High Hydride Count Rhodium Octahedra, [Rh6(PR3)6H12][BAR6F4]2: Synthesis, Structures, and Reversible Hydrogen Uptake under Mild Conditions

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Abstract: A new class of transition metal cluster is described, [Rh6(PR3)6H12][BAR6F4]2 (R = iPr (1a), Cy (2a); BAR6F4 = [B(C6H52CF3)2]4−). These clusters are unique in that they have structures exactly like those of early transition metal clusters with edge-bridging π-donor ligands rather than the structures expected for late transition metal clusters with π-acceptor ligands. The solid-state structures of 1a and 2a have been determined, and the 12 hydride ligands bridge each Rh−Rh edge of a regular octahedron. Pulsed gradient spin−echo NMR experiments show that the clusters remain intact in solution, having calculated hydrodynamic radii of 9.5(3) Å for 1a and 10.7(2) Å for 2a, and the formulation of 1a and 2a was unambiguously confirmed by ESI mass spectrometry. Both 1a and 2a take up two molecules of H2 to afford the cluster species [Rh6(PR3)6H14][BAR6F4]2 (1b) and [Rh6(PCy3)6H14][BAR6F4]2 (2b), respectively, as characterized by NMR spectroscopy, ESI-MS, and, for 2b, X-ray crystallography using the [1-H-CB11Me11]− salt. The hydride ligands were not located by X-ray crystallography, but 1H NMR spectroscopy showed a 15:1 ratio of hydride ligands, suggesting an interstitial hydride ligand. Addition of H2 is reversible: placing 1a and 2a under vacuum regenerates 1a and 2a. DFT calculations on [Rh6(PH3)6H2]2+ (x = 12, 16) support the structural assignments and also show a molecular orbital structure that has 20 orbitals involved with cluster bonding. Cluster formation has been monitored by 31P{1H} NMR spectroscopy, and mechanisms involving heterolytic H2 cleavage and elimination of [HP(iPr)3]+ or the formation of trinuclear intermediates are discussed.

Introduction

The chemistry of transition metal clusters occupies two “classical” areas.1 The first encompasses clusters with metal atoms in low to medium oxidation states combined with π-donating ligands,2 exemplified by halide edge-bridged clusters such as [Nb5Cl9]K+, Nb5Cl9(PPr3)3 (A), and by the face-bridged chalcogenides [W6S8-(PEt3)6]4− (B)3 or [Re6Se8I6]62−,4 which are molecular models for Chevrel phases.5 The second grouping is that of the later transition metals in low oxidation states with π-accepting ligands,2 exemplified by halide edge-bridged clusters such as Rh6(CO)16 (C) or [Ru6(μ-C)(CO)16]2−,5 Aside from the fascinating structural and bonding aspects of these compounds, the driving force for the study of such cluster systems is their potential to bridge the areas of heterogeneous and homogeneous catalysis1,9,10 and their unique spatial, electronic, and magnetic properties.11 The electronic descriptions for both classes of cluster are well understood, especially for octahedral species where symmetry allows for a concise account of the molecular orbital structures.12,13 The octahedral late transition metals with π-accepting ligands (C) generally have cluster valence electron counts (cve) of 86 electrons,14 although exceptions do exist.15 For clusters with π-donor edge-bridging ligands (A), electron counts of 74–78 cve have been noted, with 76 cve being usual, while the...
faced-bridged chalcogenides (B) span a larger range of cluster electron counts, from 80 cve in Mo$_6$(µ-S)$_6$(PET$_3$)$_6$ to 98 cve in Co$_6$(µ-S)$_6$(PET$_3$)$_6$.$^{16}$

The synthesis of transition metal cluster species from mono- or dinuclear starting materials often favors the isolation of what might be considered the thermodynamic product, by using moderate to high temperature and pressure, or sometimes both.$^{7,12,17}$ This invariably leads to products that are electronically and coordinatively saturated, although notable recent examples exist of electronically unsaturated clusters formed from thermolysis reactions when bulky phosphines are used, such as Pt$_3$Re$_2$(CO)$_6$(PET$_3$)$_3$. $^{18}$ Rarer are routes that offer some degree of kinetic control to cluster formation from mono- or dinuclear precursors, and, relevant to this paper, to our knowledge many of these kinetic routes often result in cluster species with attached hydride ligands, although non-hydride-containing clusters can also be synthesized.$^{19}$ Hydrogenolysis of precursor complexes and elimination of non-coordinating alkane or alcohol is a common synthetic method. For example, reaction of Pt(PR$_3$)$_3$(η$_2$-H$_2$C=C=CH$_2$) with H$_2$ gives platinum hydrido-phosphine clusters such as Pt$_4$(P$_2$P$_2$P$_2$H)$_5$,$^{20,21}$ while addition of H$_2$ to (µ-PrO)$_2$(µ-Bu)W=W=µ(µ-PrO)$_2$(µ-Bu) affords W$_6$H$_4$(C(Pr)(OPr)$_2$)$_{12,22,23}$ and reaction of H$_2$ with [µ(BuO)Cu]$_4$ in the presence of P(NMe$_2$)$_3$ gives the octahedral copper polyhydride Cu$_6$(P(NMe$_2$)$_3$)$_3$H$_6$,$^{24}$ (Scheme 2). An alternative method is to reduce a mononuclear transition metal halide with a hydride source such as H$_2$SnBu$_3$ or H$_3$SiPh to afford compounds such as Zr$_6$(PR$_3$)$_3$Cl$_4$H$_4$,$^{25}$ and [(η$_5$-C$_5$Me$_5$SiMe$_3$)-LuH$_2$]$_6$,$^{26,27}$ respectively. Kinetic routes to related metallaborane cluster species through reduction of mononuclear cyclopentadienyl halides have also been developed, $^{28}$ and hydrido clusters can also be synthesized under kinetic conditions from condensation of bimetallic hydride complexes with nonmetallic fragments.$^{29-31}$

We report in this paper the synthesis under mild conditions of a new class of octahedral cluster, [Rh$_6$(PR$_3$)$_3$H$_2$]$_{12,2+}$. Such clusters bridge the gap between early and later transition metals inasmuch as they are composed of late transition metal fragments [Rh(PR$_3$)$_2$] but have molecular geometries and

electronic structures that are more closely related to those of the early octahedral transition metal clusters. Not only do these clusters have unprecedented structures for a late transition metal cluster species but they also have an extraordinarily large number of hydride ligands associated with them and thus are potential models for nanoparticle Rh clusters used in arene hydrogenations, hydrogen storage materials, and hydrogen spillover systems. We demonstrate their relevance to these areas by describing the facile and reversible dihydrogen uptake by these clusters under very mild conditions of room temperature and pressure. The structures of these new cluster species have been probed by a combination of X-ray crystallography, NMR spectroscopy, electrospray ionization mass spectrometry, and DFT calculations, and we also report on studies to elucidate the mechanism of cluster formation from mononuclear rhodium precursor complexes. Aspects of this work have been communicated previously.

Results and Discussion

Synthesis and Solid-State Structure of \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}^\cdot\text{BARF}_4]^\cdot\) \((\text{R} = \text{iPr}, \text{Cy})\). We have recently reported that addition of \(H_2\) (\(\sim 4\) atm initially, 298 K) to \(\text{CH}_2\text{Cl}_2\) or fluorobenzene solutions of \([\text{Rh}(\text{PR}_3)_2(\text{nbd})]^{\cdot}\text{BARF}_4^\cdot\) \((\text{R} = \text{iPr}, \text{Cy}; \text{BARF}_4^\cdot = [\text{B(C}_6\text{H}_3(\text{CF}_3)_2)_2]^{\cdot}\) nbd = norbornadiene) initially results in the formation of the almost colorless dihydrogen/dihydride complexes \([\text{Rh}(\text{PR}_3)_2(\text{H})(\pi^2\text{H}_2)]^{\cdot}\text{BARF}_4^\cdot\) \((x = 1 \text{ or } 2)\). Gentle heating \((313 - 323\) K) of these solutions results in a gradual darkening to very dark red over 4 days and the formation of the dicaticionic octahedral cluster species \([\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}^{2-}\text{BARF}_4^2]^\cdot\), isolated in moderate yield as analytically pure salts on recrystallization (vide infra). The mechanism of cluster formation and hydrogen uptake experiments will be discussed in due course, and we first present the complete characterization of clusters 1a and 2a by X-ray crystallography, NMR spectroscopy, and mass spectrometry. Using \(\text{CH}_2\text{Cl}_2\) as the reaction solvent rather than fluorobenzene resulted in lower yields of cluster, and thus the latter is preferred. Anions other than \([\text{BARF}_4^\cdot]\) gave mixed results. Use of the “greasy ball” weakly coordinating anion \([1\text{-closo-HCB}_1\text{Me}_1^\cdot\text{Me}_1^\cdot\text{Me}_1^\cdot}\) afforded clusters in effectively the same yield as for \([\text{BARF}_4^\cdot]\), but \([\text{PF}_6]^-\) or \([\text{BF}_4]^-\) resulted in no cluster formation, principally because these latter two anions are not compatible with the formation of the intermediate dihydrogen complexes (Scheme 3). Compound 1a is sparingly soluble in fluorobenzene (marginally better in \(\text{CH}_2\text{Cl}_2\)), while 2a shows better solubility in either solvent. They are both insoluble in pentane and toluene.

