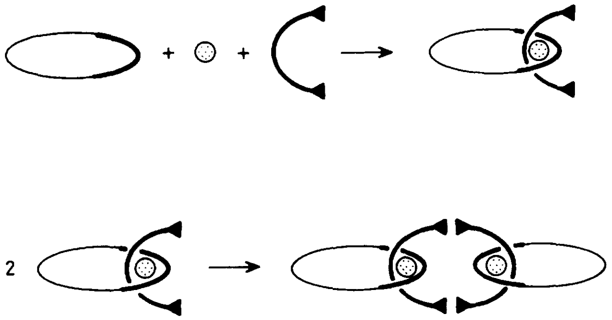
High-yield Synthesis of Multiring Copper(I) Catenates by Acetylenic Oxidative Coupling

C. O. Dietrich-Buchecker, A. Khemiss, and J. P. Sauvage

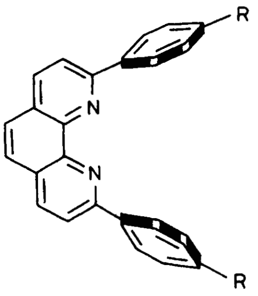
Laboratoire de Chimie Organo-Minérale, UA 422, Institut de Chimie, 1, rue Blaise Pascal, F-67000 Strasbourg Cedex, France

A [3]-catenate is prepared in 58% yield by double acetylenic oxidative coupling from a terminal diyne compound thread into a ring.

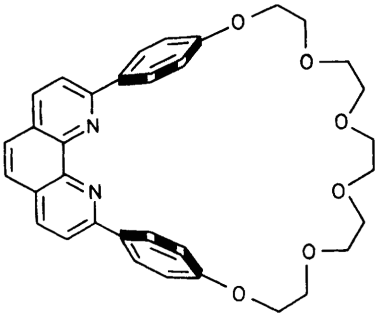
The templated synthesis of [3]-catenates, consisting of three interlocked rings and two copper(I) centres, has recently been reported,[1] as well as the preparation of the corresponding free ligands ([3]-catenands). Unfortunately, cyclisation yields were poor and work-up procedures very tedious. We now report a new and highly efficient method of preparation of [3]-catenates, based on acetylenic oxidative coupling. The strategy corresponds to a cyclo-dimerization, involving four reacting centres only, in contrast to the previously reported synthesis which required eight centres to be linked. The principle of the synthesis is given in Scheme 1. Oxidative coupling of terminal acetylenes (Glaser reaction) has been applied to diyne systems for many years. By intramolecular coupling, macrocyclic diynes have been obtained, whereas tetraynes are formed by oxidative cyclo-dimerisation.[2,3] Advantage has been taken of the latter reaction for making rigid paracyclophanes designed as molecular receptors.[4]



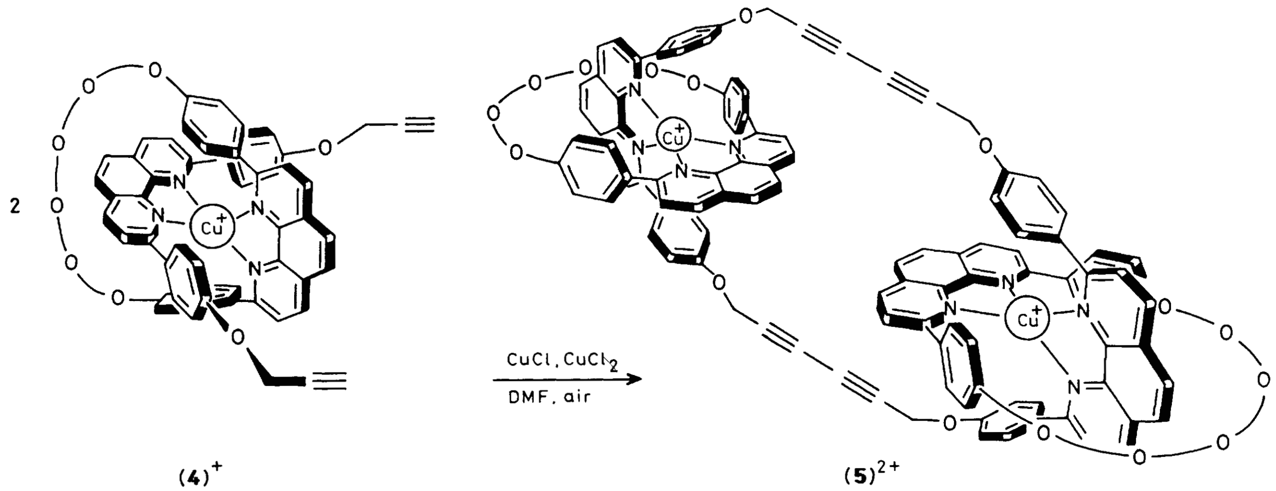
Scheme 1. Synthesis of a [3]-catenate by cyclodimerization of a difunctional precursor. The co-ordinating fragments are shown as thick lines. The circles represent the templating transition metals.



