

Cyclopentadienyl Cobalt Cluster Complexes Containing the Furyne Ligand

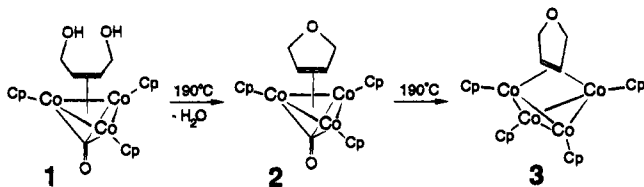
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The ability of transition metals to stabilize metastable organic ligands was first predicted by Longuet-Higgins and Orgel¹ and thereafter illustrated by the isolation² and characterization³ of the cyclobutadiene complex $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_4)$. Another family of strained ring organic molecules which are stabilized by complexation to single or assemblies of metal atoms are the cycloalkynes. Recently, examples of the first stable complexes containing four-,⁴ five-,⁵ and six-membered⁶ cycloalkynes have been described. In the course of investigating alkyne scission reactions, we have discovered a unique method of preparing the first examples of stable *furyne*-containing⁷ cluster complexes of cobalt. Here we describe a preliminary account of their syntheses and properties.

Heating the butynediol complex⁸ $\text{Cp}_3\text{Co}_3(\text{CO})(\eta^2\text{-}\mu_3\text{-RCCR})$ ($\text{R} = \text{CH}_2\text{OH}$) (**1**) in refluxing decalin for 4 h yields the trinuclear furyne complex $\text{Cp}_3\text{Co}_3(\text{CO})(\text{CCCH}_2\text{OCH}_2)$ (**2**) in 70% yield after chromatography. Prolonged heating (24 h) of **1** or **2** leads to a second furyne complex $\text{Cp}_4\text{Co}_4(\text{CCCH}_2\text{OCH}_2)$ (**3**), wherein cluster nuclearity has increased to four. The



formation of the furyne ring in **2** appears to be an intramolecular dehydration which is assisted by complexation of the alkyne to the tricobalt cluster.⁹ Both furyne complexes have been fully characterized,¹⁰ and the solid state structures of both have been determined.

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(7) IUPAC name: 1-oxa-3-cyclopentyne.

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(9) Similar formation of **2** is also observed in refluxing isoquinoline (bp 242 °C) but not in pyridine (bp 115 °C) or toluene (111 °C).

(10) Spectroscopic and analysis data. **2**: ¹H NMR (400 MHz, C₆D₆, 7.15 ppm) 4.44 (Cp), 5.26 (CH₂); ¹³C {¹H} NMR (100 MHz, CD₂Cl₂, 53.8 ppm) 85.05 (Cp), 82.23 (CH₂), 153.53 (C≡C), 284.25 (CO). Anal. Calcd for C₂₀H₁₉Co₃O₂: C, 51.31; H, 4.09. Found: C, 51.02; H, 4.02. **3**: ¹H NMR 4.43, 4.37 (Cp), 5.64 (CH₂); ¹³C {¹H} NMR 81.67, 81.23 (Cp), 87.79 (CH₂), 187.18 (C≡C); HRMS calcd for C₂₄H₂₄Co₄O 563.9155, found 563.9163.

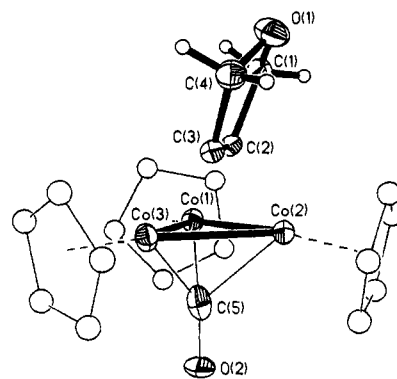


Figure 1. Molecular structure of $\text{Cp}_3\text{Co}_3(\text{CO})(\text{CCCH}_2\text{OCH}_2)$ (**2**). Selected bond distances (Å): $\text{Co}(1)\text{--Co}(2) = 2.437(1)$, $\text{Co}(2)\text{--Co}(3) = 2.461(1)$, $\text{Co}(3)\text{--Co}(1) = 2.561(1)$, $\text{C}(1)\text{--C}(2) = 1.495(8)$.

