Inorg. Chem. **2005**, *44*, 3162–3171

Dihydrogen Complexes of Rhodium: $[RhH_2(H_2)_x(PR_3)_2]^+$ (R = Cy, ^{i}Pr; x = 1, 2)

Michael J. Ingleson, Simon K. Brayshaw, Mary F. Mahon, Giuseppe D. Ruggiero, and Andrew S. Weller*

Department of Chemistry, University of Bath, Bath, BA2 7AY, United Kingdom

Received December 9, 2004

Addition of H_2 (4 atm at 298 K) to $[Rh(nbd)(PR_3)_2][BAr^F{}_4]$ [R = Cy, ^{i}Pr] affords Rh(III) dihydride/dihydrogen complexes. For R = Cy, complex **1a** results, which has been shown by low-temperature NMR experiments to be the bis-dihydrogen/bis-hydride complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2][BAr^F{}_4]$. An X-ray diffraction study on **1a** confirmed the $\{Rh(PCy_3)_2\}$ core structure, but due to a poor data set, the hydrogen ligands were not located. DFT calculations at the B3LYP/DZVP level support the formulation as a Rh(III) dihydride/dihydrogen complex with cis hydride ligands. For R = ^{i}Pr, the equivalent species, $[Rh(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2][BAr^F{}_4]$ **2a**, is formed, along with another complex that was spectroscopically identified as the mono-dihydrogen, bis-hydride solvent complex $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(P^iPr_3)_2][BAr^F{}_4]$ **2b**. The analogous complex with PCy_3 ligands, $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(PCy_3)_2][BAr^F{}_4]$ **1b**, can be observed by reducing the H_2 pressure to 2 atm (at 298 K). Under vacuum, the dihydrogen ligands are lost in these complexes to form the spectroscopically characterized species, tentatively identified as the bis hydrides $[Rh(H)_2(L)_2(PR_3)_2][BAr^F{}_4]$ (**1c** R = Cy; **2c** R = ^{i}Pr; L = CD_2Cl_2 or agostic interaction). Exposure of **1c** or **2c** to a H_2 atmosphere regenerates the dihydrogen/bis-hydride complexes, while adding acetonitrile affords the bis-hydride MeCN adduct complexes $[Rh(H)_2(NCMe)_2(PR_3)_2][BAr^F{}_4]$. The dihydrogen complexes lose $[HPR_3][BAr^F{}_4]$ at or just above ambient temperature, suggested to be by heterolytic splitting of coordinated H_2, to ultimately afford the dicationic cluster compounds of the type $[Rh_6(PR_3)_6(\mu\text{-}H)_{12}][BAr^F{}_4]_2$ in moderate yield.

Introduction

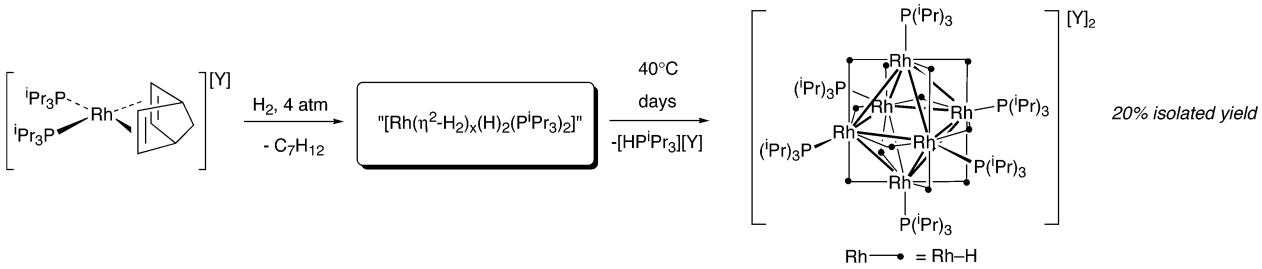
The transition metal chemistry of dihydrogen continues to be a significant area within coordination chemistry even though the first recognized example of such a complex, $W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2$, was reported by Kubas over 20 years ago.[1] Dihydrogen complexes, and the larger group of σ-complexes to which they belong, are fascinating in terms of fundamental structure and bonding as well as being central to the study of homogeneous catalysis.[2] Of the later transition metals, examples of dihydrogen acting as a ligand are known across metals of groups 8−10.[2−4] Rather surprisingly, given the important role that rhodium hydrides play in homogeneous catalysis, relatively few rhodium dihydrogen complexes have been documented: $[RhCp^*(H)(\eta^2\text{-}H_2)(PMe_3)]^+$,[5] $[RhTp(H)(\eta^2\text{-}H_2)(PPh_3)]^+$,[6] $RhTp(H)_2(\eta^2\text{-}H_2)$,[7] $Rh(\eta^2\text{-}H_2)(PCP)$,[8] $[Rh(H)_2(\eta^2\text{-}H_2)(PPP)]^+$,[9] and $[RhCp^*(\eta^2\text{-}H_2)(dmpm)]^{2+}$ [10] [Cp* = $\eta^5\text{-}C_5Me_5$, Tp = $HB(pz)_3$ or a derivative thereof, PCP = $\eta^3\text{-}C_6H_3\text{-}1,3\text{-}(P^tBu_2)_2$, PPP = $MeC(CH_2PPh_2)_3$]. No simple rhodium dihydrogen complexes of the general formula $Rh(\eta^2\text{-}H_2)_x(PR_3)_2$ have been reported, which would be of significant interest on the basis of the role that they play in homogeneous catalysis, particulary as several hydrogenation reactions have been postulated to proceed via dihydrogen intermediates.[11] Neutral $Rh(H)_x(PR_3)_y$

* Author to whom correspondence should be addressed. Tel: +44(0)-1225 383394. Fax: +44(0)1225 386231. E-mail: a.s.weller@bath.ac.uk.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.
(2) Kubas, G. J. *Metal dihydrogen and σ-bond complexes*; Kluwer: New York, 2001.
(3) McGrady, G. S.; Guilera, G. *Chem. Soc. Rev.* **2003**, *32*, 383.
(4) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.
(5) Taw, F. L.; Mellows, H.; White, P. S.; Hollander, F. J.; Bergman, R. G.; Brookhart, M.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 5100.
(6) Oldham, W. J.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028.
(7) Bucher, U. E.; Lengweiler, T.; Nanz, D.; Vonphilipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548.
(8) Xu, W. W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273.
(9) Bakhmutov, V. I.; Bianchini, C.; Peruzzini, M.; Vizza, F.; Vorontsov, E. V. *Inorg. Chem.* **2000**, *39*, 1655.
(10) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledos, A.; Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 8813.

10.1021/ic0482739 CCC: $30.25
Published on Web 04/02/2005

Scheme 1 [a]



[a] Y = $[B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-$ or [1-H-*closo*-$CB_{11}Me_{11}]^-$.

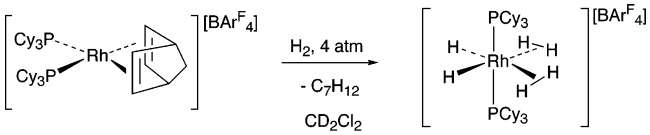
($y = 2$, $x = 3$; $y = 3$, $x = 1$) complexes were investigated by Ibers and Otsuka in the 1970s and 1980s,[12,13] although some of these latter compounds were subsequently reformulated as a dimeric species.[14] This gap in the chemistry of dihydrogen ligands is further highlighted by the fact that the closely related iridium and ruthenium complexes $[Ir(H)_2(\eta^2\text{-}H_2)_2(PR_3)_2]^+$ (R = Cy, $^{t}Bu_2Ph$)[15−17] and $Ru(H)_2(\eta^2\text{-}H_2)_2(PR_3)_2$ (R = Cy, ^{i}Pr)[18−20] have been known for almost 20 years and serve as the paradigm for compounds that contain both hydride and dihydrogen ligands.

We have recently communicated that hydrogenation of $[Rh(nbd)(P^{i}Pr_3)_2][Y]$ {nbd = norbornadiene, Y = $[B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-$($BAr^F_4$), [1-H-*closo*-$CB_{11}Me_{11}]^-$} ultimately results in the formation of a novel, high hydride content cluster: $[Rh_6(P^{i}Pr_3)_6(\mu\text{-}H)_{12}][Y]_2$ (Scheme 1), along with other (as yet unidentified) products.[21] This reaction proceeds via intermediates that we initially identified spectroscopically as the hydride/bis-dihydrogen complexes $[Rh(H)_2(\eta^2\text{-}H_2)_x(P^{i}Pr_3)_2][Y]$ ($x = 1$ or 2). In this Article, we describe in more detail the synthesis and spectroscopic characterization of these intermediate species and their related cyclohexyl phosphine congeners.

