

New “Bucky-ligands”. Potentially Monoanionic Terdentate Diamino Aryl Pincer Ligands Anchored to C₆₀

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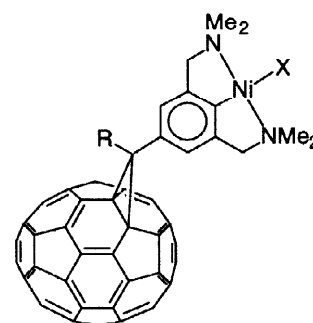
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Abstract: Two new methanofullerenes have been prepared by the reaction of C₆₀ with diazo substituted, potentially monoanionic, terdentate diamino aryl ligands, yielding a mixture of the open valence [5,6]- and closed valence [6,6]-isomers. Single isomers of the pure [6,6]-methanofullerenes were obtained by heating these mixtures in toluene solution. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Fullerenes such as C₆₀ possess a wide variety of chemical and physical properties, which make this class of carbon allotropes not only useful as building blocks in organic chemistry, but also applicable in supramolecular chemistry for the synthesis of molecular devices. The C₆₀ molecule has been shown to be an electron accepting unit¹. It has also been used in several organic donor-acceptor complexes with for example aniline² or tetrathiafulvalene³ or with ligated metal fragments as electron donor groups^{4–7}.

Herein we describe the functionalization of C₆₀ with potentially monoanionic terdentate diamino aryl fragments (*i.e.* 1,3-bis[(dimethyl-amino)methyl]benzene or “pincer ligand”⁸) and their use as precursor compounds for aryl metal complexes connected to C₆₀. Attachment of such an electronic rich metal system to C₆₀ may afford an electron push-pull system with novel electronic and photochemical properties. This work may also allow the study of the effect of a para C₆₀ fragment on the catalytic performance of pincer-metal complexes⁹. Compound A (Figure 1), comprising of C₆₀ bearing a pincer-nickel(II) unit, represents one of our target compounds.



A: C₆₀-pincer-NiX

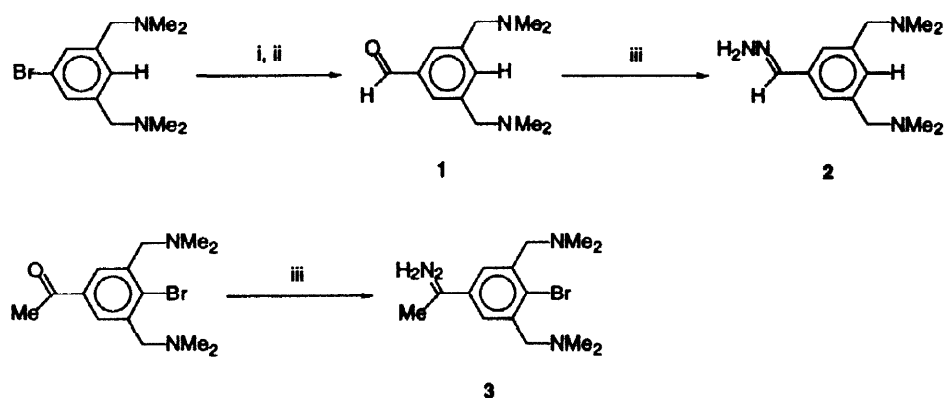
Figure 1

RESULTS AND DISCUSSION

There are many possible routes to connect organic groups to fullerenes¹⁰, but one of the most common methods is a 1,3-dipolar addition of diazo compounds to free C₆₀. This results in the formation of fulleroids and methanofullerenes^{10,11}. Using this methodology, we have developed a synthetic route towards methanofullerenes

containing a pincer ligand. This route starts with the synthesis of hydrazone appended pincer ligands (Scheme 1).

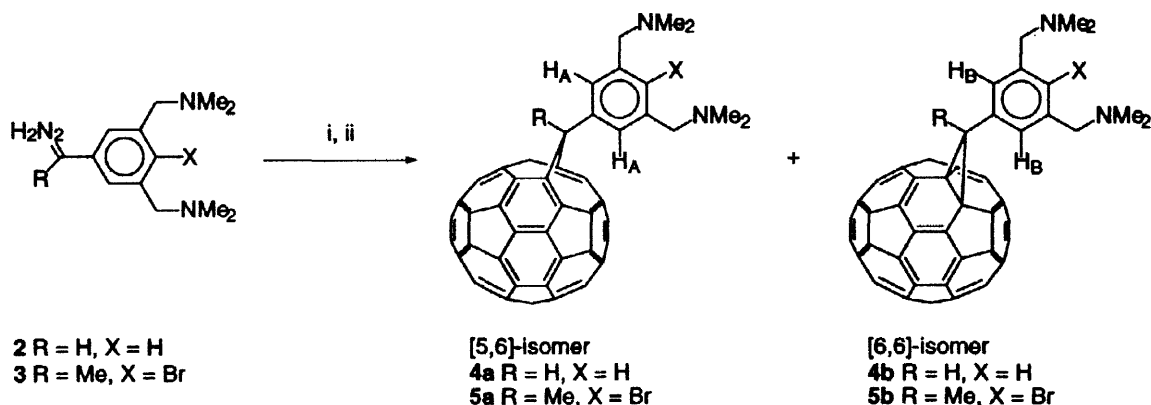
Lithiation (*via* Li-Br exchange) of 3,5-bis[(dimethylamino)methyl]-1-bromobenzene in Et₂O at low temperature, followed by a formylation reaction with DMF and a subsequent water quench, produces **1** in excellent yield (93%). The aldehyde functionality could be easily converted into a hydrazone by reaction with N₂H₄·H₂O in EtOH, yielding **2** quantitatively. In a similar way, 4-bromo-3,5-bis[(dimethylamino)methyl]acetophenone¹² was converted into **3**.