The solid-state structures of the triisopropylphosphine cluster 1a and the tricyclohexylphosphine cluster 2a are shown in Figure 1. Table 1 gives data collection and refinement details, and Table 2 presents a comparison of the key structural metrics of these clusters. Full listings of bond lengths and angles are given in the Supporting Information. 1a has a crystallographically imposed centrosymmetric structure in the solid state, while 2a does not, but both are effectively regular \(\text{Rh}_6\) octahedra. Each rhodium vertex is coordinated with a single phosphine, which is directed approximately radial to the cluster core, with the cross-cluster Rh-Rh-P angles, e.g. Rh(2)-Rh(2)-P(2) in 1a, being only a few degrees away from 180° (average 176.6-(1) and 177.8(1)° for 1a and 2a, respectively). The Rh-Rh distances are only slightly larger for 2a than measured for 1a (averages for 1a, 2.720 Å; for 2a, 2.735 Å), and there is only a slight increase in cross-cluster P-P-P distances, showing that the bulkier tricyclohexylphosphine ligands (cone angle for PCy3 is 169° vs 159° for PPr3) have only a small effect on the cluster geometry. The deviation of Rh-Rh bonding distances, \(\delta\) (Rh-Rh), is essentially the same for both and is small \((\sim 0.03\) Å), as is deviation in cross-cluster Rh-Rh distances. DiSalvo...
and co-workers have noted similar small changes to the cluster core on going from PEt₃ to the bulkier PCy₃ in the octahedral face-bridged sulfide clusters W₆S₆(PR₃)₆. The direct Rh–Rh distances in 1a and 2a are also comparable to those found in Rh₆(CO)₁₆ (average 2.750 Å). For both 1a and 2a, the 12 hydride ligands were located in the final difference map, and each Rh–Rh edge in the respective octahedra is spanned by a bridging hydride ligand, forming a cuboctahedron surrounding the metal core (Figure 2 shows 1a). Three independently synthesized samples of 1a gave similar high-quality data and are in agreement with the gross positioning of the hydride ligands over Rh–Rh edges. The location of hydride ligands in transition metal clusters by X-ray crystallography is often problematic, given the low scattering associated with the M–H bond, but, as will be reported later, NMR, mass spectral, and microanalysis data all unequivocally support the formulation as 12-hydride clusters for both 1a and 2a. Comparison of the Rh–H distances in 1a suggests that, within error, six of these hydrides are more semi-bridging than bridging in nature, although the difference between the two modes is rather subtle, especially as measured by X-ray crystallography. DFT calculations (vide infra) also suggest a mixture of bridging and semi-bridging hydrides, with four octahedral edges bridged symmetrically and the remaining eight bridged unsymmetrically, supporting such a structural assignment. Of course, a neutron diffraction study would help pin down the positioning of the hydrides, as it has for cluster hydride ligands previously, and attempts are currently underway to produce crystals of a size suitable for such an experiment.

Transition metal clusters with hydride ligands are ubiquitous, however, those with more than four hydride ligands, or a hydride:metal ratio of > 1, are significantly less well documented. Well-characterized examples of clusters with a high (>4) hydride count include Pt₅H₆(PBu₅)₆, [Pt₅H₇(PBu₅)]-[BF₄]⁻, Pt₅Os(CO)₁₀H₂, [Zr₆Cl₁₂H₂][PF₆]⁻, Cu₅(PR₃)₆H₂, Pd₅(PMe₃)(PPh₃)₂(CO)₁₂H₁₂, [Ru(η⁵-C₅H₅)₂H₂]Cl₂, Os₅Pd(CO)₁₀H₆, [CP*Ru(H)₃]₃O₅, Os₅Rh₃(CO)₁₂H₁₁, [Os₅Pt(CO)₁₀H₆], [Os-Re(PBu₅)₆][BF₄]⁻, [Re₃CuH₁₆(PMe₃)₆][PF₆]⁻, and [Ir₂(L)₃(L')₃H₆][PF₆]₂ (L = PCy₃, L' = py)⁴³. Of particular, the edge-bridging arrangement of the hydride ligands in 1a and 2a is reminiscent of that observed in octahedral W₆(CPr)/(OPr)₂H₂,⁴² the simple stoichiometry of [Rh(PR₃)H₂] is similar to that of the hydrido-platinum monophosphine clusters such as Pt₄(P₂-tBu₃)₄⁻ and especially Zr₆Cl₁₂H₂(PMe₃)₆.⁵⁻ This structural motif is unknown in the chemistry of rhodium clusters, which is dominated by complexes with carbynol ligands and [Rh(CO)₅] fragments, although a small number of non-carbonyl bi- and trimetallic hydrido-phosphine species with bridging hydride ligands have been reported, such as [Rh{P(OR)₃}₃]H₅,⁵⁷ and [Rh₃H₅{P(Pr)₃}₃]₅⁵.⁵⁹

Figure 1. Solid-state structure of the dications in 1a (top) and 2a (bottom). Thermal ellipsoids are shown at the 50% probability level. The counterrons are not shown. Apart from the hydride ligands, all other hydrogen atoms have been omitted for clarity.


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Table 1. Crystal and Structure Refinement Data for the New Cluster Compounds

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The cluster cores in both 1a and 2a are surrounded by an alkyl sheath formed by the phosphine ligands, presenting a nonpolar outer layer, shielding the inner [Rh<sub>6</sub>P<sub>6</sub>H<sub>12</sub>]<sup>2+</sup> core (Figure 3). For 1a, the Pr<sub>3</sub>P ligands appear to pack so as to allow more appreciable gaps in the alkyl sheath, whereas in 2a the cyclohexyl groups shroud the core more effectively. It is remarkable that, especially for the tricyclohexyl phosphines in 2a, enough space can be found to accommodate the six ligands, and the interdigitation of the cyclohexyl groups clearly occurs effectively. Similar packing of cyclohexyl groups has been observed in the closely related cluster W(C<sub>8</sub>H<sub>18</sub>)<sub>4</sub>Cys<sub>2</sub>. The two clusters have appreciable van der Waals diameters of 1.6 nm (1a) and 1.8 nm (2a). With reference to the unusual electronic structure of these clusters, this protective cover may well be the reason why they can be isolated.

