Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

1,4-Metal migration at a Cp*Rh(III) complex

Yousuke Ikeda, Koichi Takano, Shintaro Kodama and Youichi Ishii*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Table of Contents

This journal is © The Royal Society of Chemistry 2013

General Considerations. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. 1,2-Dichloroethane ($C_2H_4Cl_2$) was dried and distilled over P_4O_{10}, degassed and stored under an argon atomosphere. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. 1-phenyl-1-propyne, 3-hexyne, diphenylacetylene and MeMgCl (3M in THF) were purchased from Sigma-Aldrich and used as received. [Cp*RhCl(Ph)(PPh_3)] (**1**),[1] [Cp*RhCl(Ph)(PMe_3)] (**4**),[1] [Cp*$RhCl_2$(PPh_3)],[1] $NaBAr^F{}_4\cdot 2H_2O$[2] and 1-(4-tolyl)-3-phenyl-2-propyn-1-one[3] were synthesized according to the literature. ^{1}H (500 MHz), ^{13}C{^{1}H} (126 MHz), and ^{31}P{^{1}H} (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ, referenced to residual ^{1}H and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of PPh_3 (δ –5.65) as an external standard. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ^{1}H NMR spectroscopy.

[Cp*Rh{*o*-C_6H_4C(Me)=CHPh}(PPh_3)][$BAr^F{}_4$] (2a). A mixture of [Cp*RhCl(Ph)(PPh_3)] (**1**; 45.5 mg, 0.074 mmol), $NaBAr^F{}_4\cdot 2H_2O$ (76.9 mg, 0.083 mmol) and 1-phenyl-1-propyne (50 μl, 47.0 mg, 0.405 mmol, 5 equiv) in $C_2H_4Cl_2$ (2 mL) was stirred at 25 ˚C for few minutes. The resulting dark red suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was concentrated in vacuo and layered with hexane to give **2a** (86.6 mg, 0.056 mmol, 76% yield) as dark red crystals. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 35.5 (d, J_{RhP} = 161 Hz, PPh_3). ^{1}H NMR ($CDCl_3$): δ 7.71–6.74 (m, 36H, Ar), 2.33 (s, 3H, CH_3), 1.10 (d, J = 2.3 Hz, 15H, Cp*), 1.06 (t, J_{RhH} = $^2J_{PH}$ = 10.3 Hz, 1H, C=C*H*Ph). Selected ^{13}C{^{1}H} NMR data ($CDCl_3$): δ 166.7 (s, *o*-C_6H_4*C*(Me)=C), 97.5 (dd, J = 6.1, 3.0 Hz, C=*C*HPh), 21.0 (s, CH_3), 9.06 (s, CH_3 of Cp*). Anal. Calcd for $C_{75}H_{55}BF_{24}PRh$ (**2a**): C, 57.86; H, 3.56. Found: C, 57.58; H, 3.44.

[Cp*Rh{*o*-C_6H_4C(Et)=CHEt}(PPh_3)][$BAr^F{}_4$] (2b). This compound was synthesized from **1** (26.3 mg, 0.043 mmmol), $NaBAr^F{}_4\cdot 2H_2O$ (42.3 mg, 0.046 mmol) and 3-hexyne (25 μl, 0.225 mmol) by a

procedure similar to that for the synthesis of **2a** except that Et_2O/hexane was used as the solvent for recystallization. Dark red crystals (50.6 mg, 0.033 mmol, 77% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.0 (d, J_{RhP} = 159 Hz, PPh_3). ^1H NMR ($CDCl_3$): δ 7.70–6.62 (m, 31H, Ar), 2.66–2.61 (m, 2H, C=CHCH_2CH$_3$ and *o*-$C_6H_4C(CH_2CH_3)$=C), 2.52–2.48 (m, 1H, *o*-$C_6H_4C(CH_2CH_3)$=C), 1.81–1.77 (m, 1H, C=CHCH_2), 1.26 (d, J = 1.7 Hz, 15H, Cp*), 1.15 (t, J = 7.4 Hz, 3H, *o*-$C_6H_4C(CH_2CH_3)$=C), 0.34 (t, J = 7.4 Hz, 3H, C=CHCH$_2$$CH_3$), −0.34 (m, 1H, C=C$HCH_2CH_3$). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 171.8 (s, *o*-$C_6H_4C(CH_2CH_3)$=C), 98.4 (m, C=CHCH$_2$CH$_3$), 25.9 (s, *o*-$C_6H_4C(CH_2CH_3)$=C), 23.9 (s, C=CHCH_2CH$_3$), 13.8 (s, *o*-$C_6H_4C(CH_2CH_3)$=C), 13.6 (s, C=CHCH$_2$$CH_3$), 9.15 (s, CH_3 of Cp*). Anal. Calcd for $C_{72}H_{57}BF_{24}PRh$ (**2b**): C, 56.79; H, 3.77. Found: C, 56.51; H, 3.60.

