P1	C9	119.17(14)
Rh1	P1	C20	112.86(14)	Rh1	P1	C30	110.74(14)
C9	P1	C20	103.38(17)	C9	P1	C30	104.71(19)
C20	P1	C30	104.69(17)	C2	O1	B1	108.4(3)

C19	O2	B1	108.6(3)	Rh1	O3	B1	134.7(2)
C20	C1	C28	119.9(5)	O1	C2	C19	103.1(4)
O1	C2	C23	109.2(5)	O1	C2	C32	106.2(4)
C19	C2	C23	118.9(5)	C19	C2	C32	110.3(5)
C23	C2	C32	108.4(6)	C11	C3	C22	119.4(5)
C16	C4	C20	119.8(4)	C21	C5	C31	120.7(7)
Rh1	C6	C10	108.2(3)	Rh1	C6	C15	72.3(3)
C10	C6	C15	126.3(4)	C16	C7	C28	120.4(4)
C9	C8	C11	120.6(5)	P1	C9	C8	122.0(3)
P1	C9	C18	119.1(3)	C8	C9	C18	118.8(4)
C6	C10	C14	113.6(4)	C3	C11	C8	120.3(5)
C21	C13	C30	120.5(5)	C10	C14	C26	113.3(4)
Rh1	C15	C6	70.7(3)	Rh1	C15	C24	111.3(3)
C6	C15	C24	123.1(5)	C4	C16	C7	120.7(5)
C9	C18	C22	119.9(4)	O2	C19	C2	102.8(3)
O2	C19	C12	109.2(5)	O2	C19	C17	106.4(5)
C2	C19	C12	115.4(5)	C2	C19	C17	114.2(5)
C12	C19	C17	108.2(5)	P1	C20	C1	122.3(3)
P1	C20	C4	118.3(3)	C1	C20	C4	119.4(3)
C5	C21	C13	120.4(5)	C3	C22	C18	120.9(5)
C15	C24	C27	112.6(4)	Rh1	C25	C26	70.8(2)
Rh1	C25	C27	111.3(3)	C26	C25	C27	125.3(5)
Rh1	C26	C14	112.9(3)	Rh1	C26	C25	70.1(3)
C14	C26	C25	123.3(4)	C24	C27	C25	113.9(4)
C1	C28	C7	119.7(5)	C30	C29	C31	119.2(5)
P1	C30	C13	117.8(4)	P1	C30	C29	123.0(3)
C13	C30	C29	119.2(5)	C5	C31	C29	120.0(6)
O1	B1	O2	110.0(4)	O1	B1	O3	122.7(3)
O2	B1	O3	127.3(4				

3. Crystallographic data and details of structure refinement of 3

Experimental

Data Collection

A dark orange prismatic crystal of $C_{40}H_{50}PRh$ having approximate dimensions of 0.25 x 0.30 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range $18.74 < 2\square < 21.42^o$ corresponded to a primitive monoclinic cell with dimensions:

a = 10.443(3) Å
b = 22.412(3) Å β = 102.93(2)°
c = 14.037(3) Å
V = 3202(1) $Å^3$

For Z = 4 and F.W. = 664.71, the calculated density is 1.38 g/cm^3. The systematic absences of:

h0l: h+l ± 2n
0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/n$ (#14)

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.25° with a take-off angle of 6.0°. Scans of (1.15 + 0.30 tan θ)° were made at a speed of 4.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 6.0 x 6.0 mm (horizontal x vertical).

Data Reduction

Of the 7950 reflections which were collected, 7554 were unique (R_{int} = 0.017); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 6.1 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 1.00 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by heavy-atom Patterson methods[1] and expanded using Fourier

techniques[2]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[3] on F was based on 4927 observed reflections ($I > 3.00\sigma(I)$) and 337 variable parameters and converged (largest parameter shift was 4.37 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, | \, |Fo| - |Fc| \, | \, / \Sigma \, |Fo| = 0.052$$

$$R_w = [\Sigma \, w \, (|Fo| - |Fc|)^2 / \Sigma \, w \, Fo^2]^{1/2} = 0.043$$

The standard deviation of an observation of unit weight[4] was 2.04. The weighting scheme was based on counting statistics and included a factor (p = 0.010) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.44 and -0.36 $e^-/\text{Å}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) PATTY: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., Garcia-Granda, S., Gould, R.O., Smits, J.M.M. and Smykalla, C. (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized:

$$\Sigma w(|F_o| - |F_c|)^2 \text{ where}$$

$$\omega = 1/[\sigma^2(Fo)] = [\sigma^2_c(Fo) + \pi^2 Fo^2/4]^{-1}$$

$\sigma_c(Fo)$ = e.s.d. based on counting statistics

p = p-factor

(4) Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
(7) Creagh, D. C. & McAuley, W.J; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
(9) teXsan for Windows: Crystal Structure Analysis Package, Molecular Structure Corporation (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{34}H_{36}PRh \cdot C_6H_{14}$
Formula Weight	664.71
Crystal Color, Habit	dark orange, prismatic
Crystal Dimensions	0.25 X 0.30 X 0.30 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20 (18.7 - 21.4°)
Omega Scan Peak Width at Half-height	0.25°
Lattice Parameters	a = 10.443(3) Å b = 22.412(3) Å c = 14.037(3) Å β = 102.93(2) ° V = 3202(1) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.379 g/cm^3
F_{000}	1400.00
μ(MoKα)	6.10 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.51, 11.52, 42.17)
Take-off Angle	6.0°
Detector Aperture	6.0 mm horizontal