Results and Discussion

$[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2][BAr^F_4]$. The addition of H_2 (ca. 4 atm at 298 K) to a CH_2Cl_2 solution of the well-separated ion pair Rh(I) complex $[Rh(nbd)(PCy_3)_2][Y]$ results in the reductive hydrogenation of the diene and the formation, in quantitative yield by NMR spectroscopy, of the new complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2][Y]$ **1a** {Y = $[BAr^F_4]^-$, [1-H-*closo*-$CB_{11}Me_{11}]^-$} (Scheme 2). For **1a**, and all subsequent

Scheme 2



1a

compounds reported here, the anions $[BAr^F_4]^-$ and [1-H-*closo*-$CB_{11}Me_{11}]^-$ are interchangeable, and consequently, only results for $[BAr^F_4]^-$ are discussed further. The use of other anions such as $[BF_4]^-$ and $[PF_6]^-$ led to decomposition and intractable mixtures. At room temperature or just above, under a H_2 atmosphere, compound **1a** slowly loses $[HPCy_3]$-$[BAr^F_4]$ to afford the cluster species $[Rh_6(PCy_3)_6(\mu\text{-}H)_{12}]$-$[BAr^F_4]_2$, which is analogous to the $^{i}Pr_3$ derivative.[21] These cluster compounds will be reported in more detail in a future contribution. The formulation of **1** was determined by solution NMR studies and a preliminary X-ray structure. The formation of discrete Rh(III) monomers is in contrast to the analogous complexes with PPh_3 ligands, which have been shown to form dimers such as $[Rh(\eta^6\text{-}C_6H_5PPh_2)(PPh_3)]_2$-$[Y]_2$ {Y = weakly coordinating anion}, in which the unsaturation at the Rh(I) center is relieved by the coordination of an aryl group from a PPh_3 ligand.[22−24]

In the ^{1}H NMR spectrum of **1a** at 298 K under 4 atm of H_2, no hydride signals are observed. Free H_2 [δ 4.6] is also not observed, consistent with a fast exchange between free and bound H_2. A single rather broad ^{31}P environment is observed in the $^{31}P\{^1H\}$ NMR spectrum [δ − 54.3, J(RhP) 110 Hz]. On progressive cooling to 190 K, the $^{31}P\{^1H\}$ NMR spectrum is still a doublet, but at this temperature, it is sharper [δ 60.1, J(RhP) 92 Hz]. The corresponding ^{1}H NMR spectrum at 190 K reveals two signals, a broader one at δ −1.81, which integrates to 4-H relative to both the cyclohexyl phosphine and $[BAr^F_4]^-$ protons, and a sharper one at δ −14.14, integrating to 2-H (Figure 1). ^{31}P or ^{103}Rh coupling is not resolved in either of the signals. T_1 measurements on these signals at 190 K show that the integral 4-H peak has a much shorter relaxation time than the higher field resonance (14 and 216 ms, respectively). These values unambiguously place the signals as arising from dihydrogen and hydride ligands, respectively.[17] The relaxation time for the dihydrogen

(11) Esteruelas, M. A.; Ore, L. A. *Chem. Rev.* **1998**, *98*, 577.
(12) Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183.
(13) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.
(14) *Catalytic Aspects of Metal Phosphine Complexes*; Thorn, D. L.; Ibers, J. A., Eds.; American Chemical Society: Washington, DC, 1982; Vol. 196.
(15) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.
(16) Cooper, A. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **1998**, *22*, 307.
(17) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.
(18) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *180*, 381.
(19) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652.
(20) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727.
(21) Ingleson, M. J.; Mahon, M. F.; Raithby, P. R.; Weller, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 4784.
(22) Rifat, A.; Patmore, N. J.; Mahon, M. F.; Weller, A. S. *Organometallics* **2002**, *21*, 2856.
(23) Rifat, A. Exo-closo carborane compounds of rhodium and iridium. Ph.D. Thesis, Univeristy of Bath, United Kingdom, 2003.
(24) Marcazzan, P.; Ezhova, M. B.; Patrick, B. O.; James, B. R. *Comptes Rendus Chimie* **2002**, *5*, 373.

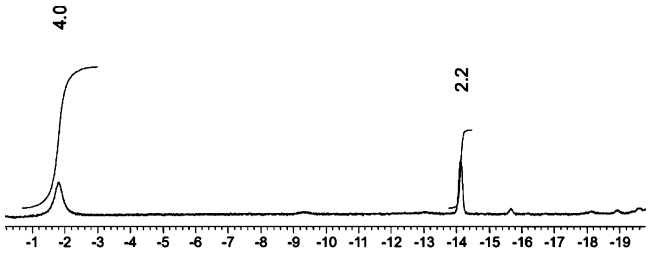
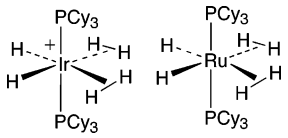


Figure 1. High-field region of the ^{1}H NMR spectrum of **1a** showing the relative integrals at 190 K.

Chart 1



ligand was still decreasing at the lowest accessible temperature (190 K); and thus T_1(minimum) was not unambiguously determined. The chemical shift and line widths of these signals are similar to those reported at low temperatures by Crabtree and by Caulton for the dihydrogen/bis-dihydrogen complexes $[Ir(H)_2(\eta^2\text{-}H_2)_2(PR_3)_2]^+$ (R = Cy, ^{t}Bu$_2$Ph).[15−17]

The observation of H/D coupling in the H−D isotopomer of a dihydrogen complex is direct proof of the existence of a coordinated H_2 ligand.[2] Exposure of a CD_2Cl_2 solution of **1a** to D_2 gas resulted in a decrease in the overall intensity of the hydride signals, indicating H/D exchange, and a broadening of the signal at δ −1.81, although unfortunately no HD coupling was observed. However, as will be shown later, under similar conditions, the P^{i}Pr$_3$ derivative does show H−D coupling. Furthermore, DFT calculations (vide infra) on a model complex $[Rh(H)_6(PMe_3)_2]^+$ indicate a dihydride/bis-dihydrogen complex as a stable isomer. This, along with chemical shifts, relative integrals, and T_1 measurements allows the confident assignment of **1a** as the bis-dihydrogen/bis-hydride complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2][BAr^F{}_4]$.

The formulation of **1a** as the bis-dihydrogen complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2][BAr^F{}_4]$ places it as being directly analogous to the complexes first reported by Crabtree, $[Ir(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$;[15,17] Chaudret, $Ru(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2$;[18,20] (Chart 1) and Shaw $[Re(H)_{8\text{-}2x})(\eta^2\text{-}H_2)_x(PCy_3)_2]^+$.[25] T_1 measurements on the dihydrogen and dihydride ligands in the iridium complex show short relaxation times for both (48 and 73 ms, respectively, at 193 K), unlike in **1a**, suggesting that the exchange is still occurring between these ligands; while for $Ru(H)_2(\eta^2\text{-}H_2)_2(PR_3)_2$ this exchange process is still extremely facile at the lowest attained temperatures, with only one time averaged signal observed for hydride and dihydride ligands. For **1a**, this exchange must be slower, leading to the observed order of magnitude difference in the T_1 times. This observation also contrasts with other rhodium hydride/dihydrogen complexes that are highly fluxional, with hydride and dihydrogen ligands exchanging at very low temperatures.[5,9] The dihydrogen ligands in **1a** are likely to be rotating around the M−H_2 axis at low temperatures as only one η^2-H_2 environment is observed; this being in accord with findings for other dihydrogen complexes in which the barrier to rotation is very small.[2,26,27]

$[Rh(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2]^+$ and $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(P^iPr_3)_2]^+$. The addition of H_2 (ca. 4 atm at room temperature) to a CH_2Cl_2 solution of $[Rh(nbd)(P^iPr_3)_2][BAr^F{}_4]$ results in a mixture of the bis-dihydrogen complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2][BAr^F{}_4]$ **2a** and the mono-dihydrogen complex $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(P^iPr_3)_2][BAr^F{}_4]$ **2b** (Scheme 3). These two complexes have been characterized by low-temperature NMR spectroscopy.

