

$[(^i\text{Pr}_3\text{P})_6\text{Rh}_6\text{H}_{12}]^{2+}$: A High-Hydride Content Octahedron that Bridges the Gap between Late and Early Transition Metal Clusters

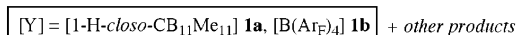
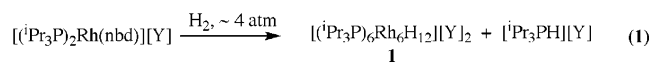
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Transition metal clusters fall into two “classical” groups. Those of the later transition metals in low oxidation states with π -acceptor ligands (i.e., CO), and their early transition metal counterparts that have π -donor ligands (i.e., halides or alkoxides).^{1,2} Paradigms for these two cluster groupings are octahedral $\text{Rh}_6(\text{CO})_{16}$ and $[\text{Nb}_6(\mu\text{-Cl})_{12}\text{Cl}_6]^{4-}$ (Figure 1). Valence electron counting affords the former 86 electrons and the latter a maximum of 76 electrons (although examples with fewer electrons are known^{2,3}). We report here the synthesis of a unique *late transition metal* cluster that has neither π -acceptor or π -donor ligands, but 12 hydride ligands instead, that shows a remarkable structural similarity to *early transition metal* halide octahedral clusters, bridging the gap between these two structural motifs that reside at opposite ends of the transition series of metals.

Treatment of $[(^i\text{Pr}_3\text{P})_2\text{Rh}(\text{kbd})][\text{Y}]$ {kbd = norbornadiene, Y = $\text{B}\{3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4^-$ [$\text{B}(\text{Ar}_F)_4$] or 1-*H-closo*- $\text{CB}_{11}\text{Me}_{11}^-$ } with H_2 (ca. 4 atm) in fluorobenzene or CH_2Cl_2 at 40 °C resulted in the isolation, in moderate yield (20% based on Rh), of a dark red crystalline air-sensitive material of empirical formula $[(^i\text{Pr}_3\text{P})_6\text{Rh}_6\text{H}_{12}][\text{Y}]_2$ (**1** (**1a** Y = 1-*H-closo*- $\text{CB}_{11}\text{Me}_{11}^-$, **1b** Y = $\text{B}(\text{Ar}_F)_4$) along with $[(^i\text{Pr}_3\text{P})_6\text{Rh}_6\text{H}_{12}][\text{Y}]_2$ (eq 1) in approximately equal proportion (by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). Other Rh-containing products are also formed but at this time remain unidentified. Characterization was initially by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and mass spectroscopy,⁵ but the identity of **1** was only elucidated by a single-crystal X-ray diffraction study⁶ of both the $[\text{1-}i\text{H-closo-CB}_{11}\text{Me}_{11}]^-$ and $[\text{B}(\text{Ar}_F)_4]$ salts (Figure 2 shows **1a**; see Supporting Information for **1b**), which showed an octahedral cluster formed from six {PRh} fragments, with the metal core surrounded by 12 hydride ligands in a cuboctahedral arrangement.



The rhodium core in **1** is not a regular octahedron, with Rh–Rh bond lengths spanning the range 2.7181(3)–3.0597(5) Å [average = 2.794 Å], this being comparable to those found in $\text{Rh}_6(\text{CO})_{16}$ [average = 2.750 Å].⁷ Each Rh vertex bears a single phosphine ligand. The cluster is completed by 12 hydride ligands that span every Rh–Rh edge (given the usual caveats about the placement of hydrides by X-ray crystallography, their positions were unequivocally located in the final difference map). They are not entirely symmetrically arranged, with the hydride that is associated with Rh1–Rh3 being disordered over two terminal sites. This Rh–Rh connectivity is also the longest [3.0597(5) Å]. However, these relatively small distortions from octahedral are ascribed to the steric influence of the six bulky $^i\text{Pr}_3\text{P}$ ligands around the metal core. Use of the HYDEX program⁸ for both **1a** and **1b** to suggest potential coordination sites for the hydride ligands reveals a preference for

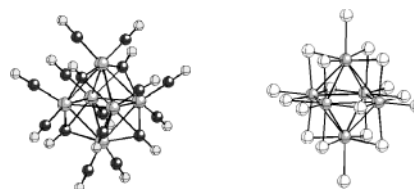


Figure 1. $\text{Rh}_6(\text{CO})_{16}$ (left) and $[\text{Nb}_6(\mu\text{-Cl})_{12}\text{Cl}_6]^{4-}$ (right).

