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A Bimetallic Zirconium Complex Containing an In-Plane Bridging Aromatic Ring

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While a large number of transition-metal complexes with bridging alkyl ligands are known, complexes with η^1-bridging aryl ligands are less common. In all but one of the structurally characterized examples of η^1-bridging aryl ligands, the axis joining the two bridged metals is roughly perpendicular to the plane of the ring. The exception is Cotton's interesting bridging aryl divanadium complex that has both of the metals in the plane of the aromatic ring.[2] We now report the synthesis and characterization of a bimetallic zirconium complex, which contains not only an in-plane bridging aryl ligand but also a bridging methyl group as well.

We recently reported[3] the synthesis and characterization of a bimetallic benzdiyne complex. In an attempt to synthesize a trimetallic benztriyne complex, we prepared 1,3,5-tris[(methylzirconocenyl)]benzene, **1** (Scheme I). Heating **1** (16 h, 80 °C) in the presence of excess trimethylphosphine gave one major new compound, **2** (70% by ^{1}H NMR). The ^{1}H NMR spectrum of **2** indicates that two of the methyl groups have been lost as methane, and one trimethylphosphine unit has been incorporated. This suggests the formation of two metal-benzyne moieties per molecule, only one of which is bound to trimethylphosphine. Since zirconocene complexes of benzynes are known[4] to be unstable without another ligand, and because of the unusual upfield shift of the remaining methyl, we surmised that the remaining methyl group might be acting as an intramolecular ligand for one zirconocene benzyne moiety (Scheme II). Unfortunately, **2** proved to be difficult to isolate in a pure state.

In order to facilitate the structural characterization of **2**, a simpler analogue, **4**, was prepared as in Scheme III. When **3** was heated to 80 °C in toluene for 1 day, needles of **4** grew from the reaction mixture. Cooling slowly to −80 °C, followed by decanting the mother liquor and drying the resulting crystals in vacuo, led to the isolation of **4** as analytically pure material in 75% yield. The ^{1}H NMR spectrum of **4** consists of four singlets, the methyl on zirconium having a shift (C_6D_6) of δ −0.71 ppm. Additionally, the ^{13}C NMR spectrum of **4** consists of seven lines, that for the methyl group at δ −25.1 ppm, with a ^{13}C–^{1}H coupling constant of 113 Hz. The number of lines observed in both spectra indicate that the molecule has two planes of symmetry in solution, and the NMR shifts of the methyl carbon and hydrogens are consistent with those reported by Grubbs[5a,b] for a (linear) $Cp_2Zr\text{-}(\mu\text{-}CH_3)\text{-}ZrCp_2$ system. The ^{13}C–^{1}H coupling constant for the bridging methyl in our case, however, is significantly lower than that reported by Grubbs (113 Hz versus 136 Hz), as would be expected in a system in which the bridging carbon atom has a different hybridization, with less p character in the C–H bonds,[5a] and thus a very different geometry. These data suggest that **4** has the structure shown in Scheme II, analogous to that proposed for **2**.

