Cluster Chemistry

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Holding onto Lots of Hydrogen: A 12-Hydride Rhodium Cluster That Reversibly Adds Two Molecules of H_2**

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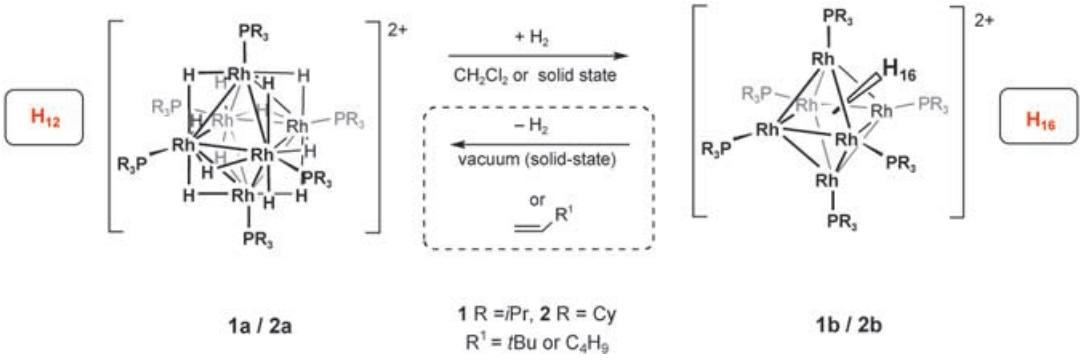
The boundary between catalysis by nanocluster and molecular materials is an area of science that is attracting considerable attention.[1] Much of this interest has centered on the role that such species play in hydrogenation reactions (especially arene hydrogenation), and in particular the nature of the actual species in catalysis (nanocluster versus molecular cluster).[2] Given the inherent difficulty in characterizing nanocluster species at atomic resolution, well-defined molecular clusters that can be considered as models for hydrogen attachment to a metal surface are key to understanding the chemistry of these species. Despite this, molecular cluster species that reversibly take up dihydrogen,[3,4] or have a hydrogen content that approaches that expected for a metal surface covered in chemisorbed H_2, are rare.[5,6] We have previously described the complex $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$ (**1a**)—a cluster complex that not only has an unexpected geometry and cluster electron count (76 cluster valence electrons (cve), 10 lower than expected for an octahedral late-transition-metal cluster) but also a rather high hydrogen content.[7] We now report that this complex, and its PCy_3 (Cy = cyclohexyl) analogue, reversibly add two molecules of H_2 to give discrete clusters with exceptionally high hydride counts: $[Rh_6(PR_3)_6H_{16}][BAr^F{}_4]_2$ (R = Cy, *i*Pr; Ar^F = 3,5-$(CF_3)_2C_6H_3$; Scheme 1).

The tricyclohexylphosphine analogue of **1a**, $[Rh_6(PCy_3)_6H_{12}][BAr^F{}_4]_2$ (**2a**), is prepared in a similar manner to **1a** in modest (≈30%) yield by gentle heating of $[(PCy_3)_2Rh(\eta^2\text{-}H_2)_2H_2][BAr^F{}_4]$[8] in fluorobenzene. Cluster **2a** was characterized by NMR spectroscopy and ESI mass spectrometry, both of which unambiguously identify the cluster as having



Scheme 1.

12-hydride ligands. Addition of dihydrogen (≈1 atm) to **1a** or **2a** in solution (CH_2Cl_2) results in the immediate formation of the sixteen-hydride cluster complexes $[Rh_6(PR_3)_6H_{16}][BAr^F{}_4]_2$ (**1b**, R = *i*Pr and **2b**, R = Cy) in quantitative yield—in which two molecules of H_2 have been added to the octahedral cluster. Hydrogen uptake also occurs in the crystalline form but at a much slower rate (hours). The ESI MS of CH_2Cl_2 solutions were unambiguous in the characterization of **1b** and **2b** (Figure 1 for **2a**/**2b** pair), and clearly demonstrate the quantitative formation of a dicationic 16-hydride species: with "flagpole" spectra observed showing excellent matches to the calculated isotope distribution patterns.