	6.0 mm vertical
Crystal to Detector Distance	258 mm
Voltage, Current	50 kV, 180 mA
Temperature	23.0 °C
Scan Type	ω-2θ
Scan Rate	4.0°/min (in ω) (up to 3 scans)
Scan Width	$(1.15 + 0.30 \tan \theta)^{o}$
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 7950
	Unique: 7554 (R_{int} = 0.017)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 1.0000 - 1.0000)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF92 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4927
No. Variables	337
Reflection/Parameter Ratio	14.62
Residuals: R; Rw	0.052; 0.043
Goodness of Fit Indicator	2.04
Max Shift/Error in Final Cycle	4.37
Maximum peak in Final Diff. Map	0.44 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.36 $e^-/Å^3$

A solvent molecule (hexane) was included in the crystal structure of compound **3**, which was treated as disordered. Three hexane molecules were placed with the occupancy of 0.2 each. DFIX and DANG commands were used for restraint and the C atoms were refined isotropically. Because the placement of H atoms for the disordered molecule resulted in failure during the refinement, the H atoms were not placed.

Table S9. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}

Rh(1)	0.06278(2)	0.17946(1)	0.22426(2)	3.422(5)
P(1)	0.01093(8)	0.10228(4)	0.31936(6)	3.19(2)
C(1)	-0.1311(3)	0.2038(1)	0.1876(2)	3.44(7)
C(2)	-0.2113(3)	0.1839(2)	0.0983(3)	4.39(8)
C(3)	-0.3412(4)	0.2030(2)	0.0695(3)	6.0(1)
C(4)	-0.3946(4)	0.2404(2)	0.1258(4)	6.7(1)
C(5)	-0.3198(4)	0.2600(2)	0.2135(3)	5.8(1)
C(6)	-0.1883(3)	0.2421(1)	0.2453(3)	4.11(8)
C(7)	-0.1598(4)	0.1403(2)	0.0342(3)	6.3(1)
C(8)	-0.1104(4)	0.2642(2)	0.3426(3)	5.6(1)
C(9)	0.2806(3)	0.1789(2)	0.2853(3)	5.4(1)
C(10)	0.2512(4)	0.1417(2)	0.2075(3)	5.5(1)
C(11)	0.2643(4)	0.1560(2)	0.1061(4)	7.0(1)
C(12)	0.2133(4)	0.2163(2)	0.0678(3)	6.4(1)
C(13)	0.1000(3)	0.2381(2)	0.1091(3)	4.60(9)
C(14)	0.1120(3)	0.2711(2)	0.1927(3)	4.41(9)
C(15)	0.2353(4)	0.2891(2)	0.2629(3)	6.3(1)
C(16)	0.3381(4)	0.2411(2)	0.2853(3)	6.4(1)
C(17)	-0.1330(3)	0.1096(1)	0.3730(3)	3.74(8)
C(18)	-0.1268(4)	0.1166(2)	0.4713(3)	4.8(1)
C(19)	-0.2393(5)	0.1265(2)	0.5055(3)	6.4(1)
C(20)	-0.3594(5)	0.1292(2)	0.4426(4)	7.1(2)
C(21)	-0.3692(4)	0.1205(2)	0.3445(4)	6.4(1)
C(22)	-0.2560(3)	0.1107(2)	0.3093(3)	4.68(9)
C(23)	0.1452(3)	0.0885(1)	0.4245(2)	3.54(7)
C(24)	0.2147(4)	0.0361(2)	0.4395(3)	4.74(9)
C(25)	0.3253(4)	0.0321(2)	0.5153(3)	6.5(1)
C(26)	0.3649(4)	0.0803(2)	0.5767(3)	6.6(1)
C(27)	0.2943(4)	0.1325(2)	0.5615(3)	5.7(1)
C(28)	0.1868(3)	0.1364(2)	0.4865(3)	4.72(9)
C(29)	-0.0165(3)	0.0287(1)	0.2619(2)	3.51(7)
C(30)	-0.0718(4)	-0.0173(2)	0.3044(3)	4.8(1)
C(31)	-0.0870(5)	-0.0730(2)	0.2618(3)	6.3(1)
C(32)	-0.0465(5)	-0.0839(2)	0.1770(3)	6.8(1)
C(33)	0.0090(5)	-0.0390(2)	0.1340(3)	6.7(1)
C(34)	0.0242(4)	0.0174(2)	0.1764(3)	5.0(1)
C(35)	0.5824(9)	0.0228(4)	0.8318(7)	19.7(4)
C(36)	0.467(2)	0.0335(7)	0.886(1)	29.7(7)
C(37)	0.508(3)	0.001(1)	0.956(2)	35.5(9)

H(1)	-0.3936	0.1895	0.0091	7.201
H(2)	-0.4833	0.2530	0.1049	8.010
H(3)	-0.3576	0.2859	0.2532	6.920
H(4)	-0.0937	0.1590	0.0079	7.526
H(5)	-0.1235	0.1066	0.0720	7.526
H(6)	-0.2296	0.1277	-0.0175	7.526
H(7)	-0.1065	0.3066	0.3418	6.670
H(8)	-0.1518	0.2517	0.3930	6.670
H(9)	-0.0239	0.2484	0.3544	6.670
H(10)	0.3061	0.1589	0.3463	6.516
H(11)	0.2621	0.1006	0.2241	6.559
H(12)	0.2176	0.1265	0.0634	8.358
H(13)	0.3549	0.1541	0.1051	8.358
H(14)	0.2831	0.2443	0.0841	7.689
H(15)	0.1848	0.2138	-0.0013	7.689
H(16)	0.0235	0.2472	0.0605	5.517
H(17)	0.0416	0.2984	0.1903	5.293
H(18)	0.2135	0.3007	0.3225	7.592
H(19)	0.2718	0.3223	0.2361	7.592
H(20)	0.3926	0.2486	0.3480	7.664
H(21)	0.3895	0.2425	0.2374	7.664
H(22)	-0.0441	0.1145	0.5163	5.760
H(23)	-0.2328	0.1315	0.5736	7.716
H(24)	-0.4358	0.1371	0.4666	8.561
H(25)	-0.4529	0.1212	0.3006	7.639
H(26)	-0.2630	0.1047	0.2414	5.609
H(27)	0.1873	0.0028	0.3982	5.689
H(28)	0.3743	-0.0040	0.5252	7.828
H(29)	0.4403	0.0774	0.6289	7.868
H(30)	0.3205	0.1658	0.6032	6.896
H(31)	0.1390	0.1728	0.4761	5.654
H(32)	-0.0997	-0.0106	0.3635	5.764
H(33)	-0.1259	-0.1042	0.2914	7.504
H(34)	-0.0570	-0.1225	0.1483	8.183
H(35)	0.0372	-0.0463	0.0753	7.993
H(36)	0.0629	0.0484	0.1464	6.025

