SUPPORTING INFORMATION

Zn-Promoted C–H Reductive Elimination and H$_2$ Activation via a Dual Unsaturated Heterobimetallic Ru-Zn Intermediate

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**S-1 Experimental Procedures and Characterization**

**General Comments.** All manipulations were carried out at room temperature under argon using standard Schlenk, high vacuum and glovebox techniques using dry and degassed solvents. C₆D₆, C₆D₅CD₃ and THF-d₈ were vacuum transferred from potassium. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400 and 500 MHz NMR spectrometers and referenced as follows: C₆D₆ (¹H, δ 7.16; ¹³C, δ 128.0), THF-d₈ (¹H, δ 1.72; ¹³C, δ 25.3). ³¹P{¹H} spectra were referenced externally to 85% H₃PO₄ (δ 0.0). Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, U.K.

[Ru(PPh₃)₃HCl]∙toluene, MgMe₂ and Na[BAr₄] were prepared according to literature methods.¹⁻³ Prior to use, [Ru(PPh₃)₃HCl]∙toluene was dried under high vacuum and ground to a fine powder affording a material with ca. 0.8 molecules of toluene per Ru (¹H NMR).

[Ru(PPh₃)(C₆H₄PPh₂)₂H][Li(THF)₂] (1). To an agitated suspension of [Ru(PPh₃)₃HCl]∙toluene (500 mg, 0.50 mmol) in THF (6 mL) was added LiCH₂TMS (1.1 mL of 1.0 M pentane solution, 2.2 equiv). After 5 min, all of the starting material had dissolved to give an orange solution, which was treated with 100 mL of hexane. After 2 h, a colorless precipitate of LiCl was removed by filtration, and the yellow filtrate concentrated and treated with THF (3 mL) and hexane (12 mL). After 16 h, orange crystals of 1 were separated, washed with hexane (2 x 5 mL) and dried under vacuum. Yield: 424 mg (82%). N.B. On a few occasions, the precipitated LiCl had a yellow color due to partial co-precipitation with 1. In such cases, 1 was extracted from the solid with hexane/THF (1:1) or benzene. ¹H NMR (500 MHz, THF-d₈):

δ 7.43 (t, J = 8.2 Hz, 2H, Ar), 7.24 (t, J = 8.0 Hz, 2H, Ar), 7.20-7.04 (m, 10H, Ar), 7.03-6.89 (m, 11H, Ar), 6.88-6.68 (m, 13H, Ar), 6.65 (br t, J = 7.2 Hz, 1H, Ar), 6.54 (ddd, J = 9.6, 5.3, 3.5 Hz, 1H, Ar), 6.48 (br t, J = 4.2 Hz, 2H, Ar), 6.44 (br q, J = 3.8 Hz, 1H, Ar), 3.64-3.58 (m, 8H, THF), 1.81-1.72 (m, 8H, THF), -9.62 (ddd, ²JHP = 83.9, 22.8, 12.8 Hz, 1H, RuH). ³¹P{¹H} NMR (202 MHz, THF-d₈): δ 53.3 (dd, ²Jpp = 22, 17 Hz, PPh₃), -20.7 (dd, ²Jpp = 22, 17 Hz, C₆H₄PPh₂ (cis to
RuH)), -25.1 (t, \(^2J_{PP} = 17\) Hz, \(\text{C}_6\text{H}_4\text{PPh}_2\) (trans to RuH)). \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, THF-\(d_8\)): \(\delta\) 180.3 (dd, \(J_{CP} = 67, 8\) Hz, Ru-C\text{metalated}), 177.5 (dd, \(J_{CP} = 66, 11\) Hz, Ru-C\text{metalated}), 161.5 (d, \(J_{CP} = 38\) Hz, C\text{ipso}-P\text{metalated}), 157.7 (d, \(J_{CP} = 41\) Hz, C\text{ipso}-P\text{metalated}), 144.2 (d, \(J_{CP} = 25\) Hz, C\text{ipso}-PPh\(_3\)), 143.2 (d, \(J_{CP} = 18\) Hz), 142.4 (d, \(J_{CP} = 12\) Hz), 141.7 (d, \(J_{CP} = 11\) Hz), 140.1 (dd, \(J_{CP} = 25, 5\) Hz), 138.9 (d, \(J_{CP} = 18\) Hz), 135.3 (d, \(J_{CP} = 22\) Hz), 135.0-134.7 (m), 134.5 (d, \(J_{CP} = 13\) Hz), 134.1 (d, \(J_{CP} = 12\) Hz), 133.0 (d, \(J_{CP} = 12\) Hz), 129.5 (s), 129.0 (s), 128.2 (s), 128.0-127.6 (m), 127.5 (s), 127.3-127.1 (m), 127.0 (d, \(J_{CP} = 8\) Hz), 126.0 (d, \(J_{CP} = 4\) Hz), 123.9 (d, \(J_{CP} = 3\) Hz), 121.2 (d, \(J_{CP} = 6\) Hz), 119.4 (d, \(J_{CP} = 7\) Hz), 68.2 (s, THF), 26.4 (s, THF). \(^7\)Li NMR (156 MHz, THF-\(d_8\)): \(\delta\) 0.85 (s). \(^7\)Li NMR (156 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) 2.58 (d, \(J = 12.0\) Hz). Anal. Found: C, 71.45; H, 5.83. Calcd. for \(\text{C}_{62}\text{H}_{60}\text{LiO}_2\text{P}_3\text{Ru}\): C, 71.74; H, 5.83.

\([\text{Li(12-crown-4)}]_2[\text{Ru(PPh}_3\text{(C}_6\text{H}_4\text{PPh}_2\text{)}_2\text{H}}] (2)\). 12-crown-4 (51 µL, 0.32 mmol, 2.1 equiv) and 1 (156 mg, 0.15 mmol) were dissolved in \(\text{C}_6\text{H}_6\) (3.5 mL) and the solution stirred for 24 h to afford a yellow precipitate. This was isolated by filtration, washed with \(\text{C}_6\text{H}_6\) (1 mL) and hexane (3 mL) and dried under vacuum. Yield: 145 mg (74%; contains 0.75 molecule of \(\text{C}_6\text{H}_6\)). \(^1\)H NMR (400 MHz, THF-\(d_8\)): \(\delta\) 7.41-7.35 (m, 2H, Ar), 7.34-7.28 (m, 2H, Ar; overlaps with signal from \(\text{C}_6\text{H}_6\)), 7.19-7.11 (m, 6H, Ar), 7.11-6.88 (m, 14H, Ar), 6.87-6.74 (m, 8H, Ar), 6.72-6.59 (m, 6H, Ar), 6.53-6.40 (m, 3H, Ar), 3.56 (s, 32H, 12-crown-4), -8.43 (ddd, \(J_{HP} = 93.3, 23.1, 12.4\) Hz, 1H, RuH). \(^{31}\)P\{\(^1\)H\} NMR (162 MHz, THF-\(d_8\)): \(\delta\) 55.2 (dd, \(J_{PP} = 20, 15\) Hz, PPh\(_3\)), -19.4 (dd, \(J_{PP} = 20, 17\) Hz, \(\text{C}_6\text{H}_4\text{PPh}_2\) (cis to RuH)), -24.3 (t, \(J_{PP} = 15\) Hz, \(\text{C}_6\text{H}_4\text{PPh}_2\) (trans to RuH)). \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, THF-\(d_8\)): \(\delta\) 188.0 (dd, \(J_{CP} = 71, 9\) Hz, Ru-C\text{metalated}), 186.7 (dd, \(J_{CP} = 72, 8\) Hz, Ru-C\text{metalated}), 159.8 (d, \(J_{CP} = 38\) Hz, C\text{ipso}-P\text{metalated}), 156.5 (dd, \(J_{CP} = 39\) Hz, 4 Hz, C\text{ipso}-P\text{metalated}), 146.0 (d, \(J_{CP} = 21\) Hz, C\text{ipso}-PPh\(_3\)), 145.0 (d, \(J_{CP} = 13\) Hz), 144.8 (d, \(J_{CP} = 7\) Hz), 143.4 (d, \(J_{CP} = 7\) Hz), 141.2-140.9 (m), 136.5 (d, \(J_{CP} = 23\) Hz), 135.1-134.9 (m), 134.5 (d, \(J_{CP} = 13\) Hz), 134.2 (d, \(J_{CP} = 13\) Hz), 133.1 (d, \(J_{CP} = 12\) Hz), 127.7-127.3 (m), 126.9-126.7 (m), 126.7-126.5 (m), 126.4 (s), 124.6 (d, \(J_{CP} = 5\) Hz), 122.3 (d, \(J_{CP} = 5\) Hz), 118.7 (d, \(J_{CP} = 6\) Hz), 117.8 (d, \(J_{CP} = 7\) Hz), 69.9 (s, 12-crown-4). \(^7\)Li NMR (156 MHz,
[Ru(PPh₃)(C₆H₄PPh₂)₂H][MgMe(THF)₂] (3). MeMgCl (37 µL of 3.0 M in THF, 0.11 mmol, 1.1 equiv) was added to a stirred C₆H₆ (1.5 mL) solution of 1 (104 mg, 0.10 mmol). The reaction mixture was then left to settle for 2 h and the precipitate of LiCl separated by filtration through the pad of Celite®. The yellow filtrate was treated with 6 mL of hexane affording a yellow crystalline solid over 72 h. The solid was collected and dried under vacuum. Yield: 87 mg (ca. 80% (product contains 6% of 1 and 1 molecule of THF per Mg, n=1)). A portion of this material (50 mg) was further purified by recrystallization from THF/hexane, yielding a product (35 mg) containing two molecules of THF per Mg. Alternatively, 3 could be obtained in ca. 85% NMR yield by reaction of [Ru(PPh₃)₃HCl]-toluene (20 mg, 0.02 mmol) with MgMe₂ (10 mg, 9.2 equiv.) in THF-d₆ (0.5 mL). ¹H NMR (500 MHz, C₆D₆): δ 7.70 (br m, 1H, Ar), 7.55 (br m, 2H, Ar), 7.45-7.35 (m, 7H, Ar), 7.41 (t, J = 8.5 Hz, 2H, Ar), 7.03-6.80 (m, 18H, Ar), 6.74-6.63 (m, 4H, Ar), 6.58 (t, J = 7.5 Hz, 1H, Ar), 2.89 (br m, 8H, THF), 0.92 (br m, 8H, THF), -0.74 (s, 3H, MgMe), -10.11 (ddd, J_HP = 65.8, 23.8, 12.4 Hz, 1H, RuH). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 51.4 (t, J_PP = 21 Hz, PPh₃), -21.6 (t, J_PP = 20 Hz, C₆H₄PPh₂ (cis to RuH)), -27.9 (t, J_PP = 20 Hz, C₆H₄PPh₂ (trans to RuH)). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 167.0 (dd, J_CP = 61, 10 Hz, Ru-C_metalated), 163.6 (d, J_CP = 40 Hz, Cipso-P_metalated), 163.1 (dd, J_CP = 59, 11 Hz, Ru-C_metalated), 155.4 (d, J_CP = 43 Hz, Cipso-P_metalated), 144.3 (dd, J_CP = 22, 4 Hz), 141.6-141.1 (m), 140.0 (d, J_CP = 21 Hz), 138.9 (d, J_CP = 19 Hz), 137.5 (d, J_CP = 20 Hz), 136.4 (d, J_CP = 26 Hz), 134.5 (d, J_CP = 14 Hz), 134.3 (d, J_CP = 11 Hz), 134.0 (d, J_CP = 9 Hz), 133.5-133.3 (m), 131.2 (s), 129.3 (s), 128.6 (s), 128.5 (s), 128.4-127.6 (m, overlaps with signal from C₆D₆), 127.6 (d, J_CP = 9 Hz), 127.4 (d, J_CP = 8 Hz), 127.2-126.9 (m), 125.5 (s), 124.2 (d, J_CP = 6 Hz), 121.5 (d, J_CP = 7 Hz), 67.6 (s, THF), 24.9 (s, THF), -12.7 (s, MgMe). Selected ¹H NMR (500 MHz, THF-d₆): δ -1.77 (s, 3H, MgMe), -10.88 (ddd, J =
68.0, 21.0, 11.8 Hz, 1H, RuH). $^{31}$P {$^1$H} NMR (202 MHz, THF-$d_8$): $\delta$ 45.8 (t, $^2J_{PP} = 21$ Hz, PPh$_3$), -25.5 (t, $^2J_{PP} = 21$ Hz, C$_6$H$_4$PPh$_2$ (cis to RuH)), -31.5 (t, $^2J_{PP} = 19.0$ Hz, C$_6$H$_4$PPh$_2$ (trans to RuH)). Anal. Found: C, 70.46; H, 5.94. Calcd. for C$_{63}$H$_{63}$MgO$_2$P$_3$Ru: C, 70.69; H, 5.93.

$[^{[Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe))] (4)}$. ZnMe$_2$ (0.5 mL of 1.2 M toluene solution, 4 equiv) was added to an agitated suspension of $[^{[Ru(PPh$_3$)$_3$HCl)]}$-toluene (150 mg, 0.15 mmol) in THF (2 mL). After 5 min, all of the starting material had dissolved to yield a red solution, to which 1 (156 mg, 0.15 mmol, 1 equiv) was added. The mixture was stirred for an additional 5 min and then treated with 6 mL of hexane and left to settle for 1 h. The resulting yellow precipitate was separated by filtration through the pad of Celite® and washed with benzene (2 mL). The filtrate and benzene washings were combined, treated with hexane (10 mL) and left to crystallize first at room temperature (24 h), and then at -20 °C (24 h). Yellow blocks of 4 were separated and washed with hexane (2 x 2 mL). Yield: 225 mg (78%). An alternative synthesis uses 1 pre-generated in-situ. A mixture of $[^{[Ru(PPh$_3$)$_3$HCl)]}$-toluene (150 mg, 0.15 mmol) and LiCH$_2$TMS (28 mg, 0.30 mmol) was treated with THF (2 mL) and agitated for 5 min. The resulting orange solution was treated with ZnMe$_2$ (0.3 mL of 2.0 M toluene solution, 4 equiv) and then with a second portion of $[^{[Ru(PPh$_3$)$_3$HCl)]}$-toluene (150 mg, 0.15 mmol). The mixture was stirred for an additional 5 min, yielding a red solution. Isolation and crystallization of 4 was then carried out as described above to yield yellow crystalline blocks. Yield: 221 mg (76%).