The ^{1}H NMR spectra of both **1b** and **2b** confirm the hydride count from the ESI MS experiments. These spectra show upfield signals that integrate to a total of 16H relative to the alkyl phosphine protons. In the room-temperature ^{1}H NMR spectrum, two hydride signals are consistently (for five independently synthesized samples) observed in the ratio 15:1. Figure 2 shows the spectrum for the **1a**/**1b** pair. This 15:1 ratio suggests a structure in which fifteen hydrides are mutually exchanging on the NMR timescale and one is not. A plausible structure that accounts for this observation is one that invokes an interstitial hydride[9,10] with 15 hydride ligands decorating the outside of the Rh_6 octahedron. On cooling the NMR sample to 200 K the hydride resonances in **1b** and **2b** become broader and resolve into many separate signals with an overall integral lower than 16H. The broad line width of some these signals indicate that any fluxional processes occurring are not completely frozen out at low temperature. T_1 measurements at 200 K indicate that all the observed

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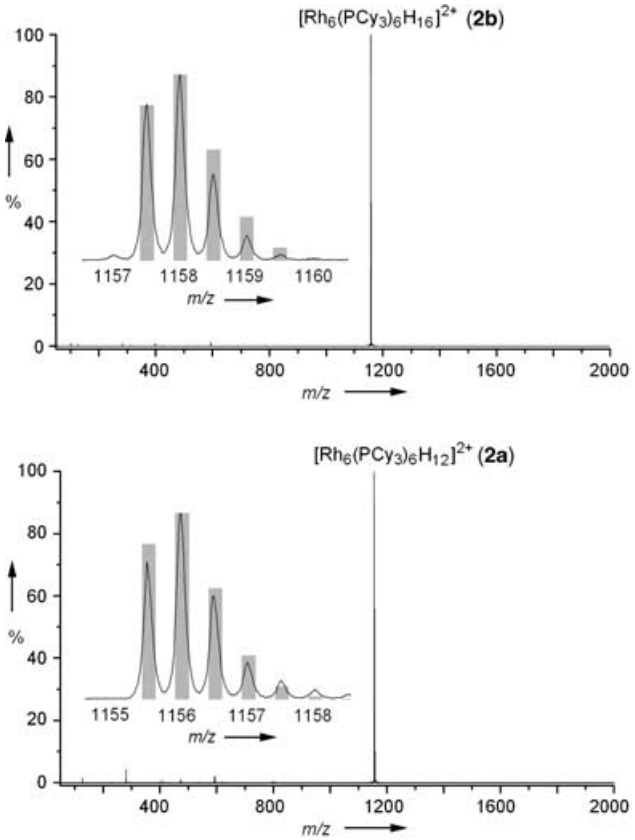

Figure 1. ESI mass spectra of **2a** and **2b**. Insets show observed isotopomer pattern overlaid with the calculated pattern (gray bars).

signals are best assigned to hydride ligands ($T_1 > 230$ ms). At higher temperatures (323 K) the 15:1 pattern is still observed, while heating further results in decomposition.

Preliminary density functional theory (DFT) calculations on model compounds $[Rh_6(PH_3)_6H_{16}]^{2+}$ and $[Rh_6(PH_3)_6H_{12}]^{2+}$ support the interstitial hydride assignment, indicating that a cluster with 15 hydride ligands on the surface and one interstitial is significantly more stable than one with 16 hydrides on the surface. Calculations also reveal the electronic reasons underlying the uptake of two molecules of H_2. Similar to recently reported $[Pt_3Re_2(CO)_6(PtBu_3)_3]$[6] which takes up three molecules of H_2 and has five low-lying unoccupied molecular orbitals, the 12-hydride octahedral clusters reported herein have a small HOMO–LUMO gap (0.50 eV) and a degenerate pair of LUMO orbitals available for the uptake of four electrons (that is, two molecules of H_2; Figure 3). The resulting 16-hydride species (80 cve) has a larger HOMO–LUMO gap (1.3 eV) and thus would be expected to take up additional H_2 less readily. This result is confirmed experimentally; under higher pressures (100 bar H_2) **1b** is the only hydride species observed in solution.

Despite repeated and extended attempts using a variety of counterions and solvents, suitable single crystals of **1b** were not forthcoming. However, crystals of **2b** were eventually obtained by using the [1-H-*closo*-$CB_{11}Me_{11}]^-$ counterion and the structural refinement showed that the $\{Rh_6(PCy_3)_6\}^{2+}$ octahedral cluster core is retained (Figure 4a) in this high-hydride species, although it is somewhat distorted showing a wide range of Rh–Rh bond lengths (2.720(1)–3.132(1) Å). A similar span of bond lengths is observed in the DFT calculated structure of $[Rh_6(PH_3)_6H_{16}]^{2+}$. The Rh–Rh bonds in $[Rh_6(PH_3)_6H_{12}]^{2+}$ show a much narrower distribution, suggesting that the observed distortion is due (in part) to the distribution of the hydride ligands in the high-hydride species. Unfortunately, the hydride ligands could not be located reliably, a common problem in cluster chemistry given the low scattering factor associated with hydrogen and the fact that the hydrides are very often distributed asymmetrically in the solid-state leading to partial occupancy of sites. This situation is taken to the extreme with the 16 hydride ligands around the octahedral core in **1b** and **2b**.

