Abstract: Cyclic voltammetry on the octahedral rhodium clusters with 12 bridging hydride ligands, [Rh₆(PR₃)₆H₁₂][BAR₄]₂ (R = Cy, Cy-H[12]²⁺; R = Pr, Pr-H[12]²⁺; [BAR₄]⁻ = [B(C₆H₄CF₃)₄]⁻) reveals four potentially accessible redox states: [Rh₆(PR₃)₆H₁₂][BAR₄]₂⁰⁻/²⁺. Chemical oxidation did not produce stable species, but reduction of Cy-H[12]²⁺ using Cr(η⁵-C₅H₅)₂ resulted in the isolation of Cy-H[12]⁻. X-ray crystallography and electrospray mass spectrometry (ESI-MS) show this to be a monocation, while EPR and NMR measurements confirm that it is a monoradical, S = ½, species. Consideration of the electron population of the frontier molecular orbitals is fully consistent with this assignment. A further reduction is mediated by Co(η⁵-C₅H₅)₂. In this case the cleanest reduction was observed with the tri-isopropyl phosphine cluster, to afford neutral Pr-[H12]. X-ray crystallography confirms this to be neutral, while NMR and magnetic measurements (SQUID) indicate an S = 1 paramagnetic ground state. The clusters Cy-[H12]¹⁺ and Pr-[H12] both take up H₂ to afford Cy-[H12]²⁺ and Pr-[H14], respectively, which have been characterized by ESI-MS, NMR spectroscopy, and UV–vis spectroscopy. Inspection of the frontier molecular orbitals of S = 1 Pr-[H12] suggest that addition of H₂ should form a diamagnetic species, and this is the case. The possibility of “spin blocking” in this H₂ uptake is also discussed. Electrochemical investigations on the previously reported Cy-[H16]²⁺ [J. Am. Chem. Soc. 2006, 128, 6247] show an irreversible loss of H₂ on reduction, presumably from an unstable Cy-[H16]¹⁺ species. This then forms Cy-[H12]³⁺ on oxidation which can be recharged with H₂ to form Cy-[H16]⁰. We show that this loss of H₂ is kinetically fast (on the millisecond time scale). Loss of H₂ upon reduction has also been followed using chemical reductants and ESI-MS. This facile, reusable gain and loss of 2 equiv of H₂ using a simple one-electron redox switch represents a new method of hydrogen storage. Although the overall storage capacity is very low (0.1%), the attractive conditions of room temperature and pressure, actuation by the addition of a single electron, and rapid desorption kinetics make this process of interest for future H₂ storage applications.

Transition metal clusters offer unique perspectives in molecular chemistry. They represent soluble molecular models for metal particles, are generally of high symmetry, have delocalized electronic structures, and have narrowly spaced frontier molecular orbitals which also show a high degree of metal character, while the core metal structure is often characterized by structural integrity. All these facets lead to a significant interest in the redox chemistry and magnetism of transition metal clusters, and many support sequential redox events and show paramagnetism in isolated species.¹–⁴ For the later transition metal clusters with π-accepting ligands, typically carbon monoxide, multiple redox steps have been observed, and up to 10 sequential reversible reductions have been reported for the high-nuclearity platinum cluster [Pt₉(CO)₁₆]⁰ (n = 0 to −10).³ Indeed such condensed metal carbonyl clusters have been termed “electron sinks”⁵ and often display rich electrochemistry associated with the reversible addition of electrons. Given this, only a handful of late-transition metal clusters with π-accepting ligands have been reported in which chemically reversible redox pairs can be isolated and characterized spectroscopically,⁵ or...
even more rarely crystallographically.\textsuperscript{4,7–10} In contrast, different redox states of transition metal clusters with $\pi$-donating ligands (such as chalogen and halides) are often synthetically more accessible, and crystallographic characterization of three members of the trigonal prismatic clusters $[W_6 Cl_{18}]^{n-}$ \textsuperscript{(n = 0 to 4)}\textsuperscript{11} and $[W_6 NC_18]^{n-}$ (n = 1 to 3),\textsuperscript{12} four of $[Fe_6 S_8 (PEt_3)_6]^{n+}$ (n = 0 to 4),\textsuperscript{13} and two of $[Mo_6 S_8 (PEt_3)_6]^{n+}$ (n = 1 to 2–3)\textsuperscript{14} have been described, among others.\textsuperscript{4} Hexanuclear cluster compounds with edge-bridged halide ligands also exhibit extensive redox behavior,\textsuperscript{15–17} and redox pairs such as $[Ta_3 Cl_2 (PEt_3)_3]^{n+}$ (n = 0, 1)\textsuperscript{18} have been structurally characterized (Scheme 1). The redox flexibility apparent in many of these clusters comes from the ease of addition or removal of electrons from metal-localized orbitals (Figure 1).

We have recently reported the synthesis of a new class of transition metal cluster, $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$ (R = Cy; $[H12]^+$, Pr$^+$Pr-[H12]$^{2+}$; $[BAr_F 4]$ = $[B(C_6 H_5)(CF_3)_2]_2^-$) which are composed of late transition metal centers (Rh) but have structures that are directly analogous to early transition metal clusters with edge-bridged halide ligands, such as $[Nb_6 Cl_{18}]^{4-}$, in that each Rh–Rh edge in the octahedron is bridged by a hydride ligand (Scheme 1).\textsuperscript{19,20} This similarity extends to the electronic structure of the rhodium clusters, which show eight orbitals involved in metal–metal bonding which are of the same symmetry as those of the halide-bridged clusters.\textsuperscript{21} However, the move from group 5 metals (e.g., Nb) with bridging halides to a group 9 metal (Rh) with phosphines and hydrides results in 12 additional metal-localized filled orbitals primarily of nonbonding nature in $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$.

