

The alkyne-anion promoted ring-contraction of hexachlorotropone: synthesis and structure of [trimethylsilyl(pentachlorobenzoyl)ethyne]-hexacarbonyldicobalt

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Abstract

The reaction of hexachlorotropone with trimethylsilylethynyl-lithium leads to contraction of the seven-membered ring via a semibenzilic acid rearrangement to yield pentachlorophenyl trimethylsilylethynyl ketone, **4**. Treatment of **4** with dicobalt octacarbonyl yields the corresponding alkyne-dicobalt hexacarbonyl, **6**, which has been characterized by X-ray crystallography. © 2003 Elsevier B.V. All rights reserved.

Keywords: Hexachlorotropone; Alkyne dicobalt hexacarbonyl; Ring contraction

1. Introduction

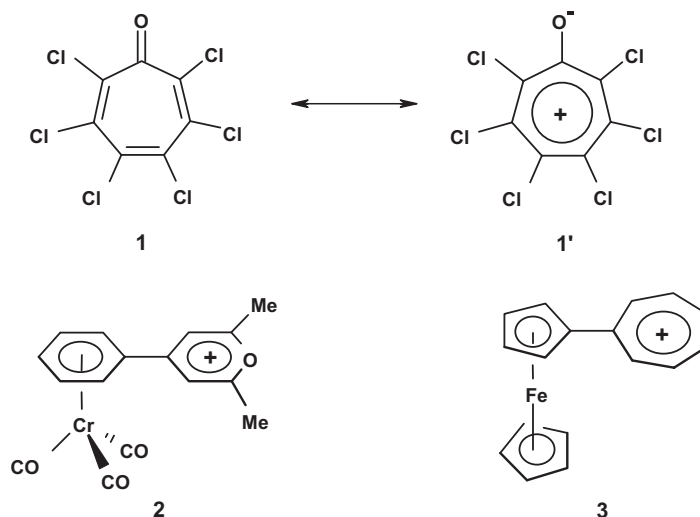
Previous reports from this laboratory have described the syntheses, structures and dynamics of a variety of metal-stabilized carbocations. These have encompassed cobalt and molybdenum complexes of formally non-classical systems, such as the 2-bornyl or 2-fenchyl cations [1–5], cobalt and iron derivatives of the cyclopentadienyl, indenyl and fluorenyl cations which possess 4π , 8π and 12π electrons, respectively, and are formally antiaromatic [6], and also chromium-stabilized benzyl cations [7]. In such cases, the cationic carbon leans toward the relatively electron-rich metal so as to alleviate the electron deficiency by direct overlap with a filled metal orbital [8].

These concepts have now been applied to another aspect of our research interests, namely sterically crowded molecules [9], in particular to chlorocarbon chemistry [10]. Since we have recently shown that the $C_7Ph_7^+$ cation adopts a shallow boat-like structure [11], one might envisage similar behaviour for the perchlo-

rotropylium cation, $C_7Cl_7^+$, which is readily synthesizable [12] but whose structure has not, to our knowledge, been reported. Moreover, the closely analogous hexachlorotropone, C_7Cl_6O **1**, has also been crystallographically characterized as a shallow boat [13,14]; apparently, the bulky chloro substituents do not permit the ring to maintain the electronically favoured planar geometry. If the canonical contributor **1'** is considered, then the geometries exhibited by C_7Cl_6O and $C_7Cl_7^+$ may be in close accord. If the polychlorinated tropylium cation is indeed puckered, then it would be of interest to probe the electronic demand that such a species would impose upon a metal center.

Our goal was to prepare a system of the type $[(C_7Cl_6)ML_n]^+$, where ML_n is an organometallic moiety, such as $(RC\equiv C)Co_2(CO)_6$ or ferrocenyl, both of which are known to stabilize a neighbouring carbocationic site [8,15]. In cases where the ligand itself is stable as a cation, such as in the $(C_6H_5)Cr(CO)_3$ -pyrylium salt, **2** [16], or the ferrocenyl-tropylium cation, **3** [17], the cyclic π system retains its planarity since it has no need for additional stabilization from the metal center. We here report an attempt to prepare an alkynyl-dicobalt hexacarbonyl derivative of the hexachlorotropylium cation, and describe the structure of the resulting product.