The 16-hydride complexes **1b** and **2b** are stable under an argon atmosphere, but under vacuum both **1b** and **2b** lose two molecules of H_2 to quantitatively regenerate **1a** and **2a**. This

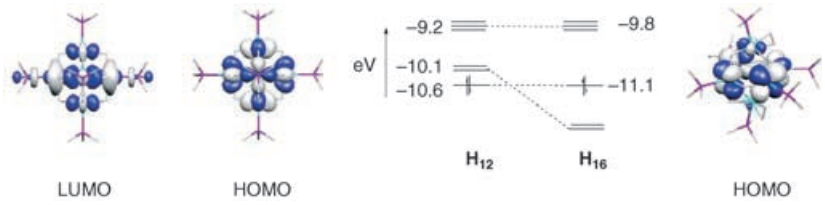

Figure 3. DFT calculated correlation diagram for $[Rh_6(PH_3)_6H_{12}]^{2+}$ and $[Rh_6(PH_3)_6H_{16}]^{2+}$.

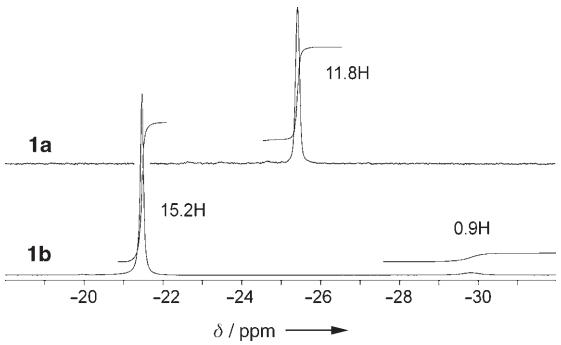

Figure 2. Upfield ^{1}H NMR spectra of **1a** and **1b**. See Supporting Information for the corresponding spectra for **2a** and **2b**.

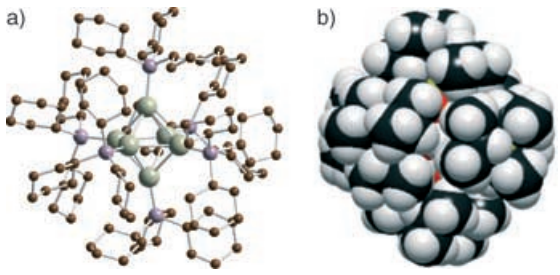

Figure 4. Molecular structure of the dicationic portion of **2b** (a; green Rh, purple P, brown C) and space-filling diagram of **2b** (b; black C, gray H, yellow P, red Rh).

process occurs both in solution and in the crystalline state, and is reversible; pressurizing with H_2 quantitatively (NMR spectroscopy, ESI MS) regenerates the H_{16} species. For **1b** H_2 loss is facile (hours), however for **2b** the process is longer (days) and this may be related to the increased steric shielding the cluster core receives from the cyclohexyl groups compared to the isopropyl groups (Figure 4b). Loss of two hydrogen molecules is also affected by addition of hydrogen acceptors such as *tert*-butylethene (tbe) or 1-hexene, as monitored by NMR spectroscopy and ESI MS (Figure 5). Interestingly, even with a large excess of alkene (>100-fold) **1a** and **2a** remain—showing that these clusters holds onto the remaining twelve hydrides very strongly.

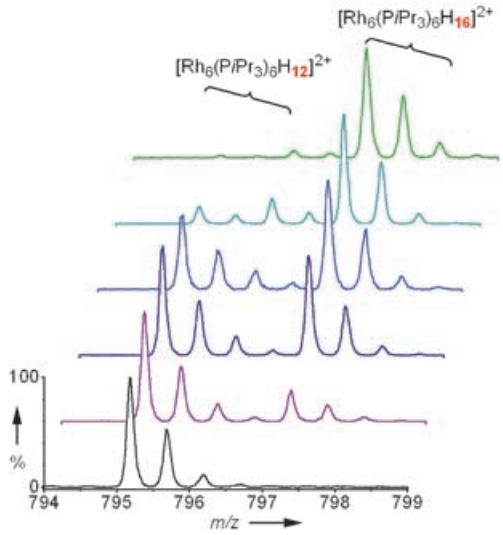

Figure 5. Stacked plot of ESI MS of **1b** on addition of the hydrogen acceptor tbe (≈100-fold excess) in CH_2Cl_2 solution. The uppermost spectrum is 5 min after addition of tbe and the bottom after 24 h.