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\square +$

$2U_{23}(bb^*cc^*)\cos\alpha)$

Table S10. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	0.0378(1)	0.0450(1)	0.0499(1)	0.0034(1)	0.0154(1)	0.0081(1)
P(1)	0.0426(5)	0.0377(4)	0.0426(5)	0.0032(4)	0.0131(4)	0.0008(4)
C(1)	0.042(2)	0.043(2)	0.048(2)	0.000(1)	0.015(1)	0.011(1)
C(2)	0.051(2)	0.057(2)	0.057(2)	-0.004(2)	0.006(2)	0.015(2)
C(3)	0.046(2)	0.090(3)	0.083(3)	-0.008(2)	-0.004(2)	0.034(3)
C(4)	0.039(2)	0.095(4)	0.120(4)	0.008(2)	0.020(2)	0.049(3)
C(5)	0.063(3)	0.060(3)	0.111(4)	0.015(2)	0.048(3)	0.027(3)
C(6)	0.052(2)	0.043(2)	0.069(2)	0.007(2)	0.029(2)	0.014(2)
C(7)	0.091(3)	0.084(3)	0.053(2)	-0.009(3)	-0.005(2)	-0.005(2)
C(8)	0.098(3)	0.050(2)	0.072(3)	0.010(2)	0.039(2)	-0.004(2)
C(9)	0.037(2)	0.090(3)	0.080(3)	0.008(2)	0.014(2)	0.026(3)
C(10)	0.050(2)	0.065(3)	0.101(3)	0.013(2)	0.032(2)	0.012(2)
C(11)	0.081(3)	0.087(3)	0.113(4)	0.002(3)	0.056(3)	-0.014(3)
C(12)	0.085(3)	0.098(4)	0.073(3)	-0.005(3)	0.044(3)	0.005(3)
C(13)	0.058(2)	0.064(2)	0.057(2)	0.001(2)	0.023(2)	0.017(2)
C(14)	0.055(2)	0.044(2)	0.071(3)	-0.000(2)	0.019(2)	0.014(2)
C(15)	0.071(3)	0.076(3)	0.089(3)	-0.021(2)	0.009(2)	0.000(3)
C(16)	0.046(2)	0.105(4)	0.088(3)	-0.013(2)	0.007(2)	-0.001(3)
C(17)	0.055(2)	0.033(2)	0.059(2)	0.001(1)	0.022(2)	0.004(2)
C(18)	0.069(3)	0.058(2)	0.062(2)	-0.002(2)	0.030(2)	-0.005(2)
C(19)	0.098(4)	0.070(3)	0.093(4)	-0.005(3)	0.058(3)	-0.017(3)
C(20)	0.103(4)	0.058(3)	0.138(5)	0.008(3)	0.086(4)	0.004(3)
C(21)	0.048(2)	0.064(3)	0.137(4)	0.006(2)	0.037(3)	0.029(3)
C(22)	0.050(2)	0.058(2)	0.074(3)	0.003(2)	0.023(2)	0.016(2)
C(23)	0.048(2)	0.044(2)	0.043(2)	0.000(1)	0.012(2)	0.001(1)
C(24)	0.056(2)	0.049(2)	0.070(3)	0.006(2)	0.004(2)	0.005(2)
C(25)	0.069(3)	0.066(3)	0.103(4)	0.014(2)	-0.001(3)	0.018(3)
C(26)	0.059(3)	0.115(4)	0.065(3)	-0.005(3)	-0.007(2)	0.015(3)
C(27)	0.068(3)	0.086(3)	0.063(3)	-0.011(2)	0.011(2)	-0.017(2)
C(28)	0.055(2)	0.060(2)	0.061(2)	0.004(2)	0.007(2)	-0.010(2)
C(29)	0.051(2)	0.040(2)	0.044(2)	0.004(1)	0.012(1)	-0.003(1)
C(30)	0.082(3)	0.046(2)	0.060(2)	-0.009(2)	0.028(2)	-0.007(2)
C(31)	0.111(4)	0.052(2)	0.080(3)	-0.022(2)	0.033(3)	-0.010(2)
C(32)	0.124(4)	0.053(3)	0.086(3)	-0.010(3)	0.032(3)	-0.020(2)
C(33)	0.122(4)	0.072(3)	0.067(3)	-0.001(3)	0.039(3)	-0.020(2)

C(34)	0.085(3)	0.052(2)	0.059(2)	-0.003(2)	0.027(2)	-0.005(2)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S11. Bond Lengths(Å)