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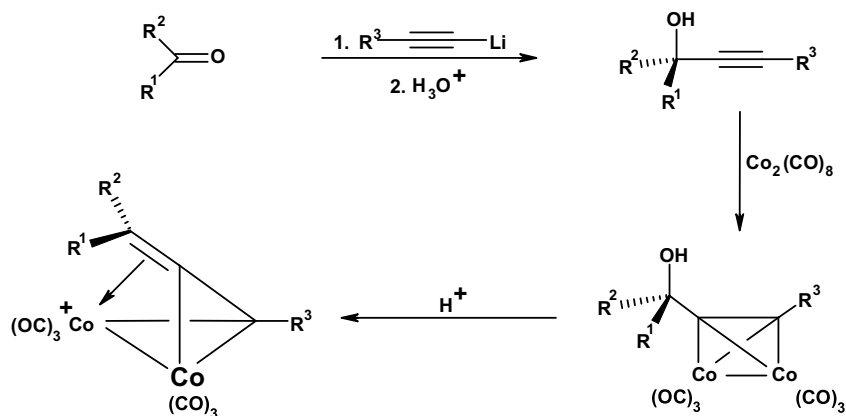
2. Results and discussion

As depicted in Scheme 1, the standard route to alkynyl-dicobalt hexacarbonyl stabilized carbocations involves (i) synthesis of an appropriate ketone, (ii) nucleophilic attack by an alkynyl anion to form the precursor alcohol, (iii) incorporation of the organometallic moiety, and (iv) protonation to generate the desired carbocation.

Consequently, hexachlorotropone was treated with trimethylsilylethynyl-lithium at $-78\text{ }^{\circ}\text{C}$ and then hydrolysed with water. The resulting product, **4**, obtained in 51% yield, was not the anticipated 7-trimethylsilylethynyl-1,2,3,4,5,6-hexachlorocycloheptatrien-7-ol, **5**, since the isotopic distribution pattern of the parent ion in the mass spectrum clearly indicated the presence of only five chlorines. The ^{13}C NMR spectrum exhibited four resonances at δ 137.5, 135.7, 132.9, and 128.8 with the intensity ratio 1:1:2:2, as well as a signal at δ 173.5 (IR ν_{CO} at 1683 cm^{-1}), suggesting the formation of a benzenoid product whereby the ketone functionality had

remained intact. These data indicated that the molecule had undergone a semibenzylic acid rearrangement [18] with concomitant ring contraction of the original seven-membered ring, as indicated in Scheme 2.

To verify that this rearrangement had indeed occurred, the alkyne unit in **4** was allowed to react with dicobalt octacarbonyl, and X-ray quality crystals of **6** were obtained. The resulting structure appears as Fig. 1, and unambiguously verifies the identity of the precursor **4**. The molecule exhibits bond lengths and angles that are within the normal ranges (Table 1), and the crystallographic collection and refinement parameters are summarized in Table 2. There are several interesting features of the structure, in particular the effects of steric hindrance on the orientation of the substituents. The carbonyl groups of the $\text{Co}(\text{CO})_3$ fragments are almost perfectly eclipsed, each having one CO aligned so as to bisect the $\text{C}\equiv\text{C}$ bond. Moreover, to avoid steric congestion, the TMS group adopts a conformation in which two of the methyl groups are directed away from the carbonyl groups. The pentachlorophenyl ring is twisted



Scheme 1.

