Highlights

An Octahedral Rhodium Cluster with Six Phosphine and 12 Hydride Ligands and 10 Too Few Electrons

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*L*ate-transition-metal (low-oxidation state) clusters, with π-acceptor ligands and early-transition-metal (high-oxidation state) clusters, with π-donor ligands, have been intensively studied for several decades.[1] Apart from the fascinating structural aspects of cluster compounds and rationalization of their bonding, much motivation for their study has been driven by potential applications. It was suggested that transition-metal clusters might prove to be effective catalysts, filling the void between mononuclear species and colloidal (or heterogeneous) catalysts and open up new possibilities in catalysis and organic synthesis.[2]

Research at the interface of late- and early-transition-metal cluster chemistry has not been forthcoming although polyoxometalates have been combined with organometallic fragments[3] and late–early-transition-metal bonds are well known.[4] However, in a recent communication by Weller et al., a late-transition-metal cluster based on an octahedral rhodium core was reported that has a structure and an electron count similar to that of an early-transition-metal cluster, and thus bridges the two largely separate and distinct re-

gimes.[5] The cluster was isolated after a remarkably simple synthesis involving reduction under hydrogen of the complex, $[\text{RhL}_2(\text{nbd})]^+$, where L is a phosphine and nbd is norbornadiene. The rhodium precursor represents a widely used class of hydrogenation catalyst, especially for asymmetric reductions where L_2 is a chiral bisphosphine.[6] Therefore, apart from the absence of any substrate, what is so different about the synthesis which leads to such an intriguing cluster? The answer to this question remains to be confirmed, but three factors appear to be important. First, commencing with a rhodium salt comprising a weakly coordinating anion, that is, $[1\text{-H-}closo\text{-CB}_{11}\text{Me}_{11}]^-$ or $[\text{B}(\text{Ar}_\text{F})_4]^-$ ($\text{Ar}_\text{F} = 3,5\text{-bis(trifluoromethyl)phenyl}$). Second, the use of relatively weakly coordinating solvents, that is, C_6H_5F or CH_2Cl_2. Third, the utilization of a phosphine which appears to have the ideal topology to form a protective sheath over the cluster (see below). The cluster in question, $[\text{Rh}_6(\text{P}i\text{Pr}_3)_6(\mu\text{-H})_{12}]^{2+}$, is prepared according to Scheme 1, and accounts for about 20% of the starting material—the other compounds formed in the reaction remain uncharacterized.
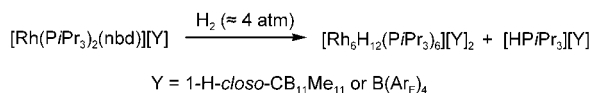
each edge bridged by a hydride (Figure 1). It resembles the early-transition-metal cluster $[\text{Zr}_6(\mu\text{-Cl})_{12}(\text{PMe}_2\text{Ph})_6(\text{H})_x]$ in the arrangement of ligands.[7]
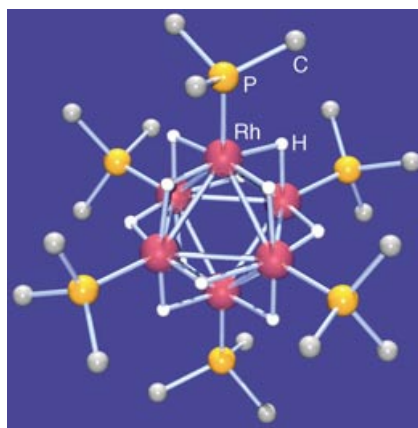
Figure 1. Ball-and-stick representation of the structure of $[\text{Rh}_6(\text{P}i\text{Pr}_3)_6(\mu\text{-H})_{12}]^{2+}$. For clarity the *iso*-propyl groups are represented by a single carbon atom. POV-RAY diagram drawn using ORTEP-3.8.[8]

What is perhaps most interesting, and could indicate why the cluster is stable, is that the *iso*-propyl groups attached to the phosphine ligand appear to cloak the metal core almost completely as can be appreciated from the space filling representation shown in Figure 2. While there are approximately 90 structurally characterized examples of $[\text{M}_6(\text{PR}_3)_6\text{L}_x]$ clusters known, the vast majority have sterically undemanding ligands (typically PEt_3) and only one, $[\text{W}_6(\mu_3\text{-S})_8(\text{PCy}_3)_6]$ (Cy = cyclohexyl)[9] has a

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$$[\text{Rh}(\text{P}i\text{Pr}_3)_2(\text{nbd})][Y] \xrightarrow{\text{H}_2\ (\approx 4\ \text{atm})} [\text{Rh}_6\text{H}_{12}(\text{P}i\text{Pr}_3)_6][Y]_2 + [\text{HP}i\text{Pr}_3][Y]$$

$$Y = 1\text{-H-}closo\text{-CB}_{11}\text{Me}_{11}\ \text{or}\ \text{B}(\text{Ar}_\text{F})_4$$

Scheme 1. The preparation of $[\text{Rh}_6(\text{P}i\text{Pr}_3)_6(\mu\text{-H})_{12}]^{2+}$.