Solution NMR and Mass Spectrometric Characterization of 1a and 2a. Complex 1a shows lower solubility in CH<sub>2</sub>Cl<sub>2</sub> solution than 2a, which is readily soluble (~40 mg/cm<sup>3</sup>). Although 1a will dissolve in CH<sub>2</sub>Cl<sub>2</sub> (~10 mg/cm<sup>3</sup>) on sonication for 10 min, overnight it tends to recrystallize, even from CH<sub>2</sub>Cl<sub>2</sub> solutions. Nevertheless, the solubility is more than adequate for the acquisition of good room-temperature solution NMR data. Both complexes are stable in CH<sub>2</sub>Cl<sub>2</sub> solutions for weeks under rigorous exclusion of air and moisture. The 31P-{1H} NMR spectrum of 1a shows a single, sharp peak centered at δ 106.2 ppm which shows coupling to 103Rh [J(RhP) = 104 Hz]. For 2a, a broadened doublet is observed at δ 91.9 ppm [J(RhP) = 103 Hz]. In its 1H NMR spectrum, 1a shows signals due to [BaF<sub>4</sub>]<sup>2-</sup> and Pr<sub>3</sub> groups in the correct ratio for a dicaticonic cluster. The high-field region displays a single, rather
broad resonance at $\delta -25.44$ ppm (fwhm = 46 Hz) that integrates to 12 H relative to both the iPr protons and the $[\text{BAr}_4\text{F}_4]$- aromatic protons. Correct integration of hydride signals can often be problematic due to slow relaxation, and long delays between pulses (5 s) and a large number of scans were used to ensure that the true integral value was obtained. Average integral values over at least three samples were also taken, with individual integrals between each sample deviating by less than 0.5 H. No fine structure to this hydride signal was observed, and decoupling $^{31}\text{P}$ did not narrow the signal significantly or reveal any coupling to $^{103}\text{Rh}$, which was unfortunate as $^1\text{H}-\{^{31}\text{P}\}$ NMR spectra are potentially useful in confirming the number of rhodium atoms with which each hydride environment couples. Cooling to 200 K broadens the hydride peak significantly and shifts it downfield by ca. 5 ppm to $\delta -19.0$ ppm. This might be indicative of a fluxional process, possibly restricted rotation of the phosphine (see later), but the low solubility of 1a could also contribute to a poorly resolved peak at low temperature. At temperatures higher than 320 K, complex 1a starts to decompose ($\text{C}_6\text{H}_4\text{F}_2$ solution). The room-temperature $^{13}\text{C}-\{^1\text{H}\}$ NMR spectrum shows only two signals for the Pr groups, which demonstrates that the phosphine ligands rotate (or at least librate) around their Rh–P axes at room temperature. A low-temperature spectrum was not possible to acquire due to the low solubility of 1a.

The room-temperature $^1\text{H}$ NMR spectrum of 2a, unlike that of 1a, displays two broad high-field peaks that consistently integrate in the ratio 9 H:3 H with respect to the other signals in the spectrum, at $\delta -27.0$ ppm (fwhm = 230 Hz) and $\delta -28.9$ ppm (fwhm = 330 Hz), respectively. The signals are invariant in ratio on slow cooling to 200 K, suggesting that they are not due to two species in dynamic equilibrium. They do sharpen significantly at the lower temperature and (as for 1a) shift to lower field ($\delta -21.7$ and $-25.2$ ppm, respectively at 248 K). At higher temperatures these signals coalesce and then become a single peak (at 353 K) shifted upfield to $\delta -36.8$ ppm, which integrates to 12.2 H (Figure 4). The $^{31}\text{P}-\{^1\text{H}\}$ NMR spectra show one phosphorus peak over all temperature ranges that also sharpens on cooling and shifts appreciably upfield by $\delta -12$ ppm. Although there are a number of possible reasons for the observation of two signals at low temperature (e.g., an alternative trigonal-prismatic structure, or a mixture of bridging and terminal hydrides), we favor the simple explanation of restricted rotation of the bulky tricyclohexyl phosphine groups at or below room temperature. This contrasts with triisopropyl phosphine ligands in 1a. This restricted rotation leads to hydride ligands that either lie directly under a cyclohexyl group or between two cyclohexyl groups, which results in different bridging hydride environments (Figure 5). Close inspection of the solid-state structure of 2a reveals three such environments, in the ratio 6:3:3, consistent with the 9:3 pattern observed in solution by $^1\text{H}$ NMR spectroscopy. The observation of different hydride environments also shows that the hydrides are not fluxional over the surface of the cluster at low temperature. A $^{13}\text{C}-\{^1\text{H}\}$ NMR spectrum of 2a at 250 K (see Supporting Information) shows 15 cyclohexyl environments (some representing coincident peaks), consistent with restricted rotation of the phosphine ligand. These signals broaden on warming, but decomposition at higher temperatures (350 K) prevented the acquisition of a
meaningful $^{13}$C($^1$H) NMR spectrum at the high temperature limit. A freely rotating ligand set would be expected to show only six separate environments for the PCy$_3$ ligands in the $^{13}$C-{$^1$H} NMR spectrum, while a static ligand set would give 18.

The gradual upfield shift of the hydride signal on warming from 200 to 353 K suggests a rapid, temperature-dependent equilibrium between two Rh–H environments (e.g., a bridging vs terminal tautomeration), one of which is favored at high temperature.

Involvement of solvent at higher temperatures is discounted, as the same spectral changes are observed in CD$_2$Cl$_2$, fluorobenzene, or 1,2-difluorobenzene solutions.

At 200 K, the longitudinal relaxation time of the hydrogen ligands on the clusters ($T_1$)$^{60,61}$ is measured as 320 ms for 1a and 890 ms for each resonance in 2a, firmly in the region associated with hydride and not dihydrogen ligands, consistent with both the X-ray structures and the structure calculated by DFT (vide infra). For comparison, the bridging hydrides in Ir$_4$H$_4$–($\mu$-H)$_3$(CO)$_4$(PPh)$_3$ have a $T_1$ of 690 to 290 ms, while in [RuH$_6$(C$_6$H$_5$)$_4$]$^2^+$ the bridging hydrides have $T_1$ of between 190 and 310 ms. This latter complex is also suggested to have a cluster dihydrogen ligand on the basis of a short ($T_1 = 34$ ms) relaxation time at 153 K.

The structure of the clusters in solution has also been probed using pulsed gradient spin–echo (PGSE) NMR experiments. Such experiments have been used to measure the size of molecules in solution by their calculated hydrodynamic radii.$^{63,64}$

A PGSE experiment on 1a in CD$_2$Cl$_2$ solution afforded a hydrodynamic radius ($r_H$) of 9.5(3) Å for the dication. As expected for the tricyclohexyl phosphate cluster 2a, a slightly larger $r_H$ value is calculated, 10.7(2) Å (Figure 6). These values are both slightly larger than those measured in the solid state (8.0 and 9.0 Å, respectively). The [BarF$_4$]$^-$ anions in each (each $r_H = 7.8(2)$ Å) are also slightly larger in solution than found in the solid state (7.2 Å). These increases in calculated radii are suggestive of ion-pairing between the anions and cation in solution, a not-uncommon feature of ion-pairs in CH$_2$Cl$_2$ solution.$^{63}$

What these values confirm is that, in solution, the clusters are intact and do not dissociate appreciably into mononuclear solvent-stabilized fragments, e.g., [Rh(PR)$_3$(H)$_2$-(solvent)], [BarF$_4$], on the NMR time scale, as these would be expected to have a significantly smaller hydrodynamic radii for the cation (ca. 7 Å or less$^{63}$).

Crucially, with regard to the solution characterization of 1a and 2a, that the clusters remain intact in solution and have 12 hydride ligands is unequivocally shown by electrospray ionization mass spectrometry (ESI-MS$^{65}$), which shows only the intact clusters and no other charged species.$^{66}$

ESI-MS on CH$_3$Cl$_2$ solutions of 1a and 2a under very soft conditions (cone voltage of 10 V, source and desolvation gas temperatures both 30 °C) are in full agreement with the formulation [Rh$_6$(PR)$_3$(H)$_2$]$^{2^+}$, with a single molecular species observed at m/z 795.1 (calcd 795.2) for 1a and 1155.5 (calcd 1155.7) for 2a, which have experimentally determined isotope patterns that are an excellent match with theory (Figure 7).

Reversible Dihydrogen Uptake by the Clusters [Rh$_6$H$_{12}$-(PR)$_3$]$^{2^+}$

The reversible uptake of hydrogen by molecular or extended materials (such as nanoclusters) is an area that is attracting significant current interest. 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).$^{1,9,10,32}$

Figure 5. Stick representation of the cluster core in 2a and the two postulated fluxional processes occurring in 1a/2a. Cyclohexyl groups apart from the ipso-carbon have been removed to more clearly demonstrate the alignment of the tricyclohexylphosphine ligands.

Figure 6. Plot of the observed intensity changes ($I/I_0$) vs arbitrary units proportional to the square of the gradient amplitude for PGSE measurements on 1a and 2a (CD$_2$Cl$_2$ solutions, 60 mM solutions). The lines represent linear least-squares fits to the experimental data.


surface and/or hydrogen storage devices, and consequently we investigated their reactivity with regard to dihydrogen uptake/loss.