[Cp*Rh{*o*-C$_6$H$_4$C(Ph)=CHPh}(PPh$_3$)][BAr$^F_4$] (2c). This compound was synthesized from **1** (33.3 mg, 0.054 mmol), $NaBAr^F_4{\cdot}2H_2O$ (58.0 mg, 0.063 mmol) and diphenylacetylene (25.0 mg, 0.140 mmol) by a procedure similar to that for the synthesis of **2a** except that the reaction was performed for 5 h and Et_2O/hexane was used as the solvent for recystallization. Dark red crystals (66.8 mg, 0.041 mmol, 76% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.4 (d, J_{RhP} = 161 Hz, PPh_3). ^1H NMR ($CDCl_3$): δ 7.71–6.44 (m, 41H, Ar), 1.16 (d, J = 2.3 Hz, 15H, Cp*), 0.72 (t, $J_{RhH} = {}^2J_{PH}$ = 10.3 Hz,, 1H, C=CHPh). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 167.1 (s, *o*-C_6H_4C(Ph)=C), 100.0 (dd, J = 6.6, 2.5 Hz, C=CHPh), 9.04 (s, CH_3 of Cp*). Anal. Calcd for $C_{80}H_{57}BF_{24}PRh$ (**2c**): C, 59.35; H, 3.55. Found: C, 58.98; H, 3.44.

[Cp*Rh{*o*-C$_6$H$_4$C(Me)=CHPh}(PMe$_3$)][BAr$^F_4$] (5a). This compound was synthesized from **4** (23.3 mg, 0.055 mmmol), $NaBAr^F_4{\cdot}2H_2O$ (62.4 mg, 0.068 mmol) and 1-phenyl-1-propyne (30 μl, 0.243 mmol) by a procedure similar to that for the synthesis of **2a**. Dark red crystals (67.1 mg, 0.049 mmol, 90% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.57 (d, J_{RhP} = 156 Hz, PMe_3). ^1H NMR ($CDCl_3$): δ 7.71 (br, 8H, BAr^F_4), 7.55–7.53 (m, 5H, Ar and BAr^F_4), 7.45–7.20 (m, 8H, Ar), 2.45 (s, 3H, CH_3), 1.37 (d, J = 10.3 Hz, 9H, $P(CH_3)_3$), 1.35 (d, J = 2.3 Hz, 15H, Cp*), 0.87 (t, $J_{RhH} = {}^2J_{PH}$ = 10.3 Hz, 1H, C=CHPh). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 167.4 (s, *o*-$C_6H_4C(CH_3)$=C), 95.3 (br, C=CHPh),

21.5 (s, *o*-$C_6H_4C(CH_3)$=C), 15.7 (d, J_{CP}= 33.6 Hz, $P(CH_3)_3$), 9.44 (s, CH_3 of Cp*). Anal. Calcd for $C_{60}H_{49}BF_{24}PRh$ (**5a**): C, 52.58; H, 3.60. Found: C, 52.58; H, 3.35.