Calculations also show that under octahedral symmetry $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$ (generically referred to as $[H12]^+$) has two, low lying, empty orbitals of $e_g$ symmetry, only ~0.3 eV higher in energy than the $a_{2g}$ HOMO. These orbitals are well set up to receive four electrons, and we have demonstrated this by the facile addition of two molecules of $H_2$ to afford $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$ ($[H16]^+$) (Scheme 2).\textsuperscript{20,22} This results in an electronic configuration that shows a significantly larger HOMO–LUMO gap (1.3 eV). A similar set of low-lying orbitals in the unsaturated cluster $Pt_3 Re_2 (CO)_6 (PBU_3)_3$ also allow the uptake of $H_2$, in this case 3 equiv per cluster.\textsuperscript{24} For $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$, $H_2$ addition is reversible (and can be cycled), as placing under a vacuum ($5 \times 10^{-3}$ Torr) or addition of a hydrogen acceptor such as tert-butylenne (tbe) regenerates $[Rh_6 (PR_3)_6 H_{12}][BAr_F 4]_2$ ($[H16]^+$), quantitatively.\textsuperscript{20,23} The $PCy_3$ functionalized cluster (Cy-$[H12]^+$) holds onto the hydrogen much more strongly than the $Pr_3$ cluster (days versus hours, respectively, when placed under a vacuum). We attribute this...
to kinetic stabilization afforded toward hydrogen loss by the bulkier cyclohexyl groups, as electronically both clusters would be expected to be very similar. Although cluster complexes with hydride ligands are common, those that can reversibly take up and release H2 are few.25–30 Both DFT calculations and H/D exchange experiments are strongly suggestive of two dihydrogen ligands on the cluster surface of this 16-hydride species;30 and the average interaction energy of the two extra H2 molecules with the cluster is calculated to be 0.62 eV (60 kJ mol−1) per dihydrogen.34 This is comparable with the binding energy both calculated and experimentally determined for dihydrogen bound to a single metal center (~60–100 kJ mol−1).31

The four electrons that can fill the low-lying eg set in [H12]2+ do not have to come from two bonding pairs in H2. In principle they can also arise from simple addition of electrons by electrochemical or chemical reduction (as in the facile uptake of electrons into an unoccupied eg set in [Pt6(m-η2-Bu2)(CO)12][PF6][PF6]).32 In this respect the structural and electronic analogies between [Rh6(PR3)6H12][BARF4]2 and clusters with η-donating ligands should extend to the observation of sequential redox events. We report here that this is the case. The clusters [Rh6(PR3)6H12][BARF4] show a reversible set of redox processes by cyclic voltammetry, two reductions and an oxidation, and we demonstrate using chemical reductants that the products of sequential addition of electrons can be isolated and fully characterized. We also comment on the ability of these reduced species to take up dihydrogen and conclude by showing that hydrogen uptake and release in these clusters can be switched electrochemically, demonstrating a new concept in the storage and release of dihydrogen that has implications for the emerging hydrogen economy.33 Aspects of this work have been communicated previously.34

Results and Discussion

Electrochemical study of [Rh6(PCy3)6H12][BARF4]2. Electrochemical investigations were performed in CH2Cl2 solvent using 0.1 M [NBu4][BARF4] as a supporting electrolyte, as use of the more common [NBu4][PF6] led to cluster decomposition, presumably by attack of the hexafluorophosphate anion (or fluoride derived from hydrolysis of this anion) on the cluster. Figure 2 shows the cyclic voltamogram of [Rh6(PCy3)6H12][BARF4]2, Cy-[H12]2+ in CH2Cl2 solution. An equivalent voltamogram was obtained for [Rh6(PR3)6H12][BARF4]2 (see Supporting Information), but as this also indicated signs of decomposition we restrict the following discussion to the tricyclohexylphosphine cluster.

Two chemically reversible reduction events are apparent, consistent with Cy-[H12]2+/1+ and Cy-[H12]1+/0 at E1/2 = −0.59 V (ΔEp = 130 mV) and E1/2 = −1.51 V (ΔEp = 140 mV) versus (η2-C6H6)2Fe0/+1. The peak to peak separations (ΔEp) are dominated by ohmic effects, and all these processes are close to reversible. A single, one-electron oxidation at E1/2 = +0.44 V (ΔEp = 220 mV) is assigned to Cy-[H12]2+/1+, and the larger peak to peak separation for this electron-transfer process indicates quasireversible characteristics. Microelectrode experiments (see Experimental Section) confirmed the consumption of one electron per redox event. Although all the redox states of the cluster are potentially chemically accessible, we demonstrated later that only the reductions led to products that could be isolated.

Consideration of the frontier molecular orbitals of [H12]2+ shows that sequential addition of electrons affords the electronic configurations shown in Scheme 3. For [H12] two possible spin states (S = 1 or S = 0) are conceptually possible, depending on the occupation of the eg set of orbitals.

Synthesis, Characterization, and Solid-state Structures of the Reduced Clusters. Addition of the oxidant [N(C6H4Br-4)][B(C6F5)4]37,38 (E1/2 = +0.70 V) to [Rh6(PCy3)6H12]+ [B(C6F5)4]2−, Cy-[H12]2+ did not result in the isolation of the electrochemically observed [H12]2+. Although 1H and 31P NMR spectroscopy indicated the formation of a paramagnetic, attempts to isolate material only resulted in Cy-[H12]2+ and another decomposition products (by NMR and electrospray ionization mass spectrometry, ESI-MS). Significantly more success was achieved with the chemical reductions. Inspection

References

of the cyclic voltammogram suggested that Cr($\eta^6$-C$_6$H$_6$)$_2$ ($E_{1/2}$ = −1.15 V) would be a suitable chemical reductant to isolate Cy-$[H12]^{+}$. Addition of excess (ca. 2 equiv) of Cr($\eta^6$-C$_6$H$_6$)$_2$ to a difluorobenzene solution of Cy-$[H12]^{2+}$ and recrystallisation afforded [Rh$_6$(PCy$_3$)$_6$H$_{12}$][BAr$_F$$_4$], Cy-$[H12]^+$, in good (76%) isolated yield, which was characterized by NMR, ESR, ESI-MS, microanalysis, and single-crystal X-ray diffraction (Scheme 4).

The $^1$H NMR spectrum of Cy-$[H12]^+$ shows no hydride resonances, consistent with a radical species in which the unpaired electron is metal-based. An Evans measurement$^{39}$ (in CH$_2$Cl$_2$) gave an effective magnetic moment of $\mu_{\text{eff}}$ = 1.82 BM, close to the value expected for a single unpaired electron ($\mu_{\text{eff}}$ = 1.73 BM). The cyclohexyl phosphine protons are paramagnetically shifted and broadened, and a 6:6:6:180 relative ratio is observed. The three resonances which integrate to six protons each are centered at $\delta$ 35.7 (fwhm 430 Hz), 16.5 (fwhm 275 Hz), and 5.4 (fwhm 380 Hz), respectively. We explain this pattern by hindered rotation of the triscyclohexylphosphine groups that affords three ipso-CH environments orientated differently with regard to the cluster core. Hindered rotation of the bulky phosphine groups is also observed in the diamagnetic precursor Cy-$[H12]^{2+}$.$^{20}$ As expected for a radical species no resonances were observed in the $^{31}$P($^1$H) NMR spectrum. ESI-MS showed the expected isotope pattern ($m/z$ 2310.9 calcld, 2311.1 obsd) which is consistent with a monocation (Figure 3). The ESR spectrum (Figure 4) showed an isotropic and strong signal with a $g$ value close to free spin (2.010), indicating the unmistakable presence of an unpaired electron in the sample. Addition of the oxidant [Fe($\eta^6$-C$_5$H$_5$)$_2$][BAr$_F$$_4$] to a CH$_2$Cl$_2$ solution of Cy-$[H12]^+$ regenerates the cation Cy-$[H12]^{2+}$, showing that this redox couple is chemically reversible.