SCHEME 1

(i). 2 eq. *t*-BuLi / Et₂O; (ii) DMF, H₂O; (iii) N₂H₄·H₂O / EtOH

Due to the stability of the hydrazone compounds and the instability of the corresponding diazo-compounds, these were made *in situ* by oxidation of **2** or **3** with MnO₂ in Et₂O. Subsequent addition of the resulting red colored solutions to C₆₀ yielded, after column chromatography, a mixture of two products **4a/b** and **5a/b**, respectively, in a good yield (Scheme 2)¹³.



SCHEME 2

(i) MnO₂, KOH/EtOH / Et₂O (ii) C₆₀ / toluene

[5,6]-isomer (**4a** and **5a**, 90%) with minor amounts of the thermodynamically more stable closed valence [6,6]-isomer (**4b** and **5b**, 10%). The compounds **4a** and **4b** exhibit a different chemical shift for the bridgehead proton; while for **5a** and **5b** different signal positions for the aryl protons H_A and H_B (Scheme 2) and the bridgehead methyl group are diagnostic NMR resonances^{11b}.

To obtain isomerically pure [6,6]-methanofullerenes, toluene solutions of the above reaction mixtures (*c.f.* scheme 2) were heated at 110 °C¹⁵. This yields the pure methanofullerenes **4b** and **5b**¹⁶, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra¹⁵, resonances of sp^3 hybridized fullerene carbons appeared at 75.6 ppm (**4b**) and 80.6 ppm (**5b**), confirming the formation of [6,6]-closed valence methanofullerenes^{10,11}.

With the preparation of the two methanofullerenes **4b** and **5b**, new routes have been opened to the development of novel C_{60} organometallic compounds that can be used as supported or homogenous catalysts, with the potential for tuning *via*, for example, modification of the C_{60} fragment. Preliminary experiments have shown that **5b** can be converted to the corresponding nickel(II) compound *via* an oxidative addition reaction. Furthermore, lithiation and subsequent transmetallation procedures are being developed to produce C_{60} -pincer metal compounds for which the oxidative addition route is not feasible¹⁷. The effect of the C_{60} moiety on these complexes will be reported in due course.

ACKNOWLEDGEMENT

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13. Yield **4a/b**: 40% (68% based on reacted C₆₀), yield **5a/b**: 61% (91% based on reacted C₆₀).
14. Selected ¹H-NMR data (300 MHz, CS₂/C₆D₆ (3/1)) for **4a**: δ = 3.93 ppm (bridgehead proton); **4b**: δ = 5.18 ppm (bridgehead proton); **5a**: δ = 7.97 ppm (H_A: Scheme 2), 1.26 ppm (bridgehead methyl); **5b**: δ = 7.99 ppm (H_B: Scheme 2), 2.54 ppm (bridgehead methyl).
15. This type of isomerization is reported to be a zero order reaction, see ref 11a. Therefore, the conversion of the isomer mixtures to **4b** or **5b** was monitored by ¹H-NMR spectroscopy.
16. Data for **4b**: ¹H-NMR (300 MHz, CS₂/C₆D₆ (3/1)): δ 7.78 (s, 2H, aromatic ortho *H*); 7.29 (s, 1H, aromatic *H*); 5.17 (s, 1H, bridge-CH); 3.39 (s, 4H, CH₂N); 2.16 (s, 12H, NCH₃); ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ 149.75, 147.81, 145.66, 145.56, 145.10, 145.05, 145.02, 145.00, 144.75, 144.60, 144.48, 144.33, 144.28, 144.05, 143.68, 143.62, 143.01, 142.95, 142.89, 142.83, 142.66, 142.22, 142.07, 142.02, 140.98, 140.71, 139.45, 138.15, 137.77, 136.40, 133.10, 130.57, 129.81 (C₆₀-C+Ar-C); 75.55 (C₆₀-sp³); 64.11 (CH₂N); 45.41 (NCH₃); 43.47 (bridgehead-C). Data for **5b**: ¹H-NMR (300 MHz, CS₂/C₆D₆ (3/1)): δ 7.99 (s, 2H, aromatic ortho *H*); 3.54 (s, 4H, CH₂N); 2.41 (s, 3H, CH₃); 2.18 (s, 12H, NCH₃); ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ 148.79, 147.92, 145.93, 145.17, 145.13, 145.11, 145.07, 145.03, 144.78, 144.73, 144.65, 144.43, 144.34, 143.97, 143.74, 143.70, 143.08, 142.98, 142.92, 142.14, 142.10, 141.98, 140.96, 140.71, 138.73, 138.26, 138.04, 137.20, 131.86, 126.07 (C₆₀-C + Ar-C); 80.63 (C₆₀-sp³); 63.80 (CH₂N); 47.19 (bridgehead-C); 45.54 (NCH₃); 22.00 (CH₃).
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