Recrystallization from THF/hexane (1:1, 6 mL) gave 4·THF, which contained 2 molecules of THF per Zn, one coordinated to Zn and one as a co-crystallite. Upon standing, the solid loses THF, such that after 2 months, only 0.5 molecules of THF remained coordinated. In solution, 4 exists as a mixture of fac-4, mer-4 and 5, in a ratio of 50:2:1 in THF-$d_8$ and 75:3:2 in C$_6$D$_6$, respectively. The Zn-bound THF molecule in 4·THF readily dissociated upon dissolution in other solvents (e.g. C$_6$D$_6$) as evident from the very similar proton chemical shifts of THF in (i) C$_6$D$_6$ solutions of 4 and (ii) free THF in C$_6$D$_6$ (4: $\delta^1$H 3.58, 1.42; free THF: $\delta^1$H 3.57, 1.40; c.f.
In THF solutions of 4, some level of THF coordination to Zn was apparent, but does not affect significantly the NMR properties of the compound (values of $^2J_{HP}$, $^2J_{PP}$ etc.).

fac-4. $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 7.46 (t, $J = 8.3$ Hz, 2H, Ar), 7.33 (td, $J = 7.3$, 1.5 Hz, 1H, Ar), 7.31-7.21 (m, 4H, Ar), 7.20-7.10 (m, 4H, Ar), 7.09-6.84 (m, 26H, Ar), 6.75 (td, $J = 7.8$, 1.9 Hz, 2H, Ar), 6.68-6.60 (m, 2H, Ar), 6.55 (br m, 1H, Ar), 6.49 (tt, $J = 7.0$, 1.8 Hz, 1H, Ar), 3.61 (m, 4H, THF), 1.77 (m, 4H, THF), -0.68 (s, 3H, ZnMe), -8.69 (ddd, $^2J_{HP} = 51.1$, 20.9, 12.2 Hz, 1H, RuH). Selected $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ -0.10 (s, 3H, ZnMe) -8.25 (ddd, $^2J_{HP} = 51.3$, 20.8, 12.2 Hz, 1H, RuH). $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$): $\delta$ 46.5 (t, $^2J_{PP} = 23$ Hz, PPh$_3$), -26.0 (dd, $^2J_{PP} = 23$, 19 Hz C$_6$H$_4$PPh$_2$ (cis to RuH)), -30.5 (dd, $^2J_{PP} = 23$, 19 Hz, C$_6$H$_4$PPh$_2$ (trans to RuH)). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ 46.3 (t, $^2J_{PP} = 23$ Hz, PPh$_3$), -26.0 (dd, $^2J_{PP} = 23$, 19 Hz C$_6$H$_4$PPh$_2$), -30.4 (dd, $^2J_{PP} = 23$, 19 Hz, C$_6$H$_4$PPh$_2$). $^{13}$C{$^1$H} NMR (126 MHz, THF-$d_8$): $\delta$ 164.1 (dt, $J_{CP} = 59$, 9 Hz, Ru-Cmetalated), 161.8 (dt, $J_{CP} = 41$, 2 Hz, C$_{ipso}$-Pmetalated), 155.6 (dd, $J_{CP} = 46$, 4 Hz, C$_{ipso}$-Pmetalated), 152.9 (dd, $J_{CP} = 52$, 13 Hz, Ru-Cmetalated), 143.5 (dq, $J_{CP} = 20$, 3 Hz), 142.6 (dd, $J_{CP} = 21$, 6 Hz), 141.5 (d, $J_{CP} = 26$ Hz), 141.1 (dd, $J_{CP} = 32$, 2 Hz, C$_{ipso}$-PPh$_3$), 138.3 (d, $J_{CP} = 22$ Hz), 137.8 (d, $J_{CP} = 19$ Hz), 135.4-134.9 (m), 134.6 (d, $J_{CP} = 11$ Hz), 134.1 (d, $J_{CP} = 9$ Hz), 133.1 (d, $J_{CP} = 11$ Hz), 132.8 (d, $J_{CP} = 12$ Hz), 130.3 (t, $J_{CP} = 3$ Hz), 130.0 (t, $J_{CP} = 4.0$ Hz), 129.9 (s), 129.1 (s), 128.9-128.8 (m), 128.7 (d, $J_{CP} = 2$ Hz), 128.6 (d, $J_{CP} = 9$ Hz), 128.5-128.3 (m), 128.3 (d, $J_{CP} = 2$ Hz), 127.9 (d, $J_{CP} = 9$ Hz), 127.7 (d, $J_{CP} = 9$ Hz), 126.3 (d, $J_{CP} = 4$ Hz).
mer-4. Selected ¹H (500 MHz, THF-d₈): δ 8.08 (ddd, J = 10.0, 6.5, 3.0 Hz, 2H, Ar), 7.71 (m, 2H, Ar), 5.95 (m, 2H, Ar), -1.42 (s, 3H, ZnMe), -6.20 (ddd, ²JHP = 16.0, 11.1, 5.1 Hz, 1H, RuH).

³¹P{¹H} NMR (202 MHz, THF-d₈): δ 54.8 (dd, ²JPP = 272, 25 Hz, PPh₃), -20.4 (br d, ²JPP = 272 Hz, C₆H₄PPh₂), -25.3 (t, ²JPP = 25 Hz, C₆H₄PPh₂).

5. Selected ¹H NMR (500 MHz, THF-d₈): δ 0.47 (s, 3H, ZnMe).

³¹P{¹H} NMR (202 MHz, THF-d₈): δ 57.5 (dd, ²JPP = 234, 13 Hz, PPh₃), 52.7 (dd, ²JPP = 22, 14 Hz, PPh₃), -34.5 (dd, ²JPP = 234, 23 Hz, C₆H₄PPh₂).

4·THF: Anal. Found: C, 67.89; H, 6.00. Calcd. for C₆₃H₆₃ZnO₂P₃Ru: C, 68.07; H, 5.71.

The reaction of [Ru(PPh₃)₃HCl]·toluene (15 mg, 0.015 mmol) and ZnMe₂ (63 µL of 1.2 M toluene solution, 5 equiv.) in THF-d₈ (0.6 mL) followed by crystallization from THF/hexane gave 4·THF co-crystallized with the ZnCl derivative, [Ru(PPh₃)(C₆H₄PPh₂)₂H(ZnCl(THF))]·THF (Figure S1). Dissolution of the crystalline material yielded two sets of signals for 4 and 4·Cl (5:3 ratio) in both the ¹H and ³¹P NMR spectra. No evidence for 4·Cl was apparent in initial reaction mixtures when ZnMe₂ was present in excess. Evaporation of solvent, together with excess ZnMe₂, and redissolution of the residue in THF-d₈ revealed (¹H NMR) small quantities of 4·Cl (4:4·Cl = 17:1). fac-4·Cl. Selected ¹H NMR (400 MHz, THF-d₈): δ -9.02 (ddd, ²JHP = 46.3, 22.1, 10.8 Hz, 1H). ³¹P{¹H} NMR (162 MHz, THF-d₈): δ 50.4 (dd, ²JPP = 23, 19 Hz, PPh₃), -24.0 (t, ²JPP = 19 Hz C₆H₄PPh₂), -30.5 (m, overlaps with signal from fac-4).
**Figure S1.** Molecular structure of 4-THF/4-Cl-THF. (a) Major disorder component (4-THF, 65% occupancy). (b) Minor disorder component (4-Cl-THF, 35% occupancy). Ellipsoids are represented at 30% probability. Solvent and hydrogen atoms, with the exception of H1, have been omitted for clarity.

**Reaction of 4 with LiCH₂TMS.** A J. Young’s resealable NMR tube was charged with a THF-d₈ (0.5 mL) solution of 4-THF (10.4 mg, 0.01 mmol) and LiCH₂TMS (15 µL of 1.0 M
pentane solution, 1.5 equiv) and the tube quickly shaken. This led to loss of the red color of 4 and appearance of a yellow color. $^1$H and $^{31}$P{$^1$H} NMR spectra showed complete conversion of 4 to 1.

$\text{[Ru(PPh}_3\text{)}_2(\text{C}_6\text{H}_4\text{PPPh}_2)(\text{ZnMe})_2]\text{[BAr}_\text{F}_4\text{]}$ (6). $\text{ZnMe}_2$ (1.0 mL of 1.2 M toluene solution, 4 equiv) was added to an agitated suspension of $\text{[Ru(PPh}_3\text{)}_3\text{HCl]}\cdot\text{toluene}$ (300 mg, 0.30 mmol) in $\text{C}_6\text{H}_5\text{F}$ (6 mL). After 10 min, all of the starting material had dissolved to give a red solution, which was treated with $\text{Na[BAr}_\text{F}_4\text{]}$ (266 mg, 0.30 mmol, 1 equiv). After 10 min, stirring was ceased and the resulting dark red-orange suspension left to settle for 3 h. A precipitate of NaCl was removed by filtration through the pad of Celite®. The reaction vessel was rinsed with $\text{C}_6\text{H}_5\text{F}$ (1 mL), which was then filtered through the same Celite® pad. The combined filtrates were treated with 10 mL hexane to give a dark red oil, which, after 72 h, crystallized to produce dark-red crystals of 6. These were collected, washed with hexane (3 mL x 2) and dried under vacuum. Yield: 475 mg (83%). 6 could be recrystallized from hot toluene. $^1$H NMR (500 MHz, $\text{C}_6\text{D}_6$): $\delta$ 8.45 (s, 8H, BAr$^2_\text{F}_4$), 7.67 (s, 4H, BAr$^2_\text{F}_4$), 7.29 (d, $J = 6.9$ Hz, 1H, Ar), 7.10 (t, $J = 7.2$ Hz, 1H, Ar), 7.06-6.77 (m, 32H, Ar), 6.75-6.67 (m, 8H, Ar), 6.58 (dd, $J = 11.8$, 7.8 Hz, 2H, Ar), 0.35 (s, 3H, ZnMe), -1.09 (s, 3H, ZnMe). $^{31}$P{$^1$H} NMR (202 MHz, $\text{C}_6\text{D}_6$): $\delta$ 42.6 (dd, $^2J_{PP} = 211$, 20 Hz, PPh$_3$), 39.2 (dd, $^2J_{PP} = 27$, 20 Hz, PPh$_3$), -19.7 (dd, $^2J_{PP} = 211$, 27 Hz, $\text{C}_6\text{H}_4\text{PPPh}_2$). $^{13}$C{$^1$H} NMR (126 MHz, $\text{C}_6\text{D}_6$): $\delta$ 162.9 (1:1:1:1 q, $^1J_{CB} = 50$ Hz, BAr$^2_\text{F}_4$), 153.0 (dd, $J_{CP} = 44$, 1 Hz, C$_\text{ipso}$-P$_\text{metalated}$), 151.6 (dt, $J_{CP} = 34$, 7 Hz, Ru-C$_\text{metalated}$), 144.6 (dd, $J_{CP} = 17$, 4 Hz), 135.9-135.4 (m), 135.7 ((overlapped with singlet at 135.5), d, $J_{CP} = 38$ Hz BAr$^2_\text{F}_4$), 134.1 (d, $J_{CP} = 11$ Hz), 133.4-133.2 (m), 132.4 (d, $J_{CP} = 11$ Hz), 132.1 (d, $J_{CP} = 44$ Hz), 132.1 (d, $J_{CP} = 2$ Hz), 131.1 (d, $J_{CP} = 2$ Hz), 130.9 (s), 130.7-130.5 (m), 130.4-129.5 (m), 130.0 (overlapped with signals at 130.1 (dd, $J_{CP} = 36$, 2 Hz) and 129.8 (d, $J_{CP} = 11$ Hz), qq, $J_{CF} = 32$, 3 Hz, BAr$^2_\text{F}_4$), 129.2 (d, $J_{CP} = 9$ Hz), 129.0-128.8 (m), 128.9 ((overlapped with doublet at 128.8 ($J_{CP} = 10$ Hz)), d, $J_{CP} = 10$ Hz), 128.7 (s), 125.3 (q, $^1J_{CF} = 273$ Hz, BAr$^2_\text{F}_4$), 118.1 (sept, $^3J_{CF} = 4$ Hz, BAr$^2_\text{F}_4$), 3.4 (s, ZnMe), -
Dissolution of 6 (10 mg) in THF-d₈ (0.5 mL) resulted in disappearance of the starting material and the formation of a light red colored solution containing fac-4 as the major species (ca. 85% by ¹H NMR spectroscopy).

Reaction of 1 with H₂. A J. Young’s resealable NMR tube was charged with a THF-d₈ (0.5 mL) solution of 1 (10.4 mg, 0.01 mmol) and placed under 1 atm of H₂. ¹H and ³¹P{¹H} NMR spectra showed no room temperature reaction. The solution was heated at 333 K (manual shaking of the NMR tube (ca. 2-3 sec) was performed every 10 min to ensure H₂ diffusion) and progress of the reaction monitored by NMR spectroscopy (Table S1). The reaction reached 50% conversion of 1 after ca. 3.5 h. In the first instance, the reaction produced [Ru(PPh₃)₂(C₆H₄PPh₂)H₂][Li(THF)₆] (7-Li), which converted to fac-[Ru(PPh₃)₃H₃][Li(THF)₃] (8-Li). After 24 h at 333 K, complete conversion to 8-Li was observed. The formation of small quantities of [Ru(PPh₃)₃(H₂)H₂] in the course of the reaction was attributed to hydrolysis by trace amounts of H₂O present or introduced during H₂ addition. Complex 7-Li was identified by the similarity of the NMR data to those reported for the potassium salt of [Ru(PPh₃)₂(C₆H₄PPh₂)H₂]⁻, specifically the presence of three triplets in the ³¹P{¹H} NMR spectrum (δ³¹P{¹H} 60.5, 53.9, -20.1; 2J⁰P= 16-18 Hz) and two multiplets in the hydride region (δ¹H -8.07 and -11.84) of the proton NMR spectrum (in a similar reaction of 2 with H₂, the hydride signals for 7-Li resolved into dddd and dtdd respectively (vide infra)). The previously reported 8-Li exhibited a singlet in the ³¹P{¹H} NMR spectrum (δ 58.8) and a multiplet in the low frequency region of the ¹H NMR spectrum, with a characteristic [AX]₃ pattern.
[Ru(PPh₃)₂(C₆H₄PPh₂)H₂][Li(THF)₃] (7-Li). Selected ¹H NMR (400 MHz, THF-d₈, 333 K): δ -8.07 (br m, ²J_HP = 76, 19 Hz, 1H, RuH), -11.84 (br m, ²J_HP = 77, 15 Hz, 1H, RuH). ³¹P {¹H} NMR (162 MHz, THF-d₈, 333 K): δ 60.5 (t, ²J_PP = 18 Hz, PPh₃), 53.9 (t, ²J_PP = 17 Hz, PPh₃), -20.1 (t, ²J_PP = 16 Hz, C₆H₄PPh₂) (c.f. [Ru(PPh₃)₂(C₆H₄PPh₂)H₂]K: Selected ¹H NMR (100 MHz, THF): δ -7.0 (ddddd, ²J_HP = 81.1, 26.5, 20.6, ²J_HH = 6.2 Hz, RuH), -11.0 (dtd, ²J_HP = 80.6, 18.6, ²J_HH = 6.2 Hz, RuH). ³¹P {¹H} NMR (81 MHz, THF): δ 62.9 (t, ²J_PP = 16 Hz), 55.0 (t, ²J_PP = 16 Hz), -18.3 (t, ²J_PP = 16 Hz)).

[Ru(PPh₃)₃H₃][Li(THF)₃] (8-Li). Selected ¹H NMR (400 MHz, THF-d₈, 333 K): δ -10.79 (br [AX]₃ pattern, 3H). ³¹P {¹H} NMR (162 MHz, THF-d₈, 333 K): δ 58.8 (s). Literature: ¹H NMR (200 MHz, THF-d₈): δ -10.58 (br m). ³¹P {¹H} NMR (81 MHz, THF-d₈): δ 59.0 (s).
Table S1. Reaction of 1 with H₂

| Time (min) | T (K) | 1, mol%\[^{[a]}\] | 7-Li, mol%\[^{[a]}\] | 8-Li, mol%\[^{[a]}\] | [Ru(PPh₃)₃(H₂)H₂]\[^{[b]}\], mol% |
|-----------|-------|----------------|----------------|----------------|-----------------------------------|
| 0         | 298   | 99             | 1              | 1              |                                   |
| 10        | 333   | 99             | 1              | 1              |                                   |
| 30        | 333   | 90             | 6              | 2              |                                   |
| 70        | 333   | 80             | 14             | 4              |                                   |
| 110       | 333   | 70             | 21             | 6              |                                   |
| 150       | 333   | 61             | 27             | 9              |                                   |
| 170       | 333   | 57             | 29             | 11             |                                   |
| 210       | 333   | 50             | 33             | 14             |                                   |

\[^{[a]}\] Determined by manual integration of signals in hydride region of ¹H NMR spectrum. \[^{[b]}\] [Ru(PPh₃)₃(H₂)H₂]: ¹H NMR (THF-\(d₈\), 333 K): \(\delta\) -7.47 (s, 4H, RuH); \(^{31}\)P\(^{[1]}\)H NMR: \(\delta\) 57.7 (s) (c.f. Literature data: ¹H NMR (THF): \(\delta\) -7.17 (s); \(^{31}\)P\(^{[1]}\)H NMR: \(\delta\) 57.8 (s)). \[^{[c]}\] Signals with relative intensity less than 3% were not integrated.

Figure S2. Hydride region of ¹H NMR spectrum (400 MHz, THF-\(d₈\), 333 K) of the reaction of 1 with H₂ (after 170 min at 333 K).
Reaction of 2 with H₂. A J. Young’s resealable NMR tube was charged with a THF-\(d_8\) (0.5 mL) solution of 2 (13.1 mg, 0.01 mmol) and placed under 1 atm of H₂. Initial \(^1\)H and \(^{31}\)P\{\(^1\)H\} NMR spectra were recorded at room temperature, and the reaction then monitored at 333 K. Every 10 min, the NMR tube was manually shaken for 2-3 sec to ensure H₂ diffusion. The reaction reached 50% conversion of 2 after ca. 1.5 h. Table S2 summarizes the composition of the reaction mixture.