Even though 1a and 2a have an exceptionally large number of hydride ligands, placing either cluster under a dynamic vacuum ($10^{-3}$ Torr, 5 days, room temperature) did not result in loss of H$_2$, as measured by NMR spectroscopy and ESI-MS. In fact, the 12 hydride ligands are so firmly placed on the clusters that 1a and 2a can be routinely recrystallized from solutions containing an excess (>100-fold) of 1-hexene, and addition of an excess (>100-fold) of the excellent hydrogen acceptor tert-butylethylene (tbe) does not remove any of the 12 hydride ligands. This was at first surprising, but in light of the electronic structure of the clusters (vide infra) that affords a very stable 76 cve count, perhaps it should not be. Although H$_2$ is not lost either under vacuum or by addition of a hydrogen acceptor, addition of H$_2$ is facile and results in the immediate uptake of two molecules of H$_2$ to afford the octahedral clusters [Rh$_6$H$_{12}$ (PR$_3$)$_6$]$_2$ (Scheme 4, R = iPr (1b), Cy (2b)). This hydrogen uptake occurs under mild conditions of temperature and pressure, happening at room temperature in CD$_2$Cl$_2$ solution under 1 atm of H$_2$ over ~10 min, and effectively instantaneously at room temperature under 4 atm of H$_2$. The uptake of hydrogen also occurs in the solid state by placing crystalline material under 4 atm of H$_2$. In this instance this solid-state reaction is, not unexpectedly, slower (16 h) and is also dependent on the size of the crystals. Pressurizing 1a to 100 bar of H$_2$ in CD$_2$Cl$_2$ solution afforded only 1b, showing that hydrogen uptake stops at two molecules of H$_2$. The ESI-MS spectra of 1b and 2b (CH$_2$Cl$_2$ solutions under the mild conditions used previously) unambiguously show the uptake of two molecules of H$_2$ (an increase of $m/z$ 2 = 4 Da for a 2$^+$ cation to $m/z$ 797.2 and 1157.5, respectively), displaying “flagpole spectra” with excellent isotope distribution match to the calculated patterns (Figure 8). Under the conditions used, the potential intermediate 14-hydride species was not observed.

The room-temperature $^1$H NMR spectra (CD$_2$Cl$_2$ solutions) of 1b and 2b show resonances due to [BARF$_4$]$^-$ anions and the alkyl phosphines in the appropriate ratio. In the high-field region, two hydride signals are observed in the ratio 15:1 with respect to both the anion and phosphine resonances. One of these is
relatively sharp, while the other is much broader, e.g., for 1b $\delta =-21.46$ ppm (15 H, fwhm 40 Hz) and $\delta =-29.81$ ppm (1 H, fwhm 200 Hz). This pattern of integrals is consistent over a number of independently synthesized, crystalline samples. Figure 9 shows the high-field region for the pair 2a/2b.

This 15:1 ratio suggests a structure in which 15 hydrides are mutually exchanging on the NMR time scale and one is not. Mutual exchange of the 15 hydrides is necessary, as it is not possible to arrange 15 hydrides around an octahedron symmetrically. To our minds, the only plausible structure that accounts for this observation is one that involves an interstitial hydride with 15 hydride ligands decorating the outside of the Rh6 octahedron. Interstitial hydrides are well-known in transition metal clusters and have been characterized by NMR spectroscopy and, in some cases, neutron diffraction techniques.45,46,67 The chemical shift of interstitial hydrides can vary over a considerable range, for example $\delta =+16.4$ ppm for [HRu6-(CO)12]68 to $\delta =-26.9$ ppm for [HNi12(CO)12]69 and it has been suggested that hydrides that are located in the center of a regular octahedron show the lowest-field chemical shifts, while those more asymmetrically oriented have high-field chemical shifts.70 For 2b, an X-ray study (vide infra) shows a rather distorted octahedron, and thus a chemical shift observed for the unique hydride around $\delta =-29$ ppm is not unreasonable. DFT studies also indicate that a structure with 15 hydride ligands on the surface and one interstitial is significantly more stable than one with 16 hydrides on the surface, and these studies also show that this central hydride sits rather asymmetrically inside the Rh6 core. Of course, in the absence of a neutron diffraction study, the assignment of an interstitial hydride must remain plausible but tentative, especially as examples exist of instances where interstitial hydrides have been originally proposed but later proven to be, in fact, located on the cluster surface.71 The room-temperature $^{31}$P[1H] NMR spectra for both 1b and 2b show broad environments, which for 1b resolves into a doublet $J(\text{Rh}P) = 140$ Hz. Within error, the hydrodynamic radii of 1b and 2b as calculated using PGSE in CD2Cl2 solutions are the same as for 1a/2a [9.5(3) and 10.3(5) Å,3 respectively].

On cooling of 1b and 2b to 200 K (CD2Cl2), their hydride resonances become broader and resolve into many separate signals with an overall integral lower than 16 H, both being nearer 12 H, showing that the hydrides are mobile over the surface of the cluster at room temperature. The broad linewidths of some of these signals indicate that any fluxional processes occurring are not completely frozen out at 200 K, as does the lower-than-expected integral value. $T_1$ measurements at 200 K indicate that all the observed signals are best assigned to hydride ligands ($T_1 > 230$ ms), although the presence of two unresolved dihydrogen ligands in the baseline cannot be discounted. Higher temperatures (up to 350 K, 1,2-difluorobenzene solvent) result in the apparent coalescence of the two peaks, possibly suggesting exchange, although as the integral 1 H peak is very broad, it could simply be unresolved in the baseline. At this temperature, partial decomposition of the cluster to unidentified material is also observed. Under a H2 atmosphere (1 atm) at 298 K, dissolved H2 is observed as a sharp resonance at $\delta =4.6$ ppm, demonstrating that exchange between free and bound H2 is slow on the NMR time scale. Slow exchange with free H2 does occur, however, as placing 1b or 2b under a D2 atmosphere (≈4 atm) results in complete H/D exchange for the hydride ligands in 72 h and the appearance of HD as a characteristic 1:1:1 triplet at $\delta =4.55$ ppm [J(DH) = 43 Hz], along with H2. The observation of HD and free H2 suggests coordinated dihydrogen on the cluster surface, resulting from H/D exchange via a dihydrogen intermediate.51,61 To our knowledge, the only cluster identified as containing a dihydrogen ligand (as identified by $T_1$ measurements and DFT calculations) is [Ru4H6(C6H6)4]12+,51 although bimetallic complexes with dihydrogen ligands are known,61,72 and dihydrogen complexes have been suggested to be possible intermediates in clusters that catalyze H2-D2 equilibrium to form HD.73,74 Interestingly, after 3 days under D2 at 313 K, for 1b some deuterium is also incorporated into the isopropyl groups on the phosphines (as shown by $^1$H NMR and ESI-MS), suggesting that these ligands do not play a completely innocent role in the clusters. We have not yet pursued the mechanism of H/D exchange, but it is likely that it involves reversible oxidative addition of an alkyl C–H bond to the cluster core.

Despite repeated attempts, the crystalline material of 1b afforded X-ray diffraction patterns that indicated high levels of disorder. Crystals suitable for X-ray diffraction for 2b where grown using the alternative anion $[1-H-CB_{11}Me_{11}]^{-}$40 from CH2Cl2/pentane solution under 1 atm of H2. Crystals of the [BARF4]− salt of 2b were of marginal quality, and the structure obtained is not reported here. Nevertheless, the resulting cluster core structural metrics are essentially the same as for that with the $[1-H-CB_{11}Me_{11}]^{-}$ anion, demonstrating that the anions do not
have a pronounced effect on the cluster geometry. Figure 10 shows the solid-state structure of \( \text{Rh}_6 \left[ \text{PCy}_3 \right]_2 \left( \text{CO} \right)_{18} \), and deviations, larger cross-cluster Rh–Rh distances in the latter by significantly larger Rh–ligands in the former.