The structure of the $[\text{Rh}_6(\text{P}i\text{Pr}_3)_6(\mu\text{-H})_{12}]^{2+}$ dication comprises an essentially regular octahedron in which each vertex is capped by a phosphine ligand and
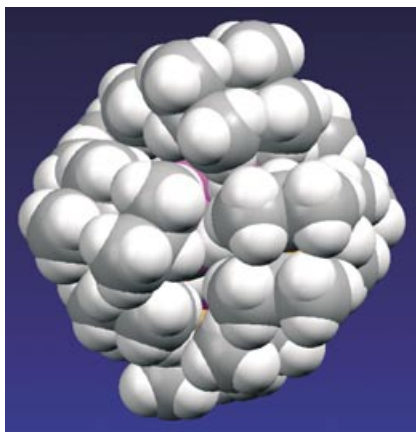
Figure 2. Space-filling representation of the structure of $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$.

ligand more bulky than $PiPr_3$. Packing six bulky phosphines around the cluster core does have a distorting effect on the geometry of the octahedral core, but the efficient packing probably helps considerably to stabilize the numerous labile hydride ligands.

The electronic structure of the cluster bears closer resemblance to early-transition-metal clusters with π-donor ligands than to late-transition-metal clusters with π-acceptor ligands. Most octahedral clusters with π-acceptor ligands have 86 electrons, and deviations from this rule for late-transition-metals are rare and usually involve clusters with unusual ligand assemblies, or Group 10 or 11 metals, or both, such as the 90 electron $[Ni_6(\eta^5\text{-}C_5H_5)_6]$.[10] There are many clusters known of the type $[M_6(\mu_3\text{-}E)_8(PR_3)_6]$ (M = Group 6, 7, 8, or 9 metal; E = S, Se, or Te)[11] that span the early–late-transition-metal divide, and these have electron counts[12] ranging from 79 for $[W_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$[13] to 98 for $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$.[14] However, $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$ has an electron count of just 76 electrons, a value entirely without precedent for the late-transition-metals and comparable only to early-transition-metal halide clusters, such as $[M_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ (M = Nb, Ta; also 76 electrons).

In addition, the ratio of hydrides to rhodium is remarkably high, and represents one of the highest ratios observed to date. High hydride to metal ratios are important with respect to hydrogen (hydride) storage and also have implications in hydrogenation catalysis where

hydrogen spillage could account for accelerated reductions.[15]

It is probably not unfair to say that cluster chemistry has been in decline since its peak in popularity in the late 1980s. However, without the high expectations that once dominated the field it remains healthy and some of the best work has since been carried out. High-nuclearity clusters, such as $[Os_{20}(CO)_{40}]^{2-}$,[16] $[Ni_{35}Pt_9(CO)_{48}]^{6-}$,[17] $[Pd_{145}(CO)_x(PEt_3)_{30}]$[18] and $[Cu_{146}Se_{73}(PPh_3)_{30}]$,[19] the larger ones exceeding the size of many colloids, have been prepared and characterized by X-ray crystallography. A fascinating series of ruthenium–palladium and ruthenium–platinum clusters prepared by condensation of preformed ruthenium clusters with the $\{M(PtBu_3)_2\}$ unit (also an active catalyst precursor—but for carbon–carbon coupling reactions) have been reported,[20] and related compounds have been used as precursors to highly active supported naked nanoparticle catalysts.[21] Also, the on-going question of whether intact clusters can act as catalysts has finally been resolved, at least for hydrogenation reactions. The answer is yes, demonstrated directly by para-hydrogen NMR spectroscopy, but the process is highly solvent dependent and this might explain why there has been so much controversy in the literature surrounding this topic.[22] However, the isolation of $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$ from $[Rh(PiPr_3)_2(nbd)]^+$ under a hydrogen atmosphere raises another question. Could clusters, especially one so electronically unsaturated and presumably as reactive as $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$, be the active catalysts in hydrogenation reactions commencing with the widely used $[Rh(PiPr_3)_2(nbd)]^+$ precursors, that operate under similar conditions to those in which the cluster was isolated, merely in the presence of a suitable substrate? It is already well established that homogeneous (mononuclear) pre-catalysts often decompose to nanoparticles which are the active catalysts,[23] but little attention has been paid to the mechanism and whether molecular cluster intermediates play an influential role. The distinctive spectroscopic properties of $[Rh_6(PiPr_3)_6(\mu\text{-}H)_{12}]^{2+}$ may well facilitate such investigations.

Further development of the unique cluster chemistry introduced by Weller

et al. could take many paths. The X-ray data notwithstanding, a neutron diffraction study to pinpoint the exact hydride locations is clearly desirable. Similarly, extension of the structural motif to other late-transition-metals, other bulky two-electron donor ligands, and perhaps other hydride ligand counts, will all provide interesting insights into what represents a new frontier for cluster chemistry.

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[1] For example, see: a) *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, New York, **1999**; b) *Early Transition Metal Clusters with pi-Donor Ligands* (Ed.: M. H. Chisholm), Wiley-VCH, New York, **1995**.

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