The solid-state structure of Cy-$[H12]^+$ confirms the monocationic formulation of the cluster, with only one [BAr$_F$$_4$]$^-$ anion associated with each rhodium octahedron (Figure 5). The crystallographic analysis also shows there are two independent cation/anion pairs in the solid state. Bond lengths and angles are effectively the same in both. Both clusters have crystallographically imposed $C_2$ symmetry in which the 2-fold axis
bisects two opposite Rh–Rh bonds. Table 1 presents selected metric data for Cy-[H12]+, alongside that for the precursor cluster Cy-[H12]2+. These show that there is no major change in the cluster core on addition of a single electron, the only notable difference being that Rh–Rh distances contract slightly (ca. 0.01 Å). The lack of significant structural change is consistent with the addition of an electron to a nonbonding Rh–Rh orbital (Figure 1).20 The hydride ligands in Cy-[H12]+ were all located in the final difference electron density map, and within error they bridge each Rh–Rh edge symmetrically.

With regard to the 1H NMR spectrum that suggests three different ipso-CH cyclohexyl environments, close inspection of the structure of Cy-[H12]2+ reveals that for each phosphine the cyclohexyl rings adopt three different orientations leading to three ipso-CH environments, two pointing more toward the cluster core (syn) and one pointing away (anti). This pattern is repeated for each phosphine ligand and, if retained in solution (i.e., the phosphine ligands were locked toward rotation), would lead to a 6:6:6 pattern in the 1H NMR spectrum for these hydrogen atoms, as is observed.

Addition of excess Co(η5-C5H5)(Ei/2) (Ei/2 = −1.33 V) or Co(η5-C5Me5)(Ei/2 = −1.94 V) to Cy-[H12]2+ resulted in a paramagnetic species that showed a 1H NMR spectrum similar to that of Cy-[H12]+. Attempts to isolate a pure, neutral, product failed due to the low solubility in pentane or toluene meaning that removal of ionic byproducts was not possible. However, addition of excess Co(η5-C5H5) to [Rh6(PPr3)6H12][BARF4]2 in 1,2-difluorobenzene ultimately resulted in a pentane-soluble blue-green product that could be recrystallized in moderate yield (56%) from cold pentane and was identified as the neutral cluster.

Table 1. Comparison of Cluster-Core Metrics for Complexes Cy-[H12]2+, Cy-[H12]+, and iPr-[H12]2+

<table>
<thead>
<tr>
<th>Metric</th>
<th>Cy-[H12]2+</th>
<th>Cy-[Rh(P2O3)6]2+[H12]+</th>
<th>Pr-[H12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh–Rh mean, Å</td>
<td>2.735(1)</td>
<td>2.735(1), 2.735(1)</td>
<td>2.741(1)</td>
</tr>
<tr>
<td>Rh–Rh, Å</td>
<td>2.743(1)–2.719(1)</td>
<td>2.753(1)–2.707(1)</td>
<td>2.742(1)–2.739(1)</td>
</tr>
<tr>
<td>δ(Rh–Rh), Å</td>
<td>0.024</td>
<td>0.046, 0.030</td>
<td>0.003</td>
</tr>
<tr>
<td>Rh⋯Rh cross-cluster, Å</td>
<td>3.869(1)–3.858(1)</td>
<td>3.870–3.866</td>
<td>3.875</td>
</tr>
<tr>
<td>δ(Rh⋯Rh), Å</td>
<td>0.011</td>
<td>0.004, 0.058</td>
<td>n/a</td>
</tr>
<tr>
<td>δ(P⋯P), deg</td>
<td>0.013</td>
<td>0.002, 0.078</td>
<td>0</td>
</tr>
<tr>
<td>Rh–P mean, Å</td>
<td>2.262(1)</td>
<td>2.254(1), 2.251(1)</td>
<td>2.227(1)</td>
</tr>
<tr>
<td>Rh⋯Rh–P, deg</td>
<td>178.3(1)–177.3(1)</td>
<td>177.9(1)–176.9(1)</td>
<td>177.5(1)</td>
</tr>
<tr>
<td>Rh–H, Å</td>
<td>1.89(5)–1.66(5)</td>
<td>1.87(4)–1.68(4)</td>
<td>1.70(2)–1.78(2)</td>
</tr>
</tbody>
</table>

a Maximum deviation in distances. b Data taken from ref 20. This paper also presents metric data for Pr-[H12]2+. c Two crystallographically independent molecules in the unit cell.

Figure 6. Variable-temperature magnetic data for compound Pr-[H12].

Reduction of High Hydride Count Rh Octahedral Clusters

ARTICLES

J. AM. CHEM. SOC. 9 VOL. 129, NO. 6, 2007 1797

Rh₆(PPr₃)₁₂H₁₂, 'Pr-[H12] (Scheme 5). Although cobaltacene should not be able to effect a two-electron reduction ($E_{1/2} - 1.33$ V versus $-1.51$ V for [H12]₀/+), we suggest that preferential crystallization of iPr-[H12] from cold difluorobenzene solution during workup, which also contains excess Co(Ł₅-C₅H₅)₂ and iPr-[H12]⁺, drives the reduction to completion. Use of the stronger reducing agent Co(Ł₅-C₅Me₅)₂ resulted in difficulties in purification due to the similarities in solubility between reductant and product.

Addition of two electrons to iPr-[H12] can conceptually result in two possible electronic configurations. If the two electrons occupy a single $e_g$ orbital then an $S=0$ ground state results, and the cluster is diamagnetic. Alternatively, one electron in each $e_g$ orbital would result in an $S=1$ ground state and a paramagnetic cluster. ¹H NMR spectroscopy is consistent with a paramagnetic complex and thus a $S=1$ ground state. The hydride ligands are not observed, while the methine isopropyl protons are observed as a single, broad, paramagnetically shifted resonance at $δ$ 30.87 (18 H, fwhm 83 Hz). Unlike Cy-[H12]⁺ restricted rotation of the slightly smaller tris-isopropylphosphine groups is not observed, just as in the diamagnetic precursor [Rh₀(PPr₃)₁₂][H₁₂][BarF₄]²⁻.¹² Evans measurements (toluene) afforded an effective magnetic moment of $μ_{eff} = 2.89$ BM, close to the value predicted for 2 unpaired electrons ($μ_{eff} = 2.83$ BM). Surprisingly, EPR measurements, even at very low temperatures ($5–10$ K), gave featureless spectra. The $S=1$ ground state was unequivocally confirmed by variable temperature magnetic susceptibility measurements. Figure 6 shows the temperature dependence of $μ_{eff}$ for 'Pr-[H12] measured in an applied magnetic field of 1 T. The moment observed at room temperature is reasonable for an $S=1$ system with two unpaired electrons, and there is essentially no variation in $μ_{eff}$ at temperatures down to 5 K. Interestingly below 5 K, $μ_{eff}$ starts to drop off which might be indicative of a singlet ground state at very low temperatures or weak, antiferromagnetic coupling between the clusters. Alternatively a gross structural rearrangement of the hydride ligands, forming a molecule with lower symmetry at very low temperature, could also account for the observed magnetic behavior. The $S=1$ groundstate observed in 'Pr-[H12] is in contrast to diamagnetic ($S=0$) Pt₀(μ-PBu₂)₄(CO)₆ which is formed on a two-electron reduction of a dicaticionic precursor which has a degenerate $e_g$ set of LUMOs. In this case a Jahn–Teller distortion is suggested to be operating.¹²