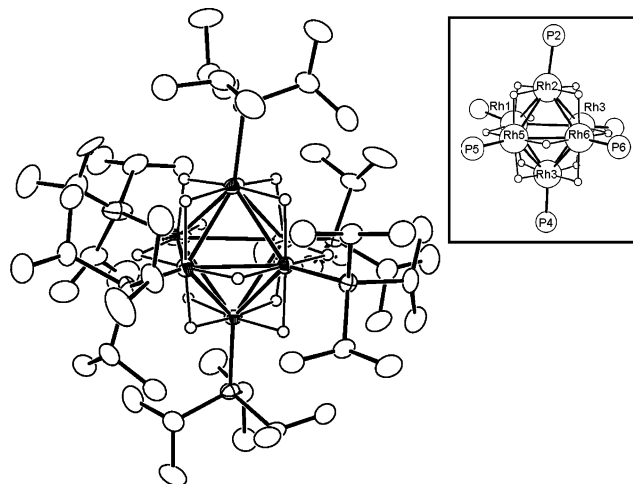


Figure 2. Molecular structure of the dicationic portion of **1a**. Phosphine hydrogen atoms have been removed. (Inset) $\text{Rh}_6\text{P}_6\text{H}_{12}$ core structure showing atom labeling scheme

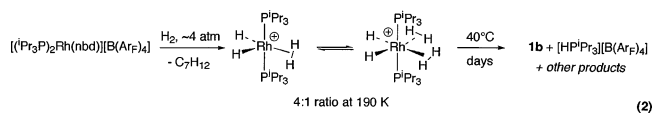
the experimentally observed structure rather than face-bridged and/or terminal Rh–H ligands.

In solution for **1a** and **1b** (CD_2Cl_2), there is one phosphorus environment [δ 110.5, $J(\text{RhP})$ 140 Hz] by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and one broad hydride environment in the ^1H NMR spectrum, in addition to signals due anion and phosphine. The hydride signal in both **1a** and **1b** integrates to 12-H, providing convincing support for the 12 hydrides located by the X-ray diffraction experiment [δ –21.4, 12 H relative to ^iPr signals, 5 s delay to avoid saturation, integration consistent over four independently synthesized samples]. The hydride ligands are fluxional at room temperature, as cooling (CD_2Cl_2 , 400 MHz) results in the hydride peak broadening into the baseline at 200 K, although the low-temperature limit was not reached. $^1\text{H}\{^{31}\text{P}\}$ NMR experiments were uninformative, with only a slight sharpening of the hydride peak observed.

The structure of **1**, with a ML_5 fragment at each vertex, is much more closely related to the early transition metal halides with edge-bridging π -donor ligands than later transition metal clusters such as $\text{Rh}_6(\text{CO})_{16}$ (Figure 1). This view is strengthened by the fact that **1** has a cluster valence electron count of 76 cve, 10 less than the 86 cve expected for an octahedron of rhodium atoms with π -accepting ligands such as $\text{Rh}_6(\text{CO})_{16}$ but identical to the 76 cve that $[\text{Nb}(\mu\text{-Cl})_{12}\text{Cl}_6]^{4-}$ possesses.⁹ Simple electron bookkeeping for

this Nb-cluster alongside **1** shows that the replacement of the halide with both hydride and phosphine ligands reduces this count by 24 electrons in total.⁹ This deficiency is exactly balanced by the move along the transition series from group 5 (Nb) to group 9 (Rh), resulting in a net gain of 24 metal electrons to the octahedron. Thus, the low ligand electron contribution in **1** is compensated for by the move to six group 9 metal centers. EHMO calculations on the model compound $[(\text{H}_3\text{P})_6\text{Rh}_6\text{H}_{12}]^{2+}$ are consistent with this showing 20 filled orbitals concerned with M–M bonding, 12 more (i.e., 24 electrons) than the 8 found for $[\text{Nb}(\mu\text{-Cl})_{12}\text{Cl}_6]^{4-}$.⁹ A close structural comparison also resides between **1** and the zirconium–phosphine clusters reported by Cotton such as $\text{Zr}_6\text{Cl}_{12}(\text{PMe}_2\text{Ph})_6$ ³ and $\text{Zr}_6\text{Cl}_{14}(\text{PMe}_3)_4$.¹⁰ These have edge-bridging halide structures but fewer valence electrons (72 and 70, respectively).

A detailed discussion of the mechanism of formation of **1** is inappropriate given that all the products of the reaction have not been identified. A number of observations can be made, however. That both a noncoordinating anion and a relativity noncoordinating solvent ($\text{C}_6\text{H}_5\text{F}$ or CH_2Cl_2) are required suggests that cluster formation may arise from the combination of unsaturated “ $\{(\text{Pr}_3\text{P})\text{-Rh}(\text{H})_x\}$ ” fragments. In support of this, NMR experiments (see Supporting Information) show that addition of H_2 (ca. 4 atm) to $[(\text{Pr}_3\text{P})_2\text{Rh}(\text{nbdt})][\text{B}(\text{Ar}_F)_4]$ initially cleanly affords a mixture of two nonclassical dihydrogen complexes $[(\text{Pr}_3\text{P})_2\text{Rh}(\text{H})_2(\eta^2\text{-H}_2)_x][\text{B}(\text{Ar}_F)_4]$ ($x = 1$ or 2) (eq 2), by comparison with the closely related iridium complexes spectroscopically characterized by Crabtree and Caulton.¹¹ Heating this mixture to 40 °C under H_2 gradually generates the previously observed mixture containing the protonated phosphine $[(\text{Pr}_3\text{P})\text{H}][\text{B}(\text{Ar}_F)_4]$ and **1b**, the former possibly arising from intramolecular heterolytic cleavage of coordinated H_2 and proton transfer to a cis phosphine ligand.¹² Labeling studies replacing H_2 with D_2 indicate the formation of $[(\text{Pr}_3\text{P})\text{D}]^+$ and the absence of a hydride signal in the ^1H NMR spectrum, consistent with this.