The ^{1}H NMR and ^{31}P NMR spectra of this mixture under a H_2 atmosphere (4 atm at 298 K) are temperature dependent. In the room temperature ^{1}H NMR spectrum, as well as signals due to phosphine and the $[BAr^F{}_4]^-$ anion, a very broad peak is observed in the hydride region centered at δ − 8.62 ppm that integrates to 3.6 protons relative to the $[BAr^F{}_4]^-$ anion signals. The line-width of this signal suggests that an exchange process is occurring. No signal due to free H_2 is observed at ca. δ 4.6, consistent with exchange between free and bound H_2. In the ^{31}P{^{1}H} NMR spectrum, a single doublet is observed at δ 60.4 [J(RhP) 107]. On progressive cooling, the broad hydride signal in the ^{1}H NMR spectrum first disappears into the baseline (240 K) eventually to be replaced at low temperature (200 K) by a more complex set of signals of varying line widths (Figure 2). At the same time, in the ^{31}P{^{1}H} NMR spectrum, two major signals are observed at δ 68.4 and δ 62.1 in a 2:1 ratio, both showing coupling to rhodium. This ratio changes to 4:1 on cooling to 190 K, showing that these two complexes are in dynamic equilibrium. On the basis of chemical shifts, relative integrals, T_1 measurements, and H/D exchange experiments, these two sets of peaks are assigned to the bis-dihydrogen/bis-hydride complex $[Rh(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2][BAr^F{}_4]$ **2a** and the mono-dihydrogen/bis-hydride solvento complex $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(P^iPr_3)_2][BAr^F{}_4]$ **2b**.

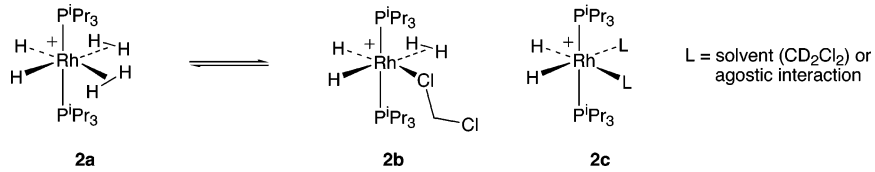
In the hydride region of the ^{1}H NMR spectrum at 200 K, two resonances at δ −1.90 and δ −14.23, in the ratio of 4:2, are assigned to complex **2a**. The measured T_1 values (at 190 K) for these two signals in **2a** provide evidence for formulation as a bis-dihydrogen/dihydride complex, showing the characteristic short T_1 times for the dihydrogen ligand as compared with the hydride: δ −1.90 (11 ms) and δ −14.23 (202 ms). As for **1a**, the relaxation time for the dihydrogen ligand was still decreasing at the lowest accessible temperature (190 K); and thus T_1(minimum) was not unambiguously determined. These chemical shifts are also similar to those observed for **1a** as well as $[Ir(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$.[15,17] Further evidence for the assignment of **2a** as a bis-dihydrogen complex is the observation of a broad 1:1:1 triplet for the higher field signal δ −1.90 when a sample is degassed and then placed under 4 atm of D_2 [$J(DH)_{average}$ ∼30 Hz] (Figure 3). This multiplet is due to a mixture of

(25) Fontaine, X. L. R.; Fowles, E. H.; Shaw, B. L. *J. Chem. Soc., Chem. Commun* **1988**, 482.

(26) Li, S.; Hall, M. B.; Eckert, J.; Jensen, C. M.; Albinati, A. *J. Am. Chem. Soc.* **2000**, *122*, 2903.

(27) Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Thoburn, J.; Ulrich, S.; Limbach, H.-H.; Barthelat, J. C.; Hussein, K.; Marsden, C. J. *Inorg. Chem.* **1998**, *37*, 3475.

Scheme 3 [a]



[a] $[BAr^F_4]^-$ anions not shown.

the partially deuterated isotopomers of **2a**: $[Rh(H)_{6-x}(D)_x(P^iPr_3)_2][BAr^F_4]$. We are reluctant to use this value to estimate[28] the H−H distance in the complex as the signal is so broad. This signal also undergoes a small upfield IPR shift of 0.044 ppm. Similar upfield shifts have been reported previously in other dihydrogen complexes $RuH_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2$ [19] and $[RhCp^*H(\eta^2\text{-}H_2)(PMe_3)][BAr^F_4]$.[5] For these latter species, and closely related complexes,[10] well-resolved coupling patterns are observed for the various H/D isotopomers. This is in contrast to the broad signal observed for **2a**. Under a D_2 atmosphere, no H/D exchange was observed for the protons on the phosphine ligands, similar to that observed for $[Ir(H)_2(\eta^2\text{-}H_2)_2(P^tBu_2Ph)_2]^+$,[29] but contrasts with $[Ru(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2]^+$ [19] in which deuterium is incorporated into the phosphine.

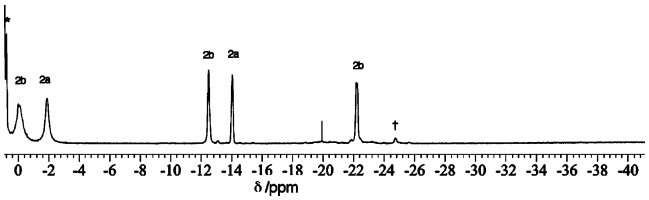


Figure 2. ^{1}H NMR spectrum (high field region, 200 K) of complexes **2a** and **2b** (asterisk marks part of resonances due to $^iPr_3P$ ligands, and † marks an unidentified compound).

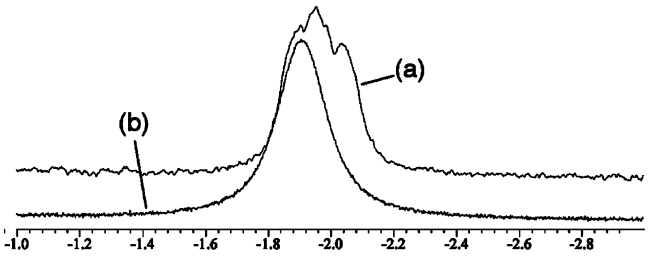


Figure 3. Partial ^{1}H NMR spectrum of the $(\eta^2\text{-}H_2)_2$ region of **2a** (b) overlaid with that of a mixture of **2a** and its partially deuterated isotopomers (a). Both were measured at 200 K.

The other major species in solution at 200 K is formulated as the solvento complex $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(P^iPr_3)_2][BAr^F_4]$ **2b**. In addition to the resonance arising from **2a**, a doublet is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 62.1 that is assigned to **2b**. In the ^{1}H NMR spectrum, three high-field signals observed at δ −0.28, −12.66, and −22.42 in the ratio 2:1:1 are assigned to **2b**. T_1 measurements (at 190 K) on these three signals assign the lowest field as a dihydrogen ligand (9 ms) and the other two as hydrides (149 and 144 ms, respectively). Unfortunately, HD coupling was not resolved in the partially deuterated sample, although the signal at δ −0.28 does broaden significantly on the addition of D_2. The two inequivalent hydride resonances observed for **2b** suggest a structure similar to that reported for the related five-coordinate complex $[Ir(H)_2(\eta^2\text{-}H_2)(P^tBu_2Ph)_2][BAr^F_4]$, which shows signals at δ −0.02 (η^2-H_2), δ −10.0 (H), and δ −41.2 (H); the latter signal being assigned to a hydride trans to an empty coordination site.[16] Related cationic iridium complexes with hydride ligands trans to vacant sites also show similar, large, upfield chemical shifts (e.g., $[Ir(H)_2(PPh(^tBu)_2)_2][BAr^F_4]$ δ −37.1[29] (trans to agostic interactions) and five-coordinate $IrH_2I(P^tBu_2Ph)_2$ δ −44.4).[30] In contrast, the highest field chemical shift observed for **2b** is δ −22.4, which suggests a different structure, possibly one in which a ligand occupies the site trans to the hydride.[30] On the basis of the chemical shifts of the hydrogen ligands and observations made on changing the solvent from CD_2Cl_2 (vide infra), we tentatively suggest that the CD_2Cl_2 solvent occupies this vacant site rather than an agostic interaction. Attempts to observe the coordinated CH_2Cl_2 spectroscopically by $^{13}C\{^1H\}$ NMR at low temperature were not successful, although bound CH_2Cl_2 is often difficult to observe due to rapid exchange with the bulk solvent.[31] Examples of dichloromethane complexed with electrophilic transition metals are now well-established, and both monodentate[31,32] and bidentate[33,34] binding modes have been observed. A Rh(III) complex with coordinated CH_2Cl_2 has recently been reported and crystallographically characterized, $[RhCp^*(PMe_3)(Me)(CH_2Cl_2)][BAr^F_4]$,[5] and in this case, coordinated CH_2Cl_2 is observed in the $^{13}C\{^1H\}$ NMR spectrum.