The cluster core in \( \text{2b} \) describes an approximate octahedron, but compared to the \( \text{H}_2 \)-hydride counterparts \( \text{1a} \) and \( \text{2a} \) it is significantly distorted. Notably, the Rh–Rh distances span a wider range, \( \delta(\text{Rh}–\text{Rh}) \) being an order of magnitude larger for the \( \text{H}_2 \) species than the \( \text{H}_2 \) clusters. The cross-cluster Rh–Rh and P–Rh–P distances are also larger and span a similarly wide range. The cross-cluster Rh–Rh–P angles also span a much wider range for \( \text{2b} \) than for \( \text{2a} \), e.g., 178.3(1)–177.3(1)° for \( \text{2a} \) and 177.1(1)–166.8(1)° for \( \text{2b} \). The hydride ligands around the \( \text{Rh}_6 \) core were not located with any certainty. As discussed, the location of hydrogen atoms near metal centers is always potentially problematic, and coupled with the fact that the hydrides in \( \text{2b} \) will be distributed asymmetrically in the solid state, potentially leading to partial occupancy of sites, this means that the definitive location of the hydrides using X-ray crystallography would always be difficult. Nevertheless, the combination of NMR and ESI-MS data unambiguously points to clusters with 16-hydride ligands. Moreover, the structural comparisons between the 12-hydride clusters, \( \text{1a/2a} \), and the 16-hydride cluster, \( \text{2b} \), indicate the accommodation of four extra hydride ligands in the latter by significantly larger Rh–Rh distances and deviations, larger cross-cluster Rh–Rh–P distances, and greater deviations from linearity for Rh–Rh–P angles. These structural variations are underscored by DFT calculations on both 12- and 16-hydride structures (vide infra) that, for comparison, are shown in Table 2. Even though the phosphine \( \text{PH}_3 \) was used in the DFT model instead of the bulky \( \text{PPPr}_3 \) or \( \text{PCy}_3 \) ligands, all the changes observed experimentally on addition of dihydrogen are reproduced satisfactorily in the calculated structures.

**Figure 10.** Solid-state structure of the dication of \( \text{2b[HCB}_3\text{Me}_{12]} \). Thermal ellipsoids are shown at the 50% probability level. The counterions are not shown. The hydride ligands around the cluster core were not located reliably. All other hydrogen atoms have been omitted for clarity. See Supporting Information for labeling scheme.

The 16-hydride complex \( \text{2a} \) slowly loses \( \text{H}_2 \) in the solid state under an argon atmosphere to give \( \text{1a} \), giving a ratio of 1:0.7 for \( \text{2a/1a} \) by \( ^1 \text{H} \) NMR spectroscopy after 1 week. By contrast, after 1 week \( \text{2b} \) is unchanged as shown by NMR and ESI-MS. Under vacuum (5 × 10⁻³ Torr), \( \text{H}_2 \) loss is faster. For the \( \text{PrP}_3 \) cluster, \( \text{1b} \), complete \( \text{H}_2 \) loss is considerably more rapid (12 h) than for the \( \text{PCy}_3 \) congener \( \text{2b} \) (~1 week). This increased resistance to \( \text{H}_2 \) loss for \( \text{2b} \) reflects the increased kinetic stabilization toward \( \text{H}_2 \) loss provided by the bulky cyclohexyl ligands, as electronically both \( \text{1b} \) and \( \text{2b} \) would be expected to be very similar. This process is completely reversible for both clusters, and repressurizing with \( \text{H}_2 \) regenerates quantitatively (NMR, ESI-MS) the \( \text{H}_2 \) species. Loss of two hydrogen molecules is also effected by addition of hydrogen acceptors such as tert-butylethene or 1-hexene, as monitored by NMR and ESI-MS (Figure 11). The loss of dihydrogen from \( \text{1b} \) or \( \text{2b} \) is not at odds with their putative interstitial hydride structure, as interstitial hydrides in octahedral complexes have been noted to be mobile between the center of the octahedron and the cluster surface. For example, protonation of \( \left[ \text{Ru}_6(\mu_5-H)(\text{CO})_{18} \right]^- \) affords \( \text{H}_2 \left[ \text{Ru}_6(\text{CO})_{18} \right] \), which has two bridging hydrides,⁶⁸ while the interstitial hydride in \( \left[ \text{Co}_6(\mu_5-H)(\text{CO})_{18} \right]^- \) undergoes rapid migration from the inside to the outside of the cluster.⁴⁶⁷⁰

Although complexes with hydride ligands are common in cluster chemistry, those that can reversibly take up and release one molecule of \( \text{H}_2 \) are few.⁷³⁷⁵⁷⁶ Of these species that reversibly take up \( \text{H}_2 \), only one approaches the high hydride count of \( \text{1b/2b} \), \( \left[ \text{Pt}_4(\text{H})_7(\text{P} \text{Bu}_3)_4 \right] \left[ \text{BF}_4 \right] \).⁴⁸ This cluster reversibly loses four molecules of \( \text{H}_2 \) on exposure to air, to afford a cluster with no hydrides (Scheme 5), or on exposure to ethanol, to give a cluster with one hydride ligand. \( \text{Pt}_5 \text{Re}_2(\text{CO})_6(\text{P} \text{Bu}_3)_3 \) has been reported to take up a relatively large amount of \( \text{H}_2 \) (3 equiv), but the process is not reported to be reversible for this cluster.¹⁸⁷⁶

![Figure 11.](image_url) Stacked plot of ESI-MS of \( \text{1b} \) on addition of the hydrogen acceptor tert-butylethene (~100-fold excess) in CH₂Cl₂ solution. The bottom spectrum was obtained 5 min after addition of the and the top after 24 h.

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The cluster species [Rh₆(PR₃)₆H₁₆][BAR F₄]²⁺ are thus unique in that H₂ uptake and loss is facile and the “low” hydride species that result still have an exceptionally high number of hydrides. To our knowledge, the complexes 1b and 2b are without precedent in cluster chemistry, combining (i) the greatest number of hydride ligands so far reported on a discrete metal cluster, (ii) a hydride:metal ratio of greater than 2:1 (Pd₂₈(PtPMe₃)₂(PtPh₃)₁₂(CO)₂₇H₁₂ has 12-hydride ligands but has 41 metals in its core, while [Ir₃(ROX)₃H₇][PF₆]₂ has a high hydride:metal ratio of 7:3 but only seven hydride ligands⁵⁵), and (iii) reversible hydrogen loss/uptake of two molecules of H₂.

DFT Calculations on the Model Cluster Pairs [Rh₆(PH₃)₆H₁₂]²⁺ and [Rh₆(PH₃)₆H₁₆]²⁺. DFT calculations on the cluster pair [Rh₆(PH₃)₆H₁₂]²⁺ and [Rh₆(PH₃)₆H₁₆]²⁺ have been carried out at the ADF/TZVP level, with the alkyl phosphine groups substituted by PH₃ for computational expediency. Full details of these calculations, the molecular orbital description of the bonding, and the hydrogen uptake will appear in a dedicated full paper. Here we briefly outline the main conclusions and highlight how these calculations mirror the experimentally determined results and support the assignment of the hydride count for the cluster pairs 1a/1b and 2a/2b. We also comment briefly on the molecular orbital structure of the 12-hydride species.

