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(Tetravinylcyclobutadiene)cyclopentadienylcobalt: Serendipity at Work

Gaby Roidl,[†,‡] Volker Enkelmann,[‡] and Uwe H. F. Bunz*[,†]

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208, and Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, 55021 Mainz, FRG

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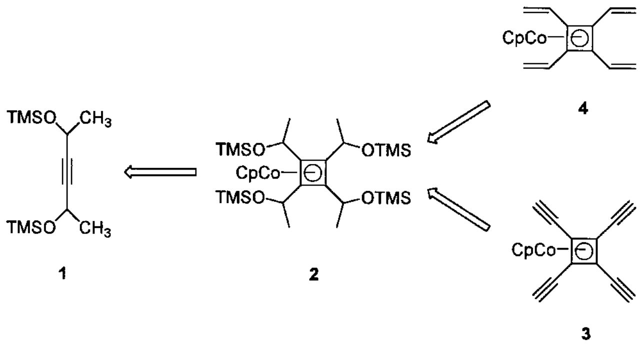
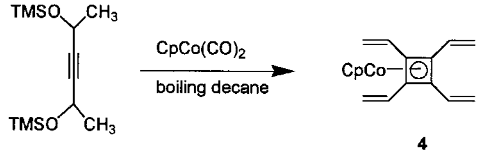
Summary: Dimerization of 2,5-bis(trimethylsilyl)-3-hexyne-2,5-diol over CpCo(CO)$_2$ in n-decane yields brown crystals of the (tetravinylcyclobutadiene)cyclopentadienylcobalt complex **4***. A single-crystal structure of* **4***, the first unsubstituted, pervinylated π-complex, was obtained.*

Multiply alkynylated π-perimeters are now an established class of fascinating compounds in organic[1] and organometallic[2] chemistry. A series of peralkynylated benzenes, cyclopentadiene/cyclopentadienyl complexes, and cyclobutadiene complexes has been made during the past decade, with the goal of accessing novel all-carbon networks radically differing in both topology and properties from graphite, diamond, or the fullerenes.[1,2]

Surprisingly enough, much less is known about the corresponding per*ethenylated* π-perimeters, and only very recently, de Meijere[3] was able to prepare a series of hexaalkenylated benzenes by Suzuki and Stille coupling of hexabromobenzene with the corresponding substituted alkenylboronic acids or alkenylstannanes. de Meijere's work includes an organometallic derivative, obtained by complexation of a substituted hexaethenylbenzene with a Cr(CO)$_3$ source. However, all of the organic and organometallic examples described were highly substituted (either tertiary or trimethylsilyl substituents), so that this route does not seem to permit access to the corresponding parent, vinylated π-perimeters.

We targeted complex **2** as a versatile module for both a solution-phase route to **3** and as a convenient precursor for the tetravinyl cyclobutadiene complex **4**. Both are attractive due to their structure and potential reactivity. From previous studies we knew that protected propargylic alcohols do undergo facile cyclobutadiene formation under the influence of CpCo(CO)$_2$, so that the exploitation of the easily accessible bis(trimethylsilyl) ether **1** should furnish the module **2** in a one-step reaction.[4]





We attempted dimerization of **1** in the presence of CpCo(CO)$_2$ in boiling *n*-decane.[5−7] Surprisingly, we were not able to obtain complex **2**, although mass spectroscopic analysis showed its presence in small amounts. Instead, we isolated as the sole product a crystalline tan material (6.4% yield) which showed in its ^{1}H NMR spectrum one singlet at δ 4.59 (5 H) and three doublets of doublets at δ 5.24, 5.48, and 6.56. The corresponding ^{13}C NMR spectrum was simple and displayed reso-

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[†] University of South Carolina.

[‡] Max-Planck-Institut für Polymerforschung.

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(6) Synthesis of 2,5-bis(trimethylsilyl)-3-hexyne-2,5-diol (**1**) and 4-(trimethylsilyl)-2-((trimethylsilyl)oxy)butyne was achieved by reaction of the unprotected alcohol with 2 equiv of BuLi/THF at 0 °C followed by reaction of the resulting dianion with chlorotrimethylsilane.

