

Ring-closing alkyne metathesis with simple catalyst systems: an access to molecular triangles and rhomboids

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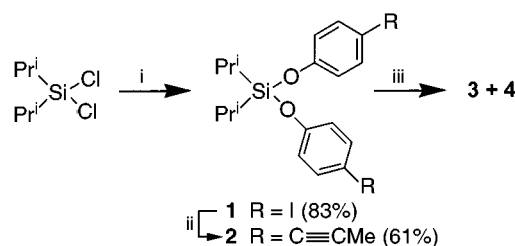
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Treatment of the siloxane monomer **2** with a mixture of molybdenum hexacarbonyl and 4-chlorophenol at 140 °C furnished the corresponding cyclotrimer **3** and the cyclotetramer **4**.

Ring-closing alkene metathesis utilizing well-defined organo-metallic catalysts^{1–4} has developed into a powerful synthetic tool. A variety of rings have been prepared by this method. Cyclic polyynes are also of great interest,⁵ but their synthesis *via* ring-closing alkyne metathesis is much less explored.⁶ Fürstner⁷ has reported the preparation of large-ring alkynes by ring-closure of suitable dipropynylated precursors utilizing Schrock's tungsten carbyne.⁸

We have recently developed an efficient and simple protocol for alkyne metathesis^{9,10} and we now report the first examples of ring-closing metathesis using our 'instant' catalyst. This powerful catalyst is formed *in situ* from Mo(CO)₆ and 4-chlorophenol using off-the-shelf quality solvents.

The synthesis of shape-persistent macrocycles, potentially useful as molecular boxes, presents a new and interesting challenge.^{11,12} We have chosen diyne **2** to be a convenient precursor to the novel molecular siloxane triangles/boxes **3** and **4**. Compound **2** was prepared in two steps from **1**, which was, itself, obtained from 4-iodophenol by treatment with Prⁱ₂SiCl₂



Scheme 1 Reagents and conditions: i, 4-IC₆H₄OH, Et₃N, THF; ii, propyne, Pd(PPh₃)₂Cl₂, CuI, piperidine; iii, Mo(CO)₆, 4-ClC₆H₄OH.

in Et₃N (Scheme 1). A palladium-catalyzed coupling of **1** with propyne affords the monomer **2** in 61% yield.¹³ Alkyne metathesis of **2** with Mo(CO)₆ and 4-chlorophenol at 140 °C in 1,2-dichlorobenzene under a steady stream of N₂ (Scheme 1) furnished the novel cycles **3** and **4**.† Sufficient dilution is an important factor for obtaining cyclic rather than polymeric products, although minor changes in concentration did not result in decreased yields of the macrocycles. Separation was difficult due to the similar retention times of **3** and **4**, and their corresponding open congeners. However, we were able to isolate **3** (14% yield) and **4** (18% yield). GC-MS confirmed that the isolated fractions of **3** and **4** were uncontaminated by other cycloisomers. The molecular structures of **3** and **4** were established by single crystal X-ray diffraction analyses.‡

The crystal of **3** contains three symmetry-independent molecules. All three display similar conformations and the molecular structure of one of these is shown in Fig. 1. The cyclotetramer **4** is crystallographically centrosymmetric. It exhibits a rhomboidal structure with a large interior cavity that contains two molecules of hexane as solvate, from which it was crystallized (Fig. 2). This feature indicates the potential of these box-shaped molecules to engage in important host-guest chemistry.

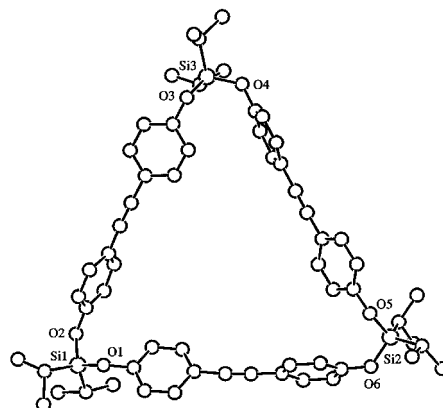
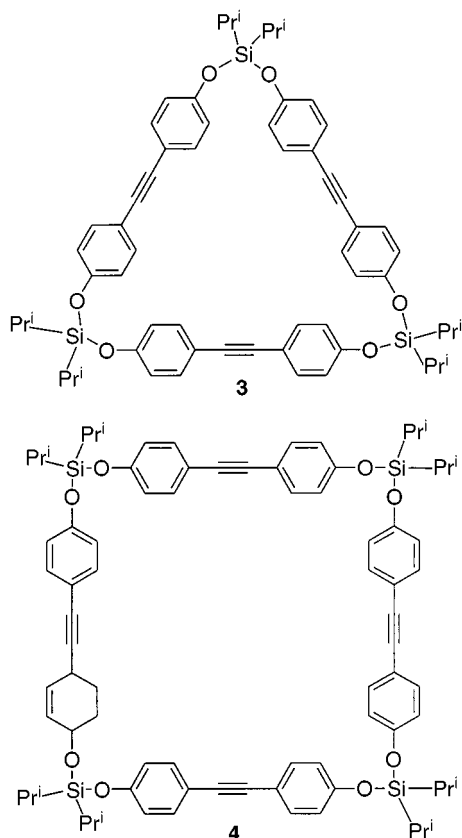


Fig. 1 A structural diagram of the cyclic triyne **3**. Selected bond distances (Å) and angles (°) are C≡C = 1.22(2), 1.20(2) and 1.16(2), Si(1)–O(1) = 1.616(9), Si(1)–O(2) = 1.624(9), Si(2)–O(5) = 1.67(1), Si(2)–O(6) = 1.63(1), Si(3)–O(3) = 1.63(1), Si(3)–O(4) = 1.66(1); O(1)–Si(1)–O(2) = 109.8(5), O(5)–Si(2)–O(6) = 106.9(5), O(3)–Si(3)–O(4) = 108.1(6).

