Attachment of Chelating Capacity to [60]Fullerene *via* Short Rigid Rods

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The cycloaddition properties of [60]fullerene containing attached olefinic centres is investigated and exploited to prepare new chelating agents attached to [60]fullerene.

Buckminsterfullerene [60]fullerene is especially reactive in cycloaddition reactions and has been shown to participate as a 2π component in [2+1], [2+2], [4+2] and higher order cycloadditions, under thermal,[1] photochemical[2] or high-pressure conditions[3] so that a wide variety of [60]fullerene adducts is now available. As there are six equivalent π centres in [60]fullerene, addition often occurs at more than one centre and polyadducts have been observed in some cases.[4]

In the development of functionalised [60]fullerene derivatives, single cycloaddition reactions have been utilised to attach prefunctionalised dienes to [60]fullerene; the 'ball and chain' adduct **1** reported by Khan *et al.*[5] typifies the type of complex product available by this approach.

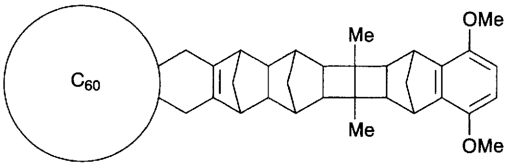
Our own interest in cycloaddition reactions, however, took us down a track which has been little explored to date in [60]fullerene chemistry. This involves the cycloaddition chemistry onto π centres already attached by σ bonds to the [60]fullerene. Thus we were interested in the cycloaddition properties of the known, norbornene-containing adducts **2**[6] and **5**.[7]

The reverse electron-demand diene 3,6-di(2-pyridyl)-*s*-tetrazine[8] reacted site-specifically at the external site with **2** and **5** to produce cycloadducts, *e.g.* **6**, which were readily oxidised to 3,6-di(2′-pyridyl)pyridazine adducts **4** and **7**, respectively (Scheme 1). These compounds represent the first example of a new class of polydentate nitrogen ligands† incorporating an attached [60]fullerene moiety. Spectral data and mass spectrometry supported the assigned structures. In particular, the downfield shift of the aliphatic proton resonances in **4** and **7** are typical of [60]fullerene adducts, while electrospray mass spectrometry confirmed their 1:1 nature. The ^{13}C NMR spectrum supported the C_s symmetry demanded by these adducts, and the sharpness of the resonances attested to the rigid nature of the carbon scaffolding linking the ligand to the [60]fullerene.

Reaction of norbornene **2** with DMAD was only productive in the presence of $[RuH_2(CO)(PPh_3)_3]$ as catalyst[11] and formed cyclobutene **3** which demonstrates further the ability of **2** to react specifically at the norbornene π centre. Spectral data‡ are consistent with the expected *exo*-specific addition occurring at the norbornenyl π centre to form cyclobutene **3**. In simple alicyclic systems, this type of activated cyclobutene undergoes Diels–Alder cycloaddition with a range of regular electron-demand dienes:[12] in contrast, efforts to conduct cycloaddition with **3** and cyclopentadiene, 3,4-dimethoxyfuran[13] and hemicyclone gave spectral evidence for the formation of polysubstitution products rather than site-selective monoadducts.§

We have conducted preliminary examination of the FMO orbitals of the [60]fullerene olefins **2**, **3** and **5**. In each case semi-empirical data¶ indicates that the electron density resides on the [60]fullerene in both the HOMO and LUMO and while this is in keeping with the lack of specificity observed in the reaction of regular dienes with these [60]fullerene derivatives it is not helpful in accounting for the external site selectivity observed in the reverse-electron demand reaction. Recourse to sub- and super-adjacent orbital contribution does not clarify these results and more extensive calculation may be required to shed light on these cycloadditions.

In conclusion, we have found a simple entry to [60]fullerene derivatives containing polydentate ligands which can be