The solid-state structure of 'Pr-[H12] is shown in Figure 7 and confirms the neutral cluster core. In the solid-state, 'Pr-[H12] crystallizes in the rhombohedral space group R₃, and this leads to each cluster {Rh(PPr₃)} vertex being crystallographically identical. The high symmetry associated with the molecule also means that there are only two crystallographically distinct hydride environments. These two different hydrides both span the Rh–Rh edges symmetrically as determined within the limits of the X-ray diffraction experiment. On reduction, compared to 'Pr-[H12]²⁺, the mean Rh–Rh distances become marginally longer [2.741 and 2.720 Å in 'Pr-[H12] and 'Pr-[H12]²⁺,
Figure 7. Solid-state structure of neutral \( ^{1}\text{Pr}[-\text{H12}] \) (50% thermal ellipsoid), showing atom labeling scheme. Inset shows an expanded view of the metal core viewed down the \( C_{3v} \) axis that demonstrates the two different hydride environments \( H(1) \) and \( H(2) \) imposed by crystallographic symmetry.

respectively) and the mean Rh–P distances become slightly smaller [2.227 and 2.246 Å, respectively]. This latter observation continues the trend observed in \( \text{Cy}[-\text{H12}]^{+} \).

Dihydrogen Uptake by the Clusters \([\text{Rh6}(\text{PR3})_{6}\text{H12}]^{0/1}\). The reversible uptake of hydrogen by molecular or extended materials (such as nanoclusters) is an area that is attracting significant current interest, and much of this interest has centered on the role that such species play in hydrogenation reactions (especially arene hydrogenation), in particular the nature of the actual species in catalysis (nanocluster versus molecular cluster), \(^{41–46}\) and potential hydrogen storage applications. \(^{33,47–51}\) We have recently demonstrated that the clusters \([\text{Rh6}(\text{PR3})_{6}\text{H12}]^{0/1}-\text{[BArF4]}_{2}\) reversibly take up two molecules of \( \text{H2} \) under ambient \( (1 \text{ atm H2}) \) conditions as a result of their electronic structure which contains two low lying, empty orbitals. Although reduction of these clusters adds electrons to these orbitals, they do not become fully filled and thus we reasoned that the reduced clusters should still be able to take up \( \text{H2} \) (Scheme 6).

Addition of \( \text{H2} \) (1 atm) to a \( \text{CH2Cl2} \) solution of \( \text{Cy}[-\text{H12}]^{+} \) led to uptake of \( \text{H2} \). Although the \( ^{1}\text{H} \) NMR spectrum of the product demonstrated a paramagnetic species, and the \( ^{31}\text{P}(^{1}\text{H}) \) NMR spectrum was featureless, ESI-MS showed the formation of the 14-hydride species \([\text{Rh6}(\text{PCy3})_{6}\text{H14}]^{+} \) (\( m/z \) calcld 2312.9, obsd 2313.1) and UV–visible spectroscopy (Supporting Information) showed a distinct change in the electronic absorption spectrum on addition of \( \text{H2} \). Efforts to isolate \( \text{Cy}[-\text{H14}]^{+} \) always led to loss of \( \text{H2} \) and the formation of \( \text{Cy}[-\text{H12}]^{+} \). Calculations\(^{34}\) suggest that the structure of \([\text{H14}]^{+} \) has a dihydrogen ligand on the surface, similar to the structure suggested for \([\text{H16}]^{2-} \).\(^{20}\) Addition of \( \text{D2} \) to a \( \text{CH2Cl2} \) solution of \( \text{Cy}[-\text{H14}]^{+} \) results in the slow (hours) appearance of \( \text{H2} \) and \( \text{HD} \) in the \( ^{1}\text{H} \) NMR spectrum, which is consistent with, although not unambiguous proof of, energetically accessible dihydrogen on the cluster surface.\(^{51}\)

In contrast to the paramagnetism of \( \text{Cy}[-\text{H14}]^{+} \), addition of \( \text{H2} \) to neutral \( ^{1}\text{Pr}[-\text{H12}] \) results in a diamagnetic cluster species which we assign as \( ^{1}\text{Pr}[-\text{H14}] \). This diamagnetism is fully consistent with the addition of an electron pair to the \( e_{g} \) orbitals in \( ^{1}\text{Pr}[-\text{H12}] \), which has a triplet spin state. Presumably \( \text{H2} \) addition occurs via a higher energy singlet intermediate, although we have not investigated this computationally. Examples exist of \( \text{H2} \) addition to triplet ground state complexes to form a singlet, diamagnetic, hydride product; for example addition of \( \text{H2} \) to \( \text{WH}([\text{CH2CH2NSiMe3}])_{3} \).\(^{52}\) This reaction has been put forward as an example of “spin-blocking”, where there is a significant barrier along the reaction coordinate.


induced by a spin change.\(^{53}\) Although we are not in a position to comment in detail on the possibility of such a process occurring here, it is interesting to note that \(\text{H}_2\) addition is significantly slower for \(\text{i-Pr-}[\text{H}_{12}]^+\) (16 h at 4 atm \(\text{H}_2\)) than that for \(\text{Cy-}[\text{H}_{16}]^+\) (effectively instantaneous under the same conditions).\(^{20}\) Also the back, dehydrogenation, reaction with 1-hexene is not observed to proceed, whereas for \(\text{Cy-}[\text{H}_{16}]^+\) this is facile, in agreement with spin change arguments. Consistent with a diamagnetic formulation, the \(\text{^1H} \) NMR spectrum of \(\text{i-Pr-}[\text{H}_{14}]^+\) shows no paramagnetically shifted resonances. In the high-field region a broad hydride resonance at \(\delta - 25.6\) is observed that integrates consistently to only 13 \(\text{H}\) (12.9 \(\text{H}\)) relative to the isopropyl groups, rather than the expected 14 \(\text{H}\). This slightly low integral (by 7%) could be a reflection of the broadness of the peak and the inherent difficulties in accurately determining hydride integral values, but it could also suggest a structure with 13 mutually exchanging surface hydride ligands and one (broad and unobserved) interstitial hydride.\(^{54–56}\) Indeed we have commented on a similar arrangement of the hydride ligands for \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{16}][\text{BAF}_4]\).\(^{20}\)

