

Preparation of [(1,4,7-Trimethyl-1,4,7-triazacyclononane)Rh(PR₃)(H)(CH₃)⁺ and Its Carbon–Hydrogen Reductive-Elimination and Oxidative-Addition Chemistry

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We report the preparation of an unusually stable rhodium methyl hydride in a unique organometallic coordination environment for rhodium, namely, [CnRh(L)(H)Me][BAR₄] (**1a**, L = PMe₃; **1b**, L = P(OMe)₃; Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane; and ⁻BAR₄ = {B[C₆H₃-3,5-(CF₃)₂]₄}⁻) (Scheme 1), wherein the principal ligand is a “hard”, facial tri-tertiary-amine chelate and the complex is cationic.² We show that the reductive elimination of methane from this species is reversible and provide evidence for involvement of a methane–rhodium “σ complex”.³ In addition to reactivating methane, the intermediate generated from methane elimination activates benzene and is trapped by ethylene to form an η²-ethylene complex.

In our exploration of the organometallic chemistry of rhodium in the unconventional “hard” coordination environment of the “Cn” ligand,⁴ we have prepared complexes **1** by the reactions shown in Scheme 1,⁵ all of which afford 90% or greater yields

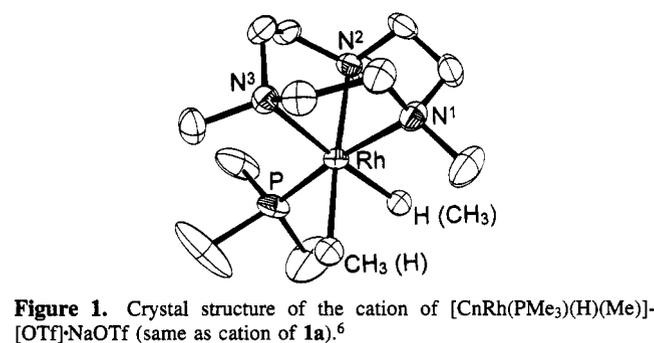
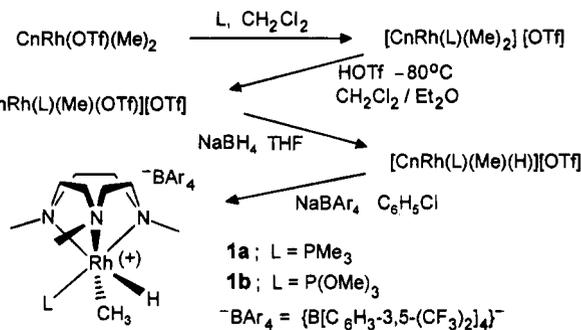


Figure 1. Crystal structure of the cation of [CnRh(PMe₃)(H)(Me)][OTf]·NaOTf (same as cation of **1a**).⁶

Scheme 1



(1) (a) University of Southern California. (b) University of California at Irvine.

(2) Other alkyl hydrides of Rh are less thermally stable than **1a** or **1b**. Also, with the exception of the complexes of tris(3,5-dimethylpyrazolyl)-borate anion (HBPz₃⁻), all of the known rhodium alkyl hydrides exist in a “soft” ligand environment whose principal ligands are Cp, Cp*, CO, PR₃, etc. It is likely that HBPz₃⁻ is significantly “harder” than Cp or Cp*. However, it is not yet clear how to compare HBPz₃⁻ anion and Cn (neutral), although it seems that Cn, having no low-lying π molecular orbitals, may be harder. (a) Cp*Rh(PMe₃)(H)Me loses methane at -17 °C: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Several Cp*Rh(PMe₃)(H)R were prepared below -60 °C. Cp*Rh(PMe₃)(H)Et loses ethane at -30 °C: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (c) (HBPz₃)Rh(CO)(H)Me is too unstable to isolate at room temperature: Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (d) (HBPz₃)Rh(CN-*t*-Bu)(H)Me loses methane at 23 °C with *t*_{1/2} = 5.6 h: Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554.