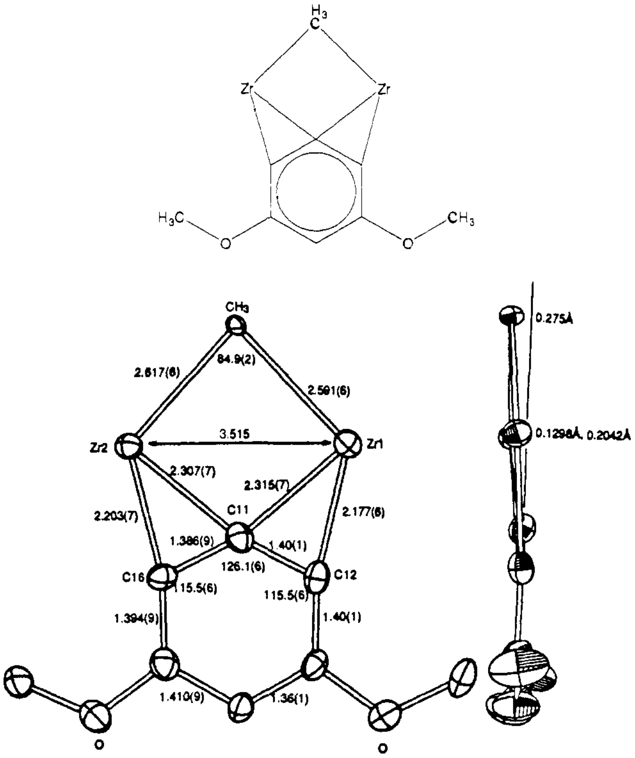
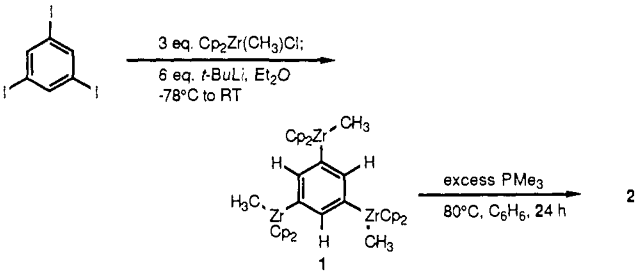
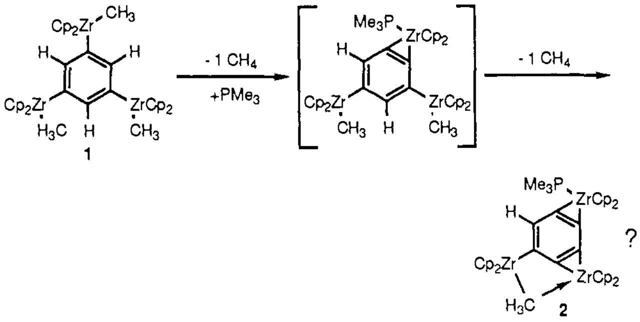


Figure 1. Front (bottom left hand) and side (bottom right hand) view ORTEP plots of **4**, including important distances and angles. Distances shown on the side view are distances of the Zr and methyl carbon atoms from the least-squares plane of the aromatic ring. (Cp rings and H atoms excluded for simplicity.)

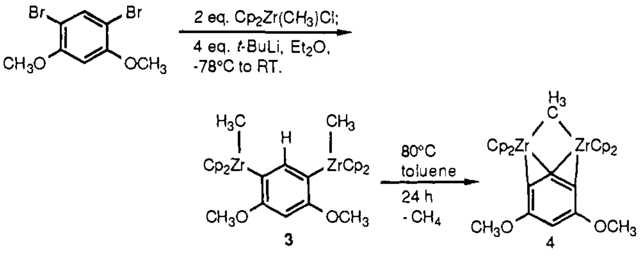
Scheme I



Scheme II



Scheme III



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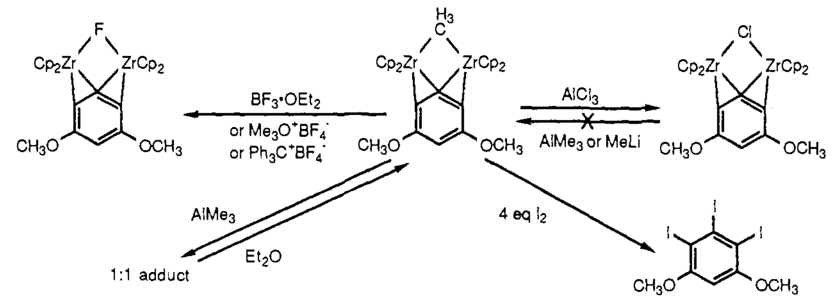
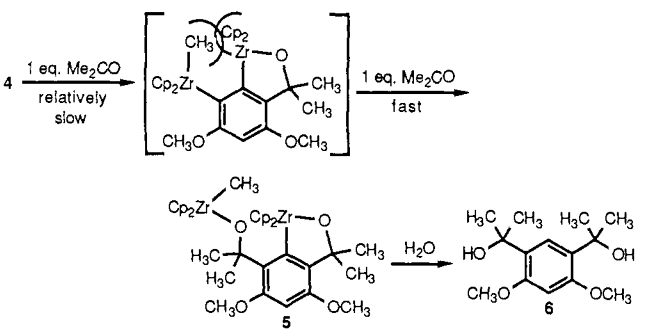
Scheme IV