The room temperature \(\text{^31P}[^1\text{H}] \) NMR spectrum shows a single broad peak. At low temperature the \(\text{^31P}[^1\text{H}] \) NMR spectrum reveals two sharper signals in the ratio 2:5 that both display Rh–P coupling. At this temperature the \(^1\text{H} \) NMR spectrum displays two hydride environments also in the approximate 2:5 ratio. Further cooling (200 K) results a 1:1.5 ratio in both the \(\text{^31P}[^1\text{H}] \) and \(^1\text{H} \) NMR spectra in the hydride region. The overall hydride integral value remains approximately 13 \(\text{H}\). This temperature-dependent behavior suggests two isomers in solution, both having exchanging hydride ligands. Longitudinal relaxation time measurements (\(T_1\)) revealed a minimum value for these hydride signals of 72 ms at 250 K (400 MHz). This relatively short relaxation time could suggest exchange between hydride and dihydrogen ligands at this temperature. Similar exchange is observed for \([\text{Ir(H)}_2(\text{η}^2-\text{H}_2\text{PCy}_3)_2]^+\) and \([\text{Ru(H)}_2(\text{η}^2-\text{H}_2\text{PCy}_3)_2]^+\).\(^{57–59}\) Intact cluster dihydrogen ligands have been suggested in \([\text{H}_6\text{Ru}_4(\text{C}_6\text{H}_6)_4]^+\) on the basis of a \(T_1\) measurement of 34 ms at 200 MHz.\(^{60}\) Given that \(T_1\) depends linearly on field strength,\(^{61}\) this value is similar to the one we observe at 400 MHz. Addition of \(\text{D}_2\) (1 atm, 313 K) to \(\text{i-Pr-}[\text{H}_{12}]^+\) slowly (4 days) results in the formation of \(\text{HD(g)}\) and the

---

complete deuteriation of the hydrides on the cluster, and although this is consistent with accessible dihydrogen on the cluster surface it is not unambiguous proof. Whatever the actual arrangement of hydride ligands in $\text{Pr}_{5}$, importantly small addition of H$_2$ to paramagnetic $\text{Pr}_{5}$ affords a diamagnetic product fully consistent with the addition of one molecule of H$_2$ (i.e., one electron pair) to the cluster. UV−vis spectroscopy (see Supporting Informations) showed a subtle, but distinct, change in the electronic absorption spectrum on addition of H$_2$.

Redox-Promoted Hydrogen Loss. Inspection of the M.O. diagram for $\text{H}_2$-coordinated clusters (Scheme 6) suggests that addition of another electron would result in the population of a high-lying orbital, and this could destabilize the cluster resulting in H$_2$ loss to re-establish a large HOMO−LUMO gap. If coupled with a sequential oxidation of the cluster, this potentially could lead to the reversible binding and release of H$_2$, triggered by a single electron redox event. Such a process has implications for the storage of hydrogen for future energy applications.

Figure 8 displays the cyclic voltammogram for Cy-[H16]$^{2+}$, which shows an irreversible one-electron reduction at $E_{1/2} \approx -1.00$ V, relative to Fe($\sigma^2$-C$_5$H$_5$)$_2$ (eq 6). Progressively increasing the scan rate to 10 V s$^{-1}$ leads to the observation of the back-oxidation, which yields a half-life for the reduced intermediate of 170 ms at 293 K (or a chemical rate constant $k = 5.9 \pm 1.0$ s$^{-1}$). The irreversible reduction is followed by a reversible reduction at exactly the same potential as Cy-[H12]$^{2+}$ ($E_{1/2} \approx -1.51$ V). The return oxidation sweep also shows Cy-[H12]$^{2+}$ ($E_{1/2} \approx -0.59$ V) and Cy-[H12]$^{3+}$ ($E_{1/2} \approx +0.44$ V) with no other new redox event observed. These redox events also show diffusion controlled kinetics. Overall these observations are very strongly suggestive of an electrochemical process in which addition of a single electron to Cy-[H16]$^{2+}$ results in elimination of 2 equiv of H$_2$ from an unstable intermediate Cy-[H16]$^{2+}$ and the formation of Cy-[H12]$^{+}$ (eq 1). Using the fully deuterated cluster Cy-[D16]$^{2+}$ (prepared from addition of D$_2$ to Cy-[H16]$^{2+}$ for 3 days)$^{20}$ resulted in an unchanged cyclic voltammogram. Calculations for the half-life of the reduced intermediate, Cy-[D16]$^{+}$, also afford the same rate constant within error for loss of D$_2$ from the cluster compared with Cy-[H16]$^{+}$. However, the error in these rates is significant, and thus we are reluctant to state with any confidence whether an isotope effect is, or is not, operating. Kinetic isotope effects have been observed for dihydrogen loss from mononuclear complexes.$^{31}$

$$\text{Cy-[H16]}^{2+} \rightarrow \text{Cy-[H16]}^{+} \rightarrow \text{Cy-[H12]}^{+} \text{H}_2$$

Use of a platinum electrode rather than a glassy carbon electrode resulted in a significant reduction in the relative observed current for the irreversible event at $E_{1/2} \approx -1.00$ V attributed to reduction of Cy-[H12]$^{2+}$ and subsequent H$_2$ loss from Cy-[H16]$^{+}$, while the redox events associated with Cy-[H12]$^{2+}$ remained unchanged (see Supporting Information). This is presumably due to the facile loss of H$_2$ to platinum and is not unexpected given the high affinity platinum has for H$_2$.$^{62,63}$ This observation further underscores that the irreversible redox event is due to H$_2$ loss. Under a H$_2$ atmosphere the same redox processes are still observed, notably the irreversible loss of H$_2$ (see Supporting Information).