The reaction products have \(^{31}\)P\{\(^1\)H\} and \(^1\)H NMR chemical shift and coupling patterns consistent with [Ru(PPh₃)₂(C₆H₄PPh₂)H₂][Li(THF)ₙ] (7-Li), and [Ru(PPh₃)₃H₃][Li(THF)₃] (8-Li) from the reaction between 1 with H₂ (see above), although the signals from 7-Li were now better resolved. At the same time, the signals from 2 remain different (both in chemical shift and with a larger \(^2\)J\(_{HP}\) coupling constant) to those from 1 over the course of the reaction, suggesting that the crown-ether coordinates to the Li-center in starting complex 2, but not in the products 7-Li and 8-Li. After 24 h at 333 K, complete conversion through to 8-Li was observed. The

Figure S3. \(^{31}\)P\{\(^1\)H\} NMR spectrum (162 MHz, THF-\(d_8\), 333 K) of the reaction of 1 with H₂ (after 170 min at 333 K).
formation of small quantities of [Ru(PPh₃)₃(H₂)H₂] in the course of the reaction was again attributed to hydrolysis by traces of H₂O.⁴

fac-[Ru(PPh₃)₂(C₆H₄PPh₂)H₂][Li(THF)₉] (7-Li). Selected ¹H NMR (400 MHz, THF-δ, 333 K): δ -8.06 (ddddd, ²J_HP = 78, 27, 19 Hz, ²J_HH = 8 Hz, 1H, RuH), -11.83 (dtd, ²J_HP = 75, 17 Hz, ²J_HH = 8 Hz, 1H, RuH).
Table S2. Reaction of 2 with H₂

| Time (min) | T (K) | 1, mol%[a] | 7-Li, mol%[a] | 8-Li, mol%[a] | [Ru(PPh₃)₃(H₂)H₂][b], mol% |
|-----------|------|-----------|-------------|-------------|-----------------|
| 0         | 298  | 99        | 1           | 1           | 1               |
| 10        | 333  | 96        | 4           | 1           | 1               |
| 20        | 333  | 89        | 9           | 1           | 2               |
| 30        | 333  | 82        | 15          | 1           | 2               |
| 40        | 333  | 76        | 20          | 2           | 2               |
| 50        | 333  | 70        | 25          | 2           | 2               |
| 60        | 333  | 65        | 30          | 3           | 2               |
| 70        | 333  | 60        | 34          | 3           | 3               |
| 80        | 333  | 56        | 36          | 4           | 4               |
| 90        | 333  | 51        | 40          | 5           | 4               |
| 100       | 333  | 48        | 43          | 5           | 4               |

[a] Determined by manual integration of signals in hydride region of ¹H NMR spectrum. [b] [Ru(PPh₃)₃(H₂)H₂]: ¹H NMR (THF-d₈, 333 K): δ -7.47 (s, 4H, RuH); ³¹P{¹H} NMR: δ 57.7 (s) (c.f. Literature data: ¹H NMR (THF): δ -7.17 (s); ³¹P{¹H} NMR: δ 57.8 (s))⁴. [c] Signals with relative intensity less than 3% were not integrated.

Figure S4. Hydride region of the ¹H NMR spectrum (400 MHz, THF-d₈, 333 K) of the reaction of 2 with H₂ (after 60 min at 333 K).
Reaction of 3 with H$_2$. A J. Young’s resealable NMR tube was charged with a THF-$_d_8$ (0.5 mL) solution of 3 (10.4 mg, 0.01 mmol) and placed under 1 atm of H$_2$ at room temperature. As in the reaction of 2, initial $^1$H and $^{31}$P{$_1^1$H} NMR spectra were recorded at room temperature, and the reaction then monitored at 333 K. Every 10 min, the NMR tube was manually shaken for 2-3 sec to ensure H$_2$ diffusion. Table S3 summarizes the composition of the reaction mixture.

Overall, the reaction was found to be less selective than for 1 or 2. The major product was assigned as [Ru(PPh$_3$)$_3$H$_3$][MgMe(THF)$_n$] (8-Mg), based on the presence of a singlet in the $^{31}$P{$_1^1$H} NMR spectrum at δ 54.6 and an $[AX]_3$ signal in the hydride region of the proton NMR spectrum, characteristic of fac-[Ru(PPh$_3$)$_3$H$_3$];$^6$ and similar to the signal for 8-Li. Two other species present at ca. 20-70% conversion of 3 exhibited signals in the $^{31}$P{$_1^1$H} and $^1$H NMR spectra suggestive of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][MgX(THF)$_n$] (3a) and [Ru(PPh$_3$)$_3$H$_3$][MgX(THF)$_n$] (8-Mg$'$. The lack of Mg-Me signals in the $^1$H NMR spectrum, leads us to tentatively assign X as OH or OR, arise from trace amounts of H$_2$O present in the reaction media. The ca. 1:1 ratio of 3a and 8-Mg$'$ also points to the possibility of a dimeric species, such as [{Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H}(THF)$_n$MgOMg(THF)$_n$][Ru(PPh$_3$)$_3$H$_3$}] (3a-O-8-
Additional signals (present in < 5 mol %) were seen by \textsuperscript{1}H-\textsuperscript{31}P\{\textsuperscript{1}H\} HMQC and are attributed to [Ru(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}PPh\textsubscript{2})H\textsubscript{2}][MgMe(THF)\textsubscript{n}] (7-Mg). The reaction reached 50% conversion of 3 and 3a after \textit{ca.} 1 h. After 40 h at 323 K, complete conversion of 3 and 3a was observed, with 8-Mg present as the major product.

[Ru(PPh\textsubscript{3})\textsubscript{3}]MgMe(THF)\textsubscript{n} (8-Mg). Selected \textsuperscript{1}H NMR (400 MHz, THF-\textit{d}_8): \(\delta\) -1.59 (s, 3H, MgMe), -11.39 ([\textit{AX}]\textsubscript{3} pattern, RuH\textsubscript{3}). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, THF-\textit{d}_8): \(\delta\) 54.6 (s).

[Ru(PPh\textsubscript{3})\textsubscript{3}]MgX(THF)\textsubscript{n} (8-Mg'). Selected \textsuperscript{1}H NMR (400 MHz, THF-\textit{d}_8): \(\delta\) -11.65 ([\textit{AX}]\textsubscript{3} pattern, RuH\textsubscript{3}). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, THF-\textit{d}_8): \(\delta\) 54.1 (s).

[Ru(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}PPh\textsubscript{2})\textsubscript{2}H][MgX(THF)\textsubscript{n}] (3a). Selected \textsuperscript{1}H NMR (400 MHz, THF-\textit{d}_8): \(\delta\) -9.68 (ddd, \(2J_{HP} = 66.5, 19.8, 12.1\) Hz, 1H, RuH). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, THF-\textit{d}_8): \(\delta\) 46.9 (dd, \(2J_{pp} = 27, 19\) Hz), -22.2 (dd, \(2J_{pp} = 27, 19\) Hz), -29.4 (t, \(2J_{pp} = 19\) Hz).

[Ru(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}PPh\textsubscript{2})H\textsubscript{2}][MgMe(THF)\textsubscript{n}] (7-Mg). Selected \textsuperscript{1}H NMR (400 MHz, THF-\textit{d}_8): \(\delta\) -9.11 (m, 1H, RuH), -12.44 (m, 1H, RuH). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, THF-\textit{d}_8): \(\delta\) 56.9 (t, \(2J_{pp} = 20\) Hz), 50.0 (t, \(2J_{pp} = 20\) Hz), -28.4 (t, \(2J_{pp} = 21\) Hz).
Table S3. Reaction of 3 with H₂

| Time (min) | T (K) | 3, mol%[a] | 3a, mol%[a] | 8-Mg + 8-Mg’, mol%[a] | Others, mol%[a] |
|-----------|-------|------------|-------------|-----------------------|-----------------|
| 0         | 298   | 92         | 0           | 0[a]                  | 8               |
| 10        | 333   | 81         | 6           | 13[b]                 | 5               |
| 25        | 333   | 63         | 8           | 24[b]                 | 5               |
| 50        | 333   | 38         | 13          | 43[b]                 | 6               |
| 60        | 333   | 33         | 13          | 48[b]                 | 6               |
| 70        | 298   | 30         | 12          | 51 (8:8-Mg’ = ca. 3:1) | 7               |

[a] Determined by manual integration of signals in hydride region in the ¹H NMR spectrum. [b] Signals with relative intensity less than 3% were not integrated.

Figure S6. Hydride region (expansion of Mg-Me region shown in inset) of the room temperature ¹H NMR spectrum (400 MHz, THF-d₈) of the reaction of 3 with H₂ (after 70 min at 333 K).
Figure S7. Room temperature $^{31}$P-$^1$H NMR spectrum (162 MHz, THF-$d_8$) of the reaction of 3 with H$_2$ (after 70 min at 333 K).
**Figure S8.** Room temperature $^1$H-$^{31}$P{$^1$H} HMQC (THF-$d_8$) spectrum of reaction of 3 with H$_2$ (after 70 min at 333 K), with expansions of the signals for 7-Mg.

**Reaction of 4 with H$_2$.** A J. Young’s resealable NMR tube was charged with a THF-$d_8$ (0.5 mL) solution of 4-THF (10.4 mg, 0.01 mmol) and placed under 1 atm of H$_2$ at 195 K. The cold NMR tube was quickly shaken to induce H$_2$ diffusion, resulting in loss of the red color of 4 and appearance of a pale-yellow color. The NMR tube was placed into pre-cooled (233 K) NMR spectrometer, and the reaction monitored by $^1$H and $^{31}$P NMR spectroscopy. Every 10 min, the NMR tube was removed and manually shaken for 2-3 sec to ensure H$_2$ diffusion. The reaction reached 50% conversion of 4 after ca. 35 min. The sample was then cooled to 210 K and $^1$H, $^{31}$P{$^1$H}, $^1$H{$^{31}$P}, $^1$H-$^{31}$P{$^1$H} HMBC and $^{31}$P-$^{31}$P COSY spectra acquired. The solution was warmed back to 233 K to bring about full conversion of fac-4 and was then monitored by $^1$H, $^{31}$P{$^1$H} and $^1$H{$^{31}$P} measurements from 210 to 233 K. These data are summarized in Table S4 and Figures S9-S15. The reaction was monitored further at 273 K and finally at 298 K. These data are summarized in Table S5 and Figures S16-S21. Prior to warming to 273 K, the major species in solution was assigned as mer-[Ru(PPh$_3$)$_3$H$_3$(ZnMe)] (mer-8-Zn), based on the presence of a singlet in the $^{31}$P{$^1$H} NMR spectrum (this resolved into a second order dd (δ 58.5))
and d (δ 57.9) at 233 K), and three second-order hydride multiplets at δ -7.53, -8.82 and -10.47 in the 1H NMR spectrum. An additional minor product observed at this stage was tentatively attributed to fac-[Ru(PPh3)2(C6H4PPh2)H2(ZnMe)] (fac-7-Zn), based on similarity of its NMR parameters with those of 7-Li. The fact that fac-7-Zn was observed only in minor amounts (< 5 mol%) at different conversions of 4, and was persistent and observed in NMR even after full consumption of 4 and at temperatures up to 298 K, suggest that fac-7-Zn is a side product of the reaction rather than an intermediate of the formation of mer-8-Zn. The characteristic hydride signal of mer-4 (δ -6.20) was observed even after full consumption of fac-4 and at temperatures up to 298 K, suggesting lower reactivity towards H2 in comparison to fac-4. Upon warming the reaction mixture to 273 K, isomerization of mer-8-Zn into fac-8-Zn started to occur. A structure for fac-8-Zn was assigned based on a singlet in the 31P{1H} NMR spectrum (δ 52.4), and an [AX]3 multiplet (δ -10.63) in the hydride region of the proton spectrum, characteristic of fac-[Ru(PPh3)3H3]-4,6 and similarity to complexes 8-Li and 8-Mg. Isomerization of mer-8-Zn into fac-8-Zn was monitored at 273 K; after 45 min, a 2.5:1 ratio of mer-8-Zn:fac-8-Zn was observed. Upon reaching room temperature, equilibrium between mer-8-Zn and fac-8-Zn is achieved (1.5:1 ratio). The reaction mixture is yellow-colored. After 4 days at room temperature the reaction had proceeded further, producing the previously reported4 fac-[{Ru(PPh3)3}2Zn] (fac-8-Zn'), together with CH4 (1H NMR: δ 0.18). Signals from mer-4 and fac-7-Zn had disappeared at this time. The color of solution was now darker, which we attribute to the likely formation of colloidal Zn.

To visualize more clearly the color change over the course of the reaction, a repeat run was carried out in a J. Young’s resealable ampule. The ampule was charged with a magnetic stir bar and a THF (3 mL) solution of 3 (56 mg, 0.054 mmol) under 1 atm of H2 at 263 K (ice / NaCl). The reaction mixture changed from red to colorless upon stirring, but upon stirring being halted, became red again. This process was reproducible was over several minutes (see accompanying ESI video file). Ultimately, complete conversion of 4 to a mixture of fac-8-Zn
and mer-8-Zn was confirmed by analysis of an aliquot of the solution by ¹H and ³¹P NMR spectroscopy.

Selected ¹H NMR (400 MHz, THF-δ₈): δ -1.34 (s, 3H, ZnMe), -8.75 (br q, J = 23.8 Hz, 1H, RuH), -8.90 (br s, 2H, RuH). Selected ¹H NMR (400 MHz, THF-δ₈, 273 K): δ -1.33 (s, 3H, ZnMe), -7.50 (br s, 1H, RuH), -8.77 (qt, ²JHP = 23.6 Hz, ²JHH = 4.3 Hz, 1H, RuH), -10.50 (br s, 1H, RuH). Selected ¹H NMR (400 MHz, THF-δ₈, 258 K): δ -1.33 (s, 3H, ZnMe), -7.48 (br s, 1H, RuH), -8.79 (qt, ²JHP = 23.9 Hz, ²JHH = 4.4 Hz, 1H, RuH), -10.51 (br s, 1H, RuH). Selected ¹H NMR (400 MHz, THF-δ₈, 233 K): δ -1.32 (s, 3H, ZnMe), -7.53 (br d, ²JHP = 20.3, 1H, RuH), -8.82 (m, ²JHP = 23.9 Hz, ²JHH = 4.4 Hz, 1H, RuH), -10.47 (br dt, ²JHP = 46.6, 23.9 Hz, 1H, RuH). Selected ¹H NMR (400 MHz, THF-δ₈, 210 K): δ -1.31 (s, 3H, ZnMe), -7.59 (dq, ²JHP = 19.6, 5.6 Hz, ²JHP = 5.6 Hz, 1H, RuH), -8.84 (m, 1H, RuH), -10.45 (m, 1H, RuH). ³¹P{¹H} NMR (162 MHz, THF-δ₈): δ 58.1 (br s). ³¹P{¹H} NMR (162 MHz, THF-δ₈, 273 K): δ 58.1 (br s). ³¹P{¹H} NMR (162 MHz, THF-δ₈, 258 K): δ 58.5 (br s), 57.9 (br s).