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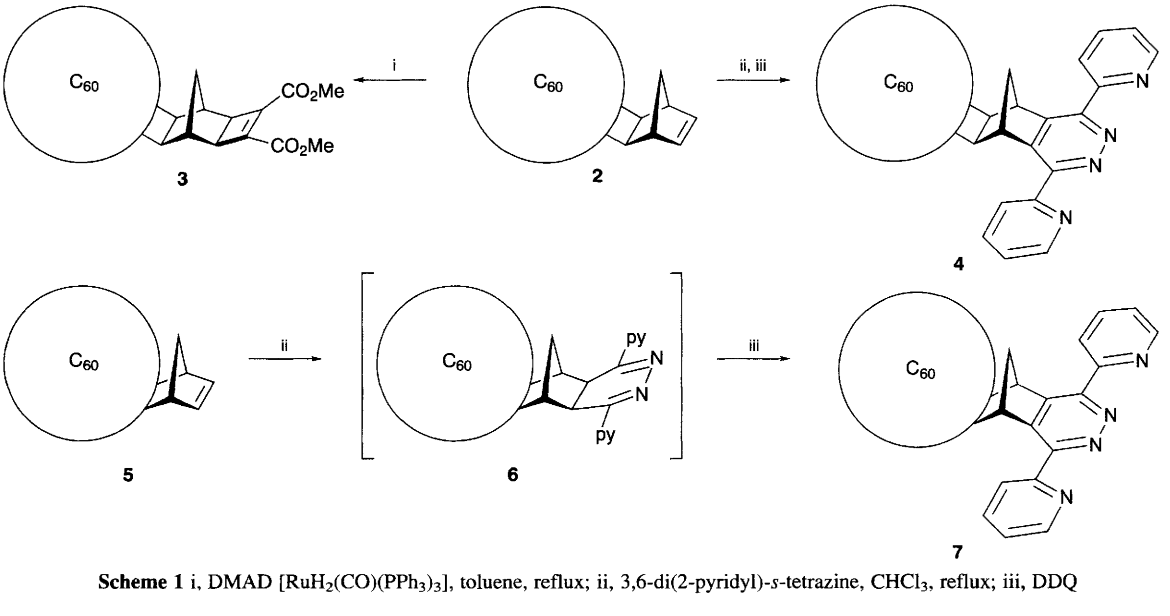

Scheme 1 i, DMAD $[RuH_2(CO)(PPh_3)_3]$, toluene, reflux; ii, 3,6-di(2-pyridyl)-*s*-tetrazine, $CHCl_3$, reflux; iii, DDQ

achieved in a two-step procedure from readily available starting materials. Metal complexation on these and other [60]fullerene ligands will be reported in due course.

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Footnotes

† 3,6-Di(2-pyridyl)pyridazine is a recognised ligand and forms complexes with a variety of metals,[9] and has recently been attached to rigid spacer molecules.[10]

‡ *Selected spectroscopic data*: **3**; mp > 300 °C; ^{1}H NMR (CDCl$_3$) δ 4.06 (d, J = 12.9 Hz, 1H), 4.04 (s, 2H), 3.81 (s, 6H), 3.23, (s, 2H), 3.08 (s, 2H), 2.02 (d, J = 12.9 Hz, 1H); ^{13}C NMR (CDCl$_3$), δ 161.31, 155.73, 150.49, 147.45, 146.95, 146.09, 146.06, 146.03, 145.97, 145.53, 145.48, 145.45, 145.40, 145.32, 145.17, 144.66, 144.52, 143.11, 143.05, 142.87, 142.81, 142.67, 142.60, 142.16, 142.13, 142.11, 142.01, 141.16, 140.70, 140.50, 140.43, 77.22, 69.83, 52.69, 52.13, 46.81, 37.94.

4; mp > 300 °C; ^{1}H NMR (CDCl$_3$) δ 8.88 (m, 2H), 8.75 (m, 2H), 7.98 (m, 2H), 7.44 (m, 2H), 5.48 (s, 2H), 4.54, (d, J = 11.1 Hz, 1H), 4.20 (s, 2H), 2.37 (d, J = 11.1 Hz, 1H); ^{13}C NMR (CDCl$_3$), δ 155.58, 152.50, 150.11, 149.60, 147.99, 146.91, 146.07, 146.02, 146.00, 145.70, 145.49, 145.28, 145.14, 144.63, 144.50, 143.09, 142.91, 142.84, 142.69, 142.61, 142.20, 142.16, 142.08, 141.18, 140.74, 140.51, 140.32, 136.97, 135.72, 124.07, 123.13, 67.62, 48.52, 46.35, 41.94; MS: *m/z* 1019.5 (M^+).

7 mp > 300 °C; ^{1}H NMR (CDCl$_3$) δ 8.75 (m, 2H), 8.65 (m, 2H), 7.85 (m, 2H), 7.25 (m, 2H), 6.28 (s, 2H), 3.81 (d, J = 11.4 Hz, 1H); 2.85 (d, J = 11.4 Hz, 1H); ^{13}C NMR (CDCl$_3$), δ 155.97, 154.88, 149.10, 147.25, 146.75, 146.36, 146.14, 146.11, 146.02, 145.88, 145.49, 145.45, 145.36, 145.02, 144.52, 144.30, 142.96, 142.78, 142.63, 142.60, 142.32, 142.08, 141.97, 141.96, 141.91, 140.22, 139.46, 137.47, 136.90, 136.02, 124.23, 122.81, 74.33, 56.36, 45.01; MS: *m/z* 993.3 (M^+).

§ Similar cycloadditions on to **2** and **3** also gave only polysubstituted products.

¶ The three semi-empirical techniques AM1, MNDO, PM3 gave essentially identical results. Calculations were performed using the SPARTAN V3.1 package.

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