(7) It is important to clean the used glassware before use thoroughly in a 2-propanol/KOH bath. 2,5-Bis((trimethylsilyl)oxy)hex-3-yne (34.4 g, 133 mmol) and CpCo(CO)$_2$ (12.0 g, 66.6 mmol) were dissolved in 100 mL of decane and refluxed for 20 h. A constant flow of nitrogen was led through the solution. Following the removal of the solvent by distillation (10^{-1} Torr, 35 °C), the residue was redissolved in hexane and this solution filtered through silica gel/Celite, followed by chromatography with hexanes as eluent to furnish **4** (2.41 g, 6.4%) as the sole product. **4**: ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 4.59 (s, 5 H, Cp H), 5.21, 5.22, 5.26, 5.27 (dd, 4 H, vinyl H), 5.43, 5.44, 5.52, 5.53 (dd, 4 H, vinyl H), 6.44, 6.49, 6.53, 6.58 (dd, 4 H, vinyl H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 74.6 (4 C, cyclobutadiene C), 82.1 (5 C, Cp C), 113.6, 133.1 (2 C, vinyl C); IR ν 3092, 3062, 3005, 2958, 2925, 1619, 1611, 886, 807 cm^{-1}; MS (EI): m/z calcd for M$^+$ (C$_{17}$H$_{17}$Co), found 279.9.

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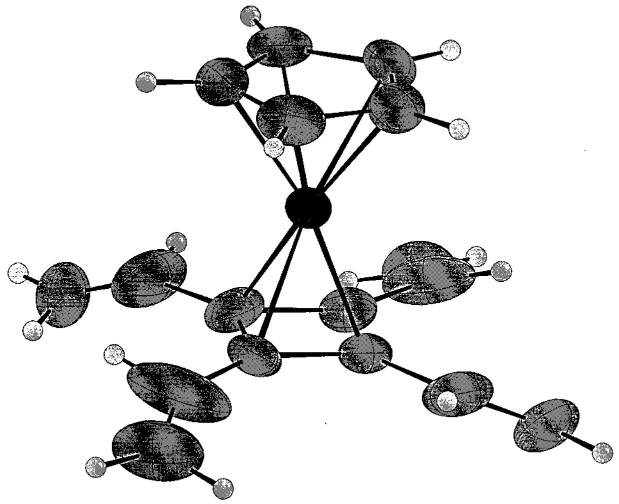


Figure 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4

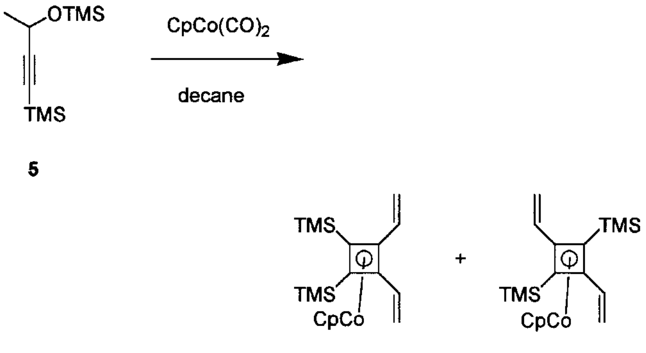
C(1)−C(2)	1.42(2)	C(4)−C(11)	1.49(2)
C(1)−C(4)	1.43(2)	C(5)−C(6)	1.18(2)
C(2)−C(3)	1.40(2)	C(7)−C(8)	1.21(2)
C(3)−C(4)	1.45(2)	C(9)−C(10)	1.06(2)
C(1)−C(5)	1.51(2)	C(11)−C(12)	1.11(2)
C(2)−C(7)	1.45(2)	C(13)−C(14)	1.38(3)
C(3)−C(9)	1.43(2)		
C(2)−C(1)−C(4)	90.2(12)	C(1)−C(5)−C(6)	131.2(27)
C(1)−C(2)−C(3)	91.0(11)	C(2)−C(7)−C(8)	134.0(23)
C(2)−C(1)−C(5)	129.4(16)	C(3)−C(9)−C(10)	148.5(32)
C(4)−C(1)−C(5)	140.5(17)	C(4)−C(11)−C(12)	141.0(33)

nances at δ 74.6 (s), 82.1 (d), 113.6 (d), and 133.1 (d). *Both ^1H and ^{13}C NMR spectral data were only compatible with structure **4**.*[6,7]