These processes may also be followed by ESI-MS, NMR spectroscopy, and chemical redox agents (Figure 9 for ESI-MS spectra). Addition of the reducing agent Cr($\pi^2$-C$_5$H$_5$)$_2$ ($E_{1/2} \approx -1.15$ V) to a CH$_2$CL$_2$ solution of Cy-[H16]$^{2+}$ results in the

Table 2. Crystal and Structure Refinement Data for the New Cluster Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>Cy-[H12][BAr$_F^6$]-5.5[C$_6$H$_5$CH$_3$]</th>
<th>Pr-[H12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{176.50}$H$</em>{255.56}$BF$_4$P$_4$Rh$_6$</td>
<td>C$_{54.16}$P$_4$Rh$_8$</td>
</tr>
<tr>
<td>formula weight</td>
<td>3681.50</td>
<td>1590.92</td>
</tr>
<tr>
<td>temperature</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>wavelength/Å</td>
<td>0.710 73</td>
<td>0.8460</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>rhombohedral</td>
</tr>
<tr>
<td>space group</td>
<td>P2/n</td>
<td>R3</td>
</tr>
<tr>
<td>a / Å</td>
<td>20.3420(1)</td>
<td>13.4673(5)</td>
</tr>
<tr>
<td>b / Å</td>
<td>24.4480(2)</td>
<td>13.4673(5)</td>
</tr>
<tr>
<td>c / Å</td>
<td>35.3600(3)</td>
<td>33.922(2)</td>
</tr>
<tr>
<td>α / deg</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ / deg</td>
<td>90.13</td>
<td>90</td>
</tr>
<tr>
<td>volume / Å$^3$</td>
<td>17585.2(2)</td>
<td>5328.1(5)</td>
</tr>
<tr>
<td>density (calculated) / mg/m$^3$</td>
<td>1.391</td>
<td>1.489</td>
</tr>
<tr>
<td>absorption coefficient / mm$^{-1}$</td>
<td>0.679</td>
<td>1.526</td>
</tr>
<tr>
<td>F(000)</td>
<td>7670</td>
<td>2466</td>
</tr>
<tr>
<td>crystal size / mm$^3$</td>
<td>0.35 x 0.35 x 0.10</td>
<td>0.10 x 0.10 x 0.05</td>
</tr>
<tr>
<td>theta range for data collection / deg</td>
<td>3.53 to 28.70</td>
<td>3.60 to 29.80</td>
</tr>
<tr>
<td>reflections collected</td>
<td>188 785</td>
<td>11 064</td>
</tr>
<tr>
<td>independent reflections</td>
<td>43989</td>
<td>2004</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>989(2)/23/2222</td>
<td>0/0/114</td>
</tr>
<tr>
<td>largest diff. peak and hole/ e/Å$^3$</td>
<td>wR$_1$ = 0.0408</td>
<td>0.1000</td>
</tr>
<tr>
<td>final R$^b$ indices [I &gt; 2σ(I)]</td>
<td>wR$_2$ = 0.0874</td>
<td>R$_1$ = 0.0179</td>
</tr>
<tr>
<td>R$^b$ indices (all data)</td>
<td>wR$_2$ = 0.0454</td>
<td>R$_2$ = 0.0185</td>
</tr>
<tr>
<td>goodness-of-fit on F$^2$</td>
<td>R$_1$ = 0.1000</td>
<td>wR$_2$ = 0.0459</td>
</tr>
<tr>
<td></td>
<td>1.019</td>
<td>1.052</td>
</tr>
</tbody>
</table>

$^a$ R$_1$ = Σ |F$_o$| − |F$_c$||/Σ|F$_o$|, $^b$ wR$_1$ = (Σ w(F$_o^2$ − F$_c^2$))/Σ w(F$_o^2$) |½|, $^c$ GOF = S = (Σ[w(F$_o^2$ − F$_c^2$)/n − p]) |½|.

clean formation of \([\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}]^{2+}\). The starting material \(\text{Cy}-[\text{H14}]^{+}\) is simply returned by oxidation of \(\text{Cy}-[\text{H14}]^{+}\) using \([\text{Fe}((\text{t}-\text{C}_3\text{H}_5)_2)\text{PF}_6]^{-}\) \((E_{1/2}: 0.00 \text{ V})\) which also results in the elimination of a further equivalent of \(H_2\). This completes a storage cycle for two molecules of \(H_2\) that is triggered by the simple addition and removal of one electron.

Calculations for this redox cycle show that addition of \(H_2\) to \(\text{Cy}-[\text{H12}]^{2+}\) gives \(\text{Cy}-[\text{H16}]^{2+}\) is an overall exothermic process taking two electrons into the degenerate \(e_g\) set of LUMO orbitals which also establishes a larger HOMO–LUMO gap.34 Reduction of \(\text{Cy}-[\text{H16}]^{2+}\) to afford unstable \(\text{Cy}-[\text{H16}]^{+}\) results in \(H_2\) loss to re-establish a large SOMO/HOMO−1 gap. Why that on chemical reduction \(\text{Cy}-[\text{H14}]^{+}\) is observed, while electrochemically \(\text{Cy}-[\text{H14}]^{+}\) is formed, is not clear at the present time. Although there is this subtle change in the order of events between the solution bulk chemical processes and electrochemical processes, the overall redox hydrogen storage/release cycle holds for both: reduction of \(\text{Cy}-[\text{H16}]^{2+}\) and subsequent reoxidation to afford starting cluster \(\text{Cy}-[\text{H12}]^{2+}\) is effectively quantitative, cyclovoltammetric, and involves 2 equiv of \(H_2\) per cluster per cycle. Redox-induced loss of hydrogen or protons has been reported previously. For example irreversible oxidation of the dihydrogen complex \([\text{Co}(\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{H}(_2)]^{2+}\text{PF}_6\) results in the loss of a proton,64 while reduction of the vinylidene complex \([\text{Rh}=(\text{C}=\text{HPPh})(\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3][\text{BF}_4]\) results in \(H_2\) loss, to form an acetylide.65 Redox promoted oxidation of \(H_2\) to afford protons (or the reverse reaction, electrocatalytic generation of \(H_2\)) is, of course, also very well documented in the study of hydrogenase chemistry.66,67

**Conclusions**

We have demonstrated here that structural similarities between \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]^{2+}\) and early transition metal clusters with \(\pi\)-donor ligands extend to the redox chemistry of these clusters, inasmuch that three different redox states of the clusters, \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]^{2+}\), can be observed electrochemically and two of these isolated using chemical reductants. These new cluster species arise from simple sequential addition of electrons to the low-lying \(e_g\) set of orbitals present in the parent cluster. Furthermore, the chemically reduced clusters also take up dihydrogen in an attempt to fill these orbitals. Just as we have suggested for \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]^{2+}\), these reduced clusters can probably be isolated due to the stabilization afforded to the cluster core by the bulky, shrouding, alkylphosphine groups.20 Pleasingly, the products of uptake of electrons and \(H_2\) can be predicted from both simple consideration of the frontier molecular orbital structure as well as more sophisticated analysis of energies using DFT techniques.20,34 Once these orbitals are predicted from both simple consideration of the frontier molecular orbitals, the overall redox hydrogen storage/release cycle completes a storage cycle for two molecules of \(H_2\) that is triggered by the simple addition and removal of one electron.