[Cp*Rh{*o*-$C_6H_4C(Et)$=CHEt}(PMe_3)][BAr^F_4] (5b). This compound was synthesized from **4** (24.0 mg, 0.056 mmmol), $NaBAr^F_4 \cdot 2H_2O$ (57.0 mg, 0.062 mmol) and 3-hexyne (32 μl, 0.288 mmol) by a procedure similar to that for the synthesis of **2a**. Red crystals (59.3 mg, 0.044 mmol, 79% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.62 (d, $^2J_{RhP}$ = 147 Hz, PMe_3). ^1H NMR ($CDCl_3$): δ 7.71 (br, 8H, BAr^F_4), 7.54 (br, 4H, BAr^F_4), 7.14–7.04 (m, 4H, Ar), 2.64, 2.31 (m, 1H each, *o*-$C_6H_4C(CH_2CH_3)$=C), 2.15 (m, 1H, C=CHC$H_2$$CH_3$), 1.94 (m, 1H, C=C$H$$CH_2CH_3$), 1.76 (m, 1H, C=CHC$H_2$$CH_3$), 1.56 (d, J = 2.9 Hz, 15H, Cp*), 1.30 (t, J = 8.0 Hz, 3H, *o*-$C_6H_4C(CH_2CH_3)$=C), 1.27 (d, J = 9.7 Hz, $P(CH_3)_3$), 1.02 (t, J = 7.4 Hz, 3H, C=$CHCH_2CH_3$). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 90.0 (br, C=$C$$HCH_2CH_3$), 26.8 (s, *o*-$C_6H_4C(CH_2CH_3)$=C), 22.9 (s, C=$CHCH_2CH_3$), 15.3 (d, J_{CP}= 34.8 Hz, $P(CH_3)_3$), 15.2 (s, *o*-$C_6H_4C(CH_2CH_3)$=C), 14.2 (s, C=$CHCH_2CH_3$), 9.52 (s, CH_3 of Cp*). Anal. Calcd for $C_{57}H_{51}BF_{24}PRh$ (**5b**): C, 51.22; H, 3.85. Found: C, 51.23; H, 3.67.

[Cp*Rh{*o*-$C_6H_4C(Ph)$=CHPh}(PMe_3)][BAr^F_4]·0.5$C_2H_4Cl_2$ (5c·0.5$C_2H_4Cl_2$). This compound was synthesized from **4** (23.2 mg, 0.054 mmmol), $NaBAr^F_4 \cdot 2H_2O$ (60.2 mg, 0.065 mmol) and diphenylacetylene (48.5 mg, 0.272 mmol) by a procedure similar to that of **2a**. Dark red crystals (74.3 mg, 0.050 mmol, 92% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.99 (d, J_{RhP} = 156 Hz, PMe_3). ^1H NMR ($CDCl_3$): δ 7.72 (br, 8H, BAr^F_4), 7.54 (br, 4H, BAr^F_4), 7.45–6.80 (m, 14H, Ar), 1.50 (d, J = 10.3 Hz, 9H, $P(CH_3)_3$), 1.34 (d, J = 2.3 Hz, 15H, Cp*), 0.38 (t, J_{RhH} = $^2J_{PH}$ = 11.2 Hz, 1H, C=CHPh). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 168.8 (s, *o*-C_6H_4C(Ph)=C), 97.2 (dd, J = 7.2, 2.4 Hz, C=CHPh), 15.7 (d, J_{CP}= 33.6 Hz, $P(CH_3)_3$), 9.49 (s, CH_3 of Cp*). Anal. Calcd for $C_{66}H_{53}BClF_{24}PRh$ (**5c·0.5$C_2H_4Cl_2$**): C, 53.48; H, 3.60. Found: C, 53.84; H, 3.46.

[Cp*Rh{C(*o*-C_6H_4Me-*p*)=CPh_2}(PPh_3)][BAr^F_4] (6). A mixture of [Cp*RhCl(Ph)(PPh_3)] (**1**; 26.6 mg, 0.043 mmol), $NaBAr^F_4 \cdot 2H_2O$ (45.0 mg, 0.049 mmol) and 1-(4-tolyl)-3-phenyl-2-propyn-1-one (40.0 mg, 0.182 mmol) in $C_2H_4Cl_2$ (2 mL) was stirred at 25 ˚C for few minutes. The resulting red suspension was filtered through a plug of Celite, and the plug was

rinsed with $C_2H_4Cl_2$. The combined filtrate was dried in vacuo, and the residue was recrystallized from toluene/hexanes to give **6** (59.6 mg, 0.036 mmol, 83% yield) as red crystals. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.1 (d, $^2J_{RhP}$ = 161 Hz, PPh_3). ^1H NMR ($CDCl_3$): δ 7.70–6.52 (m, 41H, Ar), 2.18 (s, 3H, Me), 1.17 (d, J = 2.9 Hz, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 208.1 (s, C=O), 21.4 (s, CH_3), 8.95 (s, CH_3 of Cp*). IR (cm^{-1}): 1608 (m, $\nu_{C=O}$). Anal. Calcd for $C_{82}H_{59}BF_{24}OPRh$ (**6**): C, 59.29; H, 3.58. Found: C, 59.17; H, 3.47.