Figure 12 shows the calculated structures for [Rh₆(PH₃)₆H₁₂]²⁺ and [Rh₆(PH₃)₆H₁₆]²⁺, and Table 2 presents selected structural metrics for the pair, alongside the experimentally determined structures from single-crystal X-ray diffraction. Although the substitution of bulky PiPr₃ or PCy₃ for the model phosphine PH₃ might be expected to have a significant effect on the cluster geometry, that there is a surprisingly good correlation between theory and experiment shows that, although bulky, the phosphine ligands exert less influence on the cluster core than might be expected. Dealing with the {Rh₆P₆} cluster cores first, all the observed structural trends on going from H₁₂ to H₁₆ are mirrored in the DFT-calculated structures (Table 2). Specifically, on addition of two molecules of H₂ to give [Rh₆(PH₃)₆H₁₆]²⁺ has been modeled in two ways: by 16 hydrides on the surface of the octahedron, and by 15 on the surface and 1 central (interstitial). The interstitial model comes out as being significantly more stable by 145 kJ mol⁻¹, in line with the experimental NMR data that show a 15:1 ratio of hydride ligands. Of the 15 hydrides on the outside of the octahedron, four of them (two pairs) have short H—H distances, indicative of dihydrogen ligands, d(H—H) = 1.061 and 0.965 Å. Similar structures, implicating a mixture of dihydrogen and hydride ligands, have been calculated for Pd₅H₆ clusters.⁷⁷ The presence of dihydrogen ligands is consistent with the experimental observations that the cluster undergoes H/D exchange with D₂(g) to produce HD(g) and that the low-temperature, high-field ¹H NMR spectra of both 1b and 2b show a total integral of 12 H, the four missing protons precision afforded by an X-ray diffraction experiment. Addition of two molecules of H₂ to give [Rh₆(PH₃)₆H₁₆]²⁺ has been modeled in two ways: by 16 hydrides on the surface of the octahedron, and by 15 on the surface and 1 central (interstitial). The interstitial model comes out as being significantly more stable by 145 kJ mol⁻¹, in line with the experimental NMR data that show a 15:1 ratio of hydride ligands. Of the 15 hydrides on the outside of the octahedron, four of them (two pairs) have short H—H distances, indicative of dihydrogen ligands, d(H—H) = 1.061 and 0.965 Å. Similar structures, implicating a mixture of dihydrogen and hydride ligands, have been calculated for Pd₅H₆ clusters.⁷⁷ The presence of dihydrogen ligands is consistent with the experimental observations that the cluster undergoes H/D exchange with D₂(g) to produce HD(g) and that the low-temperature, high-field ¹H NMR spectra of both 1b and 2b show a total integral of 12 H, the four missing protons.
presumably broad and not observed. Also consistent with the \(^1\)H NMR data is that the interstitial hydride is not located in the geometric center of the cluster, with the internal Rh–H distances varying between 2.082 and 1.875 Å in the model. The dissociation energy of the two H\(_2\) molecules from the H\(_{16}\) cluster, i.e., the SCF energy difference between \([\text{Rh}_6\text{H}_{12}\text{(PH}_3)_6]\)^2+ and \([\text{Rh}_6\text{H}_{16}\text{(PH}_3)_6]\)^2+, is calculated as 151 kJ mol\(^{-1}\) in favor of the \([\text{Rh}_6\text{H}_{16}\text{(PH}_3)_6]\)^2+ cluster.

In terms of simple electron book-keeping, the 12 hydride clusters \(1a\) and \(2a\) have 76 cve, this being 10 cve less than that found for late transition metal octahedral clusters (86 cve) such as \([\text{Rh}_6\text{(CO)}_{16}]\). However, the electron count is exactly like that of the early transition metal clusters such as \([\text{Nb}_6\text{Cl}_{18}]\)\(^{-}\) and is similar to that of the structurally closely related zirconium-phosphine clusters \([\text{Zr}_6\text{Cl}_{12}\text{(PMe}_2\text{Ph)}_6]\) (72 cve)\(^{16}\) and \([\text{Zr}_6\text{Cl}_{14}\text{H}_2\text{(PMe}_3)_4]\) (74 cve).\(^4\) Dicationic hexanuclear clusters \([\text{Au(PR}_3])_6]^2+\) of 76 cve are also known, and these can adopt either octahedral\(^7\) or edge-shared bieptahedral structures.\(^9\) The structural similarity between the early transition metal clusters with edge-bridged halides (Scheme 1) and \(1a/2a\), with 12 edge-bridged hydrides, is remarkable and underscores that both sets of clusters are built from \(\{\text{ML}_5\}\) fragments, e.g., \{ClNbCl\}_4 and \{(PR\(_3\))RhH\(_2\}\). The molecular orbital description of clusters such as \([\text{Nb}_6\text{Cl}_{18}]\)\(^{-}\) is well understood,\(^6\) and cluster bonding arises from 8 cluster bonding orbitals. By comparison, calculations on \([\text{Rh}_6\text{(PH}_3)_6\text{H}_{12}]\)^1+ with the Rh\(_6\)P\(_6\)H\(_{12}\) core constrained to octahedral symmetry for simplicity, revealed 20 bonding and 12 nonbonding cluster orbitals (Figure 13). Of these, 12 may be regarded as built from the 12 three-center, two-electron Rh–H–Rh bonds (1a\(_{1g}\), 1e\(_g\), 1t\(_{1u}\), 1t\(_{2u}\), and 2t\(_{2g}\) in symmetry); these are equivalent to the Nb–Cl–Nb symmetric bonding orbitals. The other 20 are principally metal-localized and correspond to the 8 Nb–Nb bonding orbitals of the niobium cluster (2a\(_{1g}\), 2t\(_{2g}\), 3t\(_{1u}\), and 1a\(_{2u}\) in symmetry) and 12 metal-localized orbitals (2t\(_{2u}\), 3t\(_{2g}\), 1e\(_u\) 1t\(_{1g}\), and 1a\(_{2g}\) in symmetry), which are numerically equal (though not symmetrically equivalent) to the 12 antisymmetric Nb–Cl–Nb bridging bonds; the \(\pi\)-donor interaction of the 12 Cl’s with the Nb\(_6\) core is replaced in the Rh\(_6\)H\(_{12}\) cluster by metal-localized electrons. The remaining 6 orbitals that complete a total orbital count of 38 (and consequently an electron count of 76) are associated with Rh–P bonding (2t\(_{1u}\), 2e\(_g\), and 3a\(_{1g}\)). Replacing the chlorides in \([\text{Nb}_6\text{Cl}_{18}]\)\(^{-}\) with hydrides and phosphines reduces the overall electron count by 24, but moving from a group 5 metal to a group 9 metal results in a net gain of 24 electrons to the cluster. Thus, the low ligand electron count of \([\text{Rh}_6\text{(PH}_3)_6\text{H}_{12}]\)^2+ is exactly balanced by the move from Nb to Rh and the subsequent use of 12 additional metal-localized orbitals (and 24 electrons). Although with regard to octahedral late transition metal clusters composed of \{ML\}_3 fragments such as \([\text{Rh}_6\text{(CO)}_{16}]\)\(^{-}\) \(1a\) and \(2a\) count less by 10 electrons, they are in fact electron-precise for a cluster constructed from \{ML\}_3 fragments such as \([\text{Nb}_6\text{Cl}_{18}]\)\(^{-}\).

The principal difference in the orbital structure when the symmetry is lowered from octahedral to that of the optimized calculated structure is that two of the three Rh–H–Rh 2t\(_{2g}\) orbitals are considerably stabilized by the shift of eight hydrogens from central bridging to semi-bridging positions as a consequence of improved overlap between the H 1s orbitals.)
and the Rh 4d orbitals. Mixing between a 3e_g orbital and the 1a_3g orbital localizes a pair of electrons in the same plane as the symmetrically bridging hydrogens.

The HOMO–LUMO gap in \([\text{Rh}_6(\text{PH}_3)_6\text{H}_6]^{2+}\) as calculated under \(O_h\) symmetry is relatively small, \(\sim 0.3\) eV, and the LUMO is of \(e_g\) degeneracy and effectively nonbonding. These two observations suggests that addition of four electrons should be facile. These four electrons can come from two molecules of \(\text{H}_2\), and addition results in the \(16\)-hydride, \(80\) cve species \([\text{Rh}_6-\text{C}_6\text{H}_5\text{F}]\)[BArF_4].

The full molecular orbital structure description, discussion of the facile uptake of \(\text{H}_2\), and electron counting for the clusters will be dealt with in detail in a future full paper. Importantly for this paper, which deals with the synthesis and structures of the cluster pair \(1\alpha/1\beta\) as well as \(2\beta\).

**Mechanism of Cluster Formation.** As discussed in the Introduction, clusters that form under kinetic conditions are relatively unusual, and the attractive time scales (5 days) and moderate temperatures involved (313–323 K) in the formation of \(1\alpha\) and \(2\alpha\) afford a rare opportunity to probe a cluster self-assembly process using NMR spectroscopy. Addition of \(\text{H}_2\) (\(\sim 4\) atm) to a fluorobenzene solution of \([\text{Rh}(\text{PPPr}_3)_2(\text{nb}d)][\text{BArF_4}]\) in a sealed J. Youngs tube initially results in the formation of the almost colorless dihydrogen/dihydride complexes \([\text{Rh}(\text{PPPr}_3)_2(\text{H})_2(\eta^6-\text{C}_6\text{H}_6)][\text{BArF_4}]\) (\(x = 1\) or \(2\)), as shown by a broad \(31^P(1H)\) NMR resonance at \(\delta\) 63 ppm and a very broad signal at \(\delta \sim 5.8\) ppm in the \(^1H\) NMR spectrum at high field. Following the reaction by NMR spectroscopy during gentle heating at 313 K over 5 days revealed a number of intermediate species, along with the final product \(1\beta\) that forms from addition of \(\text{H}_2\) to \(1\alpha\). Figure 14 shows a graph of integrated \(3^P\) resonances against time for this experiment.