Attempts to use solvents other than CD_2Cl_2 led to mixed results. The noncoordinating solvent fluorobenzene freezes at 231 K, precluding a low-temperature NMR analysis of any hydride/bis-dihydrogen complexes formed in this solvent. In a d^8-toluene solution, hydrogenation of $[Rh(nbd)(P^iPr_3)_2][BAr^F_4]$ results in a broad signal at room temperature in the ^{1}H NMR spectrum at $\sim\delta$ −8, similar to that seen in CD_2Cl_2, but at lower temperatures, the cationic products formed are not soluble. However, the solvent meta-fluorotoluene

(28) Maltby, P. A.; Schalf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.
(29) Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9069.
(30) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208.
(31) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831.
(32) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 115.
(33) Huang, D. J.; Bollinger, J. C.; Streib, W. E.; Folting, K.; Young, V.; Eisenstein, O.; Caulton, K. G. *Organometallics* **2000**, *19*, 2281.
(34) Seggen, D. M. V.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453.

Scheme 4

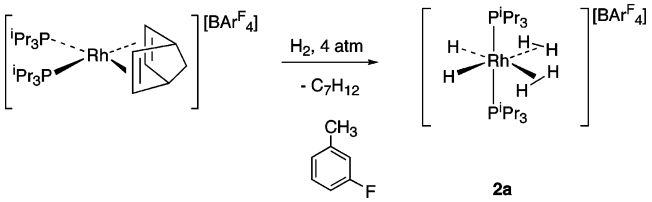
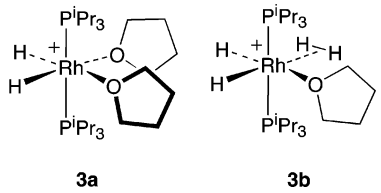


Chart 2 [a]



[a] $[BAr^F_4]^-$ anions not shown.

(3-F-C_6H_4Me) proved to be a suitable solvent that dissolved the cationic species, was noncoordinating and had a workable temperature range for NMR spectroscopy (melting point −87 °C). Although d_7-meta-fluorotoluene is not available, we successfully used a *per*-protio solvent for NMR spectroscopy (by shimming on the FID), while some of the aromatic signals due to the $[BAr^F_4]^-$ anion are not obscured by the solvent allowing for the relative integration of hydride signals. Treatment of $[Rh(nbd)(P^iPr_3)_2][BAr^F_4]$ with H_2 (4 atm at 298 K) in meta-fluorotoluene resulted in an ^1H NMR spectrum at 298 K that showed a broad high field resonance at δ −5.81 of a relative integral 4.9 and no free H_2 signal, consistent with rapid exchange between bound and free H_2. Cooling to 210 K partially (vide infra) froze this exchange out, and only two broad high field resonances are observed, at δ −3.24 and δ −15.08 in the ratio of 4:2, very similar to that observed for **1a** and **2a**. The $^{31}P\{^1H\}$ NMR spectrum at 210 K displayed a single sharp doublet at δ 67.48 [*J*(RhP) 94 Hz], similar to **2a**. T_1 measurements at 210 K indicated that the δ −3.24 resonance can be assigned to bound dihydrogen (20 ms) and that the δ −15.08 resonance is best assigned to hydride ligands (76 ms). That the signal due to the hydride ligand still shows a relatively short T_1 time indicates that there is still some exchange between hydride and dihydrogen ligands at this temperature in this solvent. Similar exchange is observed for $[Ir(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$ [15,17] and $Ru(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2$.[18,20] Cooling further to 190 K results in significant broadening into the baseline of the signal at δ −3.24 but not the signal at δ −15.08. This is different behavior to that observed in CD_2Cl_2 in which relatively sharp lines are observed at 190 K. Nevertheless, in the absence of CD_2Cl_2 solvent at low temperature, that only signals due to a bis-dihydrogen/bis-hydride complex (i.e., **2a**, Scheme 4) are observed, strongly suggests that **2b** is best assigned as a CD_2Cl_2 complex.

Use of d^8-THF in place of CD_2Cl_2 as a solvent in the initial hydrogenation of $[Rh(nbd)(P^iPr_3)_2][BAr^F_4]$ led to a low temperature (200 K) NMR spectrum that showed the presence of two compounds in a 2:1 ratio, neither of which was **2a** or **2b**. The major one showed a broad hydride peak at δ −24.33 [T_1 266 ms at 200 K] in the ^1H NMR spectrum, which we assign as the bis-THF/bis-hydride complex $[Rh(H)_2(d^8\text{-}THF)_2(P^iPr_3)_2][BAr^f_4]$, **3a**, this being similar to $[Rh(H)_2(EtOH)_2(PPh_3)_2][ClO_4]$ that was first described by Osborne and Schrock.[35] The minor component showed two hydride resonances at δ −13.08 and δ −24.89, both as complex multiplets (part of a ABM_2X system), and a broad signal at δ −0.10 characteristic of a dihydrogen ligand (T_1 at 200 K = 245, 252, and 7 ms, respectively). These signals appear in a 1:1:2 ratio, respectively. We assign these signals to $[Rh(H)_2(\eta^2\text{-}H_2)(d^8\text{-}THF)(P^iPr_3)_2][BAr^F_4]$, **3b**, on the basis of their T_1 measurements and the similarity with complex **2b** (Chart 2). The $^{31}P\{^1H\}$ NMR shows two doublets at δ 55.2 [*J*(RhP) 114 Hz] and δ 64.1 [*J*(RhP) 103 Hz], in the ratio of 2:1, respectively. Placing this solution under a partial vacuum to remove H_2 afforded NMR spectra that only showed the presence of $[Rh(H)_2(d^8\text{-}THF)_2(P^iPr_3)_2][BAr^F_4]$.

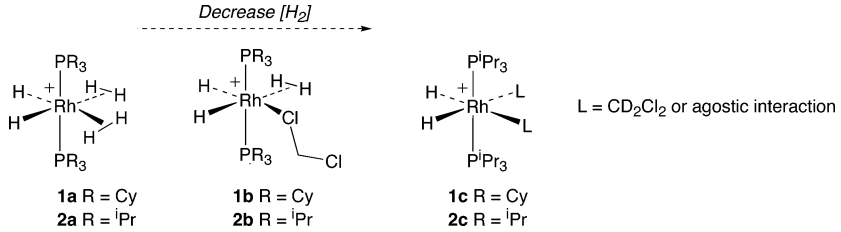
The formation of both mono- (**2a**) and bis-dihydrogen (**2b**) complexes in CD_2Cl_2 contrasts to **1a**, which is formed as the sole product. Variation in stability with respect to H_2 loss has previously been noted for the neutral $Ru(H)_2(\eta^2\text{-}H_2)_x(PR_3)$ systems. With tricyclohexyl phosphine, the stable ruthenium bis-dihydrogen adduct is formed (cf. **1a**), whereas with isopropyl phosphine, H_2 loss is facile, and dimers such as $Ru_2H_6(P^iPr_3)_4$ result.[18,19]

Pressure Dependence. All the dihydrogen complexes so far discussed are sensitive to H_2 pressure (Scheme 5). For the cyclohexyl phosphine complexes, reducing the initial H_2 pressure to ∼2 atm at 298 K results in the appearance of a mono dihydrogen complex that is formulated as $[Rh(H)_2(\eta^2\text{-}H_2)(CD_2Cl_2)(PCy_3)_2][BAr^F_4]$ **1b** on the basis of its very similar ^1H NMR spectra (at 190 K) in the hydride region as compared with **2b**, namely, a broad signal at δ −0.11 (T_1 29 ms, η^2-H_2) and sharper peaks at δ −12.3 (T_1 137 ms) and δ −22.2 (T_1 259 ms) for the now inequivalent hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum at this pressure also indicates that two compounds are present, **1a** and **1b**, the latter giving a signal at δ 54.3 [*J*(RhP) 102 Hz]. The ratio of **1a**/**1b** at 2 atm H_2 is ∼1:1. For the isopropyl derivatives under the same conditions (2 atm), the previously identified bis-dihydrogen **2a** and mono dihydrogen complexes **2b** are observed but with the latter compound by far the major species in solution.

