A Copper(I)-complexed Rotaxane with Two Fullerene Stoppers

François Diederich,*[a] Christiane Dietrich-Buchecker,[b] Jean-François Nierengarten[a] and Jean-Pierre Sauvage*[b]

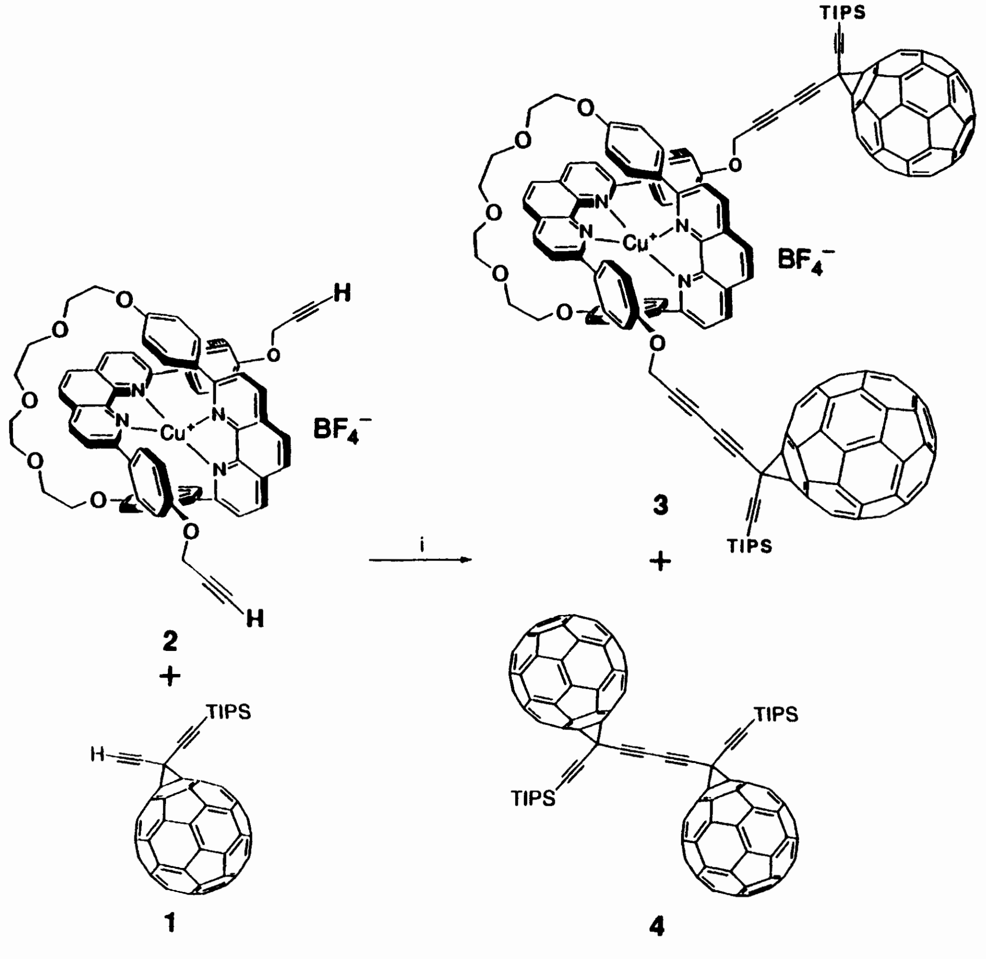
[a] *Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland*
[b] *Laboratoire de Chimie Organo-Minérale (URA 422), Institut de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal, F-67000 Strasbourg, France*

A three-component complex consisting of a coordinating ring, a copper(I) centre and a difunctionalized fragment threaded inside the ring is reacted with a C_{60} derivative to afford a soluble rotaxane with two fullerenes as stoppers in 15% yield.

The most recent syntheses of rotaxanes are based on template effects induced by transition metals[1] or electron donor–acceptor stacks.[2] The two stoppers usually used have no role other than to prevent the acyclic ribbon from being unthreaded from the ring. The use of electro- and/or photo-active species is a recent extension which allows the preparation of multicomponent molecular systems displaying novel electronic and photochemical properties.[3–5] C_{60} displays interesting electrochemical and electronic properties and being, in particular, a powerful electron acceptor,[6] it is an interesting functional stopper for rotaxanes. We now report the synthesis of such a rotaxane, assembled *via* the copper(I) templated approach, bearing two C_{60} units as chemical stoppers. Photoinduced intramolecular electron or energy transfer between the copper(I) complex and the C_{60} unit is expected to occur.