There are three new species observed after 2 h of reaction in the \(^3P(1H)\) NMR spectrum. The first is \([\text{HPPr}_3][\text{BArF_4}]\), identified by a distinctive resonance at \(\delta\) 46 ppm which splits into a doublet, \(J(\text{PH}) = 336\) Hz, in the \(^3P\) NMR spectrum. Using \(D_2\) in the reactions rather than \(\text{H}_2\) afforded \([\text{DPPr}_3]-\text{[BArF_4]}\) and, ultimately \(1\beta-d\)\(_6\). The second new species is a very small amount of cluster \(1\beta\). Both of these species continue to increase in concentration throughout the experiment. The third new species is spectroscopically identified as the fluorobenzene complex \([\text{RhH}_2(\text{PPPr}_3)(\eta^6-\text{C}_6\text{H}_6F)][\text{BArF_4}]\) (3). Complex 3 has been independently synthesized by addition of \(\text{H}_2\) to \([\text{binor}-3\text{Rh}(\text{PPPr}_3)][\text{BArF_4}]\) (a source of a reactive \{Rh(PR_3)_1\}^\text{+} fragment) \({}^\text{81}\) in fluorobenzene solution (Scheme 6), and the NMR data match exactly those observed in the reaction mixture.

After 3 h the concentration of complex 3 drops, to be replaced by a species identified as the benzene complex \([\text{RhH}_2(\text{PPPr}_3)-(\eta^6-\text{C}_6\text{H}_6)][\text{BArF_4}]\) (4). Concomitant with the appearance of 4, free benzene also appears in the \(^1H\) NMR spectrum (\(\delta\) 7.21 ppm) as well as traces of fluorocyclohexane (\(\text{C}_6\text{H}_11\)F, identified by a characteristic \(d\) of \(t\) of \(t\) at \(\delta\) 4.40 ppm)\({}^8^3\). The generation of benzene most likely comes from hydrido-defluorination of fluorobenzene by traces of colloidal Rh, while hydrogenation...

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of fluorobenzene to form fluorocyclohexane is also catalyzed by colloidal Rh.19 The benzene thus produced readily displaces the weakly bound fluorobenzene in $^3$ to give $^4$. After about 22 h, complex $^4$ starts to disappear, so by the end of the monitoring experiment the concentrations of $^3$ and $^4$ are both zero. During this time, the peak at δ 63 ppm in the $^{31}$P-$^1$H NMR spectrum gradually moves to being a doublet at δ 58.2 ppm [$^1$H($\text{RhH}$)] 110 Hz and reaches what appears to be an equilibrium concentration of approximately half the initial concentration of starting material. We assign this peak at δ 58.2 ppm to $[^\text{Rh}-(\text{P} \text{iPr}_3)^2(\text{H})_2(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$], formed from loss of one H2 from $[^\text{Rh}-(\text{P} \text{iPr}_3)^2(\text{H})_2(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$, as has been noted to happen when the H2 pressure drops from ~4 atm to ~1–2 atm.39 The final products of the reaction after 5 days are 1b, [HP$iPr_3$]−[BArF$_4$], and $[^\text{Rh}(\text{P} \text{Pr}_3)_2(\text{H})(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$. Repeating the experiment under 100 bar H2 did not afford the cluster, with the only observed species being $[^\text{Rh}(\text{P} \text{Pr}_3)_2(\text{H})(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$. Removal of H2 under vacuum after the initial hydrogenation of $[^\text{Rh}-(\text{nbdl})(\text{P} \text{Pr}_3)_2][\text{BArF}_4]$ stopped the reaction and afforded the previously spectroscopically characterized complex $[^\text{Rh}(\text{P} \text{Pr}_3)_2-(\text{H})(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$ ($\text{L} =$ solvent or agostic interaction).39 Use of less bulky phosphine ligands, such as PET$_3$ (cone angle 132° 41), starting from $[^\text{Rh}-(\text{nbdl})(\text{PET}_3)_2][\text{BArF}_4]$, cleanly affords the Rh(I) species $[^\text{Rh}(\text{Ł}^6-\text{C}_6\text{H}_5\text{F})(\text{PET}_3)_2][\text{BArF}_4]$ (5), which has a coordinated fluorobenzene ligand and no hydride ligands (see Supporting Information for full characterization). On addition of H2 no cluster is formed under 4 atm of H2 on heating to 323 K, with 5 remaining unchanged. This suggests that phosphines with sufficient steric bulk to force the trans arrangement observed in $[^\text{Rh}(\text{P} \text{iPr}_3)_2(\text{H})(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$ are required for cluster formation.

Scheme 7 outlines the species observed by NMR spectroscopy. That cluster formation does not occur under very high pressures of H2, but also requires some H2 to be available, shows that the bis-di-hydrogen complex $[^\text{Rh}(\text{P} \text{Pr}_3)_2(\text{H})(\text{Ł}^2-\text{H}_2)]^{-}[\text{BArF}_4]$. 

(Scheme 6. Synthesis of $[^\text{RhH}_2(\text{P} \text{iPr}_3)(\text{Ł}^6-\text{C}_6\text{H}_5\text{X})][\text{BArF}_4]$

(Scheme 7. Observed Species in the Cluster Buildup Reaction and Suggested Mechanistic Routes (Dashed Arrows))"
that once a significant amount of protonated phosphine has built up in the reaction, cluster formation will cease. This observation is consistent with the apparent equilibrium concentration of [Rh-(PPr3)2(H)(μ3-H1)]2[BAr4]2 observed at the end of the reaction, and the idea that repressurizing the reaction with H2 does not afford more cluster. This inhibition likely comes from a back reaction (protonation and coordination of phosphine) between [HPPPr3][BAr4]2 and a mono-phosphine intermediate involved in cluster buildup.

Although the order of all these possible events discussed, and the actual species involved, needs further clarification before a complete mechanistic picture of the cluster self-assembly can be determined, that the clusters are reproducibly isolated in a good yield (~30–40%) and are of excellent purity shows that whatever self-assembly mechanisms are operating are experimentally robust. This is an important consideration if the chemistry of these cluster species is to be developed.

Conclusions

The synthesis and characterization of octahedral rhodium cluster complexes under conditions that favor kinetically controlled cluster products has been described: [Rh6(PPr3)4(H)2]-[BAr4]2. (PPr3 = PPr3, PCy3; BAr4 = [B(C6H4(CF3)2)]2). These clusters are unique in that they have structures that are exactly like those of early transition metal clusters that have edge-bridging π-donor ligands rather than those expected for a late transition metal. These clusters reversibly take up two molecules of dihydrogen to afford clusters that have 16 hydrides surrounding the metal core. This uptake of H2 is a consequence of two low-lying unoccupied molecular orbitals that readily accept two electron pairs (or two mole equivalents of H2). The reversible uptake of dihydrogen is of clear relevance to applications in hydrogen storage, and the drivers behind the reversible storage of large amounts of H2 (>6% by mass for mobile applications) have been described extensively and will not be repeated here.33 The current best molecular materials are those based around metal–organic frameworks (MOFs),34 which can reach storage efficiencies of 2.5% at 77 K.88 Based on the cluster dication core, complex 1a can store a modest ~0.25% of H2 at room temperature for the 12-hydride to 16-hydride process, and in terms of the volume of H2 uptake, 1a can reversibly take up ~20 times its volume of H2. Clearly, they do not make suitable candidates for hydrogen storage for mobile applications. However, their well-defined molecular nature that can be probed by NMR, X-ray crystallography, and mass spectrometry as well as DFT calculations means that they make excellent models for reversible hydrogen attachment on a metal surface. Moreover, the ease of filling and emptying the frontier molecular orbitals with electrons (in this case from H2) without significant structural change suggests that these clusters should present interesting electrochemistry and magnetic behavior, especially when linked to the reversible uptake of H2 and the extremely high hydride count of the clusters. These aspects, and ways of increasing the hydrogen storage capacity of these clusters by “unlocking” the remaining 12 hydride ligands that surround the metal core, must be future goals associated with this work.