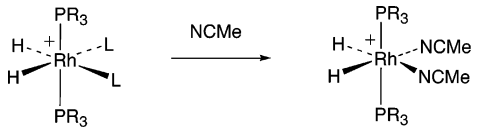
At lower H_2 pressures (1 atm at 298 K), one compound predominates for both **1** and **2** that may be more cleanly produced by removing H_2 in vacuo. These products have been spectroscopically characterized in CD_2Cl_2 solution and are tentatively identified as $[Rh(H)_2(L)_2(PR_3)_2][BAr^F_4]$ (**1c** R = Cy; **2c** R = ^{i}Pr; L = CD_2Cl_2 or agostic interaction). For both complexes, a single relatively sharp signal is observed in the region associated with terminal hydrides: **1c** δ −23.0 and **2c** δ −24.4. No signal due to coordinated dihydrogen was observed. ^{103}Rh coupling is resolved in both, and for **2c** coupling to two equivalent phosphines are also observed. The $^{31}P\{^1H\}$ NMR spectra for each is a single doublet showing coupling to rhodium [**1c** δ 53.9 *J*(RhP) 111 Hz; **2c** δ 57.6 *J*(RhP) 104 Hz]. We tentatively assign these

(35) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

Scheme 5



Scheme 6



to Rh(III) complexes with either a chelating coordinated dichloromethane or as bis-agostic complexes with no coordinated dichloromethane. The chemical shift of the hydride ligands in an agostic species is expected to be nearer δ −40 {viz. $[Ir(H)_2(PPh(^tBu)_2)_2][BAr^F_4]$ δ −37.1},[29] while the hydride signals in **1c** and **2c** are more like the dihydride complexes $Rh(H)_2\{O_2S(O)Me\}(P^iPr_3)_2$ [36] [δ −25.3] and $[Ir(H)_2(o\text{-}Cl_2C_6H_4)(PPh_3)_2][BF_4]$[37] [$\delta$ −20.8], both of which contain weakly bound ligands trans to the hydrides. This suggests that the formulation of **1c** and **2c** as weakly bound dichloromethane complexes is more appropriate. Whatever the nature of the weakly bound ligand, repressurization of **1c** or **2c** with H_2 (4 atm) immediately affords the previously observed mixtures of dihydrogen complexes at 200 K, while addition of the coordinating solvent acetonitrile to **1c** or **2c** resulted in the immediate formation of the bis-acetonitrile adducts $[Rh(H)_2(NCMe)_2(PR_3)_2][BAr^F_4]$ (Scheme 6). Both these observations are consistent with a weakly bound solvent or interaction. The acetonitrile adducts are direct congeners of $[Ir(H)_2(NCMe)_2(PR_3)_2][PF_6]$[38] first reported by Crabtree and are identified by a sharp doublet of triplets in the ^{1}H NMR spectrum for the equivalent hydrides [e.g., δ −19.1, J(RhH) 18, J(PH) 8 Hz] and a single, sharp doublet in the $^{31}P\{^1H\}$ NMR spectrum [e.g., δ 59.8 J(RhP) 107 Hz]. Attempts to isolate **1c** and **2c** led to decomposition, leading to dimeric compounds with bridging chlorides that presumably arise from the coordinated CH_2Cl_2.

Solid-State Structure of $[Rh(H)_2(\eta^2\text{-}H_2)_x(PCy_3)_2]^+$. Attempts to secure the unambiguous characterization of the dihydrogen complexes **1** and **2** in the solid state by X-ray crystallography were frustrated by the mixtures of products formed, the dependence on H_2 pressure, and the gradual formation of $[Rh_6(PR_3)_6(\mu\text{-}H)_{12}][BAr^F_4]_2$ and $[HPR_3][BAr^F_4]$ among other products. After repeated attempts, a small number of crystals were grown from the reaction of [Rh(nbd)$(PCy_3)_2$][1-H-*closo*-$CB_{11}Me_{11}$] with dihydrogen in fluorobenzene solution by layering with pentane under a H_2 atmosphere and storage at 10 °C. The crystals were poor diffractors, and the resulting data set was not of high quality, allowing only the gross structural features of the molecule to be observed. The asymmetric unit (Figure 4) consists of one cation and one [1-H-*closo*-$CB_{11}Me_{11}]^-$ anion. The cationic portion is a linear $\{Rh(PCy_3)_2\}^+$ fragment, and no other significant electron density was located near the Rh center. Given that the metal fragment would have a nominal 12-electron count, this suggests the presence of hydrogen ligands or agostic interactions;[29] however, given the poor quality of the data, the location of the hydride ligands around the metal was precluded, leaving the actual number indeterminate. Nevertheless, the structure is consistent with a $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$ fragment, showing a trans disposition of phosphine ligands [P1−Rh−P1″ = 180°]. The structure is grossly similar to the structures recently reported for $Ru(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ [39] and $Ru(H)_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2$,[19] both of which also have a P−M−P bond angle of ∼180° in the solid state. DFT calculations (vide infra) show that a trans arrangement of dihydrogen and hydride ligands in $[Rh(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$ would be expected to give a complex with a P−Rh−P angle of 180°, while cis arrangements have a slightly bent P−Rh−P angle. Interestingly, in these gas-phase calculations, the trans isomer is found to be 27 kcal mol^{-1} higher in energy as compared to the possible cis isomers, but given the poor quality of the data, discussion of the structural metrics is clearly inappropriate apart from confirming the gross overall structure.

DFT Calculations on $[Rh(H)_6(PMe_3)_2]^+$. We have briefly investigated the structure of the complex $[Rh(H)_6(PMe_3)_2]^+$, which is a model for complexes **1a** and **2a**, by the DFT method (B3LYP/DZVP). Very similar results were also obtained using the B3LYP/LANL2DZ level of theory, which has been successfully used previously to model transition metal dihydrogen complexes.[16,26,27] Optimization of $[Rh(H)_2(\eta^2\text{-}H_2)_2(PMe_3)_2]^+$ afforded a stable ground-state structure with trans phosphines, two hydrides, and two dihydrogen ligands, confirming the spectroscopic assignment as a Rh(III) bis-dihydrogen dihydride. Four possible isomers all having trans phosphines (**A**−**D**) were identified, which are very similar to those described for $RuH_2(H_2)_2(PH_3)_2$.[27] Structures **A**−**C** have cis hydrides (Figure 5) and are related to one another by a simple rotation of one or both of the dihydrogen ligands. There is only a negligible energy difference between these (less than 1 kcal mol^{-1}). Structure **D** has trans hydrides and is 27 kcal mol^{-1} higher in energy. The P−Rh−P angles in isomers **A**−**C** lie between 164 and

(36) Werner, H.; Bosch, M.; Schneider, M. E.; Hahn, C.; Kukla, F.; Manger, M.; Windmüller, B.; Weberndörfer, B.; Laubender, M. *Dalton Trans.* **1998**, 3549.
(37) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361.
(38) Crabtree, R.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.
(39) Borowski, A. F.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543.

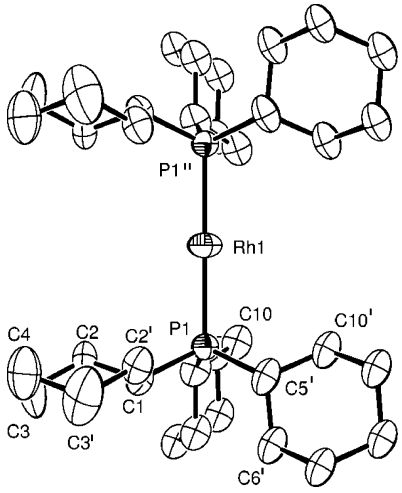


Figure 4. Solid-state structure of the cationic portion of $[Rh(H)_2(\eta^2\text{-}H_2)_x(PCy_3)_2][1\text{-}H\text{-}closo\text{-}CB_{11}Me_{11}]$. Ellipsoids shown at the 30% probability level. Only one of the disordered cyclohexyl rings is shown (see Experimental Procedures for details). Hydrogen atoms are not shown. Equivalent (primed) atoms were generated by the operations $x, y, -z + {}^3/_2$ and $-x, y, z$. Selected bond lengths (Å) and angles (deg): Rh−P1 2.352(3) and P1−Rh−P1″ 180.

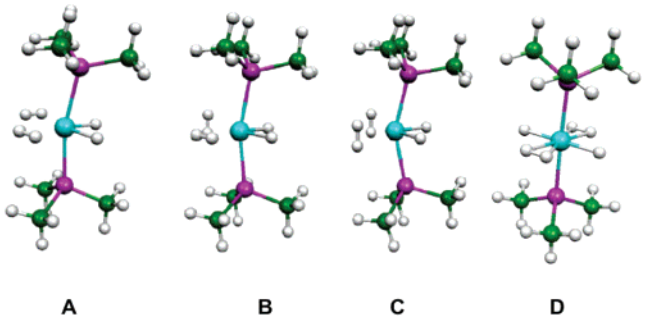


Figure 5. DFT optimized structures for $[Rh(H)_2(\eta^2\text{-}H_2)_2(PMe_3)_2]^+$ (B3LYP/DZVP level).

