

New Chemistry of Transition Metal Alkyls and Hydrides: Bonding and Reactivity

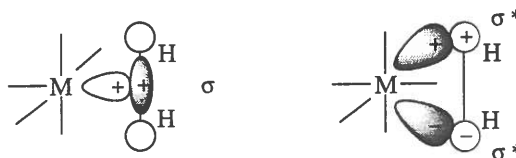
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Final Seminar

June 26, 2000

Dihydrogen was long thought incapable of bonding intact to a transition metal.¹⁻³ Although oxidative addition of H₂ to transition metal centers has long been known, the first stable molecular dihydrogen complex, W(CO)₃[P(*i*-Pr)₃](η^2 -H₂), was not reported until 1984.³ Since this initial discovery, several hundred molecular dihydrogen complexes have been described.¹⁻³

Both the choice of the metal center and the nature of the ancillary ligands greatly influence the stability of molecular dihydrogen complexes. The bonding model used to describe transition metal dihydrogen complexes, which is similar to the Dewar-Chatt-Duncanson model of the bonding in metal-olefin complexes, has two separate components: donation of electron density from the σ -orbital of the H₂ ligand to a vacant metal orbital, and back-donation of electron density from a filled metal orbital to the σ^* -orbital of the H₂ ligand:



Although both bonding components are important, in most molecular dihydrogen compounds the amount of back bonding from the metal center into the H₂ σ^* -orbital determines the nature of the M-H₂ interaction. Too little back bonding will facilitate dissociation of the dihydrogen ligand; too much will cleave the H-H bond and generate a classical metal dihydride complex. Stable molecular dihydrogen complexes are found when the amount of back bonding is between these extremes. The stability of molecular dihydrogen complexes also appears to be enhanced if the metal has a d⁶ electron configuration and an octahedral or pseudooctahedral geometry.

Protonation of the osmium(II) hydrides (C₅Me₅)Os(PR₃)₂H with tetrafluoroboric acid affords the corresponding osmium(IV) dihydride complexes of stoichiometry [(C₅Me₅)Os(PR₃)₂H₂⁺], where PR₃ = Pme₃, Pet₃, PPh₃, 1/2 dmpe, 1/2 dmpm, 1/2 dpdm, or dpdtm. If the phosphine ligand is unidentate or bidentate with a large bite angle, then the complex isolated at room temperature has a transoid geometry. In contrast, if the phosphine ligand is bidentate with a small bite angle (viz, dmpm and dpdm), then a mixture of cisoid and transoid isomers is isolated. In the cisoid compounds [(C₅Me₅)Os(dmpm)H₂⁺] and [(C₅Me₅)Os(dpdm)H₂⁺], the two hydride ligands undergo chemical exchange on the NMR time scale with activation free energies of 17.5 and 16.9 kcal mol⁻¹, respectively. Protonation of all the (C₅Me₅)Os(PR₃)₂H complexes at low temperature affords the cisoid isomers, which must be the kinetic products. For the compounds [(C₅Me₅)Os(Pme₃)₂H₂⁺] and [(C₅Me₅)Os(PPh₃)₂H₂⁺] the cisoid isomers convert to the transoid isomers by two pathways, one unimolecular and one bimolecular; the latter involves intermolecular hydride exchange between the dihydride cations and the neutral monohydride.

The structural characterization of the trigonal prismatic hexamethylzirconate dianion, [ZrMe₆]²⁻, by Girolami in 1989 provided the first experimental evidence that a transition

metal complex with six identical unidentate ligands could adopt a non-octahedral geometry.⁴ This discovery exposed the limitations of the simple points-on-a-sphere bonding models in predicting ML_6 coordination geometries. The trigonal prismatic geometry could only be rationalized in terms of a second-order Jahn-Teller effect, which causes a distortion from O_h symmetry to D_{3h} or even C_{3v} symmetry for d^0 , d^1 , or d^2 metal centers with purely σ -donating ligands.