References

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 flame-dried with a blow torch, under vacuum, three times before use. CH3F was distilled from CaH2, CHCl3, pentane, and hexane were purified using an MBraun solvent purification system. CD2Cl2 was distilled under vacuum from CaH2. [(Cy3P)2Rh(H)][H-Closo-CB11Me11], [(Cy3P)Rh(H)][BA2r4], and [(Pr2P)Rh(nbd)][BA2r4] were prepared by the published route using Ag[closo-I-I-CB11Me11],46 18K[BA2r4],18 and Pr3P or PCy3. [Rh(binor-S)(PR3)][BA2r4] was synthesized by the published procedure.88

NMR Spectroscopy. 1H and 31P NMR spectra were recorded on a Bruker Avance 400 MHz FT-NMR spectrometer. Residual proton solution was used as reference for 1H NMR spectra (CD2Cl2: δ = 5.33). 31P NMR spectra were referenced against 85% H3PO4 (external). 1H NMR spectra in fluorobenzene were referenced to the solvent signal, the position of which was determined using an external sample of TMS. For samples run in protio-fluorobenzene (reaction monitoring experiments), shimming was performed by optimization of line shapes obtained by visual inspection of a real-time Fourier-transformed FID. Coupling constants are quoted in hertz.1 H 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°). PGSE diffusion data were collected at 294 K in 5-mm NMR tubes using the previously outlined method,63 measuring integrated resonances of the PR3 groups in the 1H NMR spectrum. The diffusion coefficient was calculated from the slope of the regression line of the plot (ln[I2/I0]) vs Q2).

Mass Spectrometry. ESI-MS data were collected on a Waters Micromass Q-Tof micromass 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://jorg.chem.unc.edu/personal/moore/mwcalc.html).

Computational Details. Calculations were carried out using the ADF code version 2004.19 Vosko, Wilk, and Nusair’s local functional was used to indicate single-atmosphere disorder in the solid state. Other solvent/anion combinations did not produce better quality crystals. Alternatively, finely crystalline or finely powdered 1a (−5 mg) was treated with H2 (−4 atm) in a J. Young tube for 10 h, resulting in quantitative conversion (by ESI-MS and NMR) to 1b.

1H NMR (400 MHz, CD2Cl2): δ 7.71 (m, 16H, BarF4), 7.55 (m, 8H, BarF4), 2.32 (m, 18H, PCH), 1.23 (m, 108H, CH3), −25.44 (s, fwhm 46 Hz, 12H, Rh−H).63 31P NMR (162 MHz, CD2Cl2): δ 106.2 [d, J(RhP) = 104 Hz]. Selected low-temperature 1H NMR data: at 250 K, δ −25.44 (s, fwhm 55 Hz); at 200 K, δ −19.03 (s, fwhm 76 Hz, T2 = 320 ms).1H NMR (162 MHz, CD2Cl2): δ 29.92 (br, fwhm 30 Hz, PCH), δ 20.53 (s, CH3). ESI-MS (CH2Cl2): calc'd for [P2Rh2Cy6H12][BarF4]2: 795.2; obsd 795.1. Elemental analysis: C118H162F48B2P6 requires C 43.63, H 4.93; found C 43.48, H 4.86.

[S2]. 1H NMR (400 MHz, CD2Cl2): δ 7.71 (m, 16H, BarF4), 7.55 (m, 8H, BarF4), 2.32 (m, 18H, PCH), 1.23 (m, 108H, CH3), −25.44 (s, fwhm 46 Hz, 12H, Rh−H).63 31P NMR (162 MHz, CD2Cl2): δ 106.2 [d, J(RhP) = 104 Hz]. Selected low-temperature 1H NMR data: at 250 K, δ −25.44 (s, fwhm 55 Hz); at 200 K, δ −19.03 (s, fwhm 76 Hz, T2 = 320 ms).1H NMR (162 MHz, CD2Cl2): δ 29.92 (br, fwhm 30 Hz, PCH), δ 20.53 (s, CH3). ESI-MS (CH2Cl2): calc'd for [P2Rh2Cy6H12][BarF4]2: 795.2; obsd 795.3. Elemental analysis was not obtained due to loss of H2 under vacuum. Characterization by NMR and ESI-MS is unequivocal.

Synthesis of [Rh2(PCy3)2][BA2r4]2 (2a). In a typical experiment, a solution of [Rh(nbd)(PPR3)2]2 (200 mg, 0.145 mmol) in fluorobenzene (10 mL) in a J. Young tube was hydrogenated (ca. 4 atm of H2) by freezing a solution to 77 K, placing the tube under 1 atm of H2, sealing the tube, and warming to room temperature (298/77 °C) at 8 °C under ca. 4 atm of H2 for 5 days. Pentane (50 cm3) was added, and the mixture was crystallized at −18 °C overnight. The material that resulted was crystallized in the same manner an additional two times. The sample was dissolved in fluorobenzene, and 1-hexene was added to ensure that only [Rh2(PCy3)2][BA2r4]2 (and none of the 16-hyride species) was present. After 24 h, the solution was layered with hexanes, and slow diffusion gave [Rh2(PCy3)2][BA2r4]2 as a deep red crystalline solid (25 mg, 31%).
a deep red solid (84 mg, 40%). NMR and ESI data of the resulting crystals were unequivocal in the characterization as the 12-hydride species.

1H NMR (400 MHz, CD2Cl2, 298 K): δ 7.71 (m, 16H, BaF2), 7.55 (m, 8H, BaF2), 0.8–2.5 (m, 198H, PCy3), −27.20 (br s, fwhm 230 Hz, 9H, Rh−H), −28.9 (br s, fwhm 330 Hz, 3H, Rh−H). Selected variable-temperature 1H NMR data: at 330 K, δ −21.7 (12H); at 250 K, δ −21.7 (9H), −25.2 (3H); at 200 K, δ −19.52 (9H, T1 = 890 ms), −21.94 (3H, T1 = 890 ms). 31P(1H) (162 MHz, CD2Cl2, 298 K): δ 91.9 [d br, J(RhP) = 102Hz]; at 200 K, δ 88.2 [d, J(RhP) = 105 Hz]; at 348 K, 100.4 (vbr s, fwhm 200 Hz). ESI-MS (CH2Cl2): calcd for [PdRh6(C6H6)2]2+: 915.55; obsd, 915.57. Elemental analysis: C173 H234 B2 −6O2 −21.94 (3H, 141 Hz, 18H, CH3), 26.71 (9H, T = 21.59 Å). The solution was layered with CH2Cl2 molecules and therefore had to be restrained and refined throughout. For 2a only 5 out of 16 hydrogen atoms could be found and refined reliably in the final stages of the refinement. In 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, a symmetry-related (multiscan) absorption correction was employed.

Synthesis of [Rh6(PCy3)6H16][BaF2]2 (2b). A solution of [Rh6(PCy3)6H16][BaF2]2 (5 mg) in CD2Cl2 (0.5 mL) was shaken under a hydrogen atmosphere (4 atm) for 2 min in a J. Young NMR tube. Alternatively, placing a solution of [Rh6(PCy3)6H16][BaF2]2 (5 mg) was treated with H2 (under 1 atm of H2 effects are negligible). The solution was layered with CH2Cl2 and slow diffusion gave [Rh6(PCy3)6H16][BaF2]2 (as a deep red solid). Suitable crystals were obtained due to loss of H2 under vacuum. Characterization by NMR spectroscopy is unequivocal. The solution was shaken and allowed to stand for 15 min, resulting in quantitative conversion to 2, as determined by in situ 1H and 31P NMR spectroscopy. The NMR data for the cation are essentially the same as those reported for the [PF6]− salt.

Selected 1H NMR (400 MHz, CD2Cl2): δ 6.77 (s, 6H, CH6), 1.94–2.07 (m, 3H, PCH), 1.12 [dd, J(HH) = 16.0 Hz, J(HF) = 7.1 Hz, 1H, CH6], −14.54 [dd, J(HP) = 27.7 Hz, J(RhH) = 23.6 Hz, 2H, Rh−H], 31P(1H) NMR (162 MHz, CD2Cl2): δ 96.3 [d, J(RhP) = 142 Hz].

X-ray Crystallography. Intensity data for 1a, 2a, and 2b were collected at 150 K on a Nonius Kappa26 diffractometer equipped with a low-temperature device, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using the supplied Nonius software. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-X program. For 2a, 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 1.