167°, while that for **D** is 177°, and all are similar to that calculated for $RuH_2(H_2)_2(PH_3)_2$.[27] We have not searched for transition states between the three isomers **A**−**C**, but given that experimentally dihydrogen rotation is faster than the NMR time scale for **1a** and **2a** at 190 K, the barrier between the isomers is expected to be small. Barriers to η^2-H_2 rotation have been determined both theoretically and experimentally on related systems and are indeed small (less than 1 kcal mol^{-1}).[16,26,27] The H−H distance in all three isomers is very short, at ca. 0.77 Å. This is longer than in free H_2 (0.74 Å) but shorter than in other neutral polyhydride−dihydrogen complexes studied by DFT methods, such as $Ru(H)_2(\eta^2\text{-}H_2)_2(PH_3)_2$ [~0.85 Å][27] and $IrIH_2(\eta^2\text{-}H_2)(PMe_3)_2$ [0.86 Å].[26] Not unsurprisingly, the H−H distance is more like that calculated for cationic hydride/dihydrogen systems such as $[Ir(H)_2(\eta^2\text{-}H_2)(PH_3)_2]^+$ [0.80 Å][16] or observed by neutron diffraction in $[Fe(H)(\eta^2\text{-}H_2)(dppe)_2][BPh_4]$ [0.816(16) Å].[40] The short H−H distance calculated in $[Rh(H)_2(\eta^2\text{-}H_2)_2(PMe_3)_2]^+$ is consistent with a dihydrogen ligand showing little back-bonding with the cationic Rh(III) center, coupled with both H_2 ligands being orientated trans to the high trans influence hydrides. Optimization of a tetrahydride, Rh(V), structure $[Rh(H)_4(\eta^2\text{-}H_2)(PMe_3)_2]^+$ resulted in the Rh(III) dihydride/bis-dihydrogen structure.

Heterolytic Cleavage of Coordinated H_2. Under a H_2 atmosphere at, or just above, room temperature, the complex mixtures of **2** lose protonated phosphine, $[HP^iPr_3][BAr^F{}_4]$, over a period of days with the concomitant formation of the cluster dications $[Rh_6(P^iPr_3)_6(\mu\text{-}H)_{12}][BAr^F{}_4]_2$ in moderate yield (20%).[21] A similar cluster and the formation of $[HPCy_3][BAr^F{}_4]$ also ultimately results from mixtures of **1**. Other rhodium containing products are also formed in these reactions that currently have not been fully characterized. Although the initial organometallic product of this process is not yet known (we assume it is a neutral low coordinate $\{RhP(H)_x\}_n$ species—Scheme 7), the observation of protonated phosphine means that it could be regarded as arising from heterolytic activation of a dihydrogen ligand. Confirmation that the proton arises from H_2 comes from replacing H_2 with D_2 and the observation of $[DP^iPr_3][BAr^F{}_4]$ in the $^{31}P\{^1H\}$ NMR spectrum [1:1:1 triplet, δ 46.1, J(DP) 68 Hz]. Intramolecular heterolytic cleavage of metal-bound H_2 is now a well-known phenomenon,[2,41] for example, the proton transfer between dihydrogen and thiolate in the complex $[Os(\eta^2\text{-}H_2)(CO)(pyridine\text{-}2\text{-}thiolate)(PPh_3)_2]BF_4$.[42] As far as we are aware, the products of heterolytic H_2 cleavage and proton transfer to a phosphine have only been reported once previously. Protonation at low temperature of $Ru(H)(PCy_3)_2(CO)Cl$ with $H[BF_4]$ initially affords the dihydrogen complex $[Ru(\eta^2\text{-}H_2)_2(PCy_3)_2(CO)Cl][BF_4]$ (Scheme 8), which subsequently eliminates $[HPCy_3][BF_4]$ to leave a transient compound spectroscopically characterized as 14-electron $Ru(H)(PCy_3)(CO)Cl$.[43] On warming, a tetrametric compound, $[Ru_4Cl_7(PCy_3)_4(CO)_4][BF_4]$, is isolated. The elimination of $[HPR_3]^+$ from a cationic dihydrogen complex to give an unsaturated species that subsequently condenses to form a multimetallic product shows clear parallels with the rhodium compounds under discussion here.

The mechanism by which the protonated phosphine results from mixtures **1** and **2** could either be intramolecular (perhaps via a σ-bond metathesis-type route) or intermolecular deprotonation by traces of free PR_3 in solution. Whatever the mechanism, even though there are no π-acid ligands on **1** or **2**, the net positive charge on the rhodium center is sufficient to render the dihydrogen ligand sufficiently acidic to protonate PCy_3 or P^iPr_3. Morris has compiled extensive data on the relative pK_a values of coordinated dihydrogen ligands in nonaqueous solvents.[44] Given that, on this scale, the pK_a of $[HPCy_3][BAr^F{}_4]$ is 9.7 and that of $[HP^iPr_3][BAr^F{}_4]$ is 9.0, this places the relative pK_a of the dihydrogen ligands in **1** and **2** as being comparable to these protonated phosphines. Dihydrogen complexes that bear a positive

(40) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823.

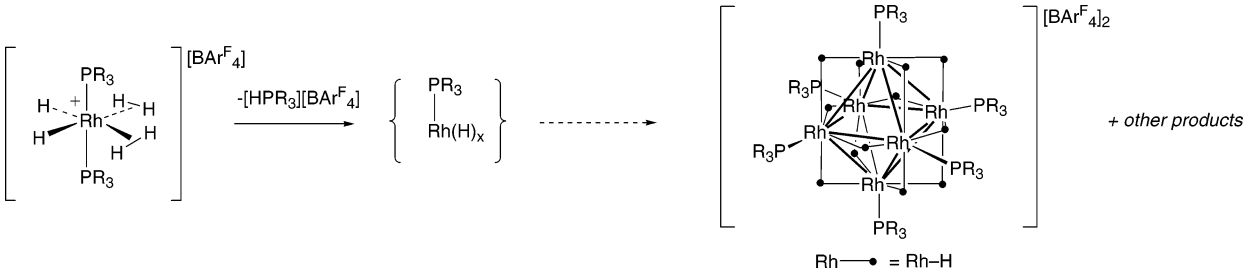
(41) Kubas, G. *Adv. Inorg. Chem.* **2004**, *56*, 127.

(42) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1996**, *15*, 4423.

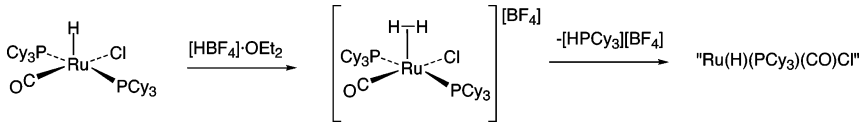
(43) Yi, C. S.; Lee, D. W.; He, Z.; Rheingold, A. L.; Lam, K.-C.; Concolino, T. E. *Organometallics* **2000**, *19*, 2909.

(44) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155.

Scheme 7



Scheme 8



charge and/or electron-withdrawing ligands are more acidic than neutral complexes,[41] and the estimated pK_a for the dihydrogen complexes **1** and **2** would be thus expected to be much lower than the neutral isoelectronic complexes Ru(H)$_2$(η^2-H$_2$)$_2$(PR$_3$)$_2$. This is the case, with the R = P^{i}Pr$_3$ complex having a pK_a of 39.[44] Consistent with this, these complexes do not eliminate protonated phosphine and decompose by simple loss of molecular H_2 instead to give bis-phosphine hydride bridged dimers.[44,45]

Conclusions

The addition of H_2 to [Rh(nbd)(PR$_3$)$_2$][BAr$^F_4$] salts (R = ^{i}Pr or Cy) in CD_2Cl_2 results in Rh(III) dihydrogen/hydride complexes of the general formula [Rh(H)$_2$(η^2-H$_2$)$_2$(PR$_3$)$_2$][BAr$^F_4$] and [Rh(H)$_2$(η^2-H$_2$)(CD_2Cl_2)(PR$_3$)$_2$][BAr$^F_4$]. These complexes have been characterized at low temperature by NMR spectroscopy by using a combination of T_1 measurements, an observed H−D coupling constant of ∼30 Hz, and a crystal structure of the cyclohexyl phosphine derivative that shows a trans disposition of phosphine ligands. Experimental characterization has been supported by DFT calculations. At room temperature, these complexes slowly lose [HPR$_3$][BAr$^F_4$], suggested to result from heterolytic cleavage of coordinated H_2, to afford the novel clusters [Rh$_6$(PR$_3$)$_6$(μ-H)$_{12}$][BAr$^F_4$]$_2$.