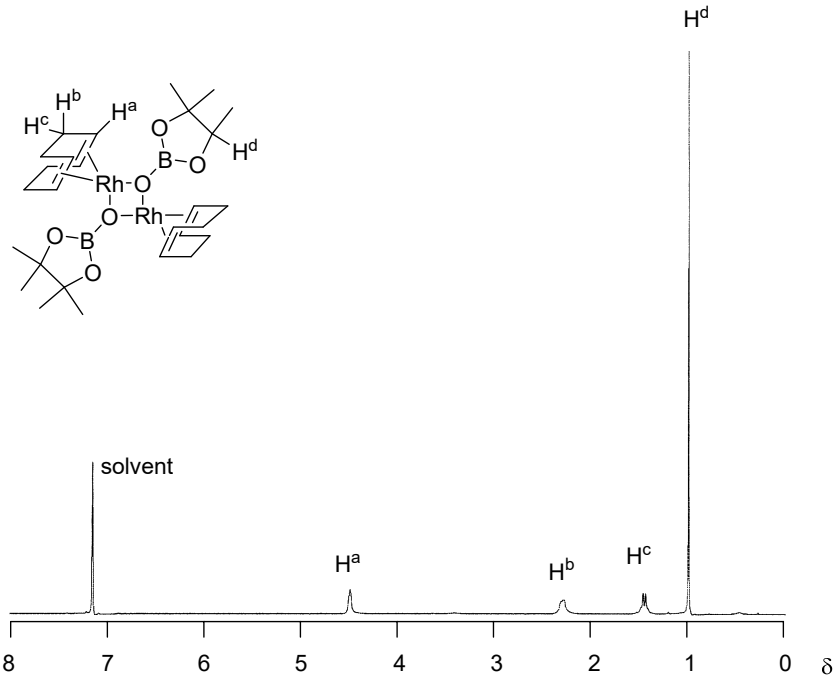
atom	atom	distance	atom	atom	distance
Rh(1)	P(1)	2.322(1)	Rh(1)	C(1)	2.049(4)
Rh(1)	C(9)	2.244(5)	Rh(1)	C(10)	2.203(5)
Rh(1)	C(13)	2.185(5)	Rh(1)	C(14)	2.187(5)
P(1)	C(17)	1.834(5)	P(1)	C(23)	1.820(5)
P(1)	C(29)	1.829(4)	C(1)	C(2)	1.415(6)
C(1)	C(6)	1.402(6)	C(2)	C(3)	1.393(7)
C(2)	C(7)	1.506(7)	C(3)	C(4)	1.354(8)
C(4)	C(5)	1.374(8)	C(5)	C(6)	1.404(7)
C(6)	C(8)	1.508(7)	C(9)	C(10)	1.354(7)
C(9)	C(16)	1.517(8)	C(10)	C(11)	1.495(8)
C(11)	C(12)	1.508(8)	C(12)	C(13)	1.511(7)
C(13)	C(14)	1.369(7)	C(14)	C(15)	1.492(7)
C(15)	C(16)	1.503(8)	C(17)	C(18)	1.375(6)
C(17)	C(22)	1.391(6)	C(18)	C(19)	1.383(7)
C(19)	C(20)	1.364(9)	C(20)	C(21)	1.371(9)
C(21)	C(22)	1.397(7)	C(23)	C(24)	1.372(6)
C(23)	C(28)	1.389(6)	C(24)	C(25)	1.387(7)
C(25)	C(26)	1.388(8)	C(26)	C(27)	1.374(8)
C(27)	C(28)	1.359(7)	C(29)	C(30)	1.382(6)
C(29)	C(34)	1.383(6)	C(30)	C(31)	1.377(7)
C(31)	C(32)	1.371(8)	C(32)	C(33)	1.368(8)
C(33)	C(34)	1.391(7)	C(35)	C(36)	1.58(2)
C(36)	C(37)	1.21(4)	C(37)	C(37)	1.30(7)

Table S12. Bond Angles(°)

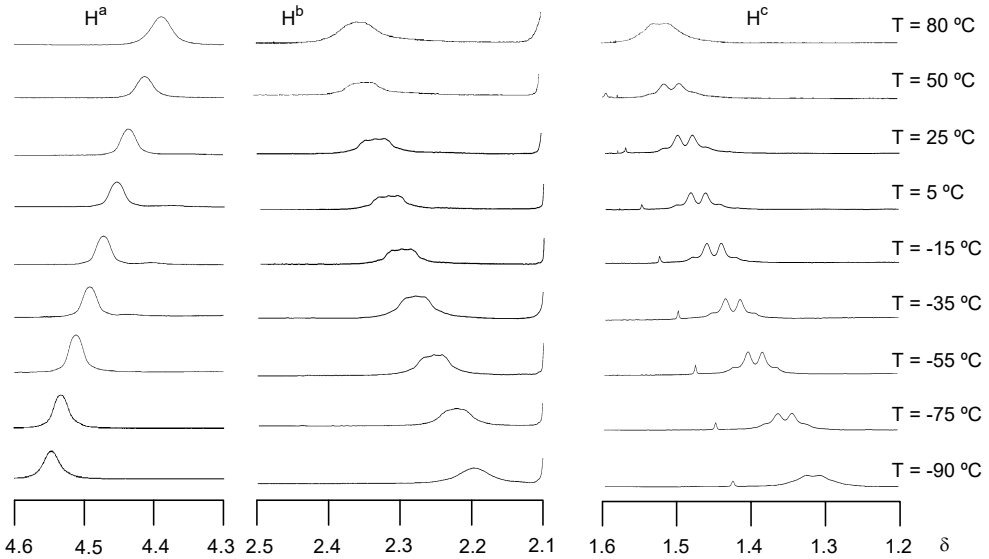
atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Rh(1)	C(1)	89.9(1)	P(1)	Rh(1)	C(9)	97.1(1)
P(1)	Rh(1)	C(10)	96.0(2)	P(1)	Rh(1)	C(13)	167.6(2)
P(1)	Rh(1)	C(14)	155.8(1)	C(1)	Rh(1)	C(9)	163.3(2)
C(1)	Rh(1)	C(10)	158.8(2)	C(1)	Rh(1)	C(13)	89.1(2)
C(1)	Rh(1)	C(14)	87.9(2)	C(9)	Rh(1)	C(10)	35.4(2)