[Cp*RhCl(Me)(PPh_3)]·0.5CH_2Cl_2 (7·0.5CH_2Cl_2). The following procedure is modified from the preparation method originally reported by Blum.[4] [Cp*$RhCl_2(PPh_3)$] (300 mg, 0.525 mmol) was suspended in anhydrous THF (20 mL), and the suspension was cooled to −40 ˚C. A THF solution of MeMgCl (0.53 mL of 3 M solution, 1.59 mmol, 3 equiv) was added dropwise to the suspension by using an airtight syringe. The reaction mixture was stirred at −40 ˚C for 15 min, warmed to room temperature, and stirring was continued until the suspension became an orange solution (almost 20 min). Then saturated aqueous NH_4Cl solution (0.2 mL) was added to quench unreacted Grignard reagent, and the solvent was removed in vacuo. The product was extracted with CH_2Cl_2 and filtered through a plug of Celite, and the plug was rinsed with CH_2Cl_2. Column chromatography on silica (4% THF–CH_2Cl_2) gave the desired complex as the first orange band. Recrystallization from CH_2Cl_2/hexane afforded pure **7**·0.5CH_2Cl_2 (167.6 mg, 0.282 mmol, 54% yield) as orange needles. ^1H NMR ($CDCl_3$): δ 7.63–7.61 (m, 6H, Ph), 7.36–7.33 (br, 9H, Ph), 1.31 (d J = 2.3 Hz, 15H, Cp*), 0.87 (dd, J = 6.6, 2.0 Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.2 (d, J = 165.7 Hz, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.5 (d, J = 9.6 Hz, Ph), 133.2 (d, J = 43.2 Hz, Ph), 129.9 (d, J = 2.4 Hz, Ph), 128.1 (d, J = 9.6 Hz, Ph), 99.1 (t, J_{RhC} = $^2J_{CP}$ = 4.2 Hz, Cp*), 8.58 (s, CH_3 of Cp*), 1.72 (dd, J = 23.4, 15.0 Hz, CH_3). Anal. Calcd for $C_{29.5}H_{34}Cl_2PRh$: C, 59.71; H, 5.78. Found: C, 59.74; H, 5.63.

Reaction of 7·0.5CH_2Cl_2 with $NaBAr^F_4$ and PhC≡CPh A mixture of **7**·0.5CH_2Cl_2 (22.7 mg, 0.038 mmol), $NaBAr^F_4$·2H_2O (36.2 mg, 0.039 mmol) and diphenylacetylene (20.5 mg, 0.115 mmol, 3 equiv) in $C_2H_4Cl_2$ (2 mL) was stirred at 25 ˚C for 21 h. The resulting dark red suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was

concentrated in vacuo, and the solution was added hexane to give **2a** (42.3 mg, 0.027 mmol, 71% yield) as dark red crystals.

Observation of 3c. A mixture of **1** (28.6 mg, 0.047 mmol), $NaBAr^F_4 \cdot 2H_2O$ (47.2 mg, 0.051 mmol) and diphenylacetylene (26.1 mg, 0.146 mmol, 3 equiv) in $C_2H_4Cl_2$ (2 mL) was stirred at 25 ˚C for 30 min. The resulting dark red suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was dried in vacuo and washed with hexane (2 mL × 3). The singal of **3c** was observed from the $^{31}P\{^1H\}$ and ^1H NMR spectrum of the $CDCl_3$ solution of the residure. When similar reaction was performed by using **1**-d_5, the diagnostic signal of **3c** (δ 5.31), which was attributed to the agostic ortho protons of the phenyl substituent, was not observed in ^1H NMR.