³¹P{¹H} NMR (162 MHz, THF-δ₈, 233 K): δ 58.5 (dd, ²JPP = 30.2, 21.8 Hz), 57.9 (d, ²JPP = 25.4 Hz). ³¹P{¹H} NMR (162 MHz, THF-δ₈, 210 K): δ 58.1 (s).
fac-[Ru(PPh₃)₃H₃(ZnMe)] (fac-8-Zn). Selected ¹H NMR (400 MHz, THF-d₈): δ -0.63 (s, 3H, ZnMe), -10.63 ([4AX₃] pattern, RuH). ³¹P{¹H} NMR (162 MHz, THF-d₈): δ 52.4 (s).

fac-[{Ru(PPh₃)₃H}(ZnMe)] (8-Zn'). Selected ¹H NMR (400 MHz, THF-d₈): δ 6.67 (t, J = 7.6 Hz, 36H), -9.66 ([4AX₃] pattern, 6H, RuH). ³¹P{¹H} NMR (162 MHz, THF-d₈): δ 55.5 (s) (c.f. Literature data:⁴ Selected ¹H NMR (400 MHz, THF-d₈): δ 6.66 (t, J = 8 Hz, 36H), -9.68 (m, 6H, RuH). ³¹P{¹H} NMR (162 MHz, THF-d₈): δ 55.3 (s).

fac-[Ru(PPh₃)₂(C₆H₄PPh₂)H₃(ZnMe)] (fac-7-Zn). Selected ¹H NMR (400 MHz, THF-d₈, 210 K): δ -0.95 (s, 3H, ZnMe), -7.96 (dtd, 2J₃P = ca. 55, 20 Hz, 2J₃H = ca. 5 Hz, 1H, RuH), -10.78 (dtd, 2J₃P = ca. 45, 15 Hz, 2J₃H = ca. 5 Hz, 1H, RuH). ³¹P{¹H} NMR (162 MHz, THF-d₈, 210 K): δ 50.8 (t, 2J₃P = 23 Hz, PPh₃), 49.5 (t, 2J₃P = 20 Hz, PPh₃), -29.0 (dd, 2J₃P = 19, 23 Hz, C₆H₄PPh₂).

Table S4. Reaction of 4 with H₂ at 210-233 K

| Time (min) | T (K) | fac-4, mol%[a] | mer-8-Zn, mol%[a] | fac-7-Zn, mol%[a] | mer-4, mol%[a] |
|------------|-------|----------------|-------------------|-------------------|----------------|
| 5          | 233   | 93             | 5                 | -[b]              | 2              |
| 15         | 233   | 70             | 26                | 2                 | 2              |
| 28         | 233   | 58             | 37                | 3                 | 2              |
| 35         | 233   | 47             | 48                | 3                 | 2              |
| 45         | 233   | 28             | 66                | 4                 | 2              |
|            | 210   | 27             | 67                | 4                 | 2              |
|            | 210   | -              | 95                | 5                 | 2              |

[a] Determined by manual integration of signals in hydride region of the ¹H and ¹H{³¹P} NMR spectra. [b] Signals with relative intensity less than 2% were not integrated. [c] After the full conversion of fac-4 was reached at 233 K. [d] fac-8-Zn was observed in less than 1 mol % quantity.
Table S5. Reaction of 4 with H₂ at 258-298 K

| Time (min) | T (K) | mer-8-Zn, mol%[a] | fac-8-Zn, mol%[a] | fac-7-Zn, mol%[a] | mer-4, mol%[a] |
|------------|-------|-----------------|-----------------|-----------------|--------------|
| 0          | 258   | 92              | 2               | 4               | 2            |
| 5          | 273   | 86              | 8               | 4               | 2            |
| 15         | 273   | 80              | 14              | 4               | 2            |
| 28         | 273   | 72              | 22              | 4               | 2            |
| 45         | 273   | 68              | 27              | 3               | 2            |
| -          | 298   | 38              | 59              | 2               | 1            |
| 4 days[b]  | 298   | 15              | 23              | -[c]            | -[c]         |

[a] Determined by manual integration of signals in hydride region of \(^1\)H\(^{31}\)P NMR spectrum. [b] After 4 days at 298 K, the reaction mixture also contained 62 mol% of 8-Zn' (calc. on Ru monomer). [c] Signals with relative intensity less than 2% were not integrated.

Figure S9. Hydride region (Zn-Me region shown in the inset) of the \(^1\)H NMR spectrum (400 MHz, THF-\(d_8\), 233 K) of the reaction of 4 with H₂ after 45 min at 233 K.
Figure S10. $^{31}$P{$^{1}$H} NMR spectrum (162 MHz, THF-$d_8$, 233 K) of the reaction of 4 with H$_2$ after 45 min at 233 K.

Figure S11. Hydride region of the $^1$H NMR spectrum (400 MHz, THF-$d_8$, 210 K) of the reaction of 4 with H$_2$ after 45 min at 233 K. Insets show the Zn-Me region and signals from fac-7-Zn.
**Figure S12.** Hydride region of the $^1H\{^{31}P\}$ NMR spectrum (400 MHz, THF-$d_8$, 210 K) of the reaction of 4 with $H_2$ after 45 min at 233 K.

**Figure S13.** $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-$d_8$, 210 K) of the reaction of 4 with $H_2$ after 45 min at 233 K.
**Figure S14.** $^1$H-$^{31}$P{$^1$H} HMQC NMR spectrum (400 MHz, THF-d$_8$, 210 K) of the reaction of 4 with H$_2$ after 45 min at 233 K.
Figure S15. $^{31}$P-$^{31}$P COSY NMR spectrum (162 MHz, THF-$d_8$, 210 K) of the reaction of 4 with H$_2$ after 45 min 233 K; correlations for fac-7-Zn are expanded.
Figure S16. Hydride region of the VT $^1$H NMR spectra (400 MHz, THF-$d_8$) of the reaction of 4 with H$_2$ after full conversion of fac-4, illustrating the isomerization of mer-8-Zn into fac-8-Zn.
Figure S17. VT $^{31}$P{$^1$H} NMR spectra (162 MHz, THF-$d_8$) of the reaction of 4 with H$_2$ after full conversion of fac-4, highlighting the isomerization of mer-8-Zn to fac-8-Zn.
Figure S18. Room temperature $^1$H NMR spectrum (400 MHz, THF-$d_8$) of the reaction of 4 with H$_2$ at 298 K, with expansions of diagnostic areas.

Figure S19. Room temperature $^{31}$P{$^1$H} NMR spectrum (162 MHz, THF-$d_8$) of reaction of 4 and H$_2$ at 298 K.
Figure S20. Room temperature $^1$H NMR spectrum (400 MHz, THF-$d_8$) of the reaction of 4 with H$_2$ after 4 days at 298 K, with expansions of diagnostic areas.

Figure S21. Room temperature $^{31}$P{$^1$H} NMR spectrum (162 MHz, THF-$d_8$) of the reaction of 4 with H$_2$ after 4 days at 298 K.
### Table S6. Selected NMR parameters of complexes 1-4 in THF-\(d_8\).

| Parameter | 2 | 1 | 3 | fac-4 |
|-----------|---|---|---|-------|
| \(^1\)H Ru\(H\) (ppm) | -8.43 | -9.62 | -10.88 | -8.69 |
| \(^2\)J Ru\(H\)-P\(A\) (Hz)\(^{[a]}\) | 93.3 | 83.9 | 68.0 | 51.1 |
| \(^2\)J Ru\(H\)-P\(B\) (Hz)\(^{[a]}\) | 12.4 | 12.8 | 11.8 | 12.2 |
| \(^2\)J Ru\(H\)-P\(C\) (Hz)\(^{[a]}\) | 23.1 | 22.8 | 21.0 | 20.9 |
| \(^{31}\)P P\(A\) (ppm) | -24.3 | -25.1 | -31.5 | -30.5 |
| \(^{31}\)P P\(B\) (ppm) | -19.4 | -20.7 | -25.5 | -26.0 |
| \(^{31}\)P P\(C\) (ppm) | 55.2 | 53.3 | 45.8 | 46.5 |
| \(^2\)J P\(A\)P\(B\) (Hz) | 17 | 17 | 20 | 19 |
| \(^2\)J P\(B\)P\(C\) (Hz) | 20 | 22 | 20 | 23 |
| \(^2\)J P\(A\)P\(C\) (Hz) | 15 | 17 | 20 | 23 |
| \(^{13}\)C Ru\(C_1\) (ppm)\(^{[b]}\) | 188.0 | 180.3 | 167.0\(^{[c]}\) | 164.1 (C\(_A\)) |
| \(^{13}\)C Ru\(C_2\) (ppm)\(^{[b]}\) | 186.7 | 177.5 | 163.1\(^{[c]}\) | 152.9 (C\(_B\)) |
| \(^2\)J Ru\(C_1\)-trans (Hz)\(^{[b]}\) | 71 | 67 | 61\(^{[c]}\) | 59 (C\(_A\)) |
| \(^2\)J Ru\(C_2\)-trans (Hz)\(^{[b]}\) | 72 | 66 | 59\(^{[c]}\) | 52 (C\(_B\)) |

\(^{[a]}\) Obtained from \(^1\)H NMR experiments with selective \(^{31}\)P decoupling. \(^{[b]}\) Due to the similarity of chemical shifts and coupling constants, signals C\(_1\) and C\(_2\) could not be attributed to C\(_A\) or C\(_B\) for complexes 1-3. \(^{[c]}\) Data in C\(_6\)D\(_6\).
Figure S22. (a) Molecular structure of the cation and anion in 2. Ellipsoids are represented at 30% probability. Solvent and hydrogen atoms, with the exception of H1, have been omitted for clarity. (b) Summary of key distances in 2. (c) Molecular structure of 1. Ellipsoids are represented at 30% probability and hydrogen atoms, with the exception of H1, have been omitted for clarity. (d) Summary of key distances in 1.
**Figure S23.** (a) Molecular structure of 3. Ellipsoids are represented at 30% probability. Only the major component of the disordered THF ligand (based on O2) is shown. Hydrogen atoms, with the exception of H1, have been also been omitted for clarity. (b) Summary of key distances in 3. (c) Molecular structure of 4·THF. Ellipsoids are represented at 30% probability. Solvent and hydrogen atoms, with the exception of H1, have been omitted for clarity. (d) Summary of key distances in 4·THF.
Table S7. Selected bond lengths (Å) and angles (°) in complexes 1-4.

| Parameter | M' | 2 Li(crown)₂ | 1 Li(THF)₂ | 3 Mg(THF)₂Me | 4 ZnMe | 4-THF Zn(THF)Me |
|-----------|----|--------------|-----------|-----------|--------|-----------------|
| Ru-M'     | -  | 2.825(6)     | 2.8250(8) | 2.4717(3) | 2.5396(3) |
| Ru-Cₐ     | 2.081(2) | 2.100(3)   | 2.125(2) | 2.0937(19) | 2.1122(18) |
| Ru-Cₜ     | 2.106(2) | 2.117(3)   | 2.127(2) | 2.173(2) | 2.1744(17) |
| Ru-Pₐ     | 2.3850(6) | 2.3491(7)   | 2.3668(6) | 2.3823(5) | 2.3648(4) |
| Ru-Pₜ     | 2.3364(6) | 2.3578(7)   | 2.3686(5) | 2.4018(5) | 2.3568(4) |
| Ru-Pₜ     | 2.3093(5) | 2.3216(7)   | 2.3543(5) | 2.3460(6) | 2.3347(4) |
| M'-Cₜ     | -  | 2.317(7)     | 2.596(2) | 2.282(2) | 2.3138(17) |
| M'-Me     | -  | -            | 2.179(3) | 1.941(2) | 1.956(2) |
| Cₐ-Ru-Cₜ  | 86.57(8) | 94.85(11)  | 91.92(8) | 89.04(7) | 94.08(7) |
| Cₐ-Ru-Pₐ  | 67.75(6) | 67.85(9)    | 67.59(6) | 67.55(6) | 67.37(5) |
| Cₜ-Ru-Pₜ  | 67.40(6) | 67.56(8)    | 67.49(6) | 67.18(5) | 67.47(5) |
| Cₚ-Ru-Pₚ  | 153.71(6) | 161.19(8)  | 158.45(6) | 156.20(6) | 160.32(5) |
| Cₚ-Ru-Pₚ  | 168.61(6) | 167.73(8)  | 167.84(6) | 174.53(5) | 170.83(5) |
S-4 Crystallographic Details

Data for 1, 3 and 4·THF were collected using an Agilent SuperNova instrument (using Cu-Kα radiation) while those for 2, 4·THF/4·Cl·THF, 4 and 6 were obtained using an Agilent Xcalibur diffractometer and a Mo-Kα source. All experiments were conducted at 150 K, with the exception of that for compound 3 (vide infra). Using Olex2, all structures were solved with the olex2.solve structure solution program and subsequently refined using the SHELXL program. While refinements were largely unremarkable, there are some points which merit note as follows.

The hydride ligand in 1 was located and refined without restraints. There is a little smearing of the electron density in the region of the THF ligands. However, efforts to model same were abandoned, on the basis that a stable disorder model could not be achieved without the inclusion of extensive restraints.

The asymmetric unit in 2 contains one cation, one anion and three molecules of benzene. The hydride ligand in the former was located and refined subject to being a distance of 1.6 Å from Ru1. The cation was (surprisingly) ordered. There is evidence for some disorder in the guest benzene based on C83, but this was not modeled. The highest, residual, electron-density maximum is located at a chemically insignificant distance from the transition metal.

C60-C62 were modeled for 60:40 disorder in the structure of 3. Distance restraints were used in the disordered region. H1 was located and refined freely. Data were collected at 200 K, as the crystal was seen to crack and degrade at 150 K – possibly due to a phase transition.

In 4·THF, the asymmetric unit comprises one molecule of the ruthenium-zinc complex and two regions of solvent. The hydride ligand (H1) was located and refined freely. Each of the two solvent regions contain one molecule of THF, with the moieties based on O2 and O3 being disordered in 70:30 and 65:35 ratios, respectively. Distance and ADP restraints were included in
disordered regions to assist convergence. The assignment of the oxygen atoms in the solvent entities is somewhat tentative due to the smearing of the electron density in these regions.

The asymmetric unit in 4·THF/4·Cl·THF contains one molecule of a ruthenium-zinc complex and two regions of solvent. The methyl ligand attached to Zn1, in the former, was seen to be disordered in a 65:35 ratio with a chloride ligand which means that the gross crystal contains two distinct compounds. The hydride ligand (H1) was located and refined freely. Each of the two solvent regions contain one molecule of THF, with both solvent molecules being disordered in a 65:35 ratio. Distance and ADP restraints were included in disordered regions to assist convergence. The assignment of the oxygen atoms in the solvent entities is somewhat tentative due to the smearing of the electron density in these regions.

The hydride ligand (H1) in the structure of 4 was located and refined without restraints. One phenyl ring (attached to P3) was modeled to take account of 55:45 disorder. The component parts therein were treated as rigid hexagons in the final least-squares and some soft ADP restraints were also included for partial occupancy carbon atoms. The asymmetric unit in 6 comprises one cation and one anion. The fluorine atoms attached to C82 were modeled to take account of 60:40 disorder in the final least-squares, while refinement of those bonded to C86 take 50:30:20 disorder into consideration. Restraints were employed in the disordered regions, to assist convergence.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1937188-1937194 for 1-3, 4·THF, 4·THF/4·Cl·THF, 4 and 6, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.
S-5  NMR Spectra of Isolated Complexes

Figure S24. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][Li(THF)$_2$] (1).
Figure S25. $^{31}$P{$^1$H} NMR spectrum (202 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][Li(THF)$_2$] (1).
Figure S26. $^{13}$C-$^1$H PENDANT NMR spectrum (126 MHz, THF-$d_8$, 298 K) of $[\text{Ru}(\text{PPh}_3)(\text{C}_6\text{H}_4\text{PPh}_2)_{2}\text{H}][\text{Li}(\text{THF})_2]$ (1).
Figure S27. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 298 K) of [Li(12-crown-4)$_2$][Ru(PPh$_3$)$_2$(C$_6$H$_6$PPh$_2$)$_2$H] (2).
Figure S28. $^{31}$P\(\left\{^1\text{H}\right\}\) NMR spectrum (162 MHz, THF-\(d_8\), 298 K) of [Li(12-crown-4)$_2$][Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H] (2).
Figure S29. $^{13}$C\(^{1}H\) PENDANT NMR spectrum (126 MHz, THF-\(d_8\), 298 K) of [Li(12-crown-4)]\(_2\)[Ru(PPh\(_3\))(C\(_6\)H\(_4\)PPh\(_2\))\(_2\)H] (2).
Figure S30. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [Ru(PPh$_3$)$_3$(C$_6$H$_4$PPh$_2$)$_2$H][Mg(THF)$_2$Me] (3).
Figure S31. $^{31}$P {$^1$H} NMR spectrum (202 MHz, C$_6$D$_6$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][Mg(THF)$_2$Me] (3).
Figure S32. $^{13}$C{^1}H} PENDANT NMR spectrum (100 MHz, C_6D_6, 298 K) of [Ru(PPh_3)(C_6H_4PPh_2)_2H][Mg(THF)_2Me] (3).
Figure S33. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_8$H$_4$PPh$_2$)$_2$H(ZnMe)] (4).
Figure S34. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H[ZnMe]] ($4$). Insets show signals for mer-4 and 5.
Figure S35. $^{31}$P{$^1$H} NMR spectrum (202 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4). Insets show signals for fac-4.
Figure S36. $^{31}$P{$^1$H} NMR spectrum (202 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4). Insets show signals for mer-4 and 5.
Figure S37. $^{13}$C{$^1$H} PENDANT NMR spectrum (126 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4).
No $^{31}$P decoupling

$^{31}$P decoupling at -30.53 ppm
$J = 51.1$ Hz suppressed

$^{31}$P decoupling at -26.01 ppm
$J = 12.2$ Hz suppressed

$^{31}$P decoupling at 46.54 ppm
$J = 20.9$ Hz suppressed

**Figure S38.** Hydride region of the $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4) with selective $^{31}$P decoupling.
Figure S39. $^1$H-$^{31}$P/$^1$H HMQC spectrum (THF-$d_8$, 298 K) of [Ru(PPh$_3$)($C_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4). Inset highlights correlations for mer-4.
Figure S40. $^{31}$P-$^{31}$P COSY spectrum (202 MHz, THF-$d_8$, 298 K) of [Ru(PPh$_3$)$_3$(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4). Inset highlights correlations for mer-4 and 5.
Figure S41. $^{31}\text{P}$($^1\text{H}$) EXSY NMR spectrum (202 MHz, THF-$d_8$, 298 K) of 4 with exchange peaks between fac-4 and 5 highlighted.
Figure S42. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 298 K) of a mixture of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4) and [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnCl)] (4-Cl).