(3) Complexes of intact alkanes have been postulated in several cases, based at least in part on an inverse isotope effect for alkane loss from alkyl hydrides, all of which lie in the range *k*_H/*k*_D = 0.5–0.8. The inverse effect is believed to come from a thermodynamic effect on the M(H)R ⇌ M(alkane) equilibrium preceding alkane loss. (a) Cyclohexane loss from Ir: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Ethane from Rh: ref 2b. (c) Methane from W: Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. (d) Methane from Re: Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502. (e) Methane from W: Parkin, G.; Bercau, J. E. *Organometallics* **1989**, *8*, 1172.

(4) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999.

(5) Both **1a** and **1b** have been fully characterized. For example, data for **1a**: ¹H NMR (500 MHz, DMSO-*d*₆) δ -19.61 (dd, *J*_{PH} = 40.3 Hz, *J*_{RhH} = 25.7 Hz, RhH), -0.01 (dd, *J*_{PH} = 3.7 Hz, *J*_{RhH} = 1.9 Hz, RhCH₃), 1.36 (d, *J*_{PH} = 9.4 Hz, PCH₃), 2.58, 2.78, 2.85 (s, NCH₃), 2.90–3.00 (m, NCH₂), 7.60 (s, -BAR₄-*o*-H), 7.67 (s, -BAR₄-*p*-H); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ -4.85 (dd, *J*_{RhC} = 25.9 Hz, *J*_{PC} = 14.0 Hz, RhCH₃), 17.97 (dd, *J*_{PC} = 32.6 Hz, *J*_{RhC} = 1.6 Hz, PCH₃), 50.55, 53.01, 54.85 (s, NCH₃), 57.14, 57.98, 58.42, 59.14, 60.48, 66.98 (s, NCH₂), 117.64 (s, -BAR₄-C₄), 123.98 (q, *J*_{FC} = 272.9 Hz, -BAR₄-CF₃), 128.46 (q, *J*_{FC} = 32.7 Hz, -BAR₄-C₃), 134.00 (s, -BAR₄-C₂), 160.92 (q, *J*_{BC} = 50.3 Hz, -BAR₄-C₁(ipso)); ³¹P{¹H decoupled, RhH coupled} (202 MHz, DMSO-*d*₆) δ 2.99 (dd, *J*_{RhP} = 144.7 Hz, *J*_{HP} = 35.6 Hz); IR (KBr) 2053 cm⁻¹, ν_{RhH}. Elemental anal. Calcd for **1a**. C₄₅H₄₆F₂₄N₃PBRh: C, 43.96; H, 3.77; N, 3.42. Found: C, 43.96; H, 3.27; N, 3.20.

of isolated material. The stability of **1** is noteworthy in view of the more limited stability of other rhodium alkyl hydrides.² It is indefinitely stable as a solid at room temperature and is water stable, but it is slowly oxidized by O₂ in solution. Both **1a** and **1b** are insoluble in alkanes, but soluble to the extent of ca. 2 mg/mL benzene and 10 mg/mL in C₆F₆. An X-ray diffraction study⁶ of [CnRh(PMe₃)(H)(Me)][OTf]·NaOTf shows the rhodium methyl group to be partially disordered into the hydride site in the crystal (optimum refinement occurred with assigned methyl site populations of 0.75 and 0.25), so the hydride could not be located. Otherwise, the data confirm the structure of the cation in **1a** (Figure 1).