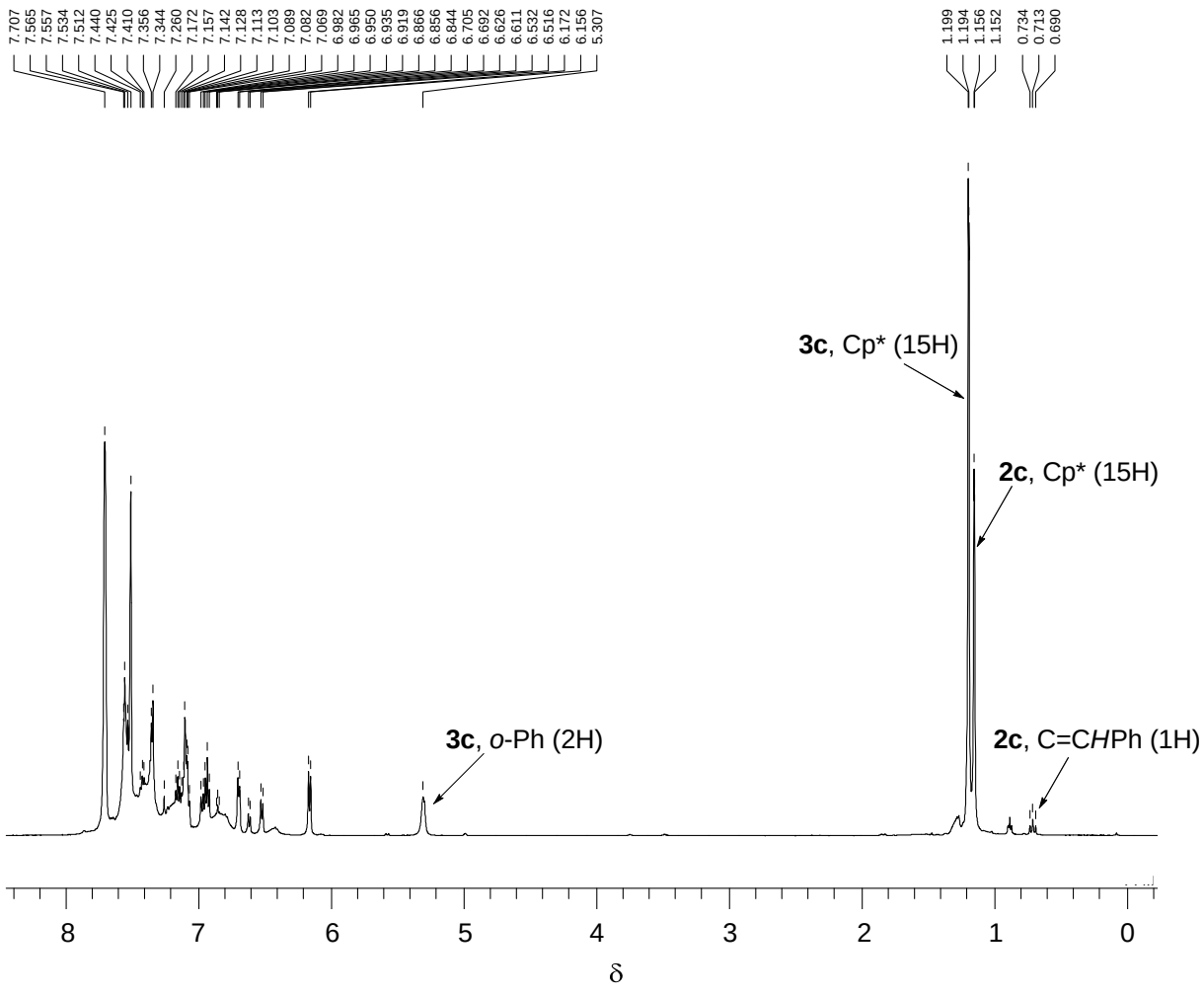

Figure S1. Full ^1H NMR spectrum of a mixture of **2c** and **3c** (**2c**:**3c** = 0.45:1)