Hydrogen storage is an area of intense current interest, being driven by the requirements for reversible storage of dihydrogen for future energy applications.33 Chemisorption of dihydrogen in the form of light metal hydrides is one approach to the problem of storing large amounts of \(H_2\) reversibly.68 Physisorption of dihydrogen onto porous network materials such as activated carbon, Metal Organic Framework (MOF) materials, or related systems presents an alternative method. Although significant and elegant advances have been made in both areas, challenges still remain. Metal hydrides require temperature cycling to encourage loss of hydrogen, this being a consequence of the chemisorption of hydrogen (binding energies of >100 kJ mol\(^{-1}\)), and while porous networks show reversible \(H_2\) uptake without temperature cycling, they generally require low temperatures (77 K) and an overpressure to retain \(H_2\), a consequence of the dihydrogen being physisorbed.69,71,74 MOF systems that hold onto \(H_2\) at reduced pressure (~0.01 atm) have been described, but these also only operate at 77 K.20

Given this, a material that both was a true store of hydrogen under ambient conditions of temperature and pressure and released the stored \(H_2\) without significant external thermal energy input would be of fundamental interest. The electrochemical cycle revealed here using clusters based upon \([\text{Rh}-\text{(PCy}_3)_6\text{H}_{12}]^{2+}\) clearly goes some way to addressing these needs. However, the hydrogen storage capacity by \(\text{Cy}-[\text{H12}]^{2+}\) is extremely modest, 0.1\% w/w, as the cluster and associated anions are of high molecular mass, and this value is clearly not sufficient for practical storage of \(H_2\) [US DOE 2010 target of 6.5\% by weight].75 This said, the ability to store \(H_2\) at no partial pressure of \(H_2\) (and even under a dynamic vacuum) at 298 K, coupled with the very rapid redox-promoted release of 2 equiv of \(H_2\) that returns the store quantitatively to its “uncharged” state, is, we believe, unique. These attractive features arise due to the special characteristics brought upon the system by the electronic and steric properties of the metal cluster: (i) two low-lying unoccupied molecular orbitals available for the uptake of bonding electron pairs from \(H_2\), (ii) the calculated binding energy of \(H_2\) to the cluster of 60 kJ mol\(^{-1}\) (lying at a value intermediate between physi- and chemisorption regimes), and (iii) the kinetic stabilization afforded toward facile hydrogen loss by the shrouding trialkylphosphine groupings.

**Experimental Section**

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 a vacuum, three times before use. \(\text{C}_6\text{H}_5\text{F}\) and \(\text{C}_6\text{H}_4\text{F}_2\) were distilled from \(\text{CaH}_2\). Toluen, \(\text{CH}_3\text{Cl}_2\), pentane, and hexane were

purified using an MBraun Solvent Purification System. CD2Cl2 was distilled under a vacuum from CaH2. CD2CD2Cl was vacuum transferred from a Na mirror. [Fe(η5-C5H5)2][BArF4]20 [Rh(PPh3)2H2][BARF4]; Cy-[H12]2+; and [Rh2(PR3)2H2][BARF4]; Pr-[H12]2+ were prepared according to the published procedures.20 Cr(η6-C6H5)3 Co(Cp-C6H5)2; and [Fe(η5-C5H5)][PF6] were purchased from Strem and Aldrich and used as received.

**NMR Spectroscopy.** 1H and 31P NMR spectra were recorded on a Bruker Avance 400 MHz FT-NMR spectrometer. Residual protio solvent was used as reference for 1H NMR spectra (CD2Cl2: δ = 5.33, CD2CD2Cl: δ = 2.09). 13C NMR spectra were referenced against 85% H3PO4 (external). Coupling constants are quoted in hertz. 1H NMR spectra were recorded using long delays between pulses (>5 s) to avoid saturation. T1 measurements were made using the standard inversion—recovery—delay method (180°—τ—90°) method.

**Mass Spectrometry.** ESI-MS data were collected on a Waters Micromass Q-Tof micro mass spectrometer in positive ion mode. Samples were infused by means of a syringe pump at 5 μL min⁻¹. Solutions were made up in an inert-atmosphere glovebox using dry CH2Cl2. Capillary voltage was set to 2000 V. To minimize fragmentation of the parent ion, the cone voltage was set to 10 V and source and desolvation gas temperatures were both set to 30 °C. Theoretical isotope patterns were calculated using Matthew Monroe’s Molecular Weight Calculator (http://www.chem.unc.edu/personal/monroe/mwtwin.html).

**X-ray Crystallography.** Intensity data for Cy-[H12]2+ were collected at 150 K on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data for Pr-[H12]2+ were recorded on a Bruker Apex II CCD diffractometer using synchrotron radiation on Station 9.8 of the SRS. Both instruments were equipped with an Oxford Cryosystems cooling device. Data for Cy-[H12]2+ were processed using the supplied Nonius Software, while those for Pr-[H12]2+ were processed using the Bruker suite of programs APEX v2.0.2. For Cy-[H12]2+ a symmetry-related (multiscan) absorption correction was employed. Crystal parameters and details on data collection, solution, and refinement for the complexes are provided in Table 2. Structure solution, followed by full-matrix least-squares refinement, was performed using the WinGX-1.70 suite of programs (Cambridge Crystallographic Data Service (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK); Telephone: (+44) 1223-336-408, Fax: (+44) 1223-336-033, E-mail: deposit@ccdc.cam.ac.uk). Cy-[H12]2+ 603 589, Pr-[H12]2+ 621 584.

**Electrochemical Experiments.** For voltammetric measurements an Autolab PGSTAT30 potentiostat system (EcoChemie, Netherlands) was employed with a Pt mesh counter electrode and a silver wire pseudo-reference electrode (calibrated versus internal ferrocene). A 3.0 mm diameter glassy carbon electrode (BASi, USA) and a 10 μm diameter platinum microdisc electrode were employed as working electrodes. Solutions in dry dichloromethane were prepared with 0.01 M [NBut4][BARF4] and under dry argon. Ferrocene was employed as an internal reference. The Digisism software package (Digism3, Cyclic Voltammetric Simulator for Windows, Version 3.03, BASi, USA) was employed for the determination of rate constants from cyclic voltammetry data. Steady state measurements at a 10 μm diameter platinum microelectrode confirmed all processes to be one electron in nature (with a diffusion coefficient of D = κTσπpa = 5.8 × 10⁻⁴ m² s⁻¹ consistent with the Stokes–Einstein equation). Although the redox processes described here appear quite straightforward, we cannot discount that they mask more complex and subtle events.

