Organometallic Chemistry

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An Intermolecular Double [2+2] Cyclodimerization of a Tetraalkyne[**]

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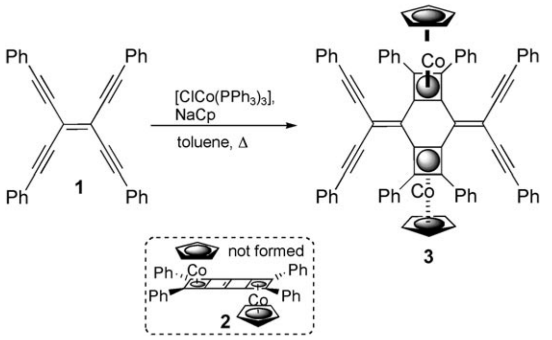
Dedicated to Professor J. Grant Buchanan on the occasion of his 80th birthday

Cobalt(I)-mediated [2+2] cycloadditions of alkynes are known to give stable organometallic compounds which contain an η^4-cyclobutadiene fragment.[1] Gleiter and co-workers exploited this chemistry in the synthesis of their trinuclear beltene system.[2] The research group of Vollhardt used cobalt to generate fused six- and four-membered ring systems discussed as models for non-delocalized benzene, that is, cyclohexatriene.[3–6] Bunz and co-workers constructed a series of highly alkynated carbon-rich derivatives.[7,8] Dinuclear $[Co_2(CO)_8]$ facilitates the Pauson–Khand reaction, a [2+2+1] cycloaddition affording extremely useful cyclopentenones.[9,10]

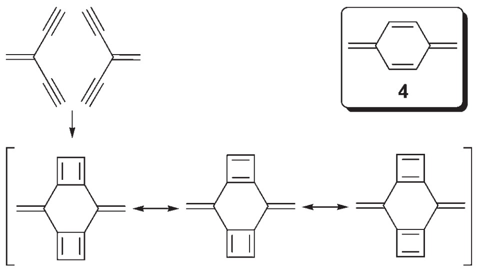
We supposed the facile nature of [2+2] cyclodimerizations mediated by cobalt(I) η^5-cyclopentadienyl complexes and the inherent stability of the 18-electron cobalt(I) η^4-cyclobutadiene η^5-cyclopentadienyl constructs could allow us to access structurally unique and potentially useful fused cyclobutenes such as **2**.[11]

It has been shown that addition of more than one equivalent of a cobalt carbonyl derivative to a vinyl tetraalkyne such as **1** leads the second metal to coordinate exclusively *trans* about the double bond.[12,13] We planned to use this phenomenon with a cobalt(I) cyclopentadienyl derivative generated in situ, thus allowing two intramolecular [2+2] reactions to take place within **1** to furnish **2**. Unfortunately, the highly strained fused tetracyclic complex **2** did not form. However, pairs of the *cis* alkynes were able to undergo intermolecular double [2+2] cyclodimerization to afford stable binuclear organometallic cobalt complexes **3** that display an extraordinary ligand motif (Scheme 1).

An intermolecular double [2+2] cyclodimerization of the vinylidene bisalkynes gives a fused carbocyclic ring system (Scheme 2). In contrast to the earlier reports of *trans* coordination of the cobalt moieties, the formation of **3** provides strong evidence for *cis* coordination of the cobalt moieties to **1** prior to the dimerization event.



Scheme 1. Synthesis of the binuclear cobalt(I) complex **3**. Cp = cyclopentadienyl.



Scheme 2. Intermolecular double [2+2] cyclodimerization of a *cis* bisalkyne.

The central six-membered ring **4** can be considered as a stable de-aromatized *p*-xylene analogue. With all the carbon atoms being sp^2 hybridized and containing two exocyclic double bonds, compounds of this type may be used for example as mechanistic probes for polymerization reactions.[14–16]

The cycloaddition reaction to form compound **3** was carried out under a dry nitrogen atmosphere, but no precautions were taken to protect the crude reaction products from external moisture or oxygen. The brown crude residue was purified by flash chromatography on silica gel and a red band was collected. ^1H NMR spectroscopy indicated this material contained four different compounds with the spectrum containing distinct η^5-cyclopentadieneyl singlet signals in a ratio of 1.1:1.3:5.5:1. On slow evaporation of a diethyl ether/hexane solution (in air), crystals suitable for X-ray analysis were obtained (Figure 1). The X-ray structure confirmed the identity of **3** and the NMR spectrum contained one singlet signal in the cyclopentadienyl region which corresponded to the major peak in the impure material.[17]

The two newly formed cyclobutadiene rings are separated by only 2.378 Å and this forces the cobalt η^5-cyclopentadienyl units to sit on opposite faces of the plane of the new ring construct. The use of an excess of **5** prepared in situ does not