Kinetic Experiment. A $C_2H_4Cl_2$ solution (1 mL) containing **1** (16.7 mg, 0.027 mmol) $NaBAr^F{}_4$ (28.0 mg, 0.030 mmol) and ca. 3 equiv of diphenylacetylene (15.0 mg, 0.084 mmol) was transferred to an NMR tube under an atomosphere of argon. The sample was kept at 25 ˚C, and the reaction was monitored by means of $^{31}P\{^1H\}$ NMR. Throughout the measurement, two distinct doublet signals were observed, which were assigned as complexes **2c** (δ 36.4) and **3c** (δ 33.2). The ratios of these copmlexes were determined on the basis of the relative intensities of the $^{31}P\{^1H\}$ NMR signals, and the apparent first-order rate constant for the isomerisation of **3c** ($k_H = 1.63 \times 10^{-4}$ s^{-1}) was obtained from the time-conversion plot (Figure S2). The k_D value ($k_D = 0.50 \times 10^{-4}$ s^{-1}, Figure S3) was obtained from a similar reaction using a $C_2H_4Cl_2$ solution (1 mL) containing **1**-d_5 (17.0 mg, 0.028 mmol), $NaBAr^F{}_4$ (28.5 mg, 0.031 mmol) and ca. 3 equiv of diphenylacetylene (15.0 mg, 0.084 mmol). The rate constant ratio k_H/k_D (25 ˚C) was determined to be 3.3. Primary KIE (k_H/k_D) values of 2.1–4.2 have been reported for Cp*Rh(III)-catalyzed *ortho* C–H activation of arenes.[5]

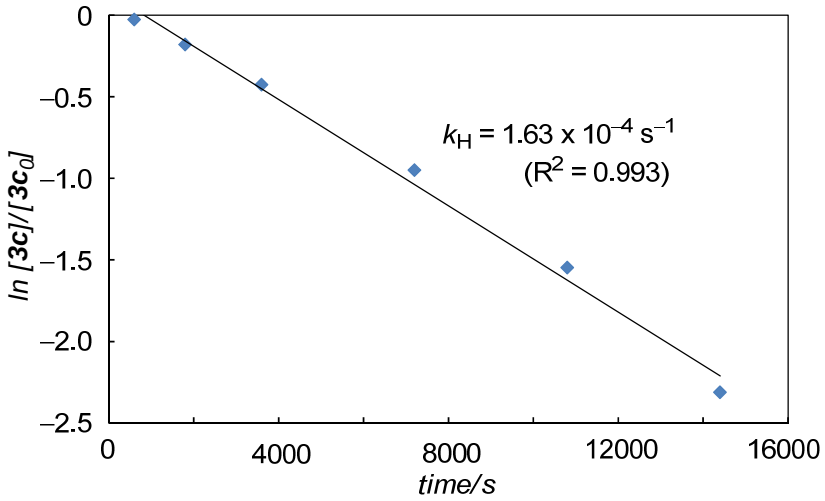

Figure S2. Plot of *ln [**3c**]/[**3c**$_0$]* versus time for the coversion of **3c** to **2c** at 25 ˚C.

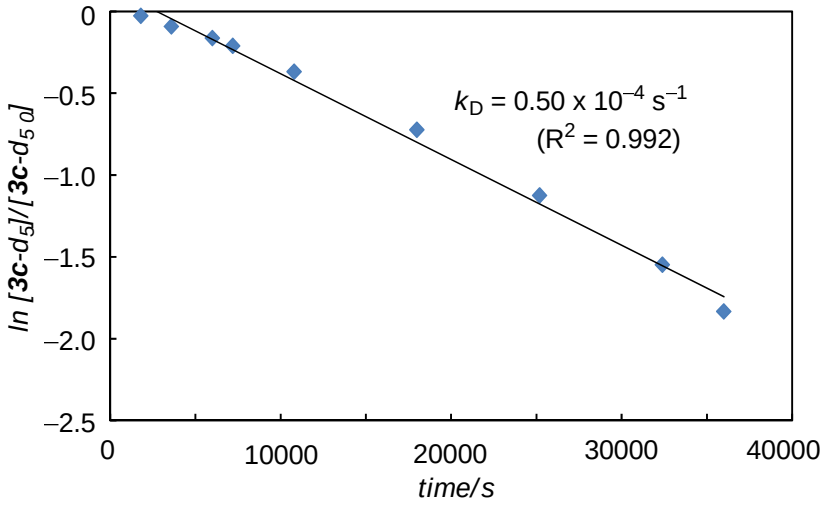

Figure S3. Plot of *ln [**3c**-d_5]/[**3c**-$d_{5\,0}$]* versus time for the coversion of **3c**-d_5 to **2c**-d_5 at 25 ˚C.