Figure S43. $^{31}$P($^1$H) NMR spectrum (202 MHz, THF-$d_8$, 298 K) of a mixture of [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnMe)] (4) and [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H(ZnCl)] (4-Cl).
Figure S44. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [Ru(PPh$_3$)$_2$(C$_6$H$_4$PPh$_2$)(ZnMe)$_2$][BAR$_4$F] (6).
Figure S45. $^{31}$P$_1$(1H) NMR spectrum (202 MHz, C$_6$D$_6$, 298 K) of [Ru(PPh$_3$)$_2$(C$_6$H$_4$PPh$_2$)(ZnMe)$_2$][BAR$_4$] (6).
Figure S46. $^{13}$C{$^1$H} DEPTQ NMR spectrum (126 MHz, C$_6$D$_6$, 298 K) of [Ru(PPh$_3$)$_2$(C$_6$H$_4$PPh$_2$)(ZnMe)$_2$][BArF$_4$] (6).
S-6. Computational Studies.

Computational Details

DFT calculations were run with Gaussian 09 (Revision D.01).\textsuperscript{10} Ru, Mg, Zn and P centers were described with the Stuttgart RECPs and associated basis sets\textsuperscript{11} and 6-31G** basis sets were used for all other atoms.\textsuperscript{12} A set of d-orbital polarization functions was also added to P ($\zeta_d = 0.387$)\textsuperscript{13} and together this combination is termed BS1. Optimizations employed the BP86 functional\textsuperscript{14} and all stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). Transition states were also characterized via IRC calculations and subsequent geometry optimizations confirmed they linked to the minima as reported in the text or in the Supporting Information. Single-point calculations were carried out with a larger basis set featuring Def2TZVP basis sets on all atoms with pseudo potentials for Ru, Mg, Zn and P (BS2).\textsuperscript{15} Single-point corrections to the BP86 results employed the $\omega$B97xD functional\textsuperscript{16} with BS2 and polarizable continuum model (PCM)\textsuperscript{17} for the effect of THF solvent. Functional testing were also conducted on the BP86-optimized geometries of \textit{fac-4, mer-4} and \textit{5} with a range of functionals including GGA functionals (PBE,\textsuperscript{18} BP86, BLYP,\textsuperscript{19} B97D\textsuperscript{20}), hybrid GGA functional (PBE0\textsuperscript{21} and B3LYP\textsuperscript{22}) and a Minnesota functional (M06\textsuperscript{23}) with BS2 in THF (see Table S8). The effect of dispersion was also considered with Grimme’s D3 parameter set with Becke-Johnson damping\textsuperscript{24} for those functionals that do not have a treatment for dispersion (i.e. BP86, PBE, PBE0 and B3LYP).

Quantum Theory of Atoms in Molecules (QTAIM)\textsuperscript{25} used the AIMALL program\textsuperscript{26} and NCI calculations were performed using the PLOT program and were based on the promolecular densities.\textsuperscript{27} QTAIM, NBO and NCI analyses were performed on the experimental heavy atom positions derived from the X-ray structure of species \textit{1, 3} and \textit{4} with the H atoms positions being optimized. Natural Bonding Orbital analyses employed the NBO 6.0 programs\textsuperscript{28} and orbital plots were produced with Chemcraft\textsuperscript{29} with an isosurface value of 0.0622. For 4 the CHOOSE option was
employed to define a Lewis structure equivalent to [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H$^-$][ZnMe$^+$] with 3 lone pairs on Ru, Ru–C$_A$, Ru–C$_B$ and Ru–H bonds and a lone pair on each of the phosphorus centers. All geometries are supplied as a separate xyz file readable by Chemcraft and Mercury.$^{30}$
Figure S47. QTAIM molecular graphs and selected BCP metrics for (a) [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H]$^-$, the molecular anion in 2, (b) [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][Li(THF)$_2$], 1, and (c) [Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$)$_2$H][MgMe(THF)$_2$], 3. Structures are truncated with phosphine phenyl substituents omitted and THF molecules (where present) truncated at the O atom for clarity. BCP metrics (in a.u.): electron densities, $\rho(r)$, values of the Laplacian of the electron density, $\nabla^2 \rho(r)$, ellipticities ($\varepsilon$) and total energy densities, $H(r)$.

| BCP  | $\rho(r)$ | $\nabla^2 \rho(r)$ | $\varepsilon$ | $H(r)$ |
|------|-----------|--------------------|--------------|--------|
| Ru—H | 0.130     | +0.116             | 0.008        | -0.061 |
| Li—H | 0.019     | +0.082             | 0.421        | +0.003 |
| Mg—H | 0.027     | +0.116             | 0.498        | -0.004 |
Figure S48. QTAIM molecular graphs and selected BCP metrics for (a) [Ru(PPh₃)(C₆H₄PPh₂)₂H][ZnMe], *fac-4*, and (b) [[Ru(PPh₃)(C₆H₄PPh₂)₂H][ZnMe(THF)]], *fac-4THF*. Structures are truncated with phosphine phenyl substituents omitted and THF molecules (where present) truncated at the O atom for clarity. BCP metrics (in a.u.): electron densities, ρ(r), values of the Laplacian of the electron density, \(\nabla^2\rho(r)\), ellipticities (ε) and total energy densities, H(r).
Figure S49. (a) Key NBO donor-acceptor pairs for *fac-*4 with NBO occupancies as indicated. (b) NCI plot for *fac-*4 with isosurfaces generated for $s = 0.3$ a.u. and $-0.07 < \rho < 0.07$ a.u.
Table S8. Functional testing on the relative free energies of fac-4, mer-4 and 5. Geometries optimized with the BP86 functional with BS1 were corrected with single point energy calculations with extended basis set BS2 and incorporating the effects of THF solvent and (for BP86, PBE, PBE0 and B3LYP) a dispersion correction (BJD3).

![Diagram of fac-4, mer-4, and 5](attachment:image.png)

| Structure | BP86 | BLYP | B3LYP | PBE | PBE0 | B97D3 | B97D | M06 | oB97xD |
|-----------|------|------|------|-----|------|-------|------|-----|-------|
| fac-4     | 0.0  | 0.0  | 0.0  | 0.0 | 0.0  | 0.0   | 0.0  | 0.0 | 0.0   |
| mer-4     | -1.3 | 0.1  | 1.0  | 1.0 | 1.6  | 0.7   | -0.5 | 1.8 | 1.8   |
| 5         | -5.4 | -11.0| -6.4 | -1.4| 2.2  | -10.5 | -7.4 | -1.5| 3.7   |
**Figure S50.** QTAIM molecular graphs and selected BCP metrics for (a) $[\text{Ru(PPh}_3)_2(\text{C}_6\text{H}_4\text{PPh}_2)\text{(ZnMe)}]$, 5, and (b) $[\text{Ru(PPh}_3)_2(\text{C}_6\text{H}_4\text{PPh}_2)\text{(MgMe)}]$, 5_Mg. BCP metrics (in a.u.): electron densities, $\rho(r)$, values of the Laplacian of the electron density, $\nabla^2 \rho(r)$, ellipticities ($\epsilon$), and total energy densities, $H(r)$. 

| BCP      | $\rho(r)$ | $\nabla^2 \rho(r)$ | $\epsilon$ | $H(r)$  |
|----------|-----------|---------------------|------------|---------|
| Ru—Zn    | 0.075     | +0.120              | 0.015      | -0.024  |
| Ru—Mg    | 0.037     | +0.116              | 0.118      | -0.011  |
Figure S51. Computed reaction profiles (free energies, kcal/mol) for C_B–H reductive elimination and C_A–H reductive elimination pathways from \textit{fac-4}_{Mg}. Selected distances are shown in Å.
Cartesian Coordinates (Å) and Computed Energies (in Hartrees).

Geometries employed in QTAIM studies

1 (QTAIM Study)

SCF = -2671.4148936400

| Energy | Cartesian Coordinates | Constraints |
|--------|------------------------|-------------|
| -3.06224 | 5.27417 | 2.26768 |
| -2.85769 | 3.80472 | 3.82240 |
| -3.60749 | 4.47762 | 4.46771 |
| -2.81961 | 2.65659 | 4.23243 |
| -2.45451 | 2.20831 | 5.20350 |
| -1.26607 | 2.66285 | 3.41952 |
| -0.75977 | 1.15535 | 3.75753 |
| 1.51988 | 0.91597 | -3.38216 |
| 1.95640 | 0.09778 | -2.78956 |
| 2.33017 | 1.68448 | -4.20893 |
| 3.39546 | 1.44326 | -4.30465 |
| 1.79168 | 2.76569 | -4.89377 |
| 2.42886 | 3.38769 | -5.53315 |
| 0.44541 | 3.02990 | -4.78146 |
| -0.00001 | 3.86843 | -3.3262 |
| -0.36314 | 2.24318 | -3.96773 |
| -1.42936 | 2.47806 | -3.90287 |
| 0.16044 | 1.18540 | -3.24627 |
| -0.44032 | -1.64332 | -4.24714 |
| 0.34077 | -0.96261 | -4.59927 |
| -0.67603 | -2.81938 | -4.95148 |
| -0.07464 | -3.04442 | -5.84037 |
| -2.25510 | -2.07587 | -5.10745 |
| 2.42159 | -3.38342 | -4.2503 |
| -3.20684 | -4.06990 | -3.09008 |
| -2.18293 | -2.21685 | -2.71169 |
| -2.78682 | -1.99395 | -1.82662 |
| -1.18697 | -1.32405 | -3.12366 |
| -2.69474 | 2.15950 | -1.43677 |
| -0.91496 | 2.42771 | -0.68735 |
| -3.86593 | 2.90725 | -1.54850 |
| -4.02377 | 3.77395 | -0.89574 |
| -4.82945 | 2.53684 | -2.46617 |
| -5.75590 | 3.19707 | -2.55048 |
| -4.62700 | 1.45049 | -3.75697 |
| -5.38809 | 1.15817 | -4.09907 |
| -3.45528 | 0.70705 | -3.17674 |
| -3.30475 | -0.14911 | -3.84004 |
| -2.47657 | 1.05193 | -2.24938 |
| 4.50173 | -3.12794 | -1.11904 |
| 5.15918 | -2.35684 | -1.58507 |
| 3.69119 | -3.32576 | -1.84599 |
| 5.27626 | -3.33212 | -0.78078 |
| 6.10343 | -4.13946 | -1.48513 |
| 4.62713 | -5.22870 | -0.80843 |
| 5.71604 | -4.06230 | 0.60156 |
| 6.64004 | -3.45145 | 0.60480 |
| 5.93855 | -4.96933 | 1.18826 |
| 4.58285 | -3.27259 | 1.19488 |
| 3.82077 | -3.91520 | 1.67309 |
| 4.88700 | -2.49849 | 1.91698 |
| 4.11036 | 1.67062 | -0.58076 |
| 3.21297 | 2.20950 | -1.01704 |
| 3.89389 | 1.62692 | -1.66462 |
| 5.31740 | 2.39056 | -0.25146 |
| 5.71909 | 2.94539 | -1.11831 |
| 5.08227 | 3.18003 | 0.48860 |
| 6.25621 | 1.45658 | 0.28146 |
| 6.84750 | 1.83942 | 1.13126 |
| 7.00213 | 1.14824 | -0.47788 |
| 5.44823 | 0.24965 | 0.67427 |
| 5.94832 | -0.71225 | 0.47106 |
| 5.15353 | 0.27063 | 1.74426 |
| 2.80765 | -0.97449 | 0.10142 |
| 1.47460 | -0.10053 | -0.86746 |

2 (Anion, QTAIM Study)

SCF = -2199.0015273700

Ru 0.177117 -0.10723 -1.02898
SCF = -2466.1278903500

107

SCP = -2466.1278903500

Ru 0.13618 -0.13539 -0.66108
Zn 1.16597 -0.63253 -2.85237
P -1.04007 1.84933 -0.06750
P 2.25801 -0.06763 0.46220
Zn -1.24080 -1.78031 0.28861
C 0.94152 -0.98472 -4.55982
H 1.54717 -0.38830 -5.35867
C 1.95511 0.05034 2.48774
C 3.08520 -0.70141 -4.51057
H -1.29101 0.40690 -2.09362
H -1.78720 1.66946 -1.70741
C -2.60222 2.44945 -2.51744
C -2.93978 3.44277 -2.19834
C -2.98105 1.94135 -3.75225
C -3.62198 2.53344 -4.41548
P -2.56269 0.67830 -4.13850
H -2.88568 0.27693 -5.10715
C -1.73250 -0.08807 -3.32712
C -1.44352 -1.09320 -3.66385
C -2.40311 2.02944 1.14852
C -2.07289 2.26742 2.47455
H -1.01970 2.32399 2.77010
C -3.05320 2.46881 3.43905
C -2.76153 2.64949 4.47925
C -4.38150 2.45125 3.07682
H -5.16035 2.61788 3.82976
C -4.72853 2.24322 1.76253
H -5.78725 2.23116 1.46274
H -3.74357 2.01568 0.79885
C -4.03240 1.85748 -0.24628
C -0.36508 3.55866 0.07627
H -1.22863 4.65514 -0.03987
C -2.30572 4.49573 -0.16029
C -0.73351 5.94866 0.01834
H -1.42303 6.79508 -0.08022
C 0.61588 6.16890 0.19884
H 1.00517 7.19279 0.23827
C 1.46988 5.09630 0.34600
H 2.54133 5.25866 0.50627
C 0.97993 3.79602 0.29229
H 1.67216 2.96105 0.40703
C 1.54045 1.23494 -1.59466
C 1.52278 2.20449 -2.59940
H 0.62656 2.35108 -3.21298

