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Pentaarylfullerenes as Noncoordinating Cyclopentadienyl Anions

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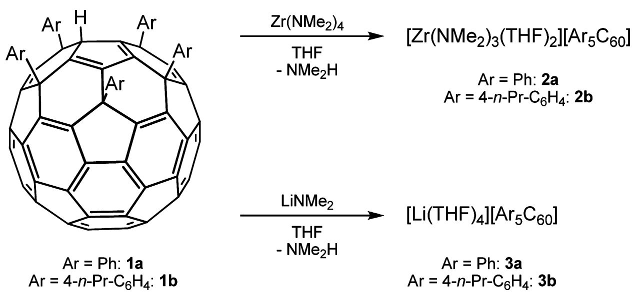
The first example of an early-transition-metal complex involving a pentaarylfullerene was prepared. Instead of half-sandwich complexes, solvent separated ion pairs were obtained in which the pentaarylfullerene moiety acts as noncoordinating cyclopentadienyl anion.

About a decade ago, the group of Nakamura introduced a new family of cyclopentadienyl ligands derived from fullerenes.[1] Since their initial report, a number of transition-metal complexes with these pentaalkyl- and pentaarylfullerene ligands have emerged, illustrating the versatility of this type of ligand. Examples include sandwich[2] and half-sandwich complexes[3] of group 6,[3h] 7,[3g] 8,[2,3a,b,e,g] 9,[3d,f,g] and 10[3c] metals. To date, however, the chemistry of these ligands is limited to the middle and right-hand sides of the periodic table, and no early-transition-metal complexes are known.[3h] Here we report our initial efforts to isolate their early-transition-metal counterparts, which resulted in the synthesis of cationic zirconium complexes with noncoordinating pentaarylfullerene anions.

The addition of tetrahydrofuran (THF) to an equimolar mixture of the pentaarylfullerene ligand precursor $Ph_5C_{60}H$ (**1a**) and zirconium amide $[Zr(NMe_2)_4]$[4] resulted in gas evolution and the disappearance of the poorly soluble ligand precursor, affording a reddish-brown solution. Monitoring the reaction by ^1H NMR spectroscopy in THF-d_8 revealed that, during the reaction, 1 equiv of dimethylamine was formed. Both the ^1H and ^{13}C NMR spectra of the product revealed the correct number of peaks expected for a half-sandwich complex of the type $[(Ph_5C_{60})Zr(NMe_2)_3]$. For example, the ^1H NMR spectrum shows resonances at δ 7.8, 7.0, and 2.87 ppm in a 10:15:18 ratio.

Scheme 1



On the other hand, a close comparison of the NMR spectroscopic data of the fullerene moiety with that of the corresponding lithium reagent $[Li(THF)_4][Ph_5C_{60}]$ (**3a**)[5] shows that the two are virtually identical. This suggests the formation of an ion pair of the type $[Zr(NMe_2)_3(THF)_n]$-$[Ph_5C_{60}]$ (**2a**; Scheme 1), in which there is no direct contact between the zirconium tris(dimethylamide) cation and the pentaphenylfullerene anion. Compound **3a** was prepared separately by the addition of 1 equiv of $LiNMe_2$ to ligand **1a** in THF (Scheme 1). To further confirm the nature of ion pair **2a**, a zirconium tris(dimethylamide) cation with a known weakly coordinating anion, $[BPh_4]^-$, was prepared as a reference by treatment of $[Zr(NMe_2)_4]$ with 1 equiv of $[PhNMe_2H][BPh_4]$ in a THF solution. The compound was obtained as its bis- or tris(THF) adduct, $[Zr(NMe_2)_3(THF)_n]$-$[BPh_4]$ ($n = 2$, **4**; $n = 3$, **4′**), depending on the workup procedure (vide infra). The NMR spectroscopic data for the $[Zr(NMe_2)_3(THF)_n]$ cation of **4** and **4′** are virtually identical with those of compound **2a**, as expected for a solvent-separated ion pair.

Recrystallization of compound **2a** from chlorobenzene/cyclohexane eventually resulted in single crystals that were

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(5) The stoichiometries of lithium salts **3a** and **3b** were determined by elemental analysis. For **3b**, this was confirmed by X-ray analysis.

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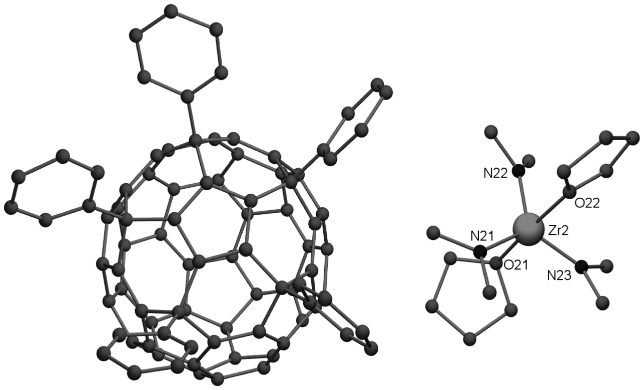

Figure 1. Ball-and-stick representation of ion pair **2a**. The hydrogen atoms were omitted for clarity.