X-ray Diffraction Studies. Diffraction data for **2a**, **5a** and **6** were collected on a Rigaku Mercury CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at –150 °C. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (REQAB).[6] All calculations were performed using the *CrystalStructure*[7] crystallographic software package except for refinements, which were performed using SHELXL-97.[8] The positions of the non-hydrogen atoms were determined by direct methods (SIR-2008)[9] and subsequent Fourier syntheses (DIRDIF-99).[10] All non-hydrogen atoms were refined on F_o^2 anisotropically by full-matrix least-square techniques. All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Details of the X-ray diffraction study are summarized in Table S1.

This journal is © The Royal Society of Chemistry 2013

Table S1. X-ray Crystallographic Data for **2a**, **5a** and **6**.

	2a	**5a**	**6**
CCDC	957816	957817	957818
formula	$C_{75}H_{55}BF_{24}PRh$	$C_{60}H_{49}BF_{24}PRh$	$C_{82}H_{59}BF_{24}OPRh$
fw	1556.91	1370.7	1661.02
crystal dimension	0.43 × 0.32 × 0.30	0.35 × 0.35 × 0.20	0.42 × 0.22 × 0.17
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$(#14)	P-1 (#2)	$P2_1/n$(#14)
a, Å	14.906(3)	12.591(2)	13.909(3)
b, Å	25.081(5)	15.472(3)	17.236(4)
c, Å	18.215(3)	17.459(3)	31.046(7)
α, deg	90	65.085(5)	90
β, deg	92.956(2)	70.167(6)	91.043(3)
γ, deg	90	81.773(7)	90
V, Å^3	6801 (2)	2901.7(8)	7442 (3)
Z	4	2	4
ρ_{calcd}, g cm^{-3}	1.521	1.569	1.482
F(000)	3144	1380	3360
μ, cm^{-1}	3.839	4.378	3.571
transmission factors range	0.857 – 0.891	0.807 – 0.916	0.901 – 0.941
index range	$-19 \le h \le 16$	$-16 \le h \le 16$	$-17 \le h \le 18$
	$-25 \le k \le 32$	$-12 \le k \le 20$	$-22 \le k \le 14$
	$-21 \le l \le 23$	$-20 \le l \le 22$	$-39 \le l \le 40$
no. reflections total	52317	22533	56972
unique (R_{int})	15429 (0.0720)	12848 (0.0408)	17012 (0.0883)
$I > 2\sigma(I)$	10917	10542	10495
no. parameters	920	788	991
R1 ($I > 2\sigma(I)$)[a]	0.0694	0.0508	0.0883
wR2 (all data)[b]	0.1796	0.1287	0.2398
GOF [c]	1.028	1.101	1.025
max diff peak / hole, e Å^{-3}	1.48/−0.85	0.90/−0.80	1.26/−0.68

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP]$ (a and b are constants suggested by the refinement program; $P = [\max(F_o^2,0) + 2F_c^2]/3$). [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$.

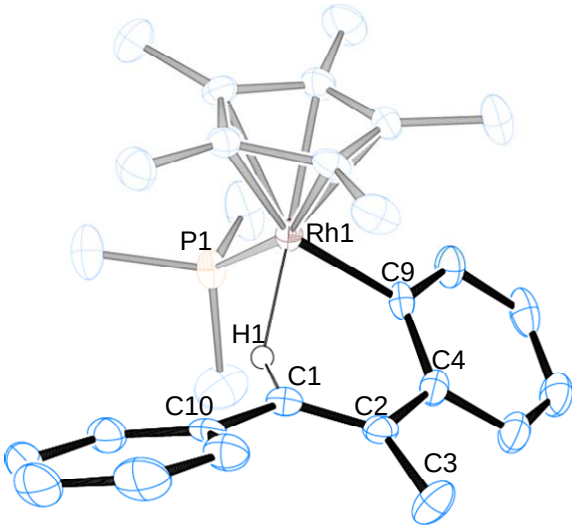

Figure S4. ORTEP drawing of **5a** (50% probability). Anionic part and hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–P1, 2.3030(10); Rh1–C1, 2.475(5); Rh1–C9, 2.033(3); Rh1–H1, 1.753; C1–C2, 1.357(4); C1–C2–C3, 122.7(3); C1–C2–C4, 118.4(3); C3–C2–C4, 118.9(3); C2–C1–C10, 130.5(4).