S72
C 2.63382 3.02546 -2.80346
H 2.59506 3.79919 -3.57969
C 3.78418 2.86800 -2.05328
H 4.65188 3.51083 -2.24227
C 3.84127 1.90538 -1.05611
H 4.74243 1.79574 -0.44103
C 2.72293 1.17859 -0.83575
H 2.66747 0.79363 2.03162
C 1.64004 1.24655 2.85040
H 0.60625 1.03931 2.55427
C 1.91375 1.93390 4.02880
H 1.08834 2.27093 4.66600
C 3.21631 2.18652 4.38582
H 3.43736 2.72571 5.31417
C 4.25522 1.76086 3.57437
H 5.29365 1.96663 3.85765
C 3.98624 1.07072 2.40087
H 4.81642 0.71451 1.78141
C 3.54883 -1.36682 0.40637
C 3.86638 -2.12118 1.53393
C 3.83008 -1.90631 2.49204
C 4.80781 -3.13650 1.45504
H 5.05841 -3.71505 2.35131
C 5.43398 -3.40541 0.25615
H 6.18296 -2.40214 0.20092
C 5.11666 -2.68324 -0.87432
H 5.60965 -2.89786 -1.82866
C 4.17933 -1.66420 -0.79600
C 3.94691 -1.07655 -1.69193
C -0.51308 -3.44450 0.63213
C -1.31641 -4.50920 1.01999
H -2.40273 -4.38275 1.08735
C -0.75685 -5.73495 1.34422
H -1.41152 -6.56154 1.63460
C 0.60805 -5.91554 1.28327
H 1.04446 -6.88713 1.54282
C 1.40232 -4.87714 0.90549
H 2.49080 -4.99216 0.85418
C 0.84270 -3.64294 0.57243
H 1.49217 -2.82516 0.25365
C -2.62813 -2.19937 -0.83480
C -3.74170 -3.15764 -0.91685
H -3.84186 -0.51620 -0.22394
C -4.70478 -1.55362 -1.89716
H 5.56229 0.87412 -1.94818
C -4.58833 -2.58528 -2.79351
H -5.34757 -2.73900 -3.56633
C -3.49327 -3.43410 -2.79110
C -3.38961 -4.26273 -3.42891
C -2.51708 -3.24104 -1.74555
H -1.65601 -3.91648 -1.70612
H 0.59721 -1.57344 -1.42755
C -2.06010 -1.57946 1.97887
C -1.20477 -1.22465 3.04348
C -3.40916 -1.86804 2.26592
H -0.14976 -1.01687 2.83426
H -4.09055 -2.16625 1.46352
C -1.68176 -1.15728 4.36029
C -3.89128 -1.78724 3.58393
H -0.99742 -0.88979 5.17297
H -4.94440 -2.01082 3.78731
C -3.03145 -1.43333 4.63449
C -3.40885 -1.37899 5.66120

fac=4

SCF = -2698.5667355000

120
Ru 0.01656 -0.02609 -0.53160
H 1.32215 -1.02324 -0.88798
Zn 1.91703 0.01453 -2.18944
P 1.22317 0.99324 1.22421
P -2.02283 1.16771 -0.56366
Reactivity Studies

fac-4

SCF =  -2466.16241426
H(0 K) =  -2465.341012
G(298 K) =  -2465.439920
Low Freq. = 12.5407cm⁻¹, 19.2869cm⁻¹

SCF BP86(BS2,D3BJ,THF) =  -5024.22179225
SCF BLYP(BS2,D3BJ,THF) =  -5022.92356995
SCF B3LYP(BS2,D3BJ,THF) =  -5023.88790446
SCF PBE(BS2,D3BJ,THF) =  -5020.16346053
SCF PBE0(BS2,D3BJ,THF) =  -5020.39923313
SCF B97D3(BS2,D3BJ,THF) =  -5023.18993665
SCF B97D(BS2,D3BJ,THF) =  -5022.93670106
SCF M06(BS2,D3BJ,THF) =  -5021.61230710
SCF wB97XD(BS2,D3BJ,THF) =  -5022.76658412

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Ru  -0.11759 -0.06428 -0.80917
H  -1.11805  0.94895  -1.6899
En  -1.40329 -0.28436 -2.9498
P  -2.00998 -0.77790  0.55980
P  1.83987 -1.33106 -0.10647
P  0.38698  2.09350  0.13583
C  -0.92888 -1.97233 -1.44106
C  -0.59858 -2.97551 -2.38808
H  0.21587 -2.80973  3.10429
C  -1.29751 -4.20066 -2.40790

H  3.81651  -5.53492  1.31387
C  2.79119  -4.30191  -0.12783
C  3.54666  -4.44846  -0.90588
C  1.69661  -3.50682  -0.38336
H  1.61848  -3.00480  -1.35302
C  -1.72287  -3.04287  -0.96546
C  -1.22678  -4.05689  -1.77727
H  -0.21919  -4.45072  -1.61618
C  -2.00283  -4.59503  -2.79447
H  -1.58821  -5.39407  -3.42028
C  -3.27823  -4.13839  -3.01014
H  -3.88871  -4.56335  -3.81534
C  -3.79395  -3.13722  -2.20434
H  -4.81089  -2.76370  -2.36628
C  -3.01821  -2.59107  -1.19782
C  -3.43622  -1.79095  -0.57926
H  -1.64516  -2.29479  1.79946
C  -1.25154  -1.05012  2.87646
H  -0.43498  -0.78870  2.74516
C  -1.90119  -1.59419  4.10037
H  -1.57312  -0.95740  4.92993
C  -2.95915  -2.46428  4.25697
H  -3.48123  -2.53003  5.21890
C  -3.35839  -2.34918  3.19946
H  -4.19658  -2.94611  3.31383
C  -2.69323  -2.17733  1.97661
C  -3.01584  -3.82202  1.15307
C  4.73470  -0.93291  -1.37983
H  4.60457  -1.35525  -2.39690
H  4.36957  -1.67225  -0.64811
C  6.14300  -0.47068  -1.13796
H  6.79005  -0.74361  -1.99008
C  6.58221  -0.94959  -0.24707
C  6.05596  1.02314  -0.96814
H  6.09657  1.29158  0.10163
C  6.86392  1.56859  -1.47525
C  4.70681  1.37503  -1.52373
C  4.21731  2.24217  -0.05520
H  4.74323  1.54142  -2.62144
C  2.43799  -0.20063  -4.05006
C  3.36715  0.34955  -4.28929
H  1.64741  0.17562  -4.72134
C  2.60901  -1.25980  -4.31847

S74
C  -4.32897  2.98660  -0.44396
H  -4.35887  3.98488  -0.06004
C  -3.51082  1.96452  0.05859
H  -2.91602  2.14683  0.95999

TS(mer-4-5)
SCF  =  -2466.13251724
H(0 K)=         -2465.312714
G(298 K)=       -2465.411366
Low Freq. = -513.2928cm^{-1}, 10.5714cm^{-1}
SCF wB97XD(BS2,D3BJ,THF) = -5022.73050500

Ru  0.05329  -0.42173  -0.22408
H  -0.06622  -2.08587  -0.01852
Zn  0.01731  -0.12301  -0.49864
P  -2.42775  -0.91501  -0.01051
P  -2.27176  -0.46186  -0.1852
C  -1.26593  -3.11172  -1.98975
C  -0.55079  -4.19130  -2.78070
Ru  -0.00109  -4.91885  -3.38930
C  -1.95596  -4.18767  -2.82117
H  -2.49486  -4.88973  -3.45655
C  -2.66759  -3.24216  -2.04556
P  -3.76142  -3.19078  -2.08774
C  -1.94517  -2.36739  -1.22862
C  -3.20984  -1.60652  1.34753
C  -3.14107  -2.98421  1.64346
H  -2.68017  -3.66971  0.92459
C  -3.66426  -3.47770  2.84983
C  -3.60380  -4.54599  3.06961
C  -4.26818  -2.60527  3.76960
C  -4.67754  -2.99212  4.70862
C  -4.34795  -1.23322  3.47686
C  -4.82132  -0.54689  4.18722
C  -3.82047  -0.73402  2.72617
C  -3.88655  0.33727  2.05820
C  -3.89971  -0.15417  -1.06931
C  -3.69672  0.81942  -2.07024
C  -2.68470  1.15905  -2.30156
C  -4.78995  1.34288  -2.77869
C  -4.61598  2.05986  -3.55459
C  -6.09420  0.90731  -2.49625
C  -6.94496  1.31945  -3.04949
C  -6.30337  -0.05932  -1.49962
C  -7.31728  -0.40604  -1.27200
C  -5.21450  -0.58724  -0.78796
C  -5.39031  -1.33525  -0.09092
C  -0.21393  0.54055  -2.15647
C  -0.26270  1.94870  -1.93289
C  -0.27150  1.94870  -2.93582
C  -0.36295  3.98451  -2.73380
C  -0.48630  2.45058  -4.27819
C  -0.57807  3.16566  -5.10300
C  -0.47603  1.06477  -4.54049
C  -0.57467  0.71806  -5.57713
C  -0.33640  0.12232  -3.50382
C  -0.33124  -0.94827  -3.74887
C  1.15138  3.24500  0.33768
C  1.07183  4.02811  1.50905
H  0.21094  3.92875  2.17813
C  2.08072  4.95547  1.81384
H  2.00131  5.56200  2.72261
C  3.17944  5.13311  0.95376

Int(mer-4-5)
SCF  =  -2466.13541872
H(0 K)=         -2465.312021
G(298 K)=       -2465.411536
Low Freq. = 11.9112cm^{-1}, 16.4712cm^{-1}
SCF wB97XD(BS2,D3BJ,THF) = -5022.73819953

Ru  0.06026  -0.30734  0.26442
H  0.04780  -2.27897  0.37946
Zn  0.07321  -0.82021  -2.18198
P  2.37777  -0.83964  0.10947
P  0.11946  1.99000  0.14744
H  -2.24805  -0.68720  0.01221
C 1.35888 1.02034 -3.86838
H 0.42455 1.34074 -4.34099
C 3.64723 -1.27516 0.27233
C 3.33173 -2.61775 -0.03587
H 2.34950 -2.86302 -0.44908
C 4.27397 -3.63586 0.17622
H 4.01271 -4.67003 -0.07162
C 5.53790 -3.33293 0.70882
H 6.26971 -4.12993 0.87916
C 5.85646 -2.00309 1.02593
H 6.83915 -1.75654 1.44307
C 4.93910 -0.97909 0.80948
H 5.18029 0.05311 0.06141
C 3.11137 1.49208 0.85429
C 2.90297 1.59539 2.24673
H 2.27745 0.85550 2.75812
C 3.48512 2.63745 2.98386
C 3.31635 2.69896 4.06441
C 4.27670 3.60125 2.33595
H 4.73060 4.41621 2.90991
C 4.47930 3.51602 0.94938
C 5.09049 4.26637 0.43622
C 3.90546 2.46658 0.21206
C 4.07477 2.40370 -0.86754
C -2.79658 2.24243 -0.32678
C -3.76546 1.22657 -0.46619
C -3.48709 0.18514 -0.27648
C -5.08578 1.53164 -0.83306
C -5.81695 0.72238 -0.92880
C -5.54952 2.86250 -1.08152
C -6.48537 3.10163 -1.38116
C -4.50660 3.88311 -0.94414
C -4.78520 4.92559 -1.13419
C -3.18824 3.57804 -0.56194
H -2.46412 4.38887 -0.45750
C -0.15335 3.36538 -0.11218
C 0.52702 4.09273 0.88504
C 0.49949 3.75075 1.92337
C 1.24432 5.25600 0.55838
C 1.76731 5.80434 1.34877
C 1.29239 5.71299 -0.76732
C 1.84728 6.62321 -1.01838
C 0.62262 4.99427 -1.77161
C 0.64833 5.34251 -2.80990
C -0.08898 3.82933 -1.44725
C -0.62494 3.29045 -2.23731
C -1.32993 1.87800 2.10111
C -2.12470 2.88482 2.69125
C -2.61254 3.63583 2.06163
C -2.30653 2.92368 4.08218
C -2.92572 3.71111 4.52586
C -1.70630 1.95308 4.90370
H -1.85765 1.98192 9.58821
C -0.91997 0.94457 4.32637
C -0.45471 0.17555 4.95251
C -0.73332 0.91260 2.93316
H -0.12840 0.12587 2.47284
C -3.06642 -0.67145 -3.87938
H -4.03473 -1.06471 -3.52468
C -2.65110 -1.37467 -4.62218
C -3.24992 0.29844 -4.37434

TS1 (fac-4-5) B
SCF = -2466.15332900
H(0 K) = -2465.331731
G(298 K) = -2465.430174
Low Freq. = -27.5155cm⁻¹, 5.4701cm⁻¹
SCF wB97XD(B2, D3BJ, THF) = -5022.75908500
C   4.23108  0.86618 -3.48847
H   4.62291 -0.41625  1.12062
C   2.77836  1.79327  1.87245
C   1.71998  1.77294  2.80622
SCF = -2466.15882527
H(0 K) = -2465.334156
C   1.91258  2.22497  4.12136
G(298 K) = -2465.433583
H   1.07959  2.20633  4.83225
Low Freq. = 13.0680cm-1, 13.4570cm-1
SCF wB97XD(BS2,D3BJ,THF) = -5022.75603871
C   3.17270  2.70114  4.51867
H   3.32893  3.05313  5.54389
C   4.23213  2.72683  3.59609
H   5.21560  3.10038  3.90145
C   4.03839  2.27801  2.27963
H   4.87095  2.30112  1.56943
C   3.19346  2.28815  1.06480
C   2.77049 -0.88512  2.33210
H   -1.80840 -0.49706  2.68314
C   -3.49705 -1.77367  3.13842
H   -3.09690 -2.07069  4.11331
C   -4.72558 -2.28813  2.68769
H   -5.29364 -2.98474  3.31347
C   -5.22102 -1.90119  1.43262
H   -6.18041 -2.29229  1.07602
C   -4.49206 -1.01020  0.62491
H   -4.88821 -0.72059 -0.35295
C   -3.22957  0.92222 -1.47122
H   -3.94690  2.08763 -1.80951
C   -3.97626  2.93209 -1.11414
C   -4.63048  2.17410 -3.03553
H   -5.17395  3.09148 -3.28666
C   -4.62125  1.09343 -3.92987
H   -5.15676  1.16179 -4.88266
C   -3.91904 -0.07770 -3.59631
C   -3.90711 -0.92998 -4.28355
C   -3.21893 -0.15984 -2.38279
H   -2.66931 -1.07627 -2.13768
C   -2.73072  2.25598  1.11385
C   -4.08137  2.44290  1.48844
H   -4.84101  1.72082  1.17179
C   -4.46039  3.53977  2.27602
H   -5.51263  3.67180  2.55066
C   -3.49348  4.45859  2.72009
H   -3.78939  5.31033  3.34202
C   -2.14918  4.27487  2.36588
H   -1.38607  4.98223  2.70778
C   -1.77064  3.18319  1.56433
H   -0.72593  3.05148  1.26988
C   0.99267  0.20683 -4.40885
H   1.07793  0.54222 -4.77528
H   -0.68700  0.86695 -4.82434
C   -0.08759 -0.82368 -4.75745
5.H2
SCF = -2467.35126205
H(0 K) = -2466.510675
G(298 K) = -2466.608606
Low Freq. = 11.3515cm-1, 17.7210cm-1
SCF wB97XD(BS2,D3BJ,THF) = -3203.42730829
C   -3.49700  1.76027 -0.63721
C   -3.23179  0.41556 -0.97642
C   -3.65607 -0.05800 -2.23625
C   -4.34080  0.78694 -3.12545
C   -4.62306  2.11334 -2.76588
C   -4.19845  2.59732 -1.51813
P   -2.28392 -0.69534  0.21255
C   -2.95438 -2.36852 -0.38259
C   -2.14319 -3.23981 -1.13556
C   -2.65880 -4.43626 -1.66098
SCF wB97XD(BS2,D3BJ,THF) = -5023.93815508
G(298 K) = -2467.33812887

TS(5.H2-Int(5-mer-8))