A suitable specimen was grown from dichloromethane to obtain an X-ray crystal structure of this complex corroborating the unexpected structure (see Figure 1).[8] It is to our knowledge the first terminally unsubstituted pervinylated π-complex. Its bond lengths and angles (Table 1) are in excellent agreement with expected values.[2]

The cyclobutadiene complex **4** is comparatively sensitive, and after isolation only part of the material redissolves in dichloromethane after 2 h at ambient temperature. The remaining substance is insoluble, infusible, and amorphous; therefore, we can exclude a topochemical solid-state reaction of **4**. The observed instability of **4** explains the low isolated yields in this reaction. We assume that the corresponding tetrahydroxy trimethylsilyl complex **2** is an intermediate, which in boiling decane quickly loses trimethylsilanol under double-bond formation catalyzed by traces of electrophilic impurities. It is known that positive charges α to a CpCo(cyclobutadiene) unit are strongly stabilized,[9] perhaps even more so than by a ferrocenyl[10] or a phenylchromium tricarbonyl unit.[11] This activation probably leads to the unexpected formation of **4** as the main product in the dimerization reaction of **1**.

To understand the system better, we attempted to synthesize the corresponding [1,2-bis(trimethylsilyl)-divinylcyclobutadiene]- and [1,3-bis(trimethylsilyl)divinylcyclobutadiene]cyclopentadienylcobalt complexes, to obtain more information about the stability of vinyl-substituted cyclobutadiene complexes. Dimerization of bis(trimethylsilyl)butyn-2-ol (**5**) over $CpCo(CO)_2$ leads to a 1:1.3 (isolated ratio) mixture of two compounds, to which we assign according to their ^1H NMR data the structures **6** and **7** (combined yield of 5.8%). Again the products are comparatively sensitive toward decomposition when kept as neat substances. Careful thick-layer chromatography led to the isolation of one isomer (purity >90%). It was fully characterized, and due to its elution behavior we tentatively assign this compound a 1,3-substitution pattern, i.e., **7**.[12]



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6 **7**

In conclusion we made divinylated cyclobutadiene complexes (**6**, **7**) and (tetravinylcyclobutadiene)cyclopentadienylcobalt (**4**) accessible by a simple one-step dimerization of trimethylsilyl-substituted propargylic alcohols mediated by $CpCo(CO)_2$. Compound **4** is the first pervinylated cyclobutadiene complex reported. It has been structurally characterized. We are currently examining **4** with respect to its thermolysis under flash vacuum pyrolytic conditions.

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Supporting Information Available: Tables of positional and thermal parameters for **4** (2 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for **4**: crystal structure analysis was carried out on a Nonius KCCD diffractometer using Mo Kα radiation at room temperature; structure was solved by heavy-atom methods (Patterson); orthorhombic, $P2_12_12_1$, $a = 8.434(1)$ Å, $b = 9.642(1)$ Å, $c = 17.913(2)$ Å, $V = 1556.7$ Å^3, $D_{calcd} = 1.278$ g/cm^3; $\mu = 11.549$ cm^{-1}; 1815 reflections, 988 observed; final $R = 0.046$, $R_w = 0.059$.

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(12) In 100 mL of decane 4-(trimethylsilyl)-2-((trimethylsilyl)oxy)-butyne (10.0 g, 47.0 mmol) and $CpCo(CO)_2$ (4.21 g, 23.4 mmol) were dissolved and refluxed for 8 h. A constant flow of nitrogen was led through the solution. Removal of the solvent by distillation (10^{-1} Torr, 35 °C) and filtration of the residue through silica gel/Celite was followed by chromatography with hexane as eluent to yield **6** and **7** as a mixture. Careful thick-layer chromatography made the isolation of one isomer (**7**) possible. **7**: ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 18 H, TMS H), 4.74 (s, 5 H, Cp H), 5.09−5.12 (d, 2 H, vinyl H), 5.27−5.28 (d, 2 H, vinyl H), 6.25−6.32 (q, 2 H, vinyl H); ^{13}C NMR (400 MHz, $CDCL_3$) δ 1.37 (6 C, TMS C), 80.3 (5 C, Cp C), 112.9 (2 C, vinyl C), 134.2 (2 C, vinyl C), 79.5, 85.0 (4 C, cyclobutadiene C); MS (EI) m/z calcd for M^+ ($C_{19}H_{29}CoSi_2$) 372.54, found 372.