On heating in C₆D₆ at 75 °C, **1** disappears with clean first-order kinetics and quantitative (NMR) formation of [CnRh(L)-(D)(C₆D₅)] [BAR₄], **2-d**.⁷ The half-life for disappearance of **1a** (*t*_{1/2} = 91 min) is about twice that of **1b**. The rate ratio for reaction of **1a** in C₆H₆ vs C₆D₆ is 1.02 ± 0.02, but the 2/2-*d*₆ ratio from reaction of **1a** in a C₆H₆/C₆D₆ mixture reveals an isotope effect of 1.29 ± 0.02. Intramolecular competition in reaction with 1,3,5-C₆H₃D₃ yields exactly the same isotope effect (1.29 ± 0.02).^{8,9} Thermolysis of **1a** in the presence of excess P(CD₃)₃ in C₆D₆ shows no inhibition of disappearance of **1a**, no incorporation of P(CD₃)₃ into **1a**, and very little formation

(6) X-ray data for **1a** with labeling as in Figure 1 except that the CH₃-(H) site (75% CH₃) is designated C^a below and the H(CH₃) site (25% CH₃) is C^b. Monoclinic in space group C2/c, *a* = 22.112(4) Å, *b* = 10.329(2) Å, *c* = 26.153(4) Å, β = 114.761(13)°, *Z* = 8; reflections used = 4925, number of variables = 315; *R*_F = 4.5%, *R*_{wF} = 5.1%; goodness of fit = 2.32. Bond lengths (Å): Rh–N¹ 2.200(4), Rh–N² 2.219(3), Rh–N³ 2.229(4), Rh–C^a (0.75 carbon) 2.099(5), Rh–C^b (0.25 carbon, Rh–H not located) 1.927(19), Rh–P 2.236(1). Bond angles (deg): N¹–Rh–N² 80.1(1), N¹–Rh–N³ 80.5(1), N²–Rh–N³ 80.5(1), P–Rh–C^a 84.2(2), P–Rh–C^b 82.2(5), C^a–Rh–C^b 83.7(4), P–Rh–N² 103.3(1), P–Rh–N³ 104.5(1), C^a–Rh–N¹ 92.6(2), C^a–Rh–N³ 96.3(2).

(7) Both **2a** and **2b** have been fully characterized. For example, data for **2a** (anion resonances given in footnote 5): ¹H NMR (500 MHz, DMSO-*d*₆) δ -19.39 (dd, *J*_{PH} = 33.5 Hz, *J*_{RhH} = 28.3 Hz, RhH), 1.17 (d, *J*_{PH} = 9.6 Hz, PCH₃), 2.77–2.89 (m, NCH₂), 2.26, 2.92, 3.03 (s, NCH₃), 6.81–7.46 (m, RhC₆H₅); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 17.63 (d, *J*_{PC} = 34.6 Hz, PCH₃), 52.44, 54.30, 54.82 (s, NCH₃), 56.29, 57.47, 59.10, 59.20, 59.57, 61.06 (s, NCH₂), 119.39, 121.95, 128.04, 147.54 (RhC₆H₅); ³¹P{¹H decoupled, RhH coupled} (145 MHz, DMSO-*d*₆) δ 2.49 (dd, *J*_{RhP} = 140.1 Hz, *J*_{HP} = 30.2 Hz); IR (KBr) 2100 cm⁻¹, ν_{RhH}. Elemental anal. C, H, N.

of **2a-d₆**. Instead free Cn is liberated and the salt¹⁰ $\{[(\text{CD}_3)_3\text{P}]_4\text{-Rh}\}[\text{BAR}_4]$ precipitates in high yield. No deuterium is detected in the methane product. In the presence of 0.1 M $\text{P}(\text{CD}_3)_3$ in C_6D_6 at 80 °C, **2a** is unchanged after 20 h. Overall, it appears that methane loss is rate determining, phosphine dissociation is not involved at any point, and the benzene activation is irreversible at 80 °C. The identical intramolecular ($\text{C}_6\text{H}_3\text{D}_3$) and intermolecular ($\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$) kinetic isotope effects indicate that if an intermediate (there may not be an intermediate), such as an arene π -complex or a C–H σ -complex, were involved on the path to benzene activation, its formation must be rapidly reversible, with the subsequent C–H oxidative addition being the slower step of the two. The isotope effect is too large for a secondary effect on simple arene coordination.⁹