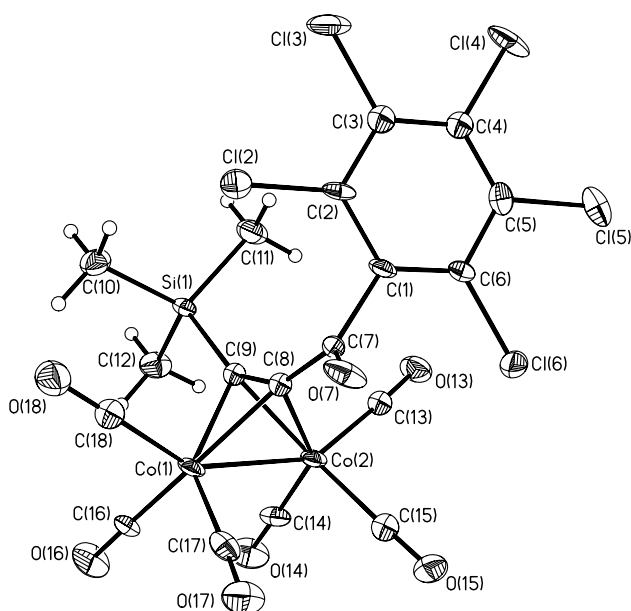
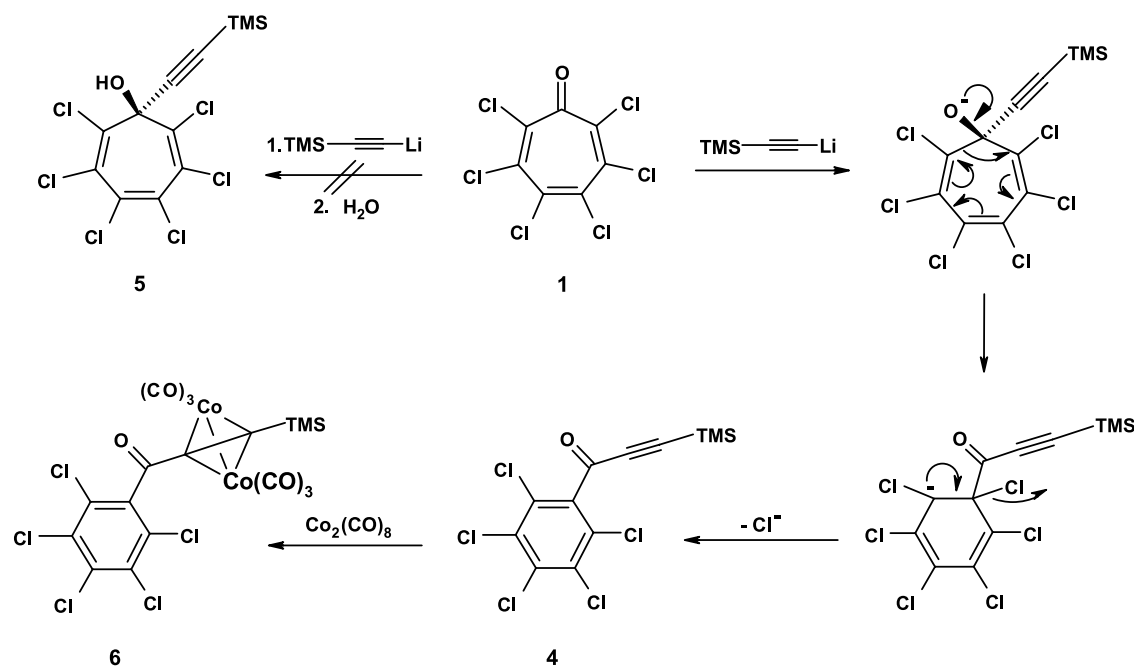


Fig. 1. X-ray crystal structure of cobalt carbonyl complex **6**.

at an angle of 22° from the plane formed by the two cobalt atoms and the center of the $C\equiv C$ bond, an arrangement that minimizes interactions of the chlorine atoms with the carbonyl groups and the methyl groups of the TMS.

