

Zirconium and Hafnium Organometallic Compounds: Molecular Geometry of Five-, Six-, and Seven-Coordinate Species

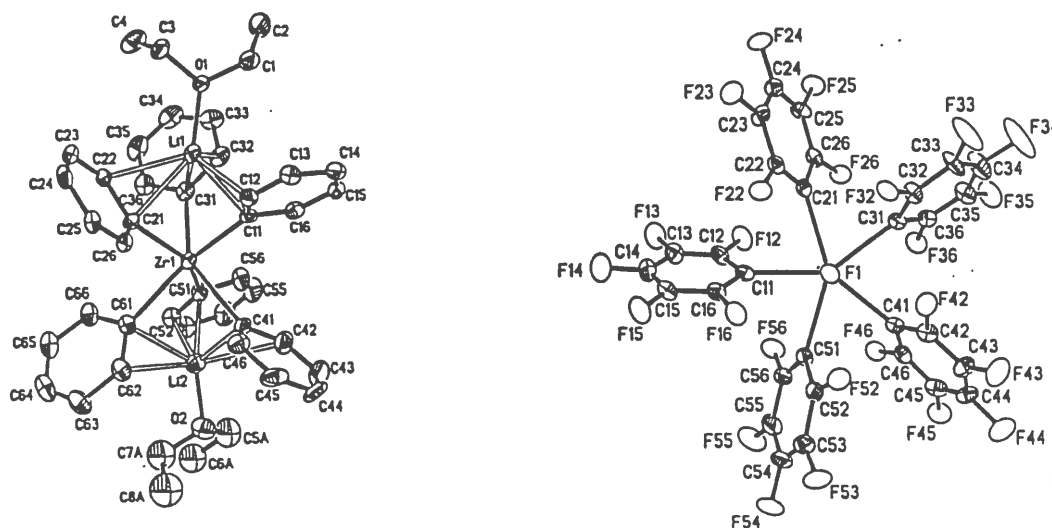
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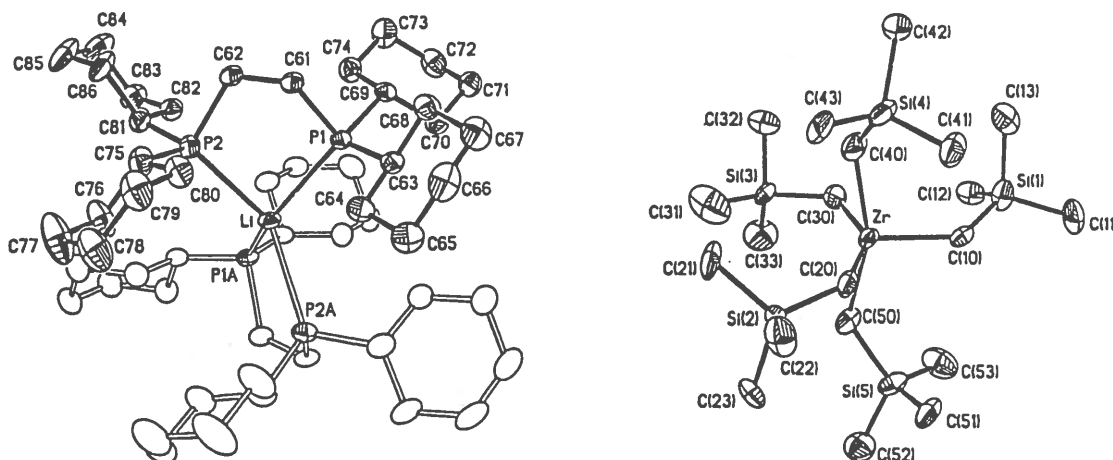
Most six coordinate transition metal complexes are octahedral, as predicted by electrostatic bonding models and by simple molecular orbital calculations. A few six-coordinate species, however, possess strikingly different geometries. Trigonal prismatic transition metal environments were first reported in extended lattice structures in 1923: the disulfides and diselenides of niobium, tantalum, molybdenum, and tungsten adopt trigonal prismatic geometries [1]. The first example of a molecular species to adopt a trigonal prismatic geometry was $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$, which was reported by Eisenberg in 1967 [2]. Since then, other trigonal prismatic compounds have been isolated, and a variety of explanations have been advanced for why the trigonal prismatic structure is adopted; many of these explanations focused on the unusual bonding properties of the dithiolene ligand. In 1989, Girolami reported the synthesis and structure of $[\text{ZrMe}_6]^{2-}$, the first example of a trigonal prismatic compound with six unidentate, electronically innocent ligands [3]. These workers attributed the geometry to a second-order Jahn-Teller effect, and predicted that WMe_6 should adopt a similar structure, a prediction that has subsequently been verified experimentally [4].