Scheme V



Proof of the structure of **4** is provided by a single-crystal X-ray analysis.[6] An ORTEP plot of **4** is shown in Figure 1, along with important bond lengths and angles. There are several interesting features to the structure. The arene ring is completely planar, and the bond lengths in the ring are the same as those in benzene[7] to within experimental error. The ring is slightly distorted from a perfect hexagon, however, with the bridging carbon atom being moved toward the center of the ring, causing an opening of the C16–C11–C12 angle to 126.1° and a concomitant decrease in both of the neighboring ring angles (C15–C16–C11 and C11–C12–C13) to 115.5°. The bonds from each zirconium to its two arene ring carbons are different (2.203 and 2.177 Å for the outer bonds, versus 2.307 and 2.315 Å for the inner bonds), making each a highly distorted zirconocene benzyne moiety.[8a] The zirconium-methyl distances, 2.617 and 2.591 Å, are considerably longer than normal terminal zirconium alkyl bond lengths (ca. 2.30 Å[9]), although they are only somewhat longer than the ones in Grubbs's μ-CH_3 complex (2.559 and 2.456 Å). Finally, the zirconium atoms and the bridging methyl carbon are all slightly displaced from the plane of the arene ring, by 0.130 Å for Zr1, 0.204 Å for Zr2, and 0.275 Å for the methyl carbon.

We have just begun to study the reactivity of **4**, and some of the reactions are shown in Scheme IV. The bridging methyl in **4** can be replaced with Cl or F, although the fluoride can be isolated in only about 90% purity. Compound **4** also forms a weak 1:1 adduct of unknown structure with $AlMe_3$ and reacts cleanly with 4 equiv of I_2 to give triiodide, **7**. Interestingly, preliminary studies show that **4** fails to react cleanly with alkynes, nitriles, and isonitriles, which are substrates for other zirconocene benzyne complexes.[8a,b] However, **4** reacts cleanly with 2 equiv of acetone to give a product with spectral and combustion analysis data consistent with structure **5** (Scheme V). Hydrolysis of **5** gives the previously unknown diol, **6**, which we have made independently to support the structure shown. Treatment of **4** with less than 2 equiv of acetone gives only a mixture of **5** and **4**, with no observable intermediate. Presumably this reaction proceeds as shown in Scheme V. Once the first equivalent of acetone adds to one benzyne moiety, there are significant steric interactions between the cyclopentadienyl groups of the oxametallacycle and the other zirconocene unit. Insertion of acetone into the acyclic zirconium aryl bond, to our knowledge an unknown reaction in normal zirconocene aryl complexes,[9] relieves this strain and produces the observed product.

In summary, we have prepared and structurally characterized only the second example of a molecule having an arene ring bridging two metals both in the plane of the ring, in this case also bridging a methyl group. Because of the unusual reactivity and structure of this compound, we are continuing to investigate its reactions and are searching for further examples of organometallic compounds with unusual structures, including other bridging aryl compounds and trimetallic complexes of benztriyne.

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Supplementary Material Available: Experimental section containing the preparation and characterization of compounds along with crystallographic procedures, a table of final positional and thermal parameters for **4**, and tables of intramolecular bond distances and angles for **4** (26 pages); table containing observed and calculated structure factor for **4** (29 pages). Ordering information is given on any current masthead page.

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[6] Details of the structure determination are included in Supplementary Material.

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Synthesis and Molecular Structure of $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$: The First Six-Coordinate Aluminum Alkyl

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The tendency of aluminum alkoxide and aryloxide compounds to maximize their coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well-documented.[1] Recent work in our laboratory[2] and by Ittel and co-workers[3] has focused on the isolation of monomeric aryloxide compounds of aluminum by use of the sterically hindered aryloxide derived from 2,6-di-*tert*-butyl-4-methylphenol. In an effort to control the oligomerization of aluminum compounds we have investigated the use of multidentate alkoxides as ligands. We report here the synthesis and structural characterization of {[N-

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