In seeking precedents for such behaviour, we note that hexachlorotroponone has been reported to undergo ring contraction to give methyl pentachlorobenzoate when treated with methanol [12,13]. Analogously, **1** reacts with dimethoxycarbene to yield methyl 2-penta-

Table 1
Selected bond lengths (\AA) and angles ($^\circ$)

| | |
|---------------------------------|-----------|
| C–Cl(average) | 1.719(10) |
| C(7)–O(7) | 1.199(12) |
| C(7)–C(8) | 1.449(13) |
| C(8)–C(9) | 1.341(13) |
| Co(1)–Co(2) | 2.476(2) |
| C(8)–Co(1) | 1.951(10) |
| C(8)–Co(2) | 1.970(9) |
| C(9)–Co(1) | 1.998(10) |
| C(9)–Co(2) | 1.977(9) |
| Si(1)–CH ₃ (average) | 1.856(11) |
| C(9)–Si(1) | 1.866(10) |
| C=O (average) | 1.133(12) |
| Aromatic C–C (average) | 1.389(15) |
| C(7)–C(8)–C(9) | 148.1(9) |
| Si(1)–C(9)–C(8) | 148.7(7) |
| Si(1)–C(9)–C(8)–C(7) | 11(3) |
| C(1)–C(7)–C(8)–C(9) | 32(2) |

chlorophenyl-2-oxo-ethanoate [19], as depicted in Scheme 3. Attempts to prepare **5** by an alternative route are continuing.

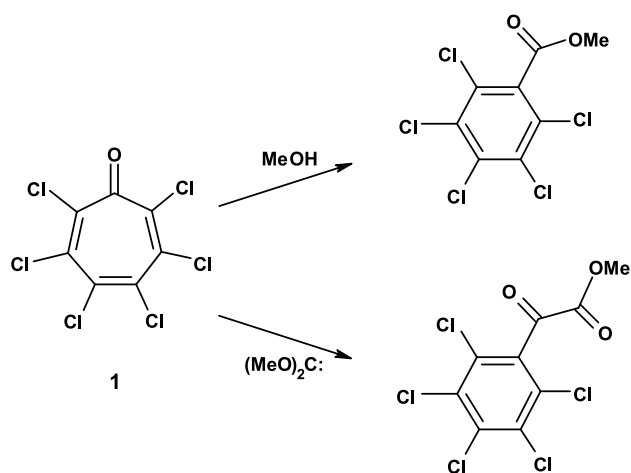
3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. Silica gel (particle size 20–45 μm) was used for flash chromatography. ^1H and ^{13}C NMR data were obtained on Bruker DRX 500 or AM 200 spec-

Table 2
Crystallographic collection and refinement parameters for **6**

| | |
|--|--|
| Empirical formula | C ₁₈ H ₉ Cl ₅ Co ₂ O ₇ Si |
| Molecular weight (g mol ⁻¹) | 660.45 |
| Description | Red plate |
| Size (mm ³) | 0.05 × 0.10 × 0.15 |
| Temperature (K) | 213(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> (Å) | 7.8366(3) |
| <i>b</i> (Å) | 31.5681(18) |
| <i>c</i> (Å) | 20.0254(11) |
| α (°) | 90 |
| β (°) | 91.535(3) |
| γ (°) | 90 |
| Volume (Å ³) | 4952.2(4) |
| <i>Z</i> | 8 |
| Calculated density (Mg/m ³) | 1.772 |
| Scan mode | ϕ - and ω -scans |
| Absorption coefficient (mm ⁻¹) | 1.964 |
| F(000) | 2608 |
| θ range for data collection (°) | 2.13–24.00 |
| Index ranges | $-4 \leq h \leq 8$ $-36 \leq k \leq 35$ $-22 \leq l \leq 21$ |
| Reflections collected | 27466 |
| Independent reflections | 7751 [<i>R</i> (int) = 0.1263] |
| Data/restraints/parameters | 7751/0/596 |
| Goodness-of-fit on F ² | 0.995 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0773, <i>wR</i> ₂ = 0.1775 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.1550, <i>wR</i> ₂ = 0.2190 |
| Transmission (ratio of max. to min.) | 1.32402 |
| Largest diff. peak and hole (e Å ⁻³) | 1.253 and -1.033 |



Scheme 3.

trometers. Mass spectra were acquired on a Finnigan 4500 spectrometer by direct electron impact (DEI), or direct chemical ionization (DCI) with NH₃. All masses quoted are for the lowest value of *m/z* in the envelope and correspond to ³⁵Cl; the observed signal intensities correctly matched the isotopic pattern required for the number of chlorine atoms in the fragment ion.

Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada.

3.2. Hexachlorotropone (**1**)

C₇Cl₆O was synthesized according to the literature procedure [12] as a yellow solid, mp 82–83 °C (82.5 lit) and identified by conventional spectroscopic techniques. ¹³C NMR (50.3 MHz, CDCl₃) δ 177.5, 136.6, 134.5, 132.4; MS (DEI; *m/z*): 310 [M]⁺, 282 [M-CO]⁺ (100%), 247 [C₆Cl₅]⁺, 212 [C₆Cl₄]⁺, 177 [C₆Cl₃]⁺, 142 [C₆Cl₂]⁺, 107 [C₆Cl]⁺; (DCI *m/z*): 328 [M+NH₄]⁺.

3.3. Pentachlorophenyl trimethylsilyl ethynyl ketone (**4**)

n-Butyllithium (0.75 ml of a 1.44 M hexane solution, 1.08 mmol) was added dropwise over a 15 min period to a solution of trimethylsilylacetylene (0.14 ml, 0.99 mmol) in ether at -78 °C *via* cannula and the solution was allowed to warm to 0 °C. After stirring for 1.5 h, the solution was then cooled to -78 °C and C₇Cl₆O (201 mg, 0.64 mmol) dissolved in ether (40 ml) was added dropwise. The solution was slowly warmed to room temperature, stirred for a further 24 h, quenched with distilled water and extracted with ether to yield a white powder (123 mg, 0.33 mmol, 51%), mp 128–130 °C. ¹H

NMR (500 MHz, CDCl₃) δ 0.24 (Me₃Si); ¹³C NMR (125 MHz, CDCl₃) δ 173.5, 137.5, 135.7, 132.9, 128.8, 105.0, 100.5, -1.0; MS (DEI, *m/z*): 275 [C₆Cl₅CO]⁺, 247 [C₆Cl₅]⁺, 212 [C₆Cl₄]⁺, 177 [C₆Cl₃]⁺, 142 [C₆Cl₂]⁺, 107 [C₆Cl]⁺; (DCI *m/z*): 390 [M+NH₄]⁺. Calc. for C₁₂H₉Cl₅SiO: C, 38.48; H, 2.42. Found: C, 38.56; H, 2.30.

3.4. (Pentachlorophenyl trimethylsilylethynyl ketone) dicobalt hexacarbonyl (**6**)

Me₃Si—C≡C—C(=O)C₆Cl₅, **4**, (70 mg, 0.19 mmol) was dissolved in THF (20 ml) and added dropwise over a 45 min period to dicobalt octacarbonyl (64 mg, 0.19 mmol) dissolved in THF (20 ml). The solution was then allowed to stir for 24 h at room temperature. After removal of solvent, the residue was subjected to flash chromatography, using hexanes as eluent, to give dark red crystals of **6** in essentially quantitative yield. ¹H NMR (200 MHz, CD₂Cl₂) δ 0.27; ¹³C NMR (125 MHz, CD₂Cl₂) δ 199.0, 191.4, 140.2, 135.0, 132.8, 128.5, 106.0, 98.2, 1.2; MS (DEI, *m/z*): 658 [M]⁺, 275 [C₇Cl₅O]⁺. Calc. for C₁₈H₉Cl₅Co₂O₇: C, 32.73; H, 1.37. Found: C, 32.98; H, 1.02. The cobalt complex was recrystallized from hexane/CH₂Cl₂ (9:1) to give crystals of X-ray diffraction quality.

3.5. Crystallographic data for **6**

X-ray crystallographic data for **6** were collected from a suitable sample mounted with epoxy on the end of a thin glass fiber. Data were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1 K CCD area detector (employing the program SMART [20]) and a rotating anode utilizing graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data processing was carried out by use of the program SAINT [21], while the program SADABS [22] was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct-methods procedure in the Bruker SHELXL [23] program library and refined by full-matrix least-squares methods on F². All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were added as fixed contributors at calculated positions with isotropic thermal parameters based on the carbon atom to which they are bonded.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 208710. Copies of this information

may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

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