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Reversible Addition of Water to the High-Hydride-Content Cluster $[Rh_6(P^iPr_3)_6H_{12}][BAr^F_4]_2$. Synthesis and Structure of $[Rh_6(P^iPr_3)_6H_{11}(OH)][BAr^F_4]_2$

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The hydroxyhydrido salt $[Rh_6(P^iPr_3)_6H_{11}(OH)][BAr^F_4]_2$ results from the addition of water to $[Rh_6(P^iPr_3)_6H_{12}][BAr^F_4]_2$. This reaction is reversible, and the addition of dihydrogen to $[Rh_6(P^iPr_3)_6H_{11}(OH)]$-$[BAr^F_4]_2$ results in the elimination of water and the regeneration of the hydride cluster.

The oxidative addition of water to transition-metal complexes to form hydroxyhydrido species has been the subject of significant interest, given the implications this has for a number of established catalytic processes (water−gas shift, olefin and nitrile hydration[1]), as well as for potential new catalytic processes involving water. The potential for solar energy conversion of water to hydrogen using transition-metal catalysts is also attracting considerable attention, and one possible mechanism for this involves intermediate hydroxyhydride species.[2] Despite this interest, only a handful of isolated examples of such species have so far been reported. All are formed from the addition of water to low-valent late-transition-metal complexes.[3−6] In addition to this, the *reversible* addition of water to metal hydrides is of considerable interest with regard to potential applications in the storage and release of dihydrogen.[7] We report herein that the addition of water to a metal hydride cluster forms a metal hydroxyhydride species that also undergoes the reverse reaction with dihydrogen to regenerate the starting hydride and water. Although the reversible addition of water with hydride complexes to liberate dihydrogen is known in a handful of late-transition-metal complexes,[4,8] as far as we are aware, this is the first time such a transformation has been reported on a metal cluster. The related reversible addition of ammonia to a trimetallic polyhydride to release dihydrogen has recently been reported by Suzuki.[9,10]

The addition of water (∼500-fold excess) to a 1,2-$F_2C_6H_4$ solution of $[Rh_6(P^iPr_3)_6H_{12}][BAr^F_4]_2$ (**1[BAr$^F_4$]$_2$**; $Ar^F = C_6H_3$-$(CF_3)_2$)[11] did not result in any observable change in the ^1H or $^{31}P\{^1H\}$ NMR spectra. However, addition in the presence of the hydrogen acceptor 3,3-dimethyl-1-butene (*tert*-butylethene, tbe, ∼65 equiv) did result in the reaction and relatively rapid (4 h at 40 °C) addition of water to form the dicationic hydroxyhydrido cluster complex $[Rh_6(P^iPr_3)_6H_{11}$-$(OH)][BAr^F_4]_2$ (**2[BAr$^F_4$]$_2$**; Scheme 1). Tbe acts as a hydrogen acceptor to remove 1 equiv of dihydrogen from the cluster, and 1 equiv of 3,3-dimethylbutane is observed in the ^1H NMR spectrum at the end of the reaction. Complex **2[BAr$^F_4$]$_2$** can be isolated in ∼70% yield as a crystalline solid after recrystallization from pentane/1,2-$F_2C_6H_4$. Samples of **2[BAr$^F_4$]$_2$** are invariably contaminated with trace (∼5%) **1[BAr$^F_4$]$_2$**, which we have not been able to remove by recrystallization. Longer reaction times result in further substitution (by ESI-MS) to give $[Rh_6(P^iPr_3)_6H_{12-x}(OH)_x]^{2+}$ (x = 1−3), but we have not been able to isolate a

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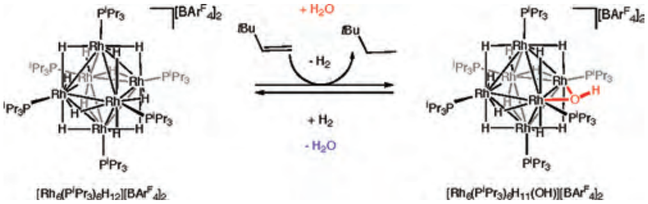
Scheme 1. Reversible Addition of Water to **1[BAr$^F{}_4$]$_2$**



compositionally pure more highly substituted material, even after extended periods of heating.