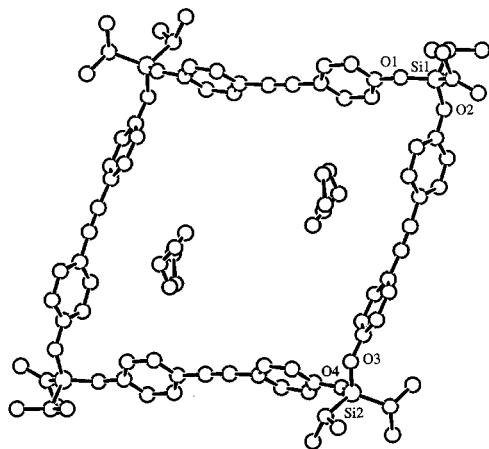


Fig. 2 A structural diagram of the cyclic tetrayne **4** showing two molecules of occluded hexane in the interior of the ring. Selected bond distances (Å) and angles (°) are C≡C = 1.179(9) and 1.213(9), Si(1)–O(1) = 1.635(4), Si(1)–O(2) = 1.646(4), Si(2)–O(3) = 1.654(4), Si(2)–O(4) = 1.652(4); O(1)–Si(1)–O(2) = 110.6(2), O(3)–Si(2)–O(4) = 109.9(2).

We have now demonstrated that ring-closing alkyne metathesis with our ‘instant’ catalyst system provides a convenient route to novel alkyne-containing macrocycles. Functionalized rings should also be accessible *via* this methodology as we have already shown that the mixtures of Mo(CO)₆ and 4-chlorophenol are metathesis-active in the presence of a variety of different functional groups.^{8,9}

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Notes and references

† Sample cyclization: **2** (1.00 g, 2.66 mmol), Mo(CO)₆ (0.66 g, 0.27 mmol), 4-chlorophenol (0.206 g, 1.60 mmol) and 1,2-dichlorobenzene (100 ml) were held at 140 °C under a steady stream of N₂ for 17 h. The solution was allowed to cool, then dissolved in hexanes and washed with dilute acid and base. Separation of the resulting products was achieved by chromatography over silica gel (Merck silica gel 60, 40–63 µm particle size; eluent 3:1 hexanes–CH₂Cl₂–). *Selected data for 3*: δ_H(400 MHz, CDCl₃) 7.31 (d, *J* 8.6, 12H), 6.71 (d, *J* 8.6, 12H), 1.30 (m, *J* 7.1, 6H), 1.16 (d, *J* 7.1, 36H); δ_C(400 MHz, CDCl₃) 154.1, 132.7, 119.9, 116.8, 88.2, 17.2, 12.7. For **4**:

δ_H(400 MHz, CDCl₃) 7.35 (d, *J* 8.8, 16H), 6.88 (d, *J* 8.8, 16H), 1.40 (m, 8H), 1.09 (d, *J* 7.3, 48H); δ_H(400 MHz, CDCl₃) 154.4, 132.9, 119.7, 116.8, 88.1, 17.2, 12.7.

‡ *Crystal data*: for **3**: Si₃O₆C₆₀H₆₈, triclinic, *M* = 936.12 g cm^{−3}, space group = *P* $\bar{1}$ (No. 2), *T* = 293 K, Mo–Kα, *a* = 23.76(2), *b* = 24.07(3), *c* = 18.7192(5) Å, α = 92.0(1), β = 96.25(7), γ = 93.70(9)°, *Z* = 6, *D* = 1.083 g cm^{−3}, μ = 0.13 cm^{−1}, 15889 measured reflections, 7703 independent reflections, *R* (*R*_w) = 0.091 (0.126), hydrogen atoms calculated, not refined. For **4**: Si₄O₈C₈₀H₁₇₆·2(C₆H₁₄), triclinic, *M* = 1378.60, Space group = *P* $\bar{1}$ (No. 2), *T* = 293 K, Mo–Kα, *a* = 13.977(8), *b* = 14.25(1), *c* = 12.144(7) Å, α = 106.29(5), β = 108.21(5), γ = 69.68(5)°, *Z* = 1, *D* = 1.083 g cm^{−3}, μ = 0.12 cm^{−1}, 4534 measured reflections, 2740 independent reflections, *R* (*R*_w) = 0.0599 (0.0814). Hydrogen atoms calculated, not refined. CCDC 182/1494. See <http://www.rsc.org/suppdata/cc/a9/a908638b/> for crystallographic data in .cif format.

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