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LETTERS

New "Bucky-ligands". Potentially Monoanionic Terdentate Diamino Aryl Pincer Ligands Anchored to C_{60}

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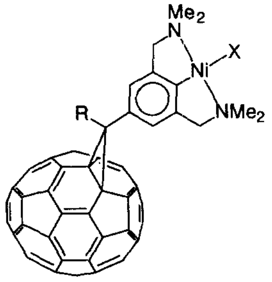
Abstract: Two new methanofullerenes have been prepared by the reaction of C_{60} with diazo substituted, potentially monoanionic, terdentate diamino aryl ligands, yielding a mixture of the open valence [5,6]- and closed valence [6,6]-isomers. Single isomers of the pure [6,6]-methanofullerenes were obtained by heating these mixtures in toluene solution. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Fullerenes such as C_{60} 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 C_{60} molecule has been shown to be an electron accepting unit[1]. It has also been used in several organic donor-acceptor complexes with for example aniline[2] or tetrathiafulvalene[3] or with ligated metal fragments as electron donor groups[4-7].

Herein we describe the functionalization of C_{60} with potentially monoanionic terdentate diamino aryl fragments (*i.e.* 1,3-bis[(dimethylamino)methyl]benzene or "pincer ligand"[8]) and their use as precursor compounds for aryl metal complexes connected to C_{60}. Attachment of such an electronic rich metal system to C_{60} 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 C_{60} fragment on the catalytic performance of pincer-metal complexes[9]. Compound **A** (Figure 1), comprising of C_{60} bearing a pincer-nickel(II) unit, represents one of our target compounds.



A: C_{60}-pincer-NiX

Figure 1

RESULTS AND DISCUSSION

There are many possible routes to connect organic groups to fullerenes[10], but one of the most common methods is a 1,3-dipolar addition of diazo compounds to free C_{60}. This results in the formation of fulleroids and methanofullerenes[10,11]. Using this methodology, we have developed a synthetic route towards methanofullerenes

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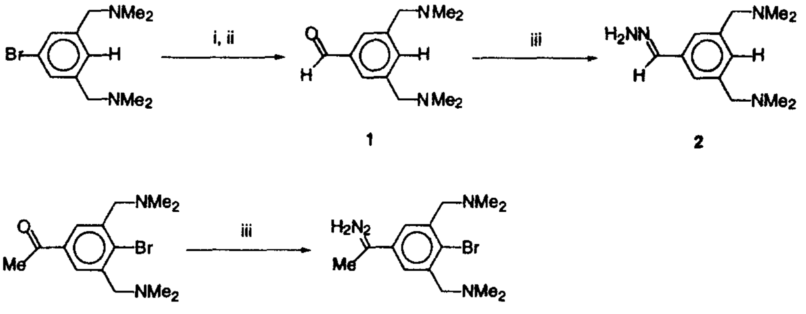
containing a pincer ligand. This route starts with the synthesis of hydrazone appended pincer ligands (Scheme 1).

Lithiation (*via* Li-Br exchange) of 3,5-bis[(dimethylamino)methyl]-1-bromobenzene in Et_2O 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 $N_2H_4 \cdot H_2O$ in EtOH, yielding **2** quantitatively. In a similar way, 4-bromo-3,5-bis[(dimethylamino)-methyl]acetophenone[12] was converted into **3**.



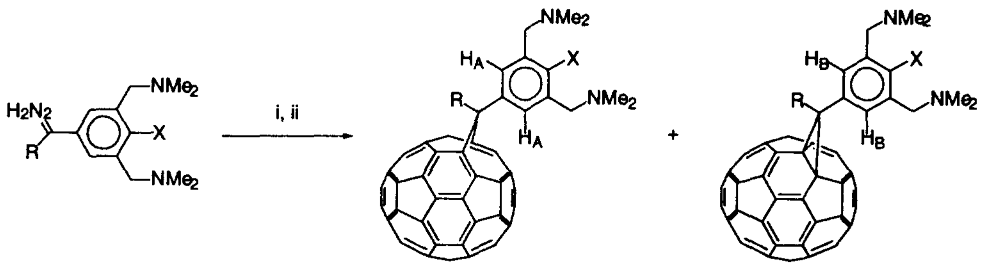
1 **2**

3

SCHEME 1

(i). 2 eq. *t*-BuLi / Et_2O; (ii) DMF, H_2O; (iii) $N_2H_4 \cdot H_2O$ / 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 MnO_2 in Et_2O. Subsequent addition of the resulting red colored solutions to C_{60} yielded, after column chromatography, a mixture of two products **4a/b** and **5a/b**, respectively, in a good yield (Scheme 2)[13].



2 R = H, X = H
3 R = Me, X = Br

[5,6]-isomer
4a R = H, X = H
5a R = Me, X = Br

[6,6]-isomer
4b R = H, X = H
5b R = Me, X = Br

SCHEME 2

(i) MnO_2, KOH/EtOH / Et_2O (ii) C_{60} / 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 °C[15]. This yields the pure methanofullerenes **4b** and **5b**[16], respectively. In the $^{13}C\{^1H\}$-NMR spectra[15], 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 feasable[17]. 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 C_{60}), yield **5a/b**: 61% (91% based on reacted C_{60}).

14. Selected ^{1}H-NMR data (300 MHz, CS_2/C_6D_6 (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 ^{1}H-NMR spectroscopy.

16. Data for **4b**: ^{1}H-NMR (300 MHz, CS_2/C_6D_6 (3/1)): δ 7.78 (s, 2H, aromatic ortho *H*); 7.29 (s, 1H, aromatic *H*); 5.17 (s, 1H, bridge-C*H*); 3.39 (s, 4H, $\mathrm{C}H_2\mathrm{N}$); 2.16 (s, 12H, $\mathrm{NC}H_3$); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 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 (C_{60}-*C*+Ar-*C*); 75.55 (C_{60}-sp^3); 64.11 ($CH_2\mathrm{N}$); 45.41 ($\mathrm{N}CH_3$); 43.47 (bridgehead-*C*). Data for **5b**: ^{1}H-NMR (300 MHz, CS_2/C_6D_6 (3/1)): δ 7.99 (s, 2H, aromatic ortho *H*); 3.54 (s, 4H, $\mathrm{C}H_2\mathrm{N}$); 2.41 (s, 3H, CH_3); 2.18 (s, 12H, $\mathrm{NC}H_3$); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 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 (C_{60}-*C* + Ar-*C*); 80.63 (C_{60}-sp^3); 63.80 ($CH_2\mathrm{N}$); 47.19 (bridgehead-*C*); 45.54 ($\mathrm{N}CH_3$); 22.00 (CH_3).

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