The reaction leading to rotaxane **3** is shown in Scheme 1 and is based on the oxidative coupling reaction of terminal alkynes which, as previously reported, is compatible with both **1**[7] and **2**.[8] *In situ* preparation of the Hay catalyst [CuCl–TMEDA–O_2 (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) in dichloromethane in the presence of **1** and **2** furnished rotaxane **3**. When **1** and **2** were used in a 2.5 : 1 molar ratio, **3** was obtained in a low yield (3.5%). The yield of **3** was improved to 15% when a 5 : 1 ratio of **1** (291 mg, 0.31 mmol): **2** (71 mg, 0.06 mmol) was used. The dark green reaction mixture was washed with water and subjected to anion exchange (KBF_4). The organic layer was then washed with water, dried over $MgSO_4$ and evaporated to dryness. Column chromatography on silica gel yielded the dimeric fullerene derivative **4**[7] (eluent: CH_2Cl_2), resulting from the homocoupling reaction of **1**, and the copper(I) complex **3** [eluent: CH_2Cl_2–MeOH (5–7%)]. An analytical sample of the rotaxane **3** (28.7 mg, 0.01 mmol, 15% yield) was obtained by crystallisation from CS_2–hexane whereas pure **4** (60 mg, 0.03 mmol, 20% yield) was isolated after further column chromatography on silica gel (eluent: cyclohexane). Surprisingly no [3]-catenate[8] resulting from the cyclodimerisation of the copper(I) complex **2** could be isolated.

The structure of **3**† is easily identified from its ^1H NMR spectrum. Signals consistent with two diphenyl-phenanthroline fragments entwined around a copper(I) centre, the



Scheme 1 *Reagents and conditions*: i, CuCl–TMEDA–O_2, CH_2Cl_2, room temp.

$CH_2(CH_2OCH_2)_3CH_2$ link, a prop-2-ynyl group and a TIPS (TIPS = $SiPr^i_3$) group are observed. The ^{13}C NMR spectrum is also in full accordance with the structure of **3**. A total of 49 resonances out of the expected 51 are distinguishable in the aromatic and typical fullerene region and the 15 expected non-aromatic signals are observed. FAB-MS confirmed the structure of the copper(I) complex **3** with a very intense signal at *m/z* = 2900.2.

The tetrahedrally coordinated copper(I) centre is usually removed by reaction with an excess of cyanide. The reaction of **3** with an excess of KCN yielded a mixture of compounds and the expected rotaxane **5** could not be isolated in a pure form. However a FAB-MS of the crude mixture showed clearly a peak at *m/z* = 2837.5 ($[M + H]^+$, 35%, calculated for $C_{210}H_{91}N_4O_7Si_2$: 2838.3) corresponding to the expected free ligand which demonstrated that the compound **5** is a rotaxane (Fig. 1). Degradation processes were previously observed during the demetallation of the copper(I) [2]-catenate constituted by two 27-membered rings due to the small size of the rings.[9] The reaction of **3** (which contains the same 27-membered ring) with cyanide results in partial destruction of the organic ligand.

Surprisingly, the redox potential of the $Cu^{I/II}$ couple appears to be significantly more anodic for **3** (+0.865 V *vs.* SCE in CH_2Cl_2) than for other similar mononuclear complexes.[10] This observation could be related to the strong electron-withdrawing effect of the fullerene, which could substantially destabilise the highest oxidation state of the copper centre. For instance the potential of the copper-localised redox process for the catenate consisting of two interlocking 27-membered rings is +0.685 V *vs.* SCE in DMF. The electronic effect evidenced for **3** and leading to a significant anodic shift of the $Cu^{I/II}$ redox potential as compared to other analogous complexes ($\Delta E^\circ \sim 0.2$ V) can be compared to what is observed in a recently reported dicopper trefoil knot.[11] In this tight dinuclear complex, oxidation of the first metal centre strongly destabilises the highest oxidation state of the second metal, leading to an unusually high $Cu^{I/II}$ redox potential ($E^\circ = +0.92$ V *vs.* SCE in MeCN). The electron-withdrawing character of the C_{60} units in **3** roughly parallels that of the first copper(II) complex in the dicopper knot. As expected, electrochemical reduction of the C_{60} units occurs around −0.6 V (irrev.).[6] Therefore, although the fullerene stoppers apparently influenced significantly the redox properties of the metal centre, the latter does not seem to change the redox properties of the fullerene. This reduction is rapidly followed by subsequent polymerisation onto the electrode surface (platinum cathode in the present case) to afford an insulating film.[12]