The 12 bridging hydride ligands surrounding the octahedral metal core of **1** are without precedent in either early or late transition metal cluster chemistry, although related complexes with high hydride content such as $(\text{PR}_3)_6\text{Cu}_6\text{H}_6$,¹³ $[\text{PPh}_4]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4]$,¹⁴ $\text{W}_6\text{H}_5(\text{OPr}^i)_{13}$,¹⁵ $\text{Pt}_5\text{H}_8(\text{PBu}^i\text{Ph})_5$,¹⁶ or $\text{H}_{12}\text{Pd}_{28}(\text{PtPMe}_3)(\text{PtPPh}_3)(\text{CO})_{27}$ ¹⁷ are known. Such cluster compounds with hydride ligands are of interest with regard to their involvement in various catalytic processes, as well as models for hydrogen storage devices.¹ Compound **1**, in particular, serves as a molecular model (stabilized by six bulky phosphine ligands) of hydrogen adsorbed onto a soluble, colloidal, nanocluster catalyst that finds application in olefin and arene hydrogenation.^{18,19} It is noteworthy that these materials are formed from routes that reductively hydrogenate a metal-bound olefin to form Rh(0) nanoclusters,¹⁹ similar to the synthesis of **1** reported here.

In summary, we have reported the synthesis of a remarkable $[\text{Rh}_6]^{2+}$ cluster, **1**, which is composed of a late transition metal but has a structure more akin to the archetypal, octahedral, early transition-metal edge-bridged halide clusters. Furthermore, the high hydrogen content of this cluster suggests that it could be a discrete molecular model for colloidal group 9 hydrogenation catalysts. We are currently exploring both the optimization of synthetic routes to **1** as well as its reactivity, especially with regard to that with arenes and other unsaturated substrates.

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Supporting Information Available: Full experimental and spectroscopic details and full data collection details, bond lengths and angles, and CIF data for **1a** and **1b**, as well as details of HYDEX analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) $[\text{Rh}_6(\text{Pr}_3\text{P})_6\text{H}_{12}][\text{CB}_{11}\text{Me}_{11}\text{H}_{12}]$ **1a**: ^1H (400 MHz, 5 s delay, 1000 scans) 2.31 (br m 18H), 1.28 (m, 108H), 1.16 (s, 2H cage_{C-H}), -0.17 (s, 30H), -0.43 (s, 30H), -0.54 (s, 6H), -2.14 (br s, 12H); ^{11}B (96 MHz) 0.17 (s, 1B), -7.89 (s, 5B), -11.14 (s, 5B); $^{31}\text{P}\{^1\text{H}\}$ (121 MHz) 110.5 [d, 140 Hz]. NMR data for the $[\text{B}(\text{Ar}_F)_4]^-$ salt are identical for the cluster dication component. $\text{C}_{78}\text{H}_{206}\text{B}_{22}\text{P}_6\text{Rh}_6$ requires C 42.9, H 9.43; found C 43.6, H 8.86. MS (FAB+, NOBA matrix): m/z 1590.3 $[\text{Rh}_6(\text{Pr}_3\text{P})_6\text{H}_{12}]^{2+}$.
- (6) **1a**: $\text{C}_{82.50}\text{H}_{206}\text{B}_{22}\text{P}_6\text{Rh}_6$, $M = 2239.57$, $0.43 \times 0.15 \times 0.13 \text{ nm}^3$, monoclinic, $P2_1/n$, $a = 21.5030(1)$, $b = 25.4890(1)$, $c = 21.8250(1) \text{ \AA}$, $\beta = 103.30^\circ$, $V = 11641.32(9) \text{ \AA}^3$, $Z = 4$, $m = 0.949 \text{ mm}^{-1}$, $D_c = 1.278 \text{ g/cm}^3$, $F(000) = 4684$, $\lambda = 0.71073 \text{ \AA}$, $T = 150(2) \text{ K}$, 33 956 unique reflections ($R_{\text{int}} = 0.0662$), $R1 = 0.0480$, $wR2 = 0.01007$ [$I > 2\sigma(I)$]. The asymmetric unit in this structure consists of one cationic cluster, two anionic carboranes, and three areas of diffuse solvent. Disorder of the isopropyl on P1 was readily modeled between two sites.
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