**EPR.** For EPR analysis a sample of Cy-[H12]2+ was placed into a quartz suprasil EPR tube in 1.2-C6H4F2 solution. The X-band (9.371 GHz) EPR spectra were recorded at room temperature on a cw-Bruker EMX spectrometer operating at 100 kHz field modulation and equipped with an ER-4119HS high-sensitivity cavity. Accurate g values were determined with respect to a DPPH standard.

**SQUID Magnetometry.** The magnetization of compound Pr-[H12]2+ was determined using a Quantum Design MPMS2 SQUID magnetometer. The sample was sealed in a 5 mm NMR tube and measured in applied fields of 0.1 and 1 T from 1.8 to 340 K. No significant difference was observed in the susceptibility, χ, as a function of field. Data were corrected for the diamagnetism of the constituent atoms, and the effective moment, μeff, deduced from these data using the relationship μeff ≈ (8γT)⁻¹, where γ is expressed in units of emu.

Synthesis of [PCy3][Rh6(H)12][BARF4]; Cy-[H12]2+; [PCy3][Rh6(H)12][BARF4]; Cy-[H12]2+ (20 mg, 4.9 μmol) and (C6D5)3Cr (2.3 mg, 11 μmol) in 1.2-difluorobenzene (2 mL) were sonicated for 5 min. The solvent was removed in vacuo, and the residue was repeatedly crystallized from fluorobenzene/toluene until minimal pale colored material crystallized. Slow diffusion of toluene into a concentrated solution of the dark solid in fluorobenzene gave [PCy3][Rh6(H)12][BARF4]; Cy-[H12]2+ as dark green crystals (12 mg, 76%). Addition of an equimolar amount of [Fe(η5-C5H5)][BARF4] to a CD2Cl2 solution of Cy-[H12]2+ returned a diamagnetic 1H NMR spectrum showing signals assigned to Cy-[H12]2+ and an ESI-MS spectrum that also showed the formation of the dicatonic dication.

31P [H] NMR (400 MHz, CD2Cl2): δ 35.75 (br s, fwhm 40 Hz, 6H, CH), 16.5 (br s, fwhm 75 Hz, 6H, CH), 7.71 (m, 8H, BAr F4), 7.53 (s, 1H, CH2), 7.35 (s, 1H, CH2), 7.35 (s, 1H, CH2). nb: Paramagnetic, no hydride signals observed, and no signals observed in the 31P [H] NMR spectrum. An Evans measurement9 (toluene) gave μeff = 1.82 (1 unpaired electron would have μeff = 1.73).

Elemental Analysis calcd for C63H82B2F25P4Rh6C12H6: %C, 54.0; %H, 7.1. Found: %C, 53.8; %H, 7.0. (Toluene was found in the X-ray structure.) ESI-MS, RbC6H5BARF4P3 calculated 2310.9, obsd 2311.0

**Hydrogen Addition to Cy-[H12]2+ To Give [PCy3][RbH8][BARF4]; Cy-[H14]4+.** A solution of Cy-[H12]2+ (2 mg) in CD2Cl2 (5 mL) was placed under an atmosphere of hydrogen (1 atm), and the solution was allowed to stand for 16 h. A change in the UV spectrum of the solution suggested hydrogen uptake had occurred. ESI-MS, RbC6H5BARF4P3 calculated 2312.9, obsd 2313.1

[Rh(PR3)2H12][C6H5BARF4]; Pr-[H12]2+, [Rh(PR3)2H12][C6H5BARF4]; Pr-[H12]2+ (5 mg, 2.90 μmol) and (η5-C5H5)Co (2.5 mg, 13 μmol) in difluorobenzene (3 mL) were shaken for 10 min. The mixture was slowly concentrated to dryness in vacuo, and the residue was (partially) dissolved in pentanes (5 mL). The solution was filtered, the filtrate was concentrated to ca. 2 mL in vacuo, and the solution was held at −20 °C overnight to give the product as dark green-blue crystals of [Rh(PR3)2H12][C6H5BARF4]; Pr-[H12]2+ (2.5 mg, 54%). Elemental Analysis C33H34PR6Rh5P5 requires: %C, 40.8; %H, 8.7. Found: %C, 41.1; %H, 8.7.

31P [H] NMR (400 MHz, C6D5CD3): δ 30.87 (s, 18H, fwhm 83 Hz, PCH), 0.59 (s, 108H, CH3).

nb: Paramagnetic, no hydride signals observed, and no signals observed in the 31P [H] NMR spectrum. An Evans measurement9 (toluene) gave μeff = 2.89 (two unpaired electrons would have μeff = 2.83).

[Rh(PR3)2H12][C6H5BARF4]; Pr-[H14]4+, A solution of Pr-[H12]2+ in CD3CD3, in a J. Youngs NMR tube, was frozen in liquid nitrogen, placed under 1 atm of hydrogen, sealed, and allowed to warm to room temperature (298/77 = 4 atm). The solution was allowed to stand for 16 h, and the product was characterized in situ by 1H and 31P NMR spectroscopy.

31P [H] NMR (400 MHz, CD3CD3, 298 K): δ 2.19 (apparent octet, splitting 7.2 Hz, 18H, PCH), 1.19 (virtual quartet, splitting 6.7 Hz, 108H, CH3), −25.60 (br s, ~13H, Rh–H).

2P [H] NMR (162 MHz, CD3CD3): δ 97.05 (br s, fwhm 530 Hz).

Selected 1H NMR (400 MHz, C6D5CD3, 250 K): δ −24.90 (s br, T1 = 72 ms), −25.82 (s br, T1 = 72 ms). Ratio of these two peaks is 0.7:1.
1H NMR (162 MHz, C6H5CD3): δ 99.1 [d, J(Rh–P) 195 Hz], 87.5 [d, J(Rh–P) 153 Hz]. Ratio of these two peaks is 2.5:1.

Acknowledgment. We thank the Royal Society (University Research Fellowship to A.S.W.) and the EPSRC (GR/T10169) for funding. Dr. Damien Murphy is thanked for the ESR measurements. Professor Jennifer Green and Dr. Nilay Hazari are thanked for insightful comments on the manuscript and stimulating discussions. Dedicated to Professor Thomas Fehlner on the occasion of his retirement.

Supporting Information Available: Cyclic voltamograms of Pr-[H12]2+, Cy-[H12]2+ on a platinum counter electrode and Cy-[H16]2+ under 1 atm of H2. Electronic absorption spectra for solutions of Cy-[H12]2+/Cy-[H16]2+; Cy-[H12]/Cy-[H14]; Pr-[H12]/Pr-[H14]. CIF files for all the crystal structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.