C(9)	Rh(1)	C(13)	87.3(2)	C(9)	Rh(1)	C(14)	79.5(2)
C(10)	Rh(1)	C(13)	80.9(2)	C(10)	Rh(1)	C(14)	94.8(2)
C(13)	Rh(1)	C(14)	36.5(2)	Rh(1)	P(1)	C(17)	119.2(1)
Rh(1)	P(1)	C(23)	110.8(2)	Rh(1)	P(1)	C(29)	116.8(2)
C(17)	P(1)	C(23)	103.6(2)	C(17)	P(1)	C(29)	101.5(2)
C(23)	P(1)	C(29)	102.8(2)	Rh(1)	C(1)	C(2)	119.6(4)
Rh(1)	C(1)	C(6)	122.9(4)	C(2)	C(1)	C(6)	117.5(4)
C(1)	C(2)	C(3)	120.3(5)	C(1)	C(2)	C(7)	120.9(5)
C(3)	C(2)	C(7)	118.7(5)	C(2)	C(3)	C(4)	121.5(6)
C(3)	C(4)	C(5)	119.7(5)	C(4)	C(5)	C(6)	120.9(6)
C(1)	C(6)	C(5)	120.2(5)	C(1)	C(6)	C(8)	120.8(4)
C(5)	C(6)	C(8)	119.0(5)	Rh(1)	C(9)	C(10)	70.6(3)
Rh(1)	C(9)	C(16)	111.2(4)	C(10)	C(9)	C(16)	125.7(5)
Rh(1)	C(10)	C(9)	74.0(3)	Rh(1)	C(10)	C(11)	107.1(4)
C(9)	C(10)	C(11)	125.7(6)	C(10)	C(11)	C(12)	115.5(5)
C(11)	C(12)	C(13)	113.5(5)	Rh(1)	C(13)	C(12)	111.9(4)
Rh(1)	C(13)	C(14)	71.8(3)	C(12)	C(13)	C(14)	125.1(5)
Rh(1)	C(14)	C(13)	71.7(3)	Rh(1)	C(14)	C(15)	109.1(4)
C(13)	C(14)	C(15)	127.8(5)	C(14)	C(15)	C(16)	114.5(5)
C(9)	C(16)	C(15)	113.2(5)	P(1)	C(17)	C(18)	124.3(4)
P(1)	C(17)	C(22)	117.5(4)	C(18)	C(17)	C(22)	118.2(5)
C(17)	C(18)	C(19)	120.9(6)	C(18)	C(19)	C(20)	120.8(6)
C(19)	C(20)	C(21)	119.7(6)	C(20)	C(21)	C(22)	119.9(6)
C(17)	C(22)	C(21)	120.5(5)	P(1)	C(23)	C(24)	123.7(4)
P(1)	C(23)	C(28)	117.0(4)	C(24)	C(23)	C(28)	119.0(5)
C(23)	C(24)	C(25)	119.7(5)	C(24)	C(25)	C(26)	120.4(6)
C(25)	C(26)	C(27)	119.5(5)	C(26)	C(27)	C(28)	119.8(6)
C(23)	C(28)	C(27)	121.6(5)	P(1)	C(29)	C(30)	121.5(4)
P(1)	C(29)	C(34)	120.0(4)	C(30)	C(29)	C(34)	118.4(4)
C(29)	C(30)	C(31)	120.5(5)	C(30)	C(31)	C(32)	120.7(5)
C(31)	C(32)	C(33)	119.7(5)	C(32)	C(33)	C(34)	119.9(5)
C(29)	C(34)	C(33)	120.7(5)	C(35)	C(36)	C(37)	97(3)
C(36)	C(37)	C(37)	135(6)				