Complex **2[BAr$^F{}_4$]$_2$** has been characterized by ESI-MS, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and X-ray crystallography (Figure 1). [Crystallographic data for **2**: intensity data were collected at 150 K on a Nonius Kappa CCD, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); $C_{118}H_{150}B_2F_{48}OP_6Rh_6 \cdot C_6H_4F_2$, M = 3435.37, triclinic, space group $P\bar{1}$ (No. 2), a = 13.3270(2) Å, b = 17.4040(2) Å, c = 17.8290(2) Å, α = 73.340(1)°, β = 68.189(1)°, γ = 88.444(1)°, V = 3663.45(8) Å^3, Z = 1, D_{calc} = 1.557 g/cm^3, μ = 0.834 mm^{-1}, $2\theta_{max}$ = 70.14°, 68 280 reflections collected, 21 290 unique [R(int) = 0.0637], wR2 = 0.1362 (all data), R1 = 0.052 [$I > 2\sigma(I)$].] In the solid state, the μ-OH group is equally disordered over the Rh−Rh edges but can be satisfactorily modeled. In addition, ESI-MS of the crystal used in the X-ray diffraction experiment confirms the formula of the cluster dication to be $[Rh_6(P^iPr_3)_6H_{11}(OH)]^{2+}$. This disorder also means that perturbations in the Rh−Rh and Rh−O bond lengths are diluted in the refined structure, and thus it is inappropriate to discuss specific metrics. The structure, nevertheless, confirms that the cluster dication has not undergone a major change upon the addition of water. The dicationic cluster has overall pseudo-C_{2v} symmetry. Crystallographically characterized complexes with Rh−OH and Rh−Rh bonds are rare, and none contain a hydride.[12]

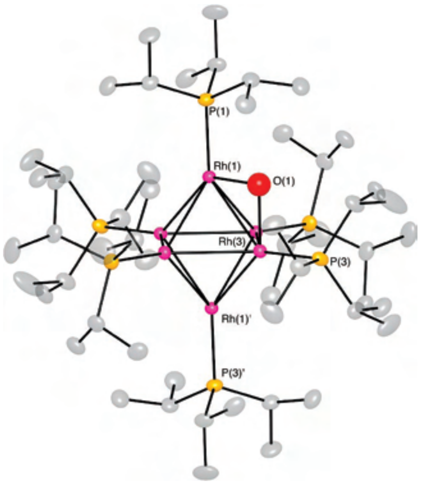
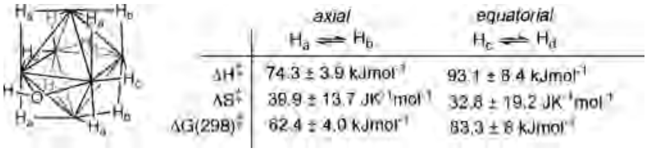


Figure 1. Solid-state structure of the cluster dication [**2**]$^{2+}$ showing the atom-labeling scheme. The hydroxide is disordered over the edges of the rhodium octahedron, and only one of these sites is shown. ESI-MS and NMR spectroscopy show 11 hydrides in total (which are not shown). Thermal ellipsoids are shown at the 30% probability level. The disordered oxygen atom was refined isotropically. Rh−Rh distances: 2.7061(4)−2.7355(4) Å. Rh−O distances (average): 1.95(2) Å.



	axial $H_a \rightleftharpoons H_b$	equatorial $H_c \rightleftharpoons H_d$
$\Delta H^\ddagger$	74.3 ± 3.9 kJmol^{-1}	93.1 ± 8.4 kJmol^{-1}
$\Delta S^\ddagger$	39.9 ± 13.7 JK^{-1}mol^{-1}	32.8 ± 19.2 JK^{-1}mol^{-1}
$\Delta G(298)^\ddagger$	62.4 ± 4.0 kJmol^{-1}	83.3 ± 8 kJmol^{-1}

Figure 2. Hydride exchange in **2[BAr$^F{}_4$]$_2$**.