The nature of the interaction of rhodium with the methane moiety was investigated. Heating of **1a-d**, $[\text{CnRh}(\text{PMe}_3)(\text{D})(\text{CH}_3)][\text{BAR}_4]$, at 50 °C in $\text{C}_6\text{D}_6/\text{C}_6\text{F}_6$ yields **2-d₆** and CH_3D very slowly, but the equilibrium $\text{Rh}(\text{D})(\text{CH}_3) \rightleftharpoons \text{Rh}(\text{H})(\text{CH}_2\text{D})$ occurs, with the equilibrium ratio of $\text{RhH}/\text{RhD} = 6.59 \pm 0.06$ being established in less than 6 h¹¹ (statistically corrected equilibrium isotope effect = 2.20 ± 0.02).¹² The scrambling is not inhibited by added $\text{P}(\text{CD}_3)_3$. Mass spectral analysis of the methane generated on reaction of a mixture of **1a** and **1a-d₄**, $[\text{CnRh}(\text{PMe}_3)(\text{D})(\text{CD}_3)][\text{BAR}_4]$, at 75 °C in $\text{C}_6\text{H}_6/\text{C}_6\text{F}_6$ revealed a mixture of CH_4 and CD_4 with less than 5% of crossover isotopomers present. Independent measurement of reaction rates of **1a** and **1a-d₄** at 75 °C showed an inverse isotope effect $k_{\text{H}}/k_{\text{D}}$ of 0.74 ± 0.02 for the loss of CH_4 vs CD_4 .^{3,13} In addition, heating **1a** at 80 °C under $^{13}\text{CH}_4$ pressure in C_6F_6 , and monitoring by ^1H and ^{13}C NMR, established that methane loss is reversible.¹⁴ The ^{13}C NMR spectrum clearly showed a very large increase in the methyl resonance corresponding to $[\text{CnRh}(\text{PMe}_3)(\text{H})(^{13}\text{CH}_3)][\text{BAR}_4]$ (**1a-¹³C**; $\delta -4.85$, dd, $J_{\text{RhC}} = 25.9$ Hz, $J_{\text{PC}} = 14.0$ Hz). The isotopic content of the methyl group, which could easily be quantitated from the new doublet of multiplets centered at $\delta 0.26$ ($J_{\text{CH}} = 125.8$ Hz) in the ^1H spectrum, increased as total **1a** disappeared, with the maximum yield of **1a-¹³C** (based on starting **1a**) of 15% occurring at ca. 30% loss of **1a**.¹⁵ The slower rate of disappearance of total **1a** (**1a-¹²C** + **1a-¹³C**) represents an inhibition of loss of **1** in the presence of added methane.

(8) $^{31}\text{P}\{^1\text{H}\}$ NMR with a 1 min pulse delay was used to determine the RhH/RhD ratio for both the $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ and the $\text{C}_6\text{H}_3\text{D}_3$ experiments. The $\text{Me}_3\text{P}-\text{RhD}$ resonance is shifted downfield from the $\text{Me}_3\text{P}-\text{RhH}$ resonance, almost to base-line separation. Computer deconvolution of the resonances allowed accurate integration. Integrals from three separate data acquisitions per sample were averaged.

(9) (a) The isotope effect for rate-determining coordination of C_6H_6 vs C_6D_6 to the intermediate $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ is 1.05, while the oxidative-addition isotope effect, measured by internal competition with $\text{C}_6\text{H}_3\text{D}_3$, is 1.4: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (b) π -Bound arene complexes of the $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ moiety have been directly observed in equilibrium with their aryl hydride isomers: Jones, W. D.; Dong, L. J. *Am. Chem. Soc.* **1989**, *111*, 8722.

(10) The salt $[(\text{Me}_3\text{P})_4\text{Rh}]\text{Cl}$ is known: Jones, R. A.; Real, F. M.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1980**, 511.