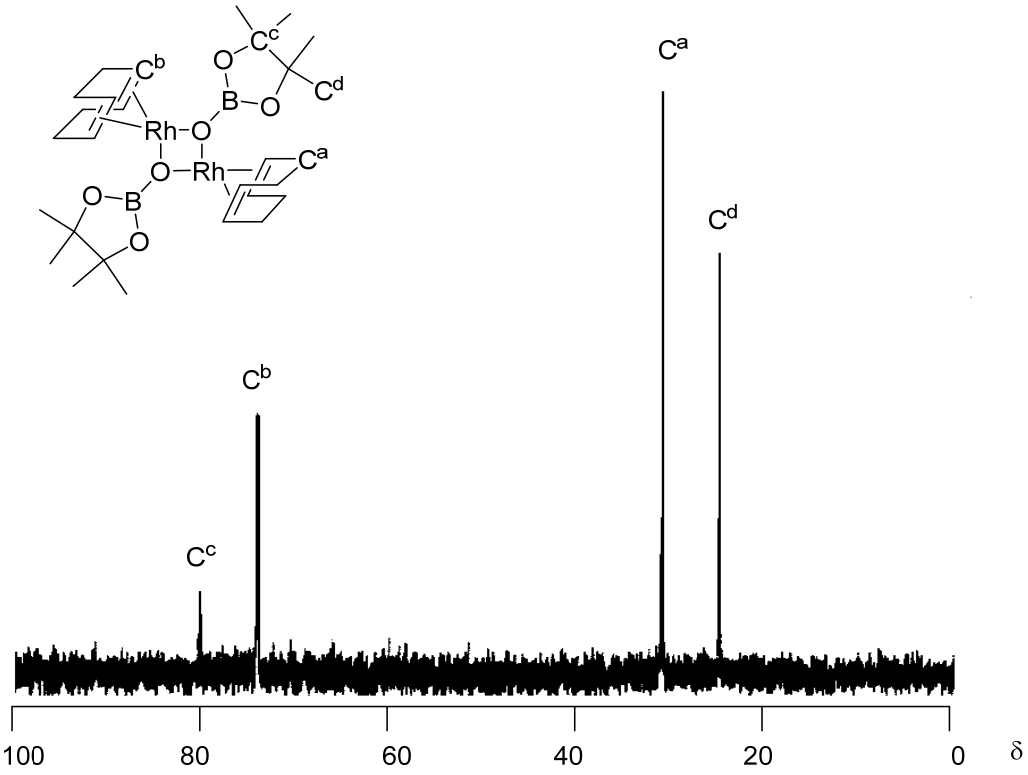
4. Copies of NMR spectra



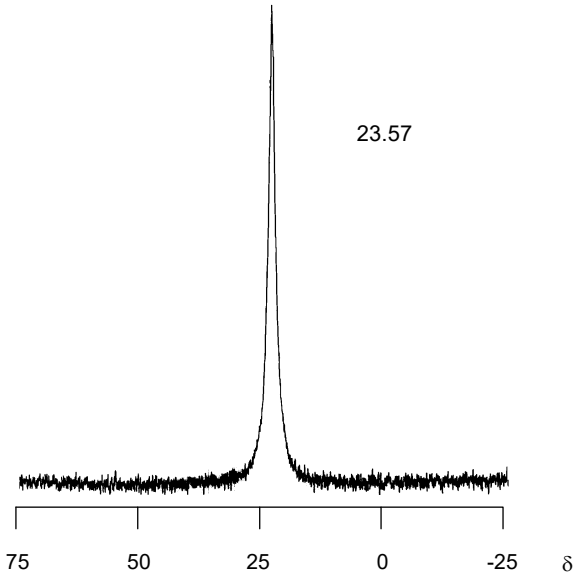
^{1}H NMR spectrum (300 MHz) of **1** (C_6D_6, rt).



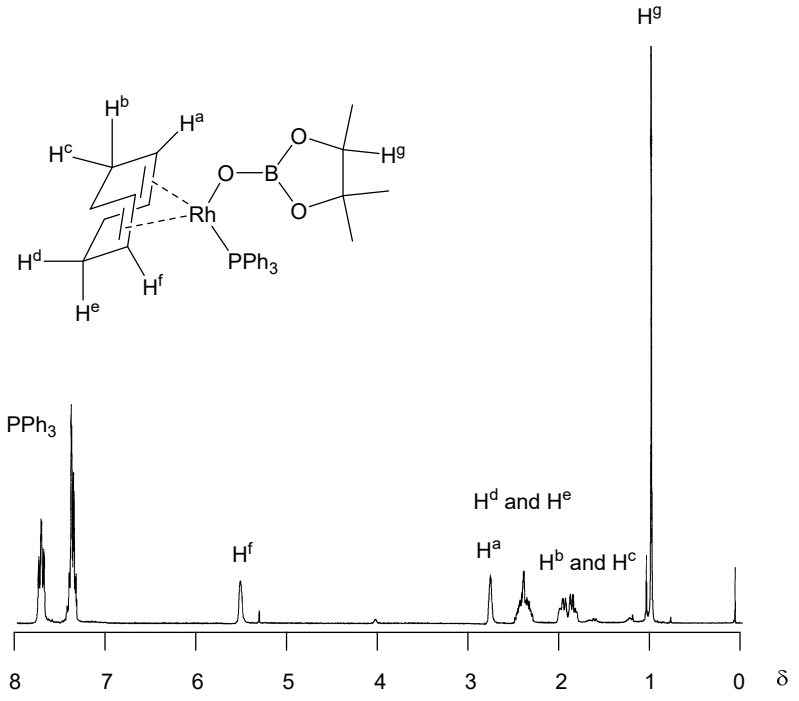
^{1}H NMR spectra (400 MHz) of the cod hydrogens of **1** in toluene-d_8 at various temperatures.



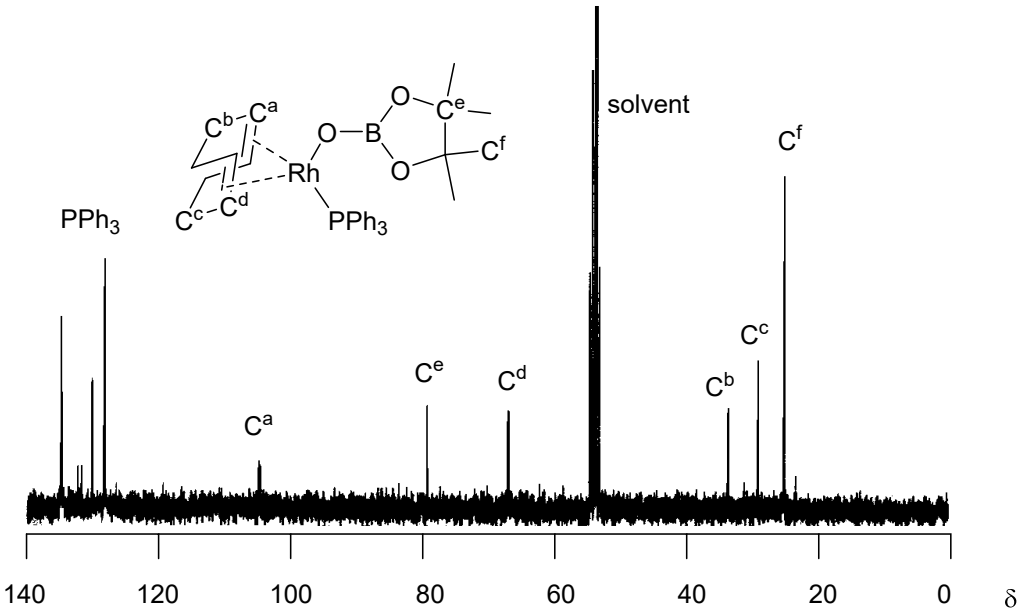
$^{13}C\{^{1}H\}$ NMR spectrum (75.3 MHz) of **1** (C_6D_6, rt).