ESI-MS of **2[BAr$^F{}_4$]$_2$** shows the expected isotope distribution and masses for the suggested formulation [obsd m/z 803.195; calcd m/z 803.175]. The ^{1}H NMR spectrum of **2-[BAr$^F{}_4$]$_2$** at 298 K shows a sharp, integral 1 H signal at δ 4.32 that disappears upon the addition of deuterated water (5 min), while ESI-MS of this solution shows that the isotope pattern has shifted by $^1/_2$ amu [obsd m/z 803.688; calcd m/z 803.678] showing H/D exchange for a single proton. These observations suggest a Rh−μ-OH group. Longer reaction times with deuterated water (1 h) result in H/D exchange into the hydrides and then alkylphosphines. In the hydride region, four environments are observed between δ −26.9 and −37.1 in the ratio 4:1:4:2 H, consistent with the C_{2v} symmetry observed in the solid state (assuming rapid inversion of the OH). The two integral 4 H signals are assigned to the "axial" hydrides (H_a and H_b in Figure 2), while the integral 2 and 1 H signals are due to those "equatorial" hydrides in the same plane as the bridging hydroxide (H_c and H_d). The axial hydrides are broadened significantly compared to the equatorial at 298 K, mutually sharpen at lower temperature, and broaden into the baseline at higher temperatures, while the equatorial hydrides only start to broaden at higher temperature (330 K). Above this temperature decomposition occurs. The OH peak remains sharp throughout, showing that the hydroxide does not partake in exchange. These data suggest that two hydride exchange processes are operating, which have been modeled (gNMR, line-shape analysis) to estimate $\Delta H^\ddagger$ = 74.3 ± 3.9 kJ mol^{-1}, $\Delta S^\ddagger$ = 39.9 ± 13.7 J K mol^{-1} [$\Delta G(298)^\ddagger$ = 62.4 ± 4.0 kJ mol^{-1}] for the axial exchange and $\Delta H^\ddagger$ = 93.1 ± 8.4 kJ mol^{-1}, $\Delta S^\ddagger$ = 32.8 ± 19.2 J K mol^{-1} [$\Delta G(298)^\ddagger$ = 83.3 ± 8.0 kJ mol^{-1}] for the equatorial exchange. These values are somewhat higher, but still reasonable, when compared to those reported for hydride exchange in other late-transition-metal hydride cluster species.[10,13] By way of contrast, the structurally closely related early-transition-metal cluster $W_6H_5(C^iPr)(O^iPr)_{12}$ does not show exchange of the hydrides.[14] The higher value for the equatorial exchange process perhaps reflects the trans orientation of these hydrides, compared to the cis-disposed axial ones. Unfortunately, an exchange spectroscopy experiment (298 K) did not show *any* exchange correlations, and thus we are unable to comment on the exchange between axial and equatorial hydrides. The ^{31}P NMR spectrum showed three separate environments over all temperatures that showed coupling to ^{103}Rh. The IR spectrum (KBr disk) shows a broad resonance at ~3450 cm^{-1}, consistent with a hydroxide.

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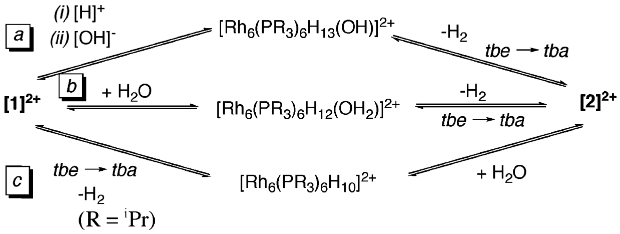
The addition of dihydrogen (1 atm, CD_2Cl_2) to **2[BAr$^{F}_{4}$]$_{2}$** rapidly forms (by NMR spectroscopy and ESI-MS) the cluster complex $[Rh_6(P^iPr_3)_6H_{16}][BAr^F_4]_2$ **3[BAr$^{F}_{4}$]$_{2}$** and 1 equiv of water (δ 1.52). **3[BAr$^{F}_{4}$]$_{2}$** is formed by the reversible addition of dihydrogen to **1[BAr$^{F}_{4}$]$_{2}$**,[11] which is presumably formed first upon reaction of **2[BAr$^{F}_{4}$]$_{2}$** with dihydrogen and then reacts with more dihydrogen to give **3[BAr$^{F}_{4}$]$_{2}$**. No other products are observed by NMR spectroscopy or ESI-MS. Thus, the addition of water to **1[BAr$^{F}_{4}$]$_{2}$** is fully reversible. The addition of D_2 to **2[BAr$^{F}_{4}$]$_{2}$** results in the observation of HDO (or D_2O) in the ^{2}H NMR, and the eventual formation of **3[BAr$^{F}_{4}$]$_{2}$-*d*$_{16}$** by H/D exchange, as we have observed previously.[15] Dissolved HD is also observed to grow in over time, which comes from H/D exchange on **3[BAr$^{F}_{4}$]$_{2}$**. The addition of dihydrogen to the mixtures $[Rh_6(P^iPr_3)_6H_{12-x}(OH)_x]^{2+}$ ($x = 1-3$) regenerates **3[BAr$^{F}_{4}$]$_{2}$** cleanly.