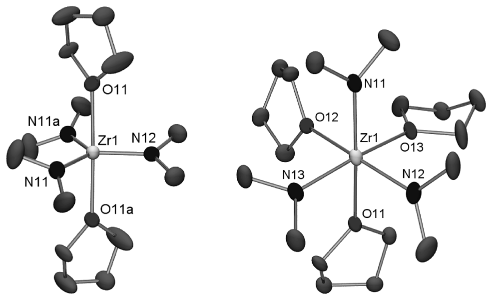

Figure 2. ORTEP representations of **4** (left) and **4′** (right) showing 50% probability levels. The hydrogen atoms and counterions were omitted for clarity.

suitable for X-ray analysis. The scattering power of the crystals was very weak, and refinement was complicated by disorder in the zirconium tris(dimethylamide) cation. Yet, the data were of sufficient quality to reveal the nature of the ion pair. A ball-and-stick representation of its structure is depicted in Figure 1. The cation of **2a** is best described as a five-coordinate zirconium tris(dimethylamide) species with trigonal-bipyramidal geometry. The amide ligands are bound in the equatorial plane, and the apical positions are occupied by two molecules of THF. No apparent interaction between the cation and the pentaphenylfullerene anion was found. As yet, there is one other example of an early-transition-metal cation with a fullerene anion. In that case, the ion pair is obtained by reduction of C_{60} using a titanium(III) compound.[6]

Because the cation of **2a** was disordered, the structure of compound **4** was determined as well, in order to obtain a better description of the cation. Single crystals suitable for an X-ray diffraction study were obtained by recrystallization of **4** from chlorobenzene/cyclohexane. Initially the compound was recrystallized from THF/cyclohexane, but this resulted in single crystals of the six-coordinate tris(THF) adduct **4′**. An ORTEP representation of both cations is depicted in Figure 2 (see Table 1 for pertinent bond distances). As expected, the metal−ligand bond distances in **4′** [average Zr−N = 2.055(3) Å; average Zr−O = 2.357(3) Å] are slightly longer compared to those in **4** [average Zr−N = 2.022(5) Å; average Zr−O = 2.261(2) Å], a result of the higher coordination number in **4′**.

Table 1. Selected Bond Distances (Å) for Compounds **4** and **4′**

	4	**4′**
Zr1−N11	2.001(4)	2.056(2)
Zr1−N12	2.042(3)	2.053(2)
Zr1−N13		2.057(2)
Zr1−O11	2.261(2)	2.3588(18)
Zr1−O12		2.3652(18)

With the hope of obtaining better crystals of an ion pair of the type **2a**, a similar compound was prepared with different ligand substituents and thus with different solubilities. Ligand (4-*n*-$PrC_6H_4)_5C_{60}H$ (**1b**)[7] was prepared in the same way as **1a**, by treatment of an excess (15 equiv) of an in situ generated arylcopper reagent to C_{60}.[8] Like in the case of **1a**, treatment of ligand **1b** with $[Zr(NMe_2)_4]$ resulted in a brownish-red reaction mixture, and the ^1H and ^{13}C NMR spectroscopic data are consistent with the formation of ion pair $[Zr(NMe_2)_3(THF)_2][(4\text{-}n\text{-}PrC_6H_4)_5C_{60}]$ (**2b**). Again, the spectroscopic data for ion pair **2b** are nearly identical with those of the corresponding ions in compounds **3b**[7] and **4**. Unfortunately, by using this ligand, no single crystals suitable for X-ray analysis were obtained.

Other attempts to prepare half-sandwich zirconium complexes using these types of pentaarylfullerene ligands include salt metathesis using $ZrCl_4$ and lithium reagent **3b** in THF and the aforementioned amine elimination reaction in a weakly coordinating solvent, such as toluene. In the case of the first, ligand precursor **1b** was obtained at room temperature in THF-d_8, suggesting the initial formation of ion pair $[ZrCl_3(THF)_n][(4\text{-}n\text{-}PrC_6H_4)_5C_{60}]$, which, in turn, abstracts a proton from the reaction mixture. Accordingly, treatment of compound **2b** with Me_3SiCl in THF-d_8 resulted in the precipitation of **1b** and concurrent formation of Me_3SiNMe_2. When ligand **1b** was treated with a solution of $[Zr(NMe_2)_4]$ in toluene-d_8, no reaction was observed by ^1H NMR spectroscopy, even at elevated temperatures (80 °C).

In summary, attempts to prepare half-sandwich complexes of zirconium bearing pentaarylfullerene ligands resulted in solvent-separated ion pairs involving a zirconium tris(dimethylamide) cation and a noncoordinating fullerene-derived cyclopentadienyl anion. This is most likely the result of the reduced nucleophilicity of the pentaarylfullerene anion compared to that of more traditional cyclopentadienyl anions.[9]

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Supporting Information Available: Experimental details and crystallographic data for compounds **1b**, **2a**, **3b**, **4**, and **4′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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