(11) Measured by ^2H NMR with pulse delay = 5 s (T_1 of ^2H is 0.91 s for RhCDH_2 and 0.48 s for RhD), from two samples each in THF and in $\text{C}_6\text{H}_6/\text{C}_6\text{F}_6$ (10% C_6H_6 by weight) at 56 °C. No solvent effect was evident.

(12) Other $\text{M}(\text{D})\text{CH} \rightleftharpoons \text{M}(\text{H})\text{CD}$ isomerizations have been observed, and in several cases equilibrium isotope effects have been measured. In the following examples all K_{HD} are statistically corrected to 1/1. (a) Ir, K not measured; ref 3a. (b) W, $K = 1.6$: Ref. 3c. (c) Rh, $K = 2.7$: Ref. 9a. (d) Rh, $K = 2.3$: ref 2b. (e) Re, $K = 3.0$: ref 3d. (f) W, K not measured; ref 3e. (g) Pt, $K = 1.6$: Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. (h) Ru, $K = 2.2$: Linn, D. E.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969.

(13) Measured by monitoring the disappearance of the PMe_3 ^1H NMR resonance of **1a** from duplicate reactions in $\text{C}_6\text{D}_6/\text{C}_6\text{F}_6$ (4% C_6D_6 by weight) at 75 °C; for **1a**, $k = 1.43 (\pm 0.02) \times 10^{-4} \text{ s}^{-1}$; and for **1a-d₄**, $k = 1.93 (\pm 0.04) \times 10^{-4} \text{ s}^{-1}$.

(14) Carried out under 18 atm of methane. Heating **1** in C_6F_6 with or without methane forms two distinct products which have not yet been identified. The solution remains clear and free of visible heterogeneity, and the rate of disappearance of **1a** is cleanly first order, with or without added methane.

The above data are most consistent with a pre-equilibrium between **1** and methane complex $[\text{CnRh}(\text{L})(\text{CH}_4)]^+$, **3**, with rate-determining dissociation of methane from **3** to form 16-electron $[\text{CnRh}(\text{L})]^+$ or its solvent complex $[\text{CnRh}(\text{L})(\text{solvent})]^+$, **4**. Then **4** coordinates another hydrocarbon, or recoordinates methane at higher methane concentrations, and oxidatively adds the C–H bond. Intermediate **4** can also be intercepted by other hydrocarbons in C_6F_6 solvent. For example, **4** is trapped by ethylene quantitatively (by NMR) to afford $[\text{CnRh}(\text{PMe}_3)(\eta^2\text{-C}_2\text{H}_4)]\text{-}[\text{BAR}_4]$, **5**,^{16,17} our first example of an isolable, formally CnRh^{I} complex. Preliminary results show that propene and **4** cleanly form a mixture of *cis*- and *trans*- $[\text{CnRh}(\text{PMe}_3)(\text{H})(\eta^1\text{-CH=CH-CH}_3)]\text{-}[\text{BAR}_4]$, **6**.¹⁸

Thus, this system exhibits extensive hydrocarbon oxidative-addition/reductive-elimination chemistry involving unusually stable rhodium alkyl hydrides in the unusual, hard Cn ligand environment of rhodium. It is hoped that this hard environment may permit functionalization of the hydrocarbon fragment, particularly by oxidative paths.

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Supplementary Material Available: Crystallographic procedure, ORTEP of complete structure, structure determination summary, atomic coordinates and equivalent isotropic displacement coefficients, interatomic distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (10 pages); listing of observed and calculated structure factors (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(15) Methyl hydride complexes have been prepared in a few cases by methane oxidative addition to reactive intermediates generated by reductive elimination of larger alkanes. However, clear examples of methane exchange with methyl hydride complexes of group 6–10 metals are still rare. (a) Ir: Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (b) Re: Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856. (c) Os: Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (d) $(\text{HBPz}^*_3)\text{Rh}(\text{CO})(\text{H})\text{Me}$ was prepared from $(\text{HBPz}^*_3)\text{-Rh}(\text{CO})(\text{H})\text{C}_y$ in cyclohexane under methane purge at 22 °C: ref 2c. (e) $(\text{HBPz}^*_3)\text{Rh}(\text{CN-}i\text{-Bu})(\text{H})\text{Me}$ was prepared from $(\text{HBPz}^*_3)\text{Rh}(\text{CN-}i\text{-Bu})(\text{H})\text{C}_y$ in cyclohexane under methane pressure at room temperature: ref 2d.