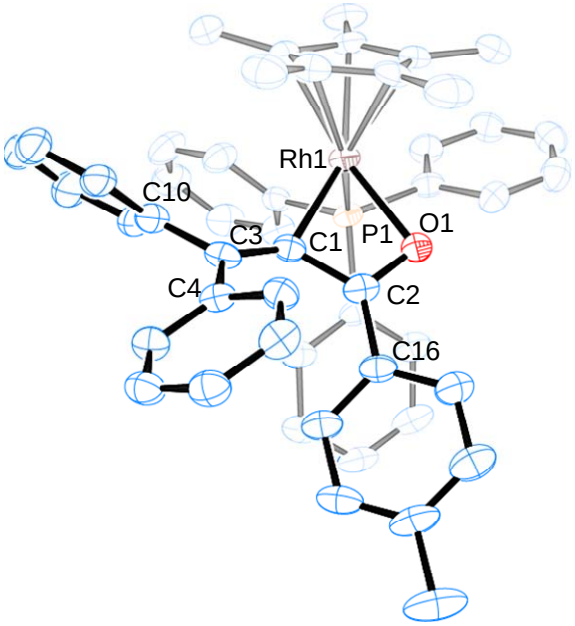

Figure S5. ORTEP drawing of **6** (50% probability). Anionic part and hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Rh1–O1, 2.141(4); Rh1–C1, 2.101(6); Rh1–P1, 2.3315(16); C1–C2, 1.449(8); C1–C3, 1.350(8); O1–C2, 1.285(7); O1–Rh1–C1, 64.32(18); Rh1–O1–C2, 93.6(3); Rh1–C1–C2, 90.6(4); Rh1–C1–C3, 134.3(4); C2–C1–C3, 130.0(6); O1–C2–C1, 111.2(5), O1–C2–C16, 117.8(5); C1–C2–C16, 130.8(6).

References

(1) (a) W. D. Jones and F. J. Feher, *Inorg. Chem*., 1984, **23**, 2376; (b) W. D. Jones and V. L. Kuykendall, *Inorg. Chem*., 1991, **30**, 2615.

(2) (a) D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem*., 2001, *40*, 3810; (b) D. L. Reger, C. A. Little, J. J. S. Lamba and K. J. Brown, *Inorg. Synth*., 2004, **34**, 5; (c) C. R. Smith, A. Zhang, D. J. Mans and T. V. BajanBabu, *Org. Synth*., 2008, **85**, 248.

(3) S. Roy, M. P. Davydova, R. Pal K. Gilmore, G. A. Tolstikov, S. F. Vasilevsky and I. V. Alabugin, *J. Org. Chem*., 2011, **76**, 7482.

(4) Y. Shi, S. A. Blum, *Organometallics*, 2011, **30**, 1776.

(5) (a) D. R. Stuart, P. Alsabeh, M. Kuhn and K. Fagnou, *J. Am. Chem. Soc*., 2010, **132**, 18326; (b) T.-J. Gong, B. Xiao, Z.-J. Liu, J. Wan, J. Xu, D.-F. Luo, Y. Fu and L. Liu, *Org. Lett*., 2011, **13**, 3235; (c) G. Song, X. Gong and X. Li, *J. Org. Chem*., 2011, **76**, 7583; (d) C. Feng and T.-P. Loh, *Chem. Commun*., 2011, **47**, 10458; (e) K.-H. Ng, Z. Zhou and W.-Y. Yu, *Org. Lett*., 2012, **14**, 272.

(6) R. A. Jacobson, *Private Communication to Rigaku Corp.; Rigaku Corp*.; Tokyo, Japan, 1998.

(7) *CrystalStructure 4.0:* Single Crystal Structure Analysis Package; Rigaku Corporation: Tokyo, Japan, 2000–2010.

(8) G. M. Sheldrick, *Acta Crystallogr., Sect A*, 2008, **64**, 112.

(9) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Crystallogr*., 2007, **40**, 609.

(10) P. T. Beurskens, G. Beurskens, R. de Gelder, S. García-Granda, R. O. Gould, R. Israël and J. M. M. Smits, *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.