The observation of simple complexes of the formula [Rh(H)$_2$(η^2-H$_2$)$_2$(PR$_3$)$_2$][BAr$^F_4$] on the hydrogenation of a norbornadiene precursor complex further underlines the role that such dihydride/dihydrogen complexes may play in the hydrogenation of olefins using cationic rhodium catalysts.[11] Intriguingly, the suggestion that heterolytic H_2 cleavage might occur in these complexes suggests that a similar mechanism could operate for the hydrogenation of olefins using these Rh(III) {RhP$_2$}$^+$ fragments, as has been suggested to operate for cationic ruthenium(II) complexes.[46,47] Alternatively, olefin may simply replace the bound dihydrogen ligands, and hydrogenation may proceed by insertion into a rhodium(III)-hydride bond.

Experimental Procedures

General. All manipulations were performed under an inert atmosphere of argon, using standard Schlenk-line and glovebox techniques. Glassware was dried in an oven at 130 °C overnight and flamed with a blowtorch, under vacuum, three times before use. CH_2Cl_2 and pentane were distilled from CaH_2, diethyl ether from sodium/benzophenone ketal, and hexane from sodium. Fluorobenzene and *m*-fluorotoluene were dried over CaH_2 and vacuum distilled. C_6D_6, d_8-THF, and d_8-toluene were dried over a potassium mirror, and CD_2Cl_2 was distilled under vacuum from CaH_2. Microanalyses were performed by Mr. Alan Carver (University of Bath Microanalytical Service). [Rh(nbd)(PR$_3$)$_2$][BAr$^F_4$] complexes were prepared by an adaptation of the published route using K[BAr$^F_4$][48] and PR$_3$.[49] [Rh(nbd)(PCy$_3$)$_2$][1-H-*closo*-CB$_{11}$Me$_{11}$] was prepared by a similar route using Ag[1-H-*closo*-CB$_{11}$Me$_{11}$].[50] All other compounds were used as received from Aldrich or Strem Chemicals. We were not able to obtain an elemental analysis of any of the unstable compounds reported in this work.

NMR Spectroscopy. ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker Avance 300 and 400 MHz FT-NMR spectrometers. Unless noted, residual protio solvent was used as reference for ^{1}H NMR spectra (CD_2Cl_2: $\delta = 5.33$). ^{11}B and ^{31}P NMR spectra were referenced against BF_3·OEt_2 (external), and 85% H_3PO_4 (external), respectively. Coupling constants are quoted in Hertz. Spectral assignments were aided by the use of T_1 measurements, which were made at 190 or 200 K using the software provided with a Bruker Avance 400 MHz spectrometer using the standard inversion−recovery−delay method (180°−τ−90°) method. In each experiment, a waiting period of 5 times longer than the expected relaxation time and 11 variable delays were used.

[Rh(H)$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$][BAr$^F_4$] (1a). A solution of [Rh(Cy$_3$P)$_2$(nbd)][BAr$^F_4$] (0.020 g) in CD_2Cl_2 (0.3 mL) in a Youngs NMR tube was degassed and backfilled with 1 atm of H_2 at 77 K. At room temperature, the H_2 pressure in the tube is ca. 4 atm (298/77 ≈ 4). On thawing, the solution rapid changed color from orange to pale yellow. Yield: quantitative by NMR spectroscopy (see text).

(45) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598.
(46) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34.
(47) Daguenet, C.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2004**, *23*, 4849.
(48) Buschmann, W. E.; Miller, J. S. *Inorg. Synth.* **2002**, *33*, 85.
(49) Rifat, A.; Laing, V. E.; Kocoik-Köhn, G.; Mahon, M. F.; Ruggiero, G. D.; Weller, A. S. *J. Organomet. Chem.* **2003**, *680*, 127.
(50) Ingleson, M. J.; Patmore, N. J.; Kociok-Köhn, G.; Mahon, M. F.; Ruggiero, G. D.; Weller, A. S.; Clarke, A. J.; Rourke, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 1503.

Attempts to isolate solid material in bulk repeatedly failed. However, small crystals of the [Y = 1-H-*closo*-$CB_{11}Me_{11}$]$^-$ salt (prepared in exactly the same manner using [$(Cy_3P)_2$Rh(NBD)][*closo*-$CB_{11}Me_{11}$H]) were obtained by slow diffusion of pentane into a solution of the complex in C_6H_5F at 10 °C.

^{1}H NMR (CD_2Cl_2, 298 K): δ 7.73 (s, 8H, BAr^F_4), 7.57 (s, 4H, BAr^F_4), 2.24−1.05 (m, 66H, PCy_3); no hydride signal visible. ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 54.3 (d, $^1J_{RhP}$ = 110 Hz). ^{11}B NMR (CD_2Cl_2, 298 K): δ −5.9 (s). Selected ^{1}H NMR (CD_2Cl_2, 190 K): δ −1.81 (br, 4H, T_1 = 14 ms, η^2-H_2), −14.14 (br s, 2H, T_1 = 216 ms, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 190 K): δ 60.1 (d, $^1J_{RhP}$ = 92 Hz)

[Rh(H)$_2$(η^2-H$_2$)(CD_2Cl_2)(PCy_3)$_2$][BAr^F_4] (1b). A solution of [Rh(Cy_3P)$_2$(nbd)][BAr^F_4] (0.018 g) in CD_2Cl_2 (0.3 mL) in a Youngs NMR tube was degassed and backfilled with 1 atm of H_2 at 170 K (∼2 atm at 298 K). On thawing, the solution rapidly changed color from orange to pale yellow to afford a mixture of **1a** and **1b** in an approximate 1:1 ratio.

Selected NMR data for 1b: ^{1}H NMR (CD_2Cl_2, 190 K): δ 0.11 (2 H, T_1 29 ms, $\eta^{2-}H_2$), −12.3 (br, 1H, T_1 137 ms, Rh−H), −22.2 (br, 1H, T_1 259 ms, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 190 K): δ 54.3 (d, $^1J_{RhP}$ = 102 Hz).

[RhH$_2$(L)$_2$(PCy_3)$_2$][BAr^F_4] (1c) (L = Solvent or Agostic Interaction). A sample of [(Cy_3P)$_2$Rh(H_2)$_2$H$_2$][BAr^F_4] was formed in situ by the hydrogenation of [(Cy_3P)$_2$Rh(nbd)][BAr^F_4] in C_6H_5F. The solvent was evaporated to dryness, and the residue was dried in vacuo for 5 h to leave a dark yellow oil. Attempts to obtain solid material repeatedly failed due to the ready decomposition of this compound.

^{1}H NMR (CD_2Cl_2, 298 K): δ 7.74 (s, 8H, BAr^F_4), 7.54 (s, 4H, BAr^F_4), 2.46−1.27 (m, 66H, PCy_3) −24.03 (br d, $^1J_{RhH}$ = 42 Hz, 2H, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 53.9 (d, $^1J_{RhP}$ = 111 Hz). ^{11}B NMR (CD_2Cl_2, 298 K): δ −5.9 (s).

[Rh(H)$_2$(η^2-H$_2$)$_2$(P^iPr_3)$_2$][BAr^F_4] (2a) and [Rh(H_2)(H)$_2$(CD_2Cl_2)-(^{i}Pr$_3$P)$_2$][BAr^F_4] (2b). A solution of [(^{i}Pr$_3$P)$_2$Rh(nbd)][BAr^F_4] (0.015 g) in CD_2Cl_2 (0.3 mL) in a Young's NMR tube was degassed and backfilled with 1 atm of H_2 at 77 K. The tube was sealed, and upon thawing to room temperature, the solution rapidly changed color from orange to pale yellow. Yield: quantitative by NMR spectroscopy (see text).

^{1}H NMR (CD_2Cl_2, 298 K): δ 7.73 (s, 8H, BAr^F_4), 7.57 (s, 4H, BAr^F_4), 2.31 (m, 6H, C*H*CH$_3$), 1.25 (doublet of heptets, 36H, $^3J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 7.1 Hz, CH_3), −8.62 (v br, 3.6H, (H_2)/H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 60.4 (d, $^1J_{RhP}$ = 107 Hz). ^{11}B NMR (CD_2Cl_2, 298K): δ −5.9 (s).

At 200 K, the ratio of **2b**/**2a** at 190 K is ∼2:1 and at 190 is ∼4:1.

[Rh(H)$_2$(η^2-H$_2$)$_2$(P^iPr_3)$_2$][BAr^F_4] (2a). ^{1}H NMR (CD_2Cl_2, 190 K): δ 7.61 (s, 8H, BAr^F_4), 7.46 (s, 4H, BAr^F_4), 2.08, (m, 6H, C*H*CH$_3$), 1.02 (m, 36H, CH_3), −1.90 (br, 4H, T_1 = 9 ms, η^2-H_2), −14.23 (br s, 1H, T_1 = 202 ms, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 190 K): δ 68.4 (d, $^1J_{RhP}$ = 92 Hz).