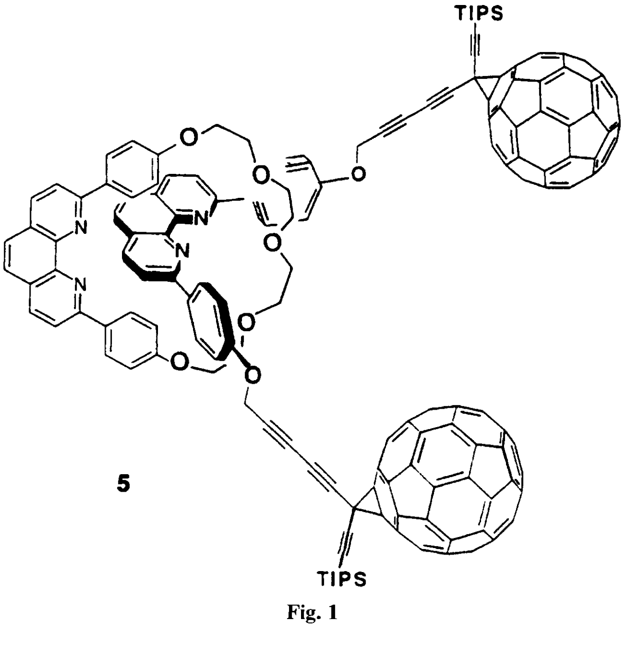


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Fig. 1

Preliminary luminescence measurements indicate that emission from the metal-to-ligand charge transfer triplet state (^3MLCT) state of the copper(I) complex **3** is completely quenched by the C_{60} stoppers at room temperature in CS_2.

We thank the CNRS and the Swiss National Science Foundation for financial support and the European Communities for a post-doctoral fellowship (Human Capital and Mobility) for J.-F. N. We also thank Dr R. Faust for helpful discussions and Mr A. Herrmann for the drawings.

Received, 11th January 1995; Com. 5/00195A

Footnote

† *Selected data* for **3**: $C_{210}H_{90}N_4O_7Si_2CuBF_4$. IR ($CHCl_3$) ν/cm^{-1} 2944 (s), 2866 (s), 2167 (w), 1600 (s), 1489 (s), 1239 (s), 1172 (m), 1094 (m), 1011 (m), 828 (m); ^1H NMR ($CDCl_3$–CS_2, 1 : 1, 300 MHz) δ 1.18 (s, 42H), 3.19 (m, 4H), 3.57 (m, 4H), 3.84 (m, 4H), 3.92 (m, 4H), 4.68 (s, 4H), 5.81 (d, 4H, *J ca.* 8 Hz), 6.19 (d, 4H, *J ca.* 8.5 Hz), 6.87 (d, 4H, *J ca.* 8.5 Hz), 7.48 (d, 4H, *J ca.* 8 Hz), 7.96 (m, 4H), 8.15 (s, 2H), 8.30 (s, 2H), 8.65 (d, 2H, *J ca.* 8.5 Hz), 8.91 (d, 2H, *J ca.* 8.5 Hz). ^{13}C NMR ($CDCl_3$–CS_2, 1 : 1, 125.8 MHz) δ 11.45, 18.82, 29.30, 56.15, 67.50, 68.92, 69.45, 71.29, 71.40, 71.52, 73.15, 74.93, 75.21, 88.76, 96.94, 113.20, 113.35, 116.31, 123.89, 124.50, 126.24, 127.12, 127.60, 128.28, 128.83, 129.40, 130.80, 132.48, 133.70, 136.78, 138.95, 139.12, 139.40, 141.19, 141.25, 142.11, 142.17, 142.38, 142.90, 142.95, 143.01, 143.08, 143.11, 143.16, 143.17, 144.02, 144.06, 144.48, 144.71, 144.75, 144.81, 144.94, 145.07, 145.20, 145.35, 145.42, 145.44, 145.47, 145.51, 145.59, 155.21, 157.47, 157.62, 158.94. UV–VIS (CH_2Cl_2) λ_{max}/nm [ε/dm^3 mol^{-1} cm^{-1}]: 225 [120 800], 254 [118 500], 325 [52 000], 434 shoulder [6500], 494 shoulder [3900]. MS (FAB, *m*-nitrobenzyl alcohol): 2900.2 ($[M - BF_4]^+$, 100%, calculated for $C_{210}H_{90}N_4O_7Si_2Cu$: 2900.8), 2179.7 ($[M - BF_4 - C_{60}]^+$, 14%, calculated for $C_{150}H_{90}N_4O_7Si_2Cu$: 2180.1).

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