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. Since their initial report, a number of transition-metal complexes with these pentaalkyl- and pentaaryl-fullerene ligands have emerged, illustrating the versatility of this type of ligand. Examples include sandwich fullerene ligands have emerged, illustrating the versatility of metal complexes with these pentaalkyl- and pentaaryl-focused precursor, affording a reddish-brown solution. Monitoring evolution and the disappearance of the poorly soluble ligand (1a) (a) Sawamura, M.; Iikura, H.; Nakamura, E. M.w.bouwkamp@rug.nl.

The addition of tetrahydrofuran (THF) to an equimolar mixture of the pentaarylfullerene ligand precursor Ph5C6H (1a) and zirconium amide [Zr(NMe2)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-d8 revealed that, during the reaction, 1 equiv of dimethylaniline was formed. Both the 1H and 13C NMR spectra of the product revealed the correct number of peaks expected for a half-sandwich complex of the type [(Ph5C60)Zr(NMe2)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.

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)]/[Ph5C60] (3a)5 shows that the two are virtually identical. This suggests the formation of an ion pair of the type [Zr(NMe2)3(THF)]/[Ph5C60] (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 LiNMe2 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, [BPh4]-, was prepared as a reference by treatment of [Zr(NMe2)3] with 1 equiv of [PhNMe2-H][BPh4] in a THF solution. The compound was obtained as its bis- or tris(THF) adduct, [Zr(NMe2)3(THF)]/[BPh4] (n = 2, 4; n = 3, 4′), depending on the workup procedure (vide infra). The NMR spectroscopic data for the [Zr(NMe2)3(THF)] 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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The stoichiometries of lithium salts 3a and 3b were determined by elemental analysis. For 3b, this was confirmed by X-ray analysis.
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-derived anion. In that case, the ion pair is obtained by reduction of C₆₀ 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′.

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-PrC₆H₅)₃C₆₀H (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 C₆₀.⁸ Like in the case of 1a, treatment of ligand 1b with [Zr(NMe₂)₄] resulted in a brownish-red reaction mixture, and the ¹H and ¹³C NMR spectroscopic data are consistent with the formation of ion pair [Zr(NMe₂)₃(THF)₂][(4-PrC₆H₅)₃C₆₀] (2b). Again, the spectroscopic data for ion pair 2b are nearly identical with those of the corresponding ions in compounds 3b⁷ 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 ZrCl₂ 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–d₈, suggesting the initial formation of ion pair [ZrCl₃(THF)₄][(4-PrC₆H₅)₃C₆₀], which, in turn, abstracts a proton from the reaction mixture. Accordingly, treatment of compound 2b with Me₃SiCl in THF–d₈ resulted in the precipitation of 1b and concurrent formation of Me₃SiNMe₂. When ligand 1b was treated with a solution of [Zr(NMe₂)₄] in toluene–d₈, 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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Table 1. Selected Bond Distances (Å) for Compounds 4 and 4′

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>4′</th>
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<tr>
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<td>2.056(2)</td>
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<td>2.3588(18)</td>
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<tr>
<td>Zr1–O12</td>
<td>2.261(2)</td>
<td>2.3652(18)</td>
</tr>
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(7) Ligand 1b and compound 3b were characterized by single-crystal X-ray analysis.