[Rh(H)$_2$(η^2-H$_2$)(CD_2Cl_2)(P^iPr_3)$_2$][BAr^F_4] (2b). ^{1}H NMR (CD_2Cl_2, 190 K): δ 7.61 (s, 8H, BAr^F_4), 7.46 (s, 4H, BAr^F_4), 2.08, (m, 6H, C*H*CH$_3$), 1.02 (m, 36H, CH_3), −0.28 (br, 2H, T_1 = 9 ms, η^2-H_2), −12.66 (s br, 1H, T_1 = 149 ms, Rh−H), −22.42 (s br, 1H, T_1 = 144 ms, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 190 K): δ 62.1 (d, $^1J_{RhP}$ = 100 Hz).

[Rh(H)$_2$(L)$_2$(P^iPr_3)$_2$][BAr^F_4] (2c) (L = Solvent or Agostic Interaction). A sample of **2a** was formed in situ as outlined previously. The solvent was evaporated to dryness, and the residue was dried in vacuo for 5 h to leave a dark yellow oil. Attempts to obtain analytically pure solid material repeatedly failed due to the ready decomposition of this compound.

Table 1. Crystal Data and Structure Refinement for **1a** [*closo*-$CB_{11}Me_{11}$H]

empirical formula	$C_{48}H_{106}B_{11}P_2Rh$
formula weight	967.09
temperature (K)	150(2)
wavelength (Å)	0.71073
crystal system	orthorhombic
space group	*Cmcm*
unit cell dimensions	a = 15.1320(4) Å; α = 90.000 b = 17.8420(4) Å; β = 90.000 c = 21.1990(8) Å; γ = 90.000
volume (Å^3)	5723.4(3)
Z	4
density (calculated) (mg/mm^3)	1.122
absorption coefficient (mm^{-1})	0.384
F(000)	2096
crystal size (mm)	0.15 × 0.15 × 0.10
theta range for data collection (deg)	3.53−27.43
index ranges	−19 ← h ← 19; −23 ← k ← 22; −27 ← l ← 27
reflections collected	44653
independent reflections	3458 [R(int) = 0.1009]
reflections observed (>2σ)	1921
data completeness	0.993
absorption correction	none
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3458/117/227
goodness-of-fit on F^2	1.807
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.1511; wR_2 = 0.4626
R indices (all data)	R_1 = 0.2208; wR_2 = 0.4920
largest diff. peak and hole (eÅ^{-3})	3.554 and −1.701

^{1}H NMR (CD_2Cl_2, 298 K): δ 7.72 (s, 8H, BAr^F_4), 7.56 (s, 4H, BAr^F_4), 2.33 (m, 6H, C*H*CH$_3$), 1.25 (doublet of heptets, $^3J_{PH}$ = 14.4, $^3J_{HH}$ = 7.6 Hz, 36H, CH_3), −24.36 (dt, $^1J_{RhH}$ = 40.4 Hz, $^2J_{PH}$ = 14.4 Hz, 2H, Rh−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 57.6 (d, $^1J_{RhP}$ = 104 Hz). ^{11}B NMR (CD_2Cl_2, 298 K): δ −5.9 (s).

[Rh(THF)$_2$(H)$_2$(P^iPr_3)$_2$][BAr^F_4] (3a) and [Rh (THF)(η^2-H$_2$)-(H)$_2$(P^iPr_3)$_2$][BAr^F_4] (3b). A solution of [Rh(^{i}Pr$_3$P)$_2$(nbd)][BAr^F_4] (0.018 g) in d_8-THF (0.3 mL) in a Youngs NMR tube was degassed and backfilled with 1 atm of H_2 at 170 K (∼2 atm at 298 K). On thawing, the solution rapidly changed color from orange to pale yellow to afford a mixture of **3a** and **3b** in an approximate 1:1 ratio.

^{1}H NMR (d_8-THF, 200 K), (3a): δ 7.89 (s, 8H, BAr^F_4), 7.76 (s, 4H, BAr^F_4), 2.27 (m, 6H, C*H*CH$_3$), 1.23 (m, 36H, CH_3), −24.33 (br, 2H, T_1 = 266 ms, Rh−H). ^{31}P{^{1}H} NMR (d_8-THF, 200 K): δ 55.17 (d, $^1J_{RhP}$ = 114 Hz). ^{1}H NMR (d_8-THF, 200 K), (**3b**): δ 7.89 (s, 8H, BAr^F_4), 7.76 (s, 4H, BAr^F_4), 2.27 (m, 6H, C*H*CH$_3$), 1.23 (m, 36H, CH_3), 0.30 (br, 2H, T_1 = 7 ms, η^2-H_2), −13.08 (m, 1H, T_1 = 245 ms, Rh−H), −24.89 (m, 1H, T_1 = 252 ms, Rh−H). ^{31}P-{^{1}H} NMR (d_8-THF, 200 K): δ 64.14 (d, $^1J_{RhP}$ = 103 Hz).

X-ray Crystallography. Single crystals were analyzed using a Nonius Kappa CCD diffractometer. Details of the data collection, solutions, and refinements are given in Table 1. The model was solved and subsequently refined using full-matrix least squares in SHELXL-97.[51] This structure presented problems from the outset of the X-ray experiment. Although the crystals appeared to be of adequate as opposed to exceptional quality under the microscope, early indexation frames on many trial samples revealed less than desirable quality diffraction spots and a rather large mosaicity (1.65°). Moreover, there was a fall off in diffraction intensity at relatively low Bragg angles, necessitating a long data collection time per frame, in an attempt to ameliorate this difficulty. The main

(51) Sheldrick, G. M. *SHELX-97. A computer program for refinement of crystal structures*, University of Göttingen, Germany, 2004.

problems arose at the structure solution stage, the first hurdle being definitive space group assignment. The two contenders after detailed scrutiny were *Cmcm* and *C*2/*c*. Integration of the data in either of the associated Laue symmetries failed to clearly reveal which of the two options was correct. Thus, parallel solutions and refinements were conducted in both space groups. Unfortunately, the model in both cases was seen to suffer from disorder. Given the quality of the data set, that the *R*(int) values for either space group differed by less than 0.6%, and that the shift/esd values were similar in both refinements, we decided to present our results in the higher symmetry option. Taking the problems outlined previously into account, we make no claim herein with regard to the metric data for this structure. The asymmetric unit in this structure was seen to consist of a cation, in which a $[Rh(PCy_3)_2]^+$ fragment was visible, and a [*closo*-$HCB_{11}Me_{11}$] anion. In the cation, the central rhodium was seen to be located at a special position with local *m2m* symmetry, while P1, C1, and C4 are all seated on a mirror plane perpendicular to the *a* axis. A 50:50 disorder of the cyclohexyl ring based on C5 was successfully modeled, with the restraint (in each of the disordered fragments) that all C−C distances be similar and that the ADPs of the partial carbons be alike. The anionic fragment as presented contains four half-occupancy boron atoms, one full-occupancy boron, four half-occupancy methyl carbon atoms, and one full-occupancy methyl carbon. All half-occupancy atoms are located on mirror planes intrinsic in the space group symmetry. The cage carbon would appear to be disordered over the two symmetry related B2 sites. However, no attempt was made to model dual occupancy of this site by both carbon and boron partials because of the data quality (*C*2/*c* did not provide any additional illumination). Hydrogen atoms were included at calculated positions throughout. Methyl hydrogens on partial occupancy carbons in the anion are included such that they are always located on the same mirror plane as the relevant parent carbon.

DFT Calculations. Gas-phase geometry optimization for all multinuclear solutes were performed using the Gaussian 03 program.[52] Structures were optimized without any symmetry constraints using DFT at the B3LYP hybrid method[53,54] with the DZVP basis set.[55] Geometry optimization for complexes used the Berny routine. The nature of each stationary point was verified through frequency calculations.

Acknowledgment. The Royal Society (A.S.W.) and the EPSRC (GR/R36824/01 and GR/T10169/01) are thanked for funding.

Supporting Information Available: CIF file for the structure of **1a** and DFT calculated structures with selected bond lengths and angles for $[RhH_6(PMe_3)_2]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0482739

(52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, Revision A.1 ed.; Gaussian, Inc.: Pittsburgh, PA, 2003.
(53) Lee, C.; Yang, W.; Parr, G. R. *Phys. Rev. B* **1988**, *37*, 785.
(54) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(55) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.