Although there are a significant number of cluster species known with a high hydride count (that is ≥5 hydride ligands)[5,6,11] and some are formed by addition of H_2 to very unsaturated cluster species,[6] only one has been shown to reversibly release H_2, $[Pt_4H_7(PtBu_3)_4][BF_4]$,[4] affording a cluster with one hydride. The species reported herein are thus unique in that H_2 uptake and loss is facile and the "low"-hydride species that result still have an exceptionally high number of hydride ligands. They thus have relevance for the modeling of surfaces that are catalytically active for hydrogenation reactions as well as hydrogen-spillover processes that result in supported catalysts showing enhanced activities.[12] The cluster pairs **1a**/**1b** and **2a**/**2b**[14] could also potentially serve as models for chemically reversible hydrogen-storage materials, albeit with a low (≈0.25% based on the Rh_6 dication) reversible hydrogen-storage capacity.

Experimental Section

Crystallographic data: Crystals were grown from CH_2Cl_2/pentane under a H_2 atmosphere. Intensity data were collected at 150 K on a Nonius Kappa CCD diffractometer, using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Structure solution and refinement was achieved using the WinGX-1.64 package.[13] $C_{132}H_{264}B_{22}P_6Rh_6 \cdot CH_2Cl_2$, $M_r = 2997.46$, $Pna2_1$, $a = 17.6720(2)$, $b = 28.0280(3)$, $c = 31.0780(5)$ Å, $V = 15393.3(3)$ Å^3, $Z = 4$, $\mu = 0.769$ mm^{-1}, unique reflections = 27469 (R(int) = 0.0614), $R_1 = 0.0565$, $wR_2 = 0.0943$ ($I > 2\sigma(I)$). Up to 11 hydrogen atoms could be found in bridging positions around the Rh_6 core. However, they could not be refined reliably and were not considered in the final stages of the refinement. CCDC-275849 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1b: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.71$ (m, 16H, BAr^F_4), 7.55 (m, 8H, BAr^F_4), 2.27 (m, 18H, PCH), 1.24 (dd, $J = 15.4$ Hz, $J = 7.1$ Hz, 108H, CH_3), −21.46 (s, full width at half maximum height (fwhm) = 40 Hz, 15H, Rh-H), −29.81 ppm (br s, fwhm = 200 Hz, 1H, Rh-H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): $\delta = 109.2$ ppm (d, J(RhP) 140 Hz). ESI MS calcd for $[P_6Rh_6C_{54}H_{142}]^{2+}$ 797.2; found: 797.3.

2a: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.71$ (m, 16H, BAr^F_4), 7.55 (m, 8H, BAr^F_4), 0.8–2.5 (m, 198H, PCy_3), −27.20 (br s, fwhm = 230 Hz, 9H, Rh-H), −28.9 ppm (br s, fwhm = 330 Hz, 3H, Rh-H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): $\delta = 91.9$ ppm (d, J(RhP) 102 Hz). ESI MS calcd for $[P_6Rh_6C_{108}H_{210}]^{2+}$ 1155.5; found: 1155.7

2b: ^{1}H NMR: $\delta = 7.71$ (m, 16H, BAr^F_4), 7.55 (m, 8H, BAr^F_4), 1.0–2.4 (m, 198H, PCy_3), −21.59 (br s, fwhm = 390 Hz, 15H, Rh-H), −28.37 ppm (br s, fwhm = 210 Hz, 1H, Rh-H). ^{31}P{^{1}H} NMR: δ = 107.4 (br s, fwhm = 1100 Hz, 2P), 89.0 ppm (br s, fwhm = 900 Hz, 4P). ESI MS calc for $[P_6Rh_6C_{108}H_{214}]^{2+}$ 1157.5, obs. 1157.8.

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[14] Note added in proof, August 31, 2005: The solid-state structure of **2a** has been determined and shows it to be an essentially regular octahedron, in line with the DFT calculated structure (Rh–Rh bond lengths span the range 2.719–2.755 Å).