H -1.73358  6.07050  -1.98973
H -1.92448  5.04877  -4.27053
H -1.21127  2.66780  -4.61915
H -0.32281  1.34243  -2.72830
H -1.72445  1.70022  2.20861
H -2.38582  3.07547  4.16616
H -1.11469  5.16599  4.72515
H  0.80641  5.86664  3.27740
H  1.44728  4.50538  1.30260
H  2.72327  1.84002  1.79365
H  5.09692  2.47979  1.49435
H  5.86547  3.50907  -0.66395
H  4.21070  7.81278  -2.09303
H  1.83148  3.24884  -2.20553
H -1.79069 -1.38633  3.02964
H -3.10345 -1.25150  5.13169
H -5.40773  0.26003  5.11965
H -6.38260  0.56637  2.96360
H -5.08191  0.40918  0.85995
H -1.08809 -2.98989 -1.28873
H -2.00610 -5.09556 -2.24271
H -4.39928 -5.72462 -1.82927
H -5.85461 -4.20737 -0.46373
H -4.94754 -2.09180  0.44765
H -3.45696 -1.09661 -2.52218
H -4.66344  0.39807 -4.09738
H -5.16793  2.76811 -3.45405
H -4.40070  3.63412 -1.23116
H -3.16746  2.15690  0.32853
H  0.51229 -0.05553  2.15252
H -0.36301 -0.15263  2.18083
TS(5,H2-Int(5-mer-8))
SCF = -2467.33812887
G(298 K) = -2466.499496

Low Freq. = -520.3196cm⁻¹, 8.5407cm⁻¹
SCF wB97XD(BS2,D3BJ,THF) = -5023.93815508

109
C -4.77450 -0.23860 -1.32730
C -3.42257 -0.64387 -1.37697
C -2.87831 -0.10488 -2.62370
C -3.65424 -0.97624 -3.79315
C -4.99311 -0.55595 -3.73400
C -5.54999 -0.18873 -2.49849
P -2.32882 -0.77958  0.16398
C -4.82017 -2.50891  0.75245
C -2.91922 -3.10570  1.80615
C -2.43936 -3.37732  2.28866
C -3.51438 -5.07979  1.72054
C -4.24435 -4.49637  0.67406
C -3.90528 -3.21875  0.19709
Ru  0.00977  0.53739  0.06689
C  0.40602 -2.48880 -0.88154
C -0.32422 -3.48188 -1.58037
C  0.35045 -4.57672 -2.15538
C  1.74544 -4.71771 -2.05691
C  2.49311 -3.75671 -1.34428
C  1.81731 -2.69054 -0.74789
P  2.31635 -1.20217  0.22918
C  2.97249 -1.83362  1.86360
C  4.02034 -2.77915  1.91704
C  4.47596 -3.26302  3.15220
C  3.90002 -2.79894  4.34788
C  2.86445 -1.85319  4.30229
C  2.39900 -1.37630  3.06475
Zn  0.36338 -0.08462 -2.35856
SCF $wB97XD(BS2,D3BJ,THF) = -5023.97676643$

Low Freq. = 6.7872cm$^{-1}$, 15.2165cm$^{-1}$

SCF $wB97XD(BS2,D3BJ,THF) = -5023.97676643$

\( \text{Int(5-mer-8)} \)

\( \text{H} -3.20031 \) 2.05951 0.11943
\( \text{H} -1.24183 \) 2.56705 2.23935
\( \text{H} -1.86058 \) -4.82120 3.10583
\( \text{H} -3.77911 \) -6.07644 2.08942
\( \text{H} -5.08382 \) -5.03514 0.22122
\( \text{H} -4.49025 \) -2.77908 -0.61555
\( \text{H} -1.82973 \) -1.33200 -2.67762
\( \text{H} -3.20730 \) -1.26888 -4.74910
\( \text{H} -5.59887 \) -0.51491 -4.64554
\( \text{H} -6.59418 \) 0.13764 -2.44112
\( \text{H} -5.22470 \) 0.04321 -0.37106
\( \text{H} -0.13865 \) -0.53625 1.71461
\( \text{H} -0.09459 \) -2.14470 0.41992

109

\( \text{Ru} -0.03760 \) -0.38683 0.04951
\( \text{C} 1.77556 \) -3.39162 -1.49049
\( \text{C} 2.14980 \) -4.46508 -2.31488
\( \text{C} 3.48213 \) -6.04393 -2.73561
\( \text{P} 4.43818 \) -3.66474 -2.31944
\( \text{C} 4.60651 \) -2.95390 -1.48995

9

\( \text{Zn} -0.08434 \) -0.68716 -2.29122

9

\( \text{C} -0.15420 \) -0.92614 -4.24784

109

\( \text{P} 0.08135 \) 1.99855 0.03038

109

\( \text{C} 1.29363 \) 2.89009 -1.10772

9

\( \text{C} 1.26900 \) 2.57368 -2.48361
\( \text{C} 2.09130 \) 3.25167 -3.39715
\( \text{C} 2.97063 \) 4.24930 -2.94416
\( \text{C} 3.01740 \) 4.55924 -1.57624
\( \text{C} 2.18149 \) 3.89088 -0.66572
\( \text{C} 3.65574 \) 0.11242 -0.05351
\( \text{C} 4.40768 \) 0.55554 1.05451
\( \text{C} 5.45278 \) 1.48036 0.88747
\( \text{C} 5.76537 \) 1.97155 -0.38859
\( \text{C} 5.01422 \) 1.54710 -1.49766
\( \text{C} 3.96201 \) 0.63592 -1.32978
\( \text{C} -1.43889 \) 3.08847 -0.25553
\( \text{C} -2.53475 \) 2.93342 0.62176
\( \text{C} -3.68342 \) 3.72540 0.48833
\( \text{C} -3.76610 \) 4.68070 -0.53876

S85
G(298 K) = -2467.829237
H(0 K) = -2467.728709
mer-8-Zn

H   0.73441 -3.28409 -1.16760
H  -0.05621 -2.01164  0.19803
H  -5.17345 -0.35335  0.95897
H  -6.61935  2.04234 -2.34069
H  -4.35685  1.92519 -3.41236
H  -4.65419 -4.19623 -2.95078
H  -3.51901 -6.21283 -1.99030
H  -1.88332 -5.93079 -0.10895
H   0.05621 -2.01164  0.19803
H   0.73441 -3.28409 -1.16760

mer-8-Zn

SCF = -2468.58851402
H(0 K) = -2467.728709
G(298 K) = -2467.829237

Low Freq. = 14.8105cm⁻¹, 18.9139cm⁻¹

SCF wB97XD(BS2,D3BJ,THF) = -3205.88374972
C  -0.17136  3.37508  0.20100
C  -0.31817  4.07872  1.41451
H   0.21180  3.73582  2.30845
C   -1.13553  5.22016  1.49044
H   -1.23458  5.75136  2.44453
C   -1.81757  5.68062  0.35332
H   -2.45095  6.57354  0.41184
C   -1.68310  4.98414  -0.86086
H   -2.21657  5.32998  -1.75516
C   -0.87299  3.84072  -0.93614
H   -0.79197  3.29304  -1.88047
C   -2.35421  2.60950  -0.90757
C   -3.27920  1.59994  -5.50127
H   -3.90143  0.68145  -1.55010
C   -4.40444  2.28576  -2.20414
H   -5.10952  1.60440  -2.69343
C   -4.61970  3.67367  -2.24021
H   -5.49237  4.08523  -2.76096
C   -3.70431  4.53022  -1.60878
C   -3.85793  5.61576  -1.63315
H   -2.58438  4.00178  -0.94246
C   -1.88040  4.68107  -0.45129

TS (2-5) H
SCF  =  -219.00584040
H(0 K)=  -219.223423
G(298 K)=  -219.318877
Low Freq.  = -89.5537cm-1, 8.9686cm-1
SCF  wB97XD(BSZ,D3BJ,THF) = -3203.41136420

102
Ru -0.01720  0.00453  -0.80313
H   0.05317  0.99411  -2.40446
P   1.50060 -1.62565  -0.04461
H   0.79313  2.08918  -0.00649
P   -2.12317 -2.97066  -0.00073
C   -0.09995  1.69434  -1.98991
H   0.83426 -2.63155  -1.45135
C   1.14672  3.86037  -2.04915
H   1.89690 -4.52983  -1.60935
C   0.48544 -4.20581  -3.24725
H   0.69839  -5.16200  -3.74016
C   -0.43944  3.30803  -3.81365
C   -0.94105 -3.57840  -4.75315
C   -0.73510 -2.07064  -3.20207
H   -1.46569 -1.39911  -3.67279
C   -3.37372 -1.72432  -0.29421
C   -3.89899 -0.98807  -1.38125
H   -3.21484 -0.41086  -2.01314
C   -5.27602  0.98838  -1.65231
H   -5.65735  0.41024  -2.50189
C   6.16044  -1.71139  -0.83144
H   7.23757  -1.70315  -1.03539
C   5.65044  -3.44005  -0.25503
H   6.32937  -3.01041  -0.90105
C   4.26962  -4.44991  -0.52006
C   3.88868  -3.02780  -1.36744
H   1.31647  -2.60169  -1.53767
C   0.61802  -3.82656  1.58602
C   0.21480 -4.25038  -0.66072
C   0.42105 -4.48926  2.80859
H   -0.13400 -5.43407  2.82558
C   0.92330 -3.94514  4.00190
H   0.76948  -4.46467  4.95475
C   1.61480  -2.72088  3.96641
C   2.00472  -2.28196  4.89255
H   1.80089  -2.05059  2.74816
H   2.33003  -1.09013  2.73149

5H
SCF  =  -219.00584040
H(0 K) = -2198.22745
G(298 K) = -2198.32065
Low Freq. = 8.7521 cm^{-1}, 15.1499 cm^{-1}
SCF wB97XD(BS2,D3BJ,THF) = -3203.42730829

102
Ru 0.06614 -0.56581 0.18748
H -0.94055 -1.80681 -2.28804
P -2.21181 -0.75112 0.04135
P 2.31335 -1.21995 0.01037
P 0.25266 1.73065 0.04553
C -1.91537 -2.31542 -2.28969
C -2.79026 -2.05232 -2.14887
C -0.42321 -2.73337 -1.16206
H -4.70941 -2.55989 -0.32676
C -4.37671 -6.52532 -2.16473
H -5.35556 -4.18125 -2.10363
C -3.50600 -3.89527 -3.24001
H -3.78393 -4.61152 0.04227
C -2.27346 -3.22391 -3.29929
H -1.58036 -3.41763 -4.12629
C -3.11664 -1.31311 1.61980
C -4.50762 -1.19512 1.83956
C -5.14420 -0.74654 0.06942
C -5.08401 -1.61630 3.05052
C -6.16523 -1.51315 3.20274
C -4.27845 -2.15928 4.06493
C -4.72785 -2.48248 5.01140
C -2.89287 -2.27406 3.86212
C -2.25365 -2.69012 4.64980
C -2.31739 -1.85025 2.65252
H -1.23402 -1.91118 2.48306
C -3.39797 0.64100 -0.46252
C -3.88226 0.76291 -1.78236
C -3.60577 0.01358 -2.53034
C -4.72303 1.82645 -2.14831
C -5.08558 1.89690 -3.18037
C -5.10022 2.79202 -2.10160
C -5.76150 3.61854 -1.48632
C -4.61400 2.69194 0.11225
C -4.89207 3.44151 0.86245
C -3.76817 1.63220 0.47478
H -3.40052 1.57039 1.50354
H -0.28034 -2.66650 0.31867
C 1.67948 -2.93432 0.17213
C 2.27697 -4.20292 0.23494
H 3.36328 -4.32253 0.13341
C 1.44136 -5.31670 0.44003
H 1.96410 -6.32742 0.49330
C 0.05314 -5.11670 0.58190
H -0.59816 -5.98639 0.74569
H -0.51718 -3.83188 0.52140
H -1.60499 -3.74729 0.63556
C 3.35133 -1.13307 -1.54197
C 4.13412 0.01063 -1.82822
C 4.18915 0.83042 -1.10430
C 4.84219 0.10733 -3.03644
H 5.44033 1.00350 -3.23857
C 4.78137 -0.92982 -3.98270
H 5.33279 -0.85041 -4.92671
C 4.00456 -2.06923 -3.70786
H 3.95065 -2.88665 -4.34638
C 2.29555 -2.16956 -2.50085
H 2.69014 -3.05763 -2.28944
C 3.61801 -1.08733 1.36568
C 5.00383 -1.26324 1.7667
H 5.39603 -1.44038 0.16961
C 5.88702 -1.20533 2.26886

TS (5-7) H

SCF = -2200.19076050
H(0 K) = -2199.393703
G(298 K) = -2199.490549
Low Freq. = -43.5606 cm^{-1}, 8.6938 cm^{-1}
SCF wB97XD(BS2,D3BJ,THF) = -3204.60690315

104
Ru 0.01553 -0.36427 -0.63528
H -5.23484 -0.04991 0.01896
P -2.16959 -0.71176 -0.13893
P 2.12137 -1.29314 -0.22569
P 0.36779 1.85574 -0.00425
C -4.91959 -0.01320 -1.02949
C -3.57372 -0.27970 -1.36586
C -3.19915 -0.20594 -2.72436
H -2.14633 -0.38467 -2.97947
C -4.13840 0.10722 -3.72055
H -3.82404 0.15412 -4.76988
C -5.47362 0.37208 -3.37131
H -6.20720 0.62923 -4.14440
C -5.86012 0.31413 -2.02210
H -6.89870 0.52495 -1.73909
C -2.64987 -2.51439 0.24533
C -3.92863 -3.06258 0.01741
H -4.70818 -2.45485 -0.45250
C -4.21642 -4.39107 0.37544
| Atom  | X         | Y         | Z       |
|-------|-----------|-----------|---------|
| H     | -0.02292  | -5.41412  | -3.74352|
| C     | -0.84059  | -3.40284  | -3.92167|
| H     | -1.39870  | -3.64264  | -4.83722|
| C     | -0.92169  | -2.10362  | -3.38189|
| H     | -1.53898  | -1.35106  | -3.88909|
| C     | 3.17161   | -1.97108  | -0.45105|
| C     | 3.72445   | -2.31562  | -1.70291|
| H     | 3.05462   | -2.61140  | -2.51725|
| C     | 5.11448   | -2.28066  | -1.90608|
| H     | 5.52541   | -2.55524  | -2.88489|
| C     | 5.97466   | -1.89952  | -0.86308|
| H     | 7.05883   | -1.87207  | -1.02228|
| C     | 5.43349   | -1.54786  | 1.13864|
| H     | 6.09388   | -1.23971  | 1.20428|
| C     | 4.04509   | -1.58076  | 0.58921|
| C     | 3.63489   | -1.29332  | 1.56379|
| C     | 1.17227   | -0.04800  | 1.29649|
| C     | 0.16674   | -2.77829  | 2.24664|
| H     | -0.47134  | -1.89685  | 2.10880|
| C     | -0.02586  | -3.62167  | 3.35427|
| H     | -0.81410  | -3.38958  | 4.07937|
| C     | 0.79171   | -4.74193  | 3.50218|
| C     | 0.67637   | -5.09022  | 4.39372|
| C     | 1.80197   | -5.02736  | 2.59132|
| C     | 2.44581   | -5.09546  | 2.72228|
| C     | 1.99275   | -4.18223  | 1.48666|
| C     | 2.79246   | -4.39089  | 0.76958|
| C     | 2.40881   | 2.65352   | -1.19088|
| C     | 2.50436   | 4.03217   | -1.47047|
| C     | 1.71529   | 4.72150   | -0.07326|
| C     | 3.55272   | 4.53735   | -2.62619|
| C     | 3.59872   | 5.61182   | -2.47724|
| C     | 4.53347   | 3.67362   | -2.77133|
| C     | 5.35115   | 4.06661   | -3.38715|
| C     | 4.45470   | 2.29875   | -2.48839|
| C     | 5.21209   | 1.60977   | -2.87920|
| C     | 3.39940   | 1.79395   | -1.71464|
| C     | 3.32625   | 0.71817   | -1.52622|
| C     | 2.00352   | 1.79553   | 1.50831|
| C     | 1.58798   | 0.83835   | 2.45598|
| C     | 0.74240   | 0.18904   | 2.20319|
| C     | 2.25653   | 0.69716   | 3.68367|
| C     | 1.91553   | -0.05641  | 4.40255|
| C     | 3.36495   | 1.50859   | 3.97874|
| C     | 3.89660   | 1.39326   | 4.93063|
| C     | 3.79372   | 2.46292   | 0.30112|
| C     | 4.66262   | 3.09565   | 3.25904|
| C     | 3.11687   | 2.60684   | 1.87153|
| C     | 3.46413   | 3.34973   | 1.09144|
| C     | 0.02146   | 3.45524   | 0.19017|
| C     | -0.94904  | 3.78365   | -0.78168|
| C     | -1.06755  | 3.12317   | -1.64769|
| C     | -1.76428  | 4.91523   | -0.63029|
| C     | -2.51780  | 5.14274   | -1.39222|
| C     | -1.63571  | 5.73176   | 0.50682|
| C     | -2.28173  | 6.60826   | 0.63385|
| C     | -0.68088  | 5.40986   | 1.48418|
| C     | -0.57390  | 6.03845   | 2.37660|
| C     | 0.14633   | 4.28342   | 1.32467|
| C     | 0.89463   | 4.05063   | 2.08920|
| C     | -0.57530  | 0.81300   | -2.25354|
| C     | 1.26292   | 0.09650   | -2.08702|

| TS1(7-8)H | SCF = -2200.21384950 |
| H(0 K) | = -2199.41164 |
| G(298K) | = -2199.505534 |
| Low Freq. | = -90.5689cm-1, 13.1869cm-1 |