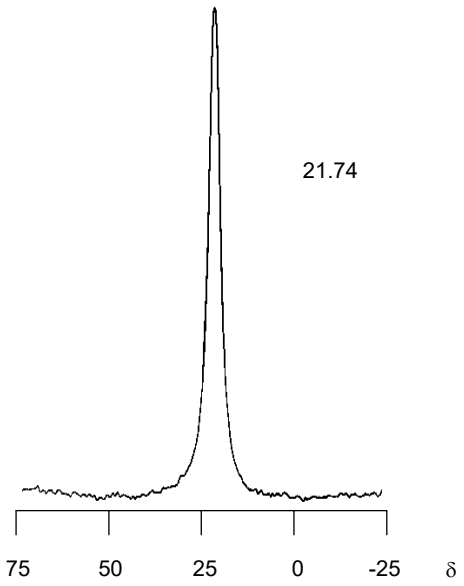
$^{11}B\{^{1}H\}$ NMR Spectrum (160.4 MHz) of **1** (C_6D_6, rt).



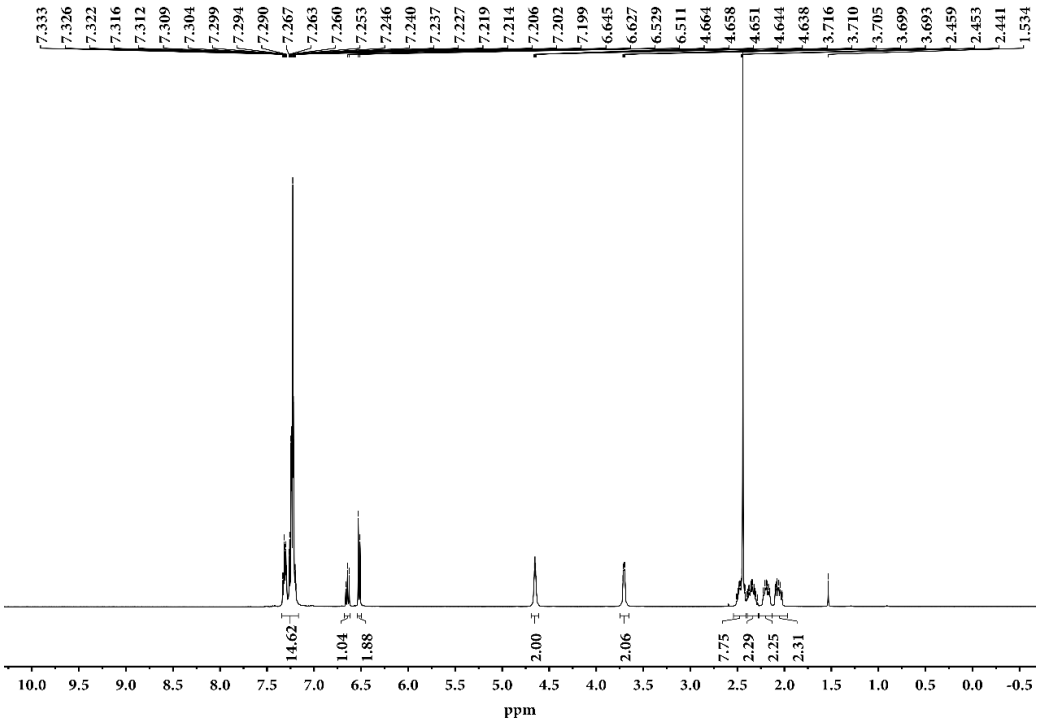
^{1}H NMR spectrum (300 MHz) of **2** (CD_2Cl_2, rt).



