One step synthesis of [7]metacyclophanediyne complexes from bis(propargyldicobalt) dication equivalents

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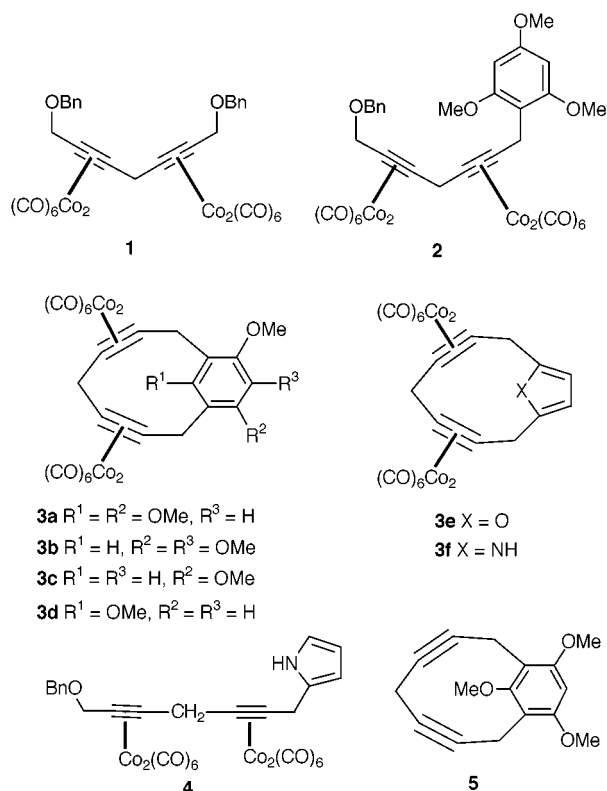*Chemistry and Biochemistry, School of Physical Sciences, University of Windsor, Windsor, Ontario, Canada N9B 3P4. E-mail: jgreen@uwindsor.ca*

The $BF_3 \cdot OEt_2$ mediated addition reactions of electron-rich arenes to 1,3-dialkoxyhepta-2,5-diyne(dodecacarbonyl)-tetracobalt complex **1** directly afford [7]metacyclophane-diyne(dodecacarbonyl)tetracobalt complexes.

The chemistry of small cyclophanes has been the focus of much attention, due to their structural and electronic properties, and their ability to include either metal ions or neutral or charged organic molecules.[1–3] Syntheses of these classes of compounds, however, are rarely straightforward. Access to the smaller [*n*]metacyclophanes ($n \leqslant 8$), for example, is most often accomplished by rearrangement of propellanes or spirocyclo-alkadienones, intramolecular Diels–Alder reactions of die-nynes, or extrusion reactions of sulfoxides.[1,2] Direct inter-molecular cycloaddition approaches towards these systems have not been efficient ones.[4]

The use of hexacarbonyldicobalt alkyne complexes has become important in organic synthesis.[5–7] Among the note-worthy features of these complexes is their ability to serve as protected versions of alkynes that would be severely or prohibitively strained.[8] This property has seen application as a tactic in the chemistry of cyclohexynes and cycloheptynes,[9] Bergman cyclization precursors,[10] and other polyacetylenic macrocycles.[11]

We have begun a program on the investigation of the chemistry of dodecacarbonyltetracobalt complexes of hepta-2,5-diynyl 1,7-diethers **1** and closely related compounds as latent 1,4-diynes, dienes, or enynes, based on the known ability of hexacarbonyldicobalt complexes of propargyl alcohols and their derivatives to form cations readily.[5] The diether complex **1** underwent ready reaction with electron-rich arenes in the presence of $BF_3 \cdot OEt_2$, but did not stop cleanly at the monoarylation products. When **1** was subjected to equimolar amounts of $BF_3 \cdot OEt_2$ and 1,3,5-trimethoxybenzene at 0 °C (at 10^{-2} M each in CH_2Cl_2), only a 24% yield of **2** could be isolated. The predominant product (26%) proved to be [7]meta-cyclophanediyne complex **3a**, stemming from two substitution reactions by trimethoxybenzene on **1**. The yields of **3a** realized could be improved considerably by increasing the amounts of both $BF_3 \cdot OEt_2$ and trimethoxybenzene to 2 equiv; **3a** was then obtained in 92% yield after 5 h at 0 °C.†

Other electron-rich benzenes also gave [7]metacyclophane-diyne complexes under analogous conditions (Table 1). 1,2,3-Trimethoxybenzene gave **3b** in a more modest yield (34%), while 1,3-dimethoxybenzene gave two separable cyclo-phanes, **3c** and **3d**, in 78% combined yield (63% **3c** + 15% **3d**). Among heterocycles tested, furan gave [7](2,5)furanocyclo-phane complex **3e** in 30% yield. Pyrrole, unlike the other electron rich arenes, afforded monocondensation product **4** as the only tractable product in 51% yield. Subsequent addition of **4** to excess $BF_3 \cdot OEt_2$ (4 equiv.) at 0 °C in CH_2Cl_2 (24 h, 10^{-2}M) then gave [7](2,5)pyrrolophane **3f** in 40% yield. Thiophene proved insufficiently reactive to give any condensation product with **1**. Conducting the reactions at lower concentration (10^{-3} M) increased the necessary reaction time considerably (3 d at 0 °C), but gave some improvement in the yields of **3c** (68% **3c** + 15% **3d**) and **3e** (43%). The yield of **3b** was actually inferior (19%) at the lower concentration.