In order to further explore the geometries of six-coordinate d^0 complexes of the transition metals, we have synthesized the new complex $[\text{Li}(\text{Et}_2\text{O})]_2[\text{ZrPh}_6]$. The C-Zr-C angles in the $[\text{ZrPh}_6]^{2-}$ anion clearly show that the overall geometry about the zirconium center is trigonal prismatic. Despite the presence of orbitals on the phenyl ligands that are of the right symmetry to serve as π -donors, the trigonal prismatic geometry of the $[\text{ZrPh}_6]^{2-}$ anion clearly shows that the phenyl groups in this molecule are not acting as π -donors. As in the previously described hexamethylzirconate complex $[\text{Li}(\text{tmed})]_2[\text{ZrMe}_6]$, the anion is involved in weak interactions with the lithium cations.

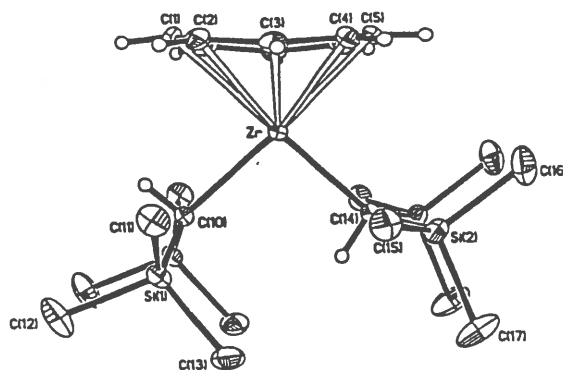


Metal-coordinated phenyl rings bear partial negative charges on the ipso carbon atoms, so it is not surprising that lithium cations would be found within bonding distance of these carbons. A natural question to ask is whether the cation-anion interactions stabilize the trigonal prismatic geometry. In an attempt to prepare a d^0 zirconium homoleptic species that lacks $\text{Li}\cdots\text{C}$ interactions, and also to assess the ability of pentafluorophenyl ligands to engage in π -bonding, the synthesis of zirconium complexes of the pentafluorophenyl ligand was investigated. The compounds $[\text{Li}(12\text{-crown-4})]_2[\text{ZrCl}_2(\text{C}_6\text{F}_5)_4]$ and $[\text{Li}(\text{tmed})]_2[\text{ZrF}_2(\text{C}_6\text{F}_5)_5]$ were isolated; the first adopts an octahedral structure owing to the π -donor

character of the chloride ligands, while the latter adopts a regular pentagonal bipyramidal structure. The latter compound also shows that C-F bond activation has occurred.



As part of an effort to prepare other examples of d^0 six-coordinate group 4 compounds, we investigated the alkylation of the phosphine complexes $ZrCl_4(PP)$ and $HfCl_4(PP)$ complexes with $LiCH_2SiMe_3$; the phosphine ligands employed were 1,2-bis(dicyclohexylphosphino)ethane (dcype) or 1,2-bis(diisopropylphosphino)ethane (dippe). In the course of this work, we isolated an unusual lithium salt of a five-coordinate zirconium alkyl: $[Li(dcype)_2][Zr(CH_2SiMe_3)_5]$. The structure of the anion is best described as a distorted square pyramid; this is the first structure of pentaalkyl derivative of the group 4 elements, and the structure is consistent with molecular orbital calculations which predict that square pyramidal structures should be adopted for such d^0 species. More interesting, however, is the structure of the cation, which consists of a lithium atom surrounded by a distorted tetrahedral array of two diposphine ligands. These results bear on important issues such as whether five-coordinate d^0 alkyls are susceptible to Jahn-Teller distortions, and whether trialkylphosphine ligands should be classified as hard or soft Lewis bases.



Treatment of $(C_8H_8)ZrCl_2(thf)_2 \cdot 2KCl$ with one equivalent of *p*-tolyllithium in diethyl ether at room temperature, followed by the addition of *N,N,N',N'*-tetramethylethylenediamine (tmed) yields red crystals of the mono(*p*-tolyl) complex $[Li(tmed)][(C_8H_8)Zr(p-C_6H_4Me)Cl_2]$; this compound has been crystallographically characterized. Treatment of $(C_8H_8)MCl_2 \cdot 2KCl$ ($M = Zr, Hf$) with three equivalents of methyl-, phenyl-, or *p*-tolyllithium in tetrahydrofuran or diethyl ether, followed by addition of *N,N,N',N'*-tetramethylethylenediamine, yields several new organozirconium and -hafnium compounds of stoichiometry $[Li(tmed)_2][(C_8H_8)MR_3]$ where $R = Me, Ph, \text{ or } p-C_6H_4Me$. With larger alkyl groups, electrically neutral organozirconium and -hafnium complexes can be isolated: treatment of $(C_8H_8)MCl_2(thf)_2 \cdot 2KCl$ with 2 equiv. of $LiCH(SiMe_3)_2$ gives products of stoichiometry $(C_8H_8)M[CH(SiMe_3)_2]_2$. The

structure of this latter complex has been determined. Interestingly, this latter 14-electron molecule reacts reversibly with carbon monoxide but is unaffected by dihydrogen even at elevated pressures.

References

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