(**1**) R = OH
(**2**) R = $OCH_2C{\equiv}CH$



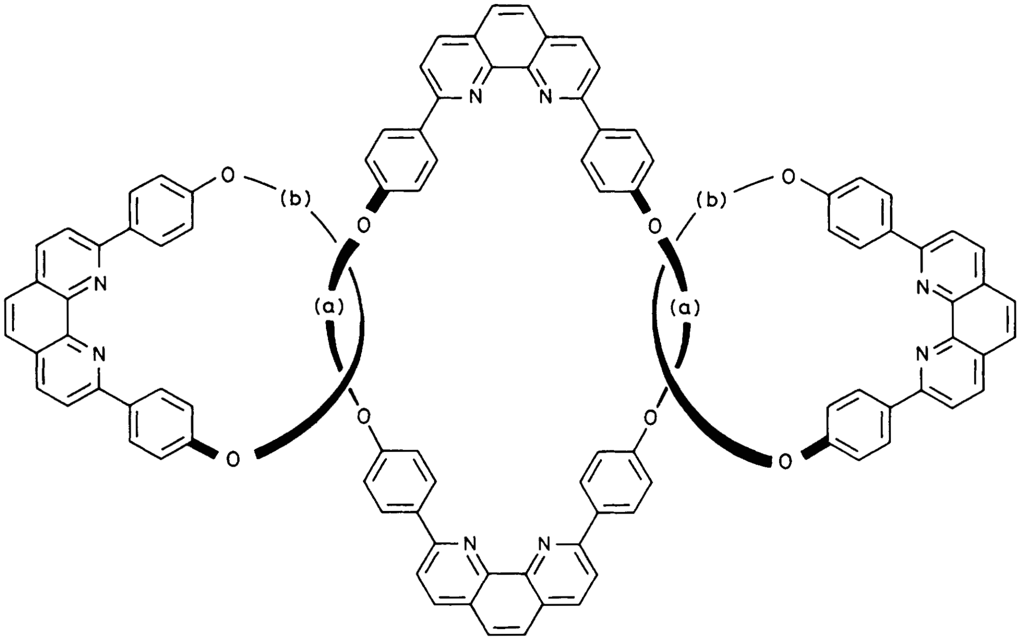
(**3**)



(**4**)$^+$

(**5**)$^{2+}$

Scheme 2



(**6**)

(a) = $-CH_2C{\equiv}C-C{\equiv}CCH_2-$
(b) = $-CH_2CH_2[OCH_2CH_2]_4-$

Furthermore, cyclo-dimerisation of a triyne has recently been carried out with a surprisingly high yield.[5]

The precursors used and the reaction scheme are represented in Scheme 2.† The open chain diyne (**2**) (m.p. 273—274 °C) was prepared in 80% yield from the diphenol (**1**)[6] and prop-2-ynyl bromide in dimethylformamide (DMF) at 65 °C, under argon, in the presence of a large excess of Cs_2CO_3. Complex $(\mathbf{4})^+$ was obtained quantitatively, as a red solid, by mixing stoicheiometric amounts of (**3**),[6] $Cu(MeCN)_4{}^+BF_4{}^-$, and (**2**) in CH_2Cl_2–MeCN (~2 : 1). The oxidative coupling leading to $(\mathbf{5})^{2+}$ was performed in DMF, with large amounts of CuCl and $CuCl_2$, in the presence of air.‡ After work-up and chromatographic separation (silica; CH_2Cl_2 and small amounts of MeOH as eluant) a 58% yield of $(\mathbf{5})^{2+}$ (red solid; m.p. >300 °C, decomp.) was obtained. This strikingly high yield allows gram scale preparation of the latter compound. Besides $(\mathbf{5})^{2+}$, another copper(I) catenate was formed in 22% yield. Based on high resolution ^1H n.m.r. data, this second product is likely to be the trimetallic complex formed by cyclo-trimerisation of $(\mathbf{4})^+$ consisting of four interlocked rings: a central hexayne 66-membered ring and three peripheral rings composed of (**3**).

Demetallation of $(\mathbf{5})^{2+}$ was performed with KCN, as for other copper(I) catenates.[7] Compound (**6**) was obtained in 75% yield as an insoluble white solid (m.p. 183—184 °C), its ^1H n.m.r. spectrum (CD_3SOCD_3 at 100 °C) clearly showing the disentangling of the 2,9-diphenyl-1,10-phenanthroline fragments.

The new co-ordinating system (**6**) is relatively flexible and adaptable owing to its catenane nature but, on the other hand, the rigidity of the central ring (44 atoms) is ensured by the two diyne spacers.

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† The new compounds reported gave satisfactory elemental analysis (C, H, and N). ^1H N.m.r. and mass spectra were in agreement with their structures.

‡ Stirring (**4**) (0.26 mmol), CuCl (35 mmol), and $CuCl_2$ (6.2 mmol) in DMF (36 ml) for 3 days at room temperature yielded $(\mathbf{5})^{2+}$ (0.075 mmol). It is puzzling that under anaerobic conditions analogous to those used by Breslow *et al.*,[5] almost no reaction takes place.