(16) Spectral data for the cation of **5** (anion resonances given in footnote 5): ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 1.19 (d, $J_{\text{PH}} = 8.8$ Hz, PCH_3), 1.28–1.38 (m, $\text{Rh}(\text{C}_2\text{H}_4)$), 2.10 (s, NCH_3), 2.55–2.97 (m, NCH_2), 3.00 (s, 2NCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO-}d_6$) δ 14.81 (d, $J_{\text{PC}} = 31.6$ Hz, PCH_3), 24.47 (dd, $J_{\text{RhC}} = 18.4$ Hz, $J_{\text{PC}} = 4.2$ Hz, $\text{Rh}(\text{C}_2\text{H}_4)$), 45.23, 53.86 (s, NCH_3), 57.33, 58.00, 58.41 (s, NCH_2); $^{31}\text{P}\{^1\text{H}\}$ (145 MHz, $\text{DMSO-}d_6$) δ 6.36 (d, $J_{\text{RHP}} = 159.2$ Hz).

(17) Several examples exist of trapping of ethylene by reactive metal complexes generated by thermolysis of metal alkyl or aryl hydrides. (a) Ir: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (b) Fe: Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436. (c) Rh: ref 2a. (d) Os: Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. Struck, G. E.; Harper, T. G. P.; Shinomoto, R. S.; Flood, T. C. Manuscript in preparation. (e) Of particular relevance is the chemistry of $(\text{HBPz}^*_3)\text{M}(\text{CO})(\text{C}_2\text{H}_4)$ for Rh and Ir: Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480.

(18) The structures of *cis*- and *trans*- $[\text{CnRh}(\text{PMe}_3)(\text{H})(\eta^1\text{-CH=CH}_3)]\text{-}[\text{BAR}_4]$, **6**, are clearly established by their NMR spectra. For example (anion resonances are given in footnote 5; Cn and PMe_3 ^1H , ^{13}C , and ^{31}P resonances are very similar to those of **1** or **2**), for *trans*-**6**: ^1H NMR (360 MHz, $\text{DMSO-}d_6$) δ -18.54 (dd, $J_{\text{RHH}} = 36.6$ Hz, $J_{\text{PH}} = 27.4$, RhH), 1.67 (d, $J = 6.4$ Hz, RhCH=CHCH_3), 5.10 (dq, $J = 14.5$ Hz, $J = 6.4$ Hz, RhCH=CHCH_3), 6.05 (d, $J = 14.5$ Hz, RhCH=CHCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, $\text{DMSO-}d_6$) δ 23.09 (s, RhCH=CHCH_3), 133.67 (s, RhCH=CHCH_3), 146.52 (dd, $J_{\text{RHC}} = 32.0$ Hz, $J_{\text{PC}} = 20.4$ Hz, RhCH=CHCH_3); *cis*-**6**: ^1H NMR (360 MHz, $\text{DMSO-}d_6$) δ -17.76 (dd, $J_{\text{RHH}} = 37.3$ Hz, $J_{\text{PH}} = 26.9$, RhH), 1.69 (d, $J = 6$ Hz, RhCH=CHCH_3), 5.79 (dq, $J = 6$ Hz, $J = 6$ Hz, RhCH=CHCH_3), 6.39 (d, $J = 6$ Hz, RhCH=CHCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, $\text{DMSO-}d_6$) δ 150.79 (dd, $J_{\text{RHC}} = 32$ Hz, $J_{\text{PC}} = 20$ Hz, RhCH=CHCH_3).