Scheme 2



Water addition to transition-metal complexes can occur by oxidative addition,[16] by protonation mechanisms,[17] and where a hydride is also present by hydrogen transfer[6] (or σ-bond metathesis[18]), and possible mechanisms for water addition to **1[BAr$^{F}_{4}$]$_{2}$** are shown in Scheme 2.[4b]

Pathway a invokes a protonolysis mechanism. Pathway b involves the addition of water, oxidative addition or hydrogen transfer, and then dehydrogenation of the cluster, while in pathway c, this order of addition is reversed. Unfortunately, the hydride exchange process described above, the relatively rapid H/D exchange into the hydrido and alkylphosphine groups[11] in both **1[BAr$^{F}_{4}$]$_{2}$** and **2[BAr$^{F}_{4}$]$_{2}$** upon the addition of deuterated water, coupled with the slow decomposition of both salts at 40 °C made detailed mechanistic studies problematic. The following observations have, however, been made: The addition of $[H(OEt_2)_2][BAr^F_4]$[19] (20 mol %) to **1[BAr$^{F}_{4}$]$_{2}$**/excess tbe/excess H_2O does not increase the rate of formation of **2[BAr$^{F}_{4}$]$_{2}$**. This rules out route a, which would be expected to be accelerated by the addition of catalytic amounts of acid. The addition of a hindered base (Hunig's or proton sponge), which would also probe this mechanism, resulted in cluster decomposition to, as yet, unidentified materials. Dihydrogen loss must be facilitated by tbe because no reaction is observed in its absence at room temperature and pressure or under a vacuum (5×10^{-2} Torr). Mechanism b suggests the addition of water and then dehydrogenation. We observe no evidence for a water adduct in the absence of tbe (the hydride signals in **1[BAr$^{F}_{4}$]$_{2}$** are unchanged in chemical shift and line width upon the addition of a ~500-fold excess of water). Adding deuterated water to **1[BAr$^{F}_{4}$]$_{2}$** in the *absence* of tbe gives H/D exchange of the cluster hydrides within 4 h at 298 K (longer times introduce deuterium into the phosphine CH groups). Given the base sensitivity of **1[BAr$^{F}_{4}$]$_{2}$**, we cannot determine whether this occurs by protonolysis or reversible water addition. Mechanism c invokes dihydrogen loss before water addition. The addition of tbe (large excess) to **1[BAr$^{F}_{4}$]$_{2}$** and analysis by ESI-MS/NMR show that a number of new species are formed, some of which have lost multiple dihydrogens from the cluster dication **[1]**$^{2+}$ (by ESI-MS). Although we have not been able to isolate these dehydrogenated materials, their observation suggests that mechanism c is a reasonable route.[4b] ^{1}H NMR spectroscopy also shows the formation of 3,3-dimethylbutane, consistent with dehydrogenation of the cluster dication. Labeling experiments that could help distinguish between routes b and c by following a deuterium label into the alkene[4b] were not useful because H/D exchange with deuterated water on **1[BAr$^{F}_{4}$]$_{2}$** occurs on a time scale similar to that of water addition/hydrogen loss. Details of the mechanism are currently under investigation computationally and will be reported in due course.[20]

The addition of excess ethanol or tetradecanol to **1-[BAr$^{F}_{4}$]$_{2}$**/tbe led to the observation of **2[BAr$^{F}_{4}$]$_{2}$** and not an alkoxide complex. Even though strictly anhydrous conditions were used, this indicates the affinity for water addition over alcohols. Similar selectivity has been reported with $[Ir(coe)_2(O{=}CMe_2)_2][PF_6]$ and methanol.[5] Finally, the addition of H_2O/tbe to the cluster $[Rh_6(PCy_3)_6H_{12}][BAr^F_4]_2$,[11] which contains the bulkier PCy_3 groups, resulted in no reaction. Presumably, the access of water or tbe to the cluster core through the tightly interdigited cyclohexyl groups is inhibited.

In conclusion, we report the synthesis of a rhodium cluster that has a hydroxyhydrido motif by the addition of water to a hydrido cluster and elimination of dihydrogen. This reaction is reversible upon the addition of dihydrogen to regenerate the starting 12-hydride cluster. Given that clusters based upon **[1]**$^{2+}$ show rich electrochemistry,[15] it is interesting to speculate whether hydroxyhydride formation can be linked with the redox-promoted elimination of oxygen. Such a process would be of significant interest with regards to the splitting of water for future energy applications.[2]

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Supporting Information Available: Full experimental details and data, including NMR/ESI-MS spectra and details of the crystallographic refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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