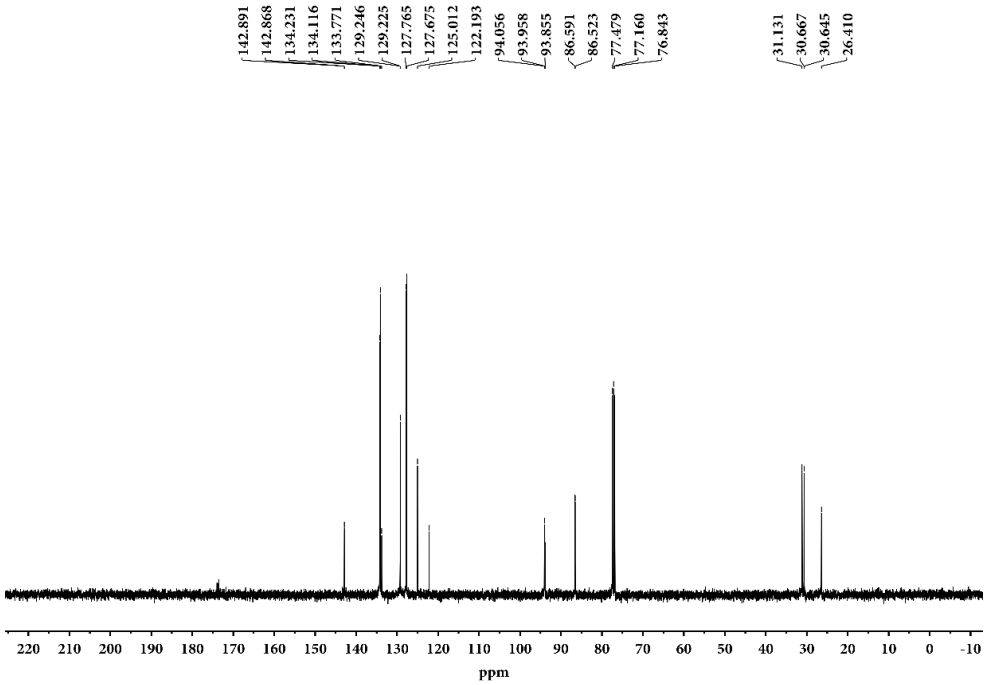
^{13}C{^{1}H} NMR spectrum (75.3 MHz) of **2** (CD_2Cl_2, rt).



$^{11}B\{^{1}H\}$ NMR spectrum (160.4 MHz) of **3** (C_6D_6, rt).

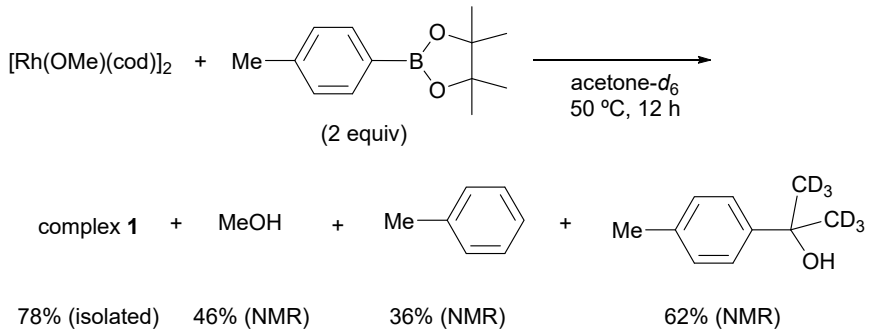


^{1}H NMR spectrum (300 MHz) of **3** ($CDCl_3$, rt).

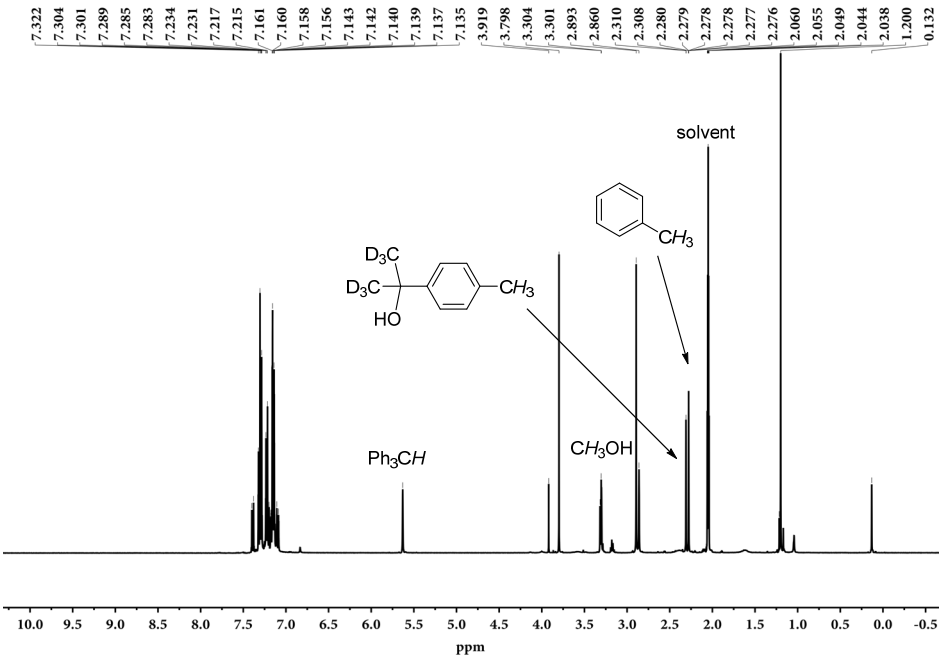


^{13}C{^{1}H} NMR (100 MHz) of **3** ($CDCl_3$, rt).

5. Identification of byproducts in the reaction of $[Rh(OMe)(cod)]_2$ with 4-methylphenylboronic acid pinacol ester.



In 25 mL pf Schlenk tube were added $[Rh(OMe)(cod)]_2$ (24 mg, 0.05 mmol), 4-methylphenylboronic acid pinacol ester (22 mg, 0.10 mmol), and triphenylmethane (24 mg, 0.10 mmol) as an internal standard in acetone-d_6 (2.5 mL), and the reaction was heated at 50 ºC under N_2 atmosphere. After 12 h, the reaction mixture was filtered and the filtrate was transferred to an NMR tube. The residue was dried in vacuo to give complex **1** as pale yellow powder (28 mg, 0.039 mmol, 78%). The ^{1}H NMR measurement indicated the formation of 46% of methanol, 36% of toluene, and 62% of 2-(4-methylphenyl)-2-propanol.



^{1}H NMR spectrum (300 MHz) of the crude mixture ($(CD_3)_2CO$, rt).