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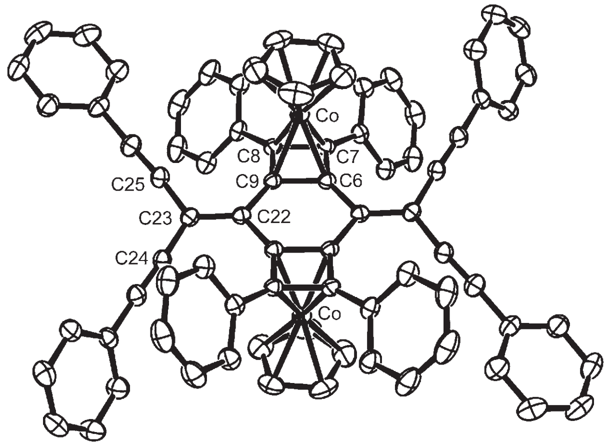
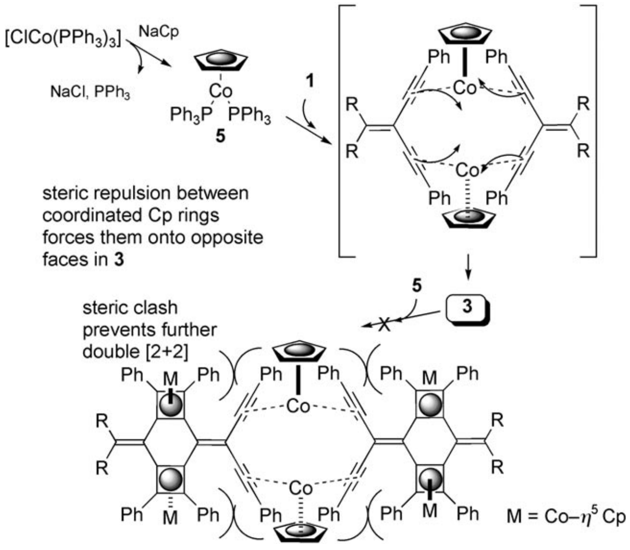


Figure 1. X-ray crystal structure of **3** with the solvent of crystallization and protons omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths [Å], angles [°] and torsions [°]: C6–C7 1.468(2), C7–C8 1.474(2), C8–C9 1.475(2), C9–C22 1.458(2), C22–C23 1.380(2); C6-C9-C22 124.55(14), C22-C9-C8 144.18(15), C9-C22-C23-C25 16.56.[18]

lead to formation of oligomers since steric congestion prevents the alkynes of **3** adopting the necessary conformation (Scheme 3). The steric congestion within **3** is reflected in a C9-C22-C23-C25 torsion angle of 16.6°, widening of the C22-C23-C24 and C22-C23-C25 angles (121.35(15)° and 123.30(15)°, respectively), and reduction in the C24-C23-C25 angle (115.30(15)°). However, a C22–C23 distance of 1.380(2) Å clearly indicates the dominance of double bond character in this portion of the molecule.

We are looking to exploit this novel reaction for the assembly of less sterically congested constructs which will allow oligomerization. Incorporation of similar binuclear motifs into polynuclear systems for advanced materials and molecular electronics is another application we are actively investigating.[19,20]



Scheme 3. Proposed mechanism for the formation of **3** and rationale for the hindrance of subsequent reactions.

Experimental Section

NMR spectra were recorded on Bruker AV250, AV300, and AV400 spectrometers in $CDCl_3$, residual chloroform peaks served as internal standards. X-ray analyses were performed on a Nonius KappaCCD diffractometer. $[CoCl(PPh_3)_3]$ was freshly prepared according to a standard method.[21] Tetraphenylethynylethylene (**1**) was prepared according to the literature procedure and the spectroscopic data obtained were in agreement with those reported.[12,22]

Synthesis of the binuclear cobalt complex **3**: $[CoCl(PPh_3)_3]$ (0.31 g, 0.35 mmol) and **1** (0.17 g, 0.40 mmol) were added to a dried flask under nitrogen. Toluene (3 mL) and sodium cyclopentadiene in THF (0.1 mL of a 1M solution, 1.07 mmol) were then added and the reaction mixture heated to reflux for 17 h. The mixture was cooled and the solvent removed in vacuo. The resulting brown oil was purified by flash chromatography on silica gel (hexane/CH_2Cl_2 4:1) and a yellow band (**1**) and a red band were collected. Slow evaporation of a portion of the red band from hexane/Et_2O in air afforded an initial crop of deep red crystals of **3** (Figure 1). Further crops were obtained by slow evaporation from hexane to give an overall yield of 3%. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.01$ (10H, s, Cp C*H*), 6.82 (8H, d $J = 7.5$, Ar C*H*), 6.91 (4H, t, $J = 7.0$, Ar C*H*), 7.03 (8H, t, $J = 7.5$, Ar C*H*)), 7.10 (8H, t, $J = 7.5$, Ar C*H*), 7.20 (4H, t, $J = 7.5$, Ar C*H*), 7.61 ppm (8H, d, $J = 8.4$, Ar C*H*); ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): $\delta = 68.1$ (cyclobutadiene *C*), 69.2(cyclobutadiene *C*), 81.8 (Cp *C*H), 93.7 (C≡*C*), 123.8 (Ar *C*H), 126.5 (Ar *C*H), 126.9 (Ar *C*H), 127.6 (Ar *C*H), 130.6 (Ar *C*H), 130.6 (Ar *C*H),135.7 (Ar *C*), 135.9 (Ar *C*), 148.1 (C=*C*), 174.8 ppm (*C*=C), second (*C*≡C) not observed.

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[11] We envisaged a metal-binding contribution to the stability of the central alkene in which communication between the metals would be possible, and considered how rearrangement/retro reaction sequences would be useful in synthesis.

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[17] With the NMR spectroscopic data of **3** in hand, retrospective analysis of the NMR spectrum of the mixture suggested that the other three compounds were isomers of alkyne-coordinated cobalt η^5-cyclopentadienyl (that is, noncyclized) complexes.

[18] Space group = $P2_1/n$, $Z=4$, $a=13.2770(2)$, $b=11.9070(2)$, $c=19.0580(3)$ Å, $\beta=92.584(1)°$, $U=3009.80(8)$ Å^3. The asymmetric unit contains $^1/_2$ of a dimer **3** and $^1/_2$ of a hexane molecule. Both fragments are proximate to crystallographic inversion centers which serve to generate the remaining portions of each entity. CCDC-624438 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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