3a $R^1 = R^2 = OMe$, $R^3 = H$
3b $R^1 = H$, $R^2 = R^3 = OMe$
3c $R^1 = R^3 = H$, $R^2 = OMe$
3d $R^1 = OMe$, $R^2 = R^3 = H$

3e X = O
3f X = NH

The ^{1}H NMR spectra of these [7]metacyclophanediyne complexes possessed characteristics that fell into two distinctly different groups. Those which contained a methoxy function between the two termini of the bridge (**3a** and **3d**) revealed highly diastereotopic methylene groups; the bispropargylic methylene function of **3a**, for example, gave resonances at δ 4.99 and 4.31, whereas the benzylic methylene function gave resonances at δ 4.34 and 4.09. The other cyclophanediyne complexes (**3b**, **3c**, **3e**, **3f**) showed methylene groups whose protons were isochronous.

The number of alkyne containing cyclophanes is relatively modest,[11,12] and dominated by cases where the alkyne function serves simply as a spacer,[13] but there is much interest in the demonstrated coordinating ability of the alkyne function of

Table 1 Additions between diyne complexes **1** or **4** with arenes

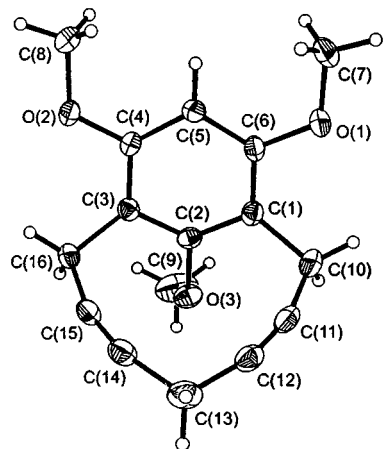| Diyne	Nucleophile	Product (% yield)
1	1,3,5-trimethoxybenzene	**3a** (92)
1	1,2,3-trimethoxybenzene	**3b** (34)
1	1,3-dimethoxybenzene[a]	**3c** (68)
		3d (15)
1	Furan[a]	**3e** (43)
1	Pyrrole	**4** (51)
4	—	**3f** (40)

[a] Conducted at [**1**] = 10^{-3} M.

Fig. 1 ORTEP drawing of **5** (30% probability). H atoms not shown. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.398(3), C(14)–C(15) 1.186(3), C(13)–C(14)–C(15) 164.0(2), C(14)–C(15)–C(16) 162.9(2), C(12)–C(14) 106.1(2), C(2)–C(3)–C(16) 117.2(2).

cyclic polyynes.[14] As a result, we deemed it of interest to determine whether or not decomplexation of **3** could be accomplished. In fact, attempted removal of the hexacarbonyldicobalt units from **3a** by the usual reagents [Me$_3$NO, (NH$_4$)$_2$Ce(NO$_3$)$_6$, CuCl$_2$, FeCl$_3$] resulted in complete destruction of the cyclophanediyne unit. On the other hand, stirring complex **3a** in a pyridine–Et$_2$O solvent mixture (1:1, in air) over a 10 d period resulted in the formation of **5** in 56% yield. The ^{1}H NMR spectrum of **5** also showed the presence of diastereotopic methylene groups; the resonances for the benzylic hydrogen atoms appeared at δ 3.48 and 3.41, while the bispropargylic hydrogen atoms gave resonances at δ 2.92 and 2.61. Compound **5** gave crystals suitable for X-ray diffraction, which revealed the structure represented in Fig. 1.‡ It is apparent that there is strain in this molecule, which is reflected in several ways. Among the most notable of these are the bond angles at the alkynyl carbon atoms, which have been bent to 164 (at C-11 and C-15) and 163° (at C-12 and C-14). The arene ring also shows these effects, as the benzylic carbon atoms are pulled out of the plane of the C-1, C-3, C-4, C-6 arene ring carbons by 32.9° (β), and the benzene ring itself deviates slightly from planar at both C-2 (α = 11.2°) and at C-5 (γ = 5.5°) (Fig. 2). Nevertheless, compound **5** has good thermal stability. The structural data also suggest strongly that the diastereotopic methylene groups in **3a**, **3d** and **5** are consequences of the ring inversion represented in Fig. 2 at the slow exchange limit (Fig. 2, shown for **5**). The singlets observed for **3b**, **3c**, **3e** and **3f** stem from molecules at the fast exchange limit of the analogous inversion process.[15]

The [7]metacyclophanediyne **5** is the smallest [*n*]metacyclophane containing a triple bond reported to date. Nevertheless, a small number of reported metacyclophanes have larger deformation angles (α, β, γ),[16] and a number alkynes with smaller

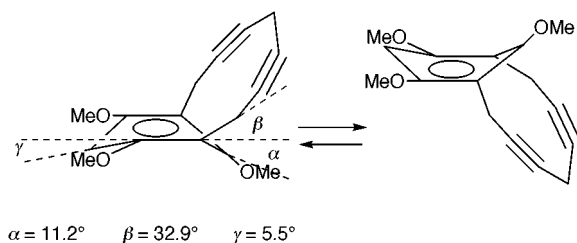$\alpha = 11.2°$ $\beta = 32.9°$ $\gamma = 5.5°$

Fig. 2 Distortion angles and fluxional process for **5**.

bond angles also exist.[17] These data suggest that smaller alkyne containing [*n*]metacyclophanes may be accessible.

We are grateful to NSERC (Canada) for support of this research. We wish to thank Professor Doug Stephan and Professor Stephen Loeb (WINMOL) for the crystallographic structural work on **5**.

Notes and references

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Communication 9/07991B