Since the synthesis and structural characterization of the hexamethylzirconate dianion, a growing number of non-octahedral six-coordinate complexes have been structurally characterized. For example, the molecules $MoMe_6$, Wme_6 , $ReMe_6$, $[NbMe_6]$, $[TaMe_6]$, $[TaPh_6]$, $[Ta(p\text{-tolyl})_6]^-$, and $[ZrPh_6]^{2-}$ display either trigonal prismatic or distorted trigonal prismatic geometries.⁵⁻⁹ Interestingly, there are some exceptions to this trend. Wolczanski has shown that $[Zr(C_2Si^tBu_3)_6]^{2-}$ and $[Hf(C_2Si^tBu_3)_3]^{2-}$ both adopt octahedral geometries whereas $[Ta(C_2Si^tBu_3)_6]^-$ adopts a trigonal prismatic geometry.¹⁰ The hexamethylhafnate salt, $[Li(tmed)_2][Li(tmed)][HfMe_6]$, also has an unexpected geometry:

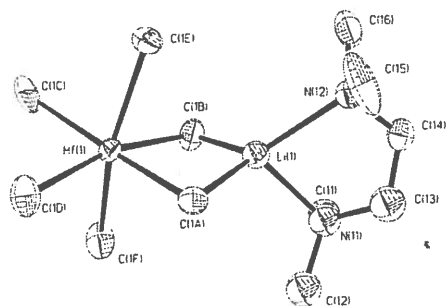


Figure 1.

The unexpected octahedral structure of $[Li(tmed)_2][Li(tmed)][HfMe_6]$ can be rationalized in terms of the relative energies of metal d-orbitals and the ligand σ -donor abilities. Until now, it has been thought that d^0 - d^2 metal centers with purely σ -donating ligands, should adopt trigonal prismatic or distorted trigonal prismatic structures. The driving force to adopt this structure is a second-order Jahn-Teller effect involving the mixing of HOMO (d-orbitals) and LUMO (ligand donor) orbitals. If the HOMO-LUMO gap is sufficiently large, the energetic stabilization associated with lowering the molecular symmetry is insufficient to overcome the increased ligand – ligand repulsions in the trigonal prismatic structure. Rather than being a structural anomaly that confounds our current understanding of bonding theory, the structure of $[HfMe_6]^{2-}$ further refines our current understanding of bonding.

The structures of binary metal alkyl and metal aryl complexes continue to be of interest, as shown, for example, by the finding that the zirconium centers in $[ZrMe_6]^{2-}$ and $[ZrPh_6]^{2-}$ both adopt trigonal prismatic (rather than octahedral) geometries. In 1983, Shilov et al. reported the synthesis and crystal structure of an organoiron compound of stoichiometry $[Li(Et_2O)]_4[FePh_4]$. Of particular interest was the claim that $[Li(Et_2O)]_4[FePh_4]$ reacted with N_2 to form a species that produced N_2H_4 when decomposed by HCl .¹¹

The iron center in “ $[Li(Et_2O)]_4[FePh_4]$ ” had been reported to adopt an unprecedented coordination geometry described as “flat rectangular”: the four ipso carbon atoms formed a planar array in which the C-Fe-C angles were 61° and 119° . A remarkably short “non-bonded” $C \cdots C$ contact of 2.09 Å was said to be formed between the ipso carbon atoms of pairs of adjacent phenyl groups.

We propose that the structure should have been solved in the space group $P\bar{4} 2_1c$ instead of $P4_22_12$. In the correct space group, the phenyl groups actually describe a regular square planar geometry with cis C-Fe-C angles that are exactly 90° . The coordination geometries about the lithium cations, and the Li \cdots C contacts formed with the phenyl rings, also differ rather substantially from those reported for the original structure but agree with those seen for lithium salts of other arylmetalate anions. Finally, the formulation of the compound as a derivative of zerovalent iron is almost certainly incorrect. We propose that the compound actually is an iron(II) dihydride of stoichiometry $[\text{Li}(\text{Et}_2\text{O})]_4[\text{trans-FeH}_2\text{Ph}_4]$.¹²

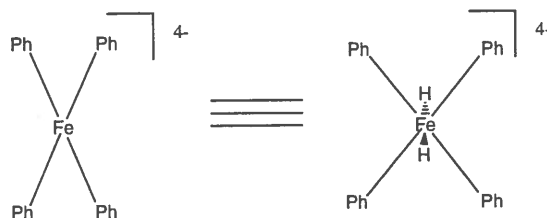


Figure 3. Reformulation of “[Li(Et₂O)]₄[FePh₄]” as [Li(Et₂O)]₄[*trans*-FeH₂Ph₄].

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