SCF wB97XD(BS2,D3BJ,THF) = -3204.62969321
H  -2.68562  -0.65815  -2.65928
H  -4.46724  -0.81935  -4.23839
H  -6.72672  0.50309  -3.77476
H  -6.84192  1.95723  -1.73791
H  -4.90199  2.08509  -0.18057
H  -0.88064  0.12737  2.34579
H  -1.59191  -0.95723  4.47124
H  -3.92293  -1.87125  4.70301
H  -5.53463  -1.62726  2.79933
H  -4.84258  -0.47280  0.71113
H  2.40170  -4.25379  -1.50097
H  3.33289  -4.20944  -3.83522
H  2.63541  -2.40535  -5.19022
H  1.00909  -0.64470  -4.70017
H  -2.57655  -2.23137  -0.61262
H  -4.31425  -4.03838  -0.68215
H  -3.66174  -6.41690  -0.22836
H  -1.27733  -6.96538  0.31284
H  0.43078  -5.15698  0.40759
H  3.32047  -2.40677  -0.01208
H  4.85755  -2.95246  1.85373
H  3.94561  -3.60243  4.10141
H  1.46130  -3.68637  4.44467
H  -0.07939  -3.14229  2.57254
H  2.40545  -0.27491  2.33128
H  2.01876  0.06109  4.75073
H  0.87033  2.13971  5.57860
H  0.10934  3.86332  3.91738
H  0.50363  3.53177  1.49709
H  0.95375  2.59201  -2.62483
H  1.54935  4.79413  -3.68962
H  2.92635  4.46191  -2.41895
H  3.72405  5.90029  -0.10932
H  3.15960  3.70583  0.90921
H  3.00935  -0.22103  -2.17051
H  5.34739  -0.99683  -2.57435
H  7.12401  -0.58720  -0.84431
H  6.53224  0.63477  1.26308
H  4.21105  1.43452  1.63771

Int(7-8)H
SCF = -2200.21766961
H(0 K)= -2199.414582
G(298 K)=-2199.511414
H(0 K)= -2199.414582
Low Freq. = 9.2277 cm⁻¹, 15.7115 cm⁻¹
SCF wB97XD(BS2,D3BJ,THF) = -3204.63568300

104
C  4.60884  0.54360  0.66882
C  3.60347  0.40553  -0.29163
C  3.89839  -0.35425  -1.44432
C  5.15808  -0.94795  -1.62122
C  6.14721  -0.81076  -0.63159
C  5.86520  -0.06555  0.52470
P  1.85765  1.18878  -0.22590
C  2.41949  2.82758  -1.03723
C  1.86901  3.18923  -2.28101
C  2.29588  4.34942  -2.95126
C  3.27737  5.17355  -2.37869
C  3.83418  4.82496  -1.13572
C  3.41354  3.65900  -0.47670
Ru  -0.08725  0.18455  -0.80308
C  0.86152  -2.07023  -2.84288
C  0.89218  -2.86798  -1.67650
C  1.38328  -4.18425  -1.76083
C  1.85479  -4.69157  -2.98649
C  1.82158  -3.89259  -4.14043
C  1.31851  -2.58003  -4.06969

S92
H  -0.22640 -2.52949  2.75321  
C   2.34568 -0.24240  2.34712  
H   2.01338  0.35169  4.72660  
C   1.20176  2.64585  5.36224  
H   0.73459  4.32618  3.55679  
P   1.08657  3.73642  1.17408  
H   1.08719  2.54297 -2.70127  
C   1.85566  4.61070 -3.92117  
C   3.60853  6.08204 -2.89567  
H   4.60262  5.46126 -0.68010  
C   3.86418  3.39274  0.48556  
P   3.11543 -0.48994 -2.20005  
C   5.36215 -1.52983 -5.25777  
H   7.12758 -1.28472 -0.75888  
P   6.62782  0.04598  1.30535  
C   4.04700  1.12077  1.59724  

8H

SCF = -2201.45188282
H(0 K)= -2200.630395
G(298 K)= -2201.45188282
Low Freq. = 19.8209cm-1, 19.8211cm-1

H   4.40700  1.12077  1.59724  
C   2.10631  2.77523 -1.61312  
C   2.13623  1.37272 -1.43288  
C   2.04977  0.55367 -2.58310  
C   1.97554  1.11640 -3.86677  
C   1.96350  2.52127 -4.03293  
P   2.01960  3.33798 -2.89751  
P   -2.04040  0.59574  0.28541  
C   -3.38241 -0.75080  0.11992  
C   -4.41242 -0.73562 -0.84459  
C   -5.39695 -1.73785 -0.86425  
C   -5.37937 -2.76764  0.09045  
C   -4.36647 -2.78632  1.06351  
C   -3.37651 -1.78997  0.07290  
Ru  0.00000  0.00000  1.25493  
C   0.54539 -2.05199 -2.58310  
P   -0.12069 -2.53639 -1.43288  
C   -1.35027 -3.21173 -1.61312  
C   -1.88094 -3.41808 -2.89751  
C   -1.19385 -2.95653 -4.03293  
P   0.02094 -2.26907 -3.86677  
P   0.50427 -2.06491  0.28541  
P   2.34142 -2.55385  0.11992  
P   2.84327 -3.45345 -0.84459  
P   4.20350 -3.80497 -0.86425  
P   5.08653 -3.27485  0.09045  
P   4.59626 -2.38832  1.06351  
P   3.23841 -2.02915  1.07290  
Ru  0.14571  1.15178  2.40252  
C   1.07033 -0.44970  2.40252  
P   1.53613  1.46917  0.28541  
P   1.04099  3.30465  0.11992  
P   0.13809  3.81913  0.07290  
P   -0.22979  5.17464  1.06351  
P   0.29284  6.04249  0.09045  
P   1.19346  5.54282 -0.86425  
P   1.56914  4.18907 -0.84459  
P   3.14061  1.84074  1.25565  
P   3.19931  1.48141  2.61601  
P   4.32517  1.79706  3.39665  
P   5.41454  2.47439  2.82680  
P   5.36550  2.84270  1.47137  
P   4.23559  2.53524 -0.69705  
P   2.25692  1.16367 -1.43288  

fac=4Mg

SCF = -2239.78274002
H(0 K)= -2238.961988
G(298 K)= -2239.060668
Low Freq. = 13.8470cm-1, 17.1286cm-1
SCF wB97XD(BS2,D3BJ,THF) = -3443.40711332

Ru  0.02161  0.01197 -0.75544

S93
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| C       | 4.68795  | -3.72492 | -4.15350 |
| H       | 4.68795  | -3.72492 | -4.15350 |
| C       | 3.53155  | -1.97744 | 3.58201  |
| H       | 3.53155  | -1.97744 | 3.58201  |
| C       | 3.40643  | -1.61769 | 4.60831  |
| H       | 3.40643  | -1.61769 | 4.60831  |
| C       | 2.95721  | -1.25962 | 2.51902  |
| H       | 2.95721  | -1.25962 | 2.51902  |
| C       | 2.42047  | -0.32434 | 2.72642  |
| H       | 2.42047  | -0.32434 | 2.72642  |
| C       | 2.77956  | -1.58890 | 1.74485  |
| C       | 4.12984  | -1.62810 | 2.16048  |
| C       | 4.90055  | -1.13930 | 1.55536  |
| H       | 4.90055  | -1.13930 | 1.55536  |
| C       | 4.49312  | -2.27895 | 3.59992  |
| H       | 4.49312  | -2.27895 | 3.59992  |
| C       | 5.54284  | -2.30572 | 3.65592  |
| H       | 5.54284  | -2.30572 | 3.65592  |
| C       | 3.50780  | -2.88513 | 4.15078  |
| H       | 3.50780  | -2.88513 | 4.15078  |
| C       | 2.16298  | -2.84137 | 2.75266  |
| C       | 2.95721  | -1.25962 | 2.51902  |
| H       | 2.95721  | -1.25962 | 2.51902  |
| C       | 1.80167  | -2.20056 | 2.55503  |
| C       | 1.75720  | -2.17189 | 2.22583  |
| C       | 3.44515  | 0.67018  | 0.31615  |
| C       | 3.34214  | 1.57206  | 1.46790  |
| C       | 2.57321  | 1.35929  | 2.21642  |
| C       | 4.22415  | 2.64189  | 1.67668  |
| C       | 4.12858  | 3.25204  | 2.58132  |
| C       | 5.25213  | 2.92536  | 0.73239  |
| C       | 5.91810  | 3.75785  | 0.89506  |
| C       | 3.53227  | 2.13056  | -0.41801 |
| C       | 6.11008  | 2.33909  | -1.16066 |
| C       | 4.45209  | 1.05355  | -0.62423 |
| C       | 4.56773  | 0.43538  | -1.51860 |
| C       | -0.30040 | -2.12425 | -4.33345 |
| C       | 0.35615  | -2.98177 | -4.57440 |
| C       | -0.04515 | -1.31014 | -5.03920 |
| C       | -1.33876 | -2.43293 | -4.55801 |

**TS (fac-4-5) A-Mg**

**SCF = -2239.73749964**

**H(0 K)= -2238.919392**

**G(298 K)= -2239.020520**

**Low Freq. = -658.4086cm⁻¹, 6.9754cm⁻¹**

**SCF wB97XD(BS2,D3BJ,THF) = -3443.35543954**
H  -0.53298  0.11431  4.81621  
C  -2.03666  1.67679  4.66473  
H  -2.32874  1.61467  5.71856  
C  -2.67149  2.59422  3.81027  
H  -3.45745  3.25220  4.19693  
C  -2.30513  2.67037  2.45643  
H  -2.80861  3.38449  1.79701  
C  -3.43970  -0.59587  -4.12146  
H  -4.47358  -0.34068  -3.82226  
H  -3.45934  -1.62542  -4.52701  
H  -3.17722  0.07482  -4.96276  

Int(fac=4-5)A-Mg  
SCF = 0.029373707  
H(0 K)= -2238.921736  
G(298 K)= -2238.921736  
Low Freq. = 8.8805cm^{-1}, 11.9185cm^{-1}  
SCF wB97XD(BS2,D3BJ,THF) = -3443.36467758  

107  
Ru  -0.03648  -0.20709  -0.75662  
H  0.54469  1.27195  -1.87379  
P  -1.03822  -1.95774  0.35310  
P  2.31718  0.06929  -0.03593  
P  -1.16090  1.70460  0.12347  
Mg  -1.73202  -0.68402  -2.65107  
C  0.27186  -2.05725  -1.76215  
C  0.93427  -2.53513  -2.92703  
H  1.43459  -1.83495  -3.60720  
C  0.98229  -3.91641  -3.20931  
C  1.50487  -4.29592  -4.11077  
C  0.38793  -4.86848  -2.35895  
C  0.44813  -5.93511  -2.59661  
C  -0.29410  -4.43923  -1.20058  
C  -0.76222  -5.16247  -0.52232  
C  -0.35201  -3.06399  -0.95058  
P  -2.88573  -2.21213  0.41082  
P  -3.65384  -1.60331  1.43012  
P  -3.15701  -1.03257  2.22209  
P  -5.05203  -1.72342  1.43160  
P  -5.63401  -1.24723  2.22781  
P  -5.70387  -2.44493  0.41650  
P  -6.79511  -2.53542  0.41983  
P  -4.94804  -3.05497  -0.59832  
P  -5.44537  -3.62886  -1.38746  
P  -3.54708  -2.94433  -0.60034  
P  -2.96259  -3.44324  -1.38176  
P  -0.51279  -2.66769  0.01112  
P  -1.29776  -3.61819  2.69852  
P  -2.27455  -3.91284  2.30284  
P  -0.83444  -4.18720  3.89588  
P  -1.45428  -4.92243  4.42056  
P  0.41458  -3.81614  4.42000  
P  0.77207  -4.26022  5.35518  
P  1.20336  -2.87508  3.73833  
P  2.18287  -2.58582  4.13386  
P  0.73968  -2.30435  2.54264  
P  1.35283  -1.57531  2.00096  
P  2.61490  0.45662  -1.83435  
P  1.42324  0.87384  -2.47917  
P  1.38525  1.06102  -3.87217  
P  0.46276  1.39821  -4.35809  
P  2.54241  0.81423  -4.63334  
P  2.52561  0.96764  -5.71737  
P  3.71472  0.36061  -4.00443  
P  4.60956  0.15739  -4.60263  
P  3.74944  0.16246  -2.61080  
P  4.65276  -0.22631  -2.12930  

fac=4Mg.THF  
SCF = -2472.24514205  
H(0 K)= -2471.309145  
G(298 K)= -2472.24514205  
Low Freq. = 10.8674cm^{-1}, 16.0164cm^{-1}  
SCF wB97XD(BS2,D3BJ,THF) = -3675.90382811  

120
| Atom  | X-Coordinate | Y-Coordinate | Z-Coordinate |
|-------|--------------|--------------|--------------|
| C     | -2.08180     | -3.70516     | -2.20050     |
| C     | -2.93595     | -3.95624     | -3.28602     |
| H     | -3.37998     | -4.95090     | -3.40609     |
| C     | -3.22010     | -2.94162     | -4.21427     |
| H     | -3.88429     | -3.14055     | -5.06231     |
| C     | -2.65322     | -1.66916     | -4.04358     |
| H     | -2.87208     | -0.86709     | -4.75649     |
| C     | -1.80783     | -1.41645     | -2.95086     |
| H     | -3.05158     | 0.89046      | -0.32101     |
| C     | -4.50885     | 1.65405      | 0.01845      |
| C     | 4.39643      | 2.16106      | 0.98180      |
| C     | 5.51287      | 2.06399      | -0.87484     |
| H     | 6.18928      | 2.87912      | -0.59401     |
| C     | 5.65512      | 1.42728      | -2.12014     |
| H     | 6.44065      | 1.74500      | -2.81422     |
| C     | 4.78380      | 0.38204      | -2.46939     |
| C     | 4.88275      | -0.12063     | -3.43694     |
| C     | 3.77725      | -0.02929     | -1.57868     |
| H     | 3.10711      | -0.84676     | -1.86336     |
| C     | -3.05158     | 0.89046      | 2.08501      |
| C     | -4.42688     | 1.16228      | 2.26300      |
| H     | -5.05324     | 1.38985      | 1.39400      |
| C     | -5.00326     | 1.12811      | 3.54200      |

SCF = -2704.68019924
H(0 K) = -2703.624738
G(298 K) = -2703.738261

Low Freq. = 15.6862 cm⁻¹, 18.0096 cm⁻¹
SCF wB97XD(BS2,D3BJ,THF) = -3908.3665743

Mg.2THF

Ru -0.23231 0.06660 -0.44654
H -2.66465 -3.03781 2.66855
P -0.50036 -1.17221 1.57082
P -2.52623 0.73103 -0.73135
P 1.71992 -0.85376 -1.34098
Mg 0.55233 2.20890 0.92736
O 2.41507 2.08060 2.12309
O 1.46532 3.84057 -0.28107
C -2.95787 -2.00916 2.89770
C -4.15054 -1.77205 3.60361
H -4.77594 -2.61917 3.90715
C -4.53642 -0.46052 3.92263
H -5.46600 -0.27668 4.47201
C -3.72382 0.61429 3.52740
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