Figure 1 illustrates the X-ray crystal structure of **2**.¹¹ The alkyne bond of the furyne ring interacts with the triangle of cobalt atoms in an $\eta^2\text{-}\mu_3$ fashion while the carbonyl ligand is found bridging the opposite side of the triangle of metal atoms. Both ligands are unsymmetrically disposed over the Co_3 triangle with the furyne ligand shifted toward one edge of the triangle and tilted by an angle of 18° toward the opposite cobalt atom. The oxygen atom of the five-membered furyne ligand deviates significantly (15°) from the mean plane of the carbons, leading to a puckering of this ring. There is, however, no interaction between the furyne oxygen and any part of the metal skeleton. The furyne ligand can be formally considered a four-electron donor ligand to the trinuclear cluster such that the overall valence count for the complex is 48, as expected for a closed shell trinuclear ring cluster.¹²

The combination of σ -donation and π -acceptance between the alkyne carbons and the metal atoms leads to two well-known structural changes in the alkyne group: lengthening of the C–C bond distance and bending of the alkyne substituents away from a linear orientation preferred by this group. Complexation and formation of the five-membered ring reduces the angle through the alkyne unit to 109° ($\text{C}_2\text{--C}_3\text{--C}_4$) and causes appreciable elongation of the $\text{C}_2\text{--C}_3$ separation to 1.374(9) Å.¹³ A measure of the *additional* deformation in the alkyne structural parameters caused by ring formation in **2** may be obtained by comparison with the corresponding parameters observed in the analogous 3-hexyne complex⁸ wherein the alkyne bond length and bending angle are found to be 1.370(5) Å and 127°. Thus, formation of the five-membered furyne ring in **2** causes no significant lengthening of the alkyne C–C bond but does reduce the angle of the alkyne unit by approximately 18°.

The structure of the tetranuclear furyne complex **3** is illustrated in Figure 2.¹⁵ To our knowledge **3** is the second butterfly-type, Cp-based cobalt cluster to be reported.¹⁶ The planar furyne ligand sits symmetrically over the Co–Co hinge, interacting both with the hinge and “wingtip” cobalt atoms.

(11) Crystal data for **2** at –100 °C: black plate, $a = 9.138(2)$ Å, $b = 23.327(6)$ Å, $c = 8.835(2)$ Å, $\beta = 117.23(2)^\circ$, $V = 1674.7(7)$ Å³, monoclinic, $P2_1/c$, $Z = 4$, $D_{\text{calc}} = 1.857$ g cm^{–3}. Of the 2959 independent reflections collected, 2445 with $F_o^2 > 4\sigma(F_o^2)$ were used and gave a final $R = 0.0482$ and $R_w = 0.0615$.

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(13) Representative values for C–C bond lengths: single C–C, 1.54 Å; double C=C, 1.34 Å; triple C≡C, 1.20 Å (Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 109).

(14) The ethyl substituents of the hexyne ligand in the complex $\text{Cp}_3\text{Co}_3(\text{CO})(\text{CH}_3\text{CH}_2\text{CCCH}_2\text{CH}_3)$ are tilted away from the perpendicular to the Co_3 plane in the solid state in a manner similar to what is observed for **2**. This structural feature, however, may be due to solid state packing effects in these complexes as both ligands are observed to be highly fluxional in solution.

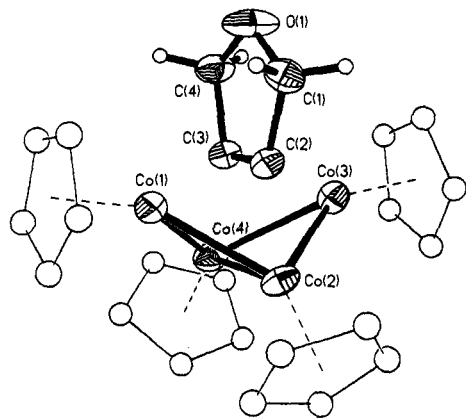


Figure 2. Molecular structure of $\text{Cp}_4\text{Co}_4(\text{CCCH}_2\text{OCH}_2)$ (**3**). Selected bond distances (Å): $\text{Co}(1)\text{--Co}(2) = 2.375(1)$, $\text{Co}(1)\text{--Co}(4) = 2.388(1)$, $\text{Co}(3)\text{--Co}(2) = 2.376(1)$, $\text{Co}(3)\text{--Co}(4) = 2.369(1)$, $\text{Co}(2)\text{--Co}(4) = 2.485(1)$, $\text{C}(1)\text{--C}(2) = 1.516(5)$.

Although traditionally considered a four-electron donor to the tetracobalt valence sphere, according to polyhedral skeletal electron pair theory, the two alkyne carbons occupy two positions of an M_4C_2 , 66-electron octahedron.¹² The structural parameters for the Co_4 butterfly unit are quite similar to those exhibited by carbonyl-alkyne analogues.¹⁷ The unsaturated C–C bond length (1.473(5) Å) observed in the furfuryne ligand in **3** is among the longest observed in any alkyne cluster complex reported to date¹⁷ and illustrates the effect that increasing the number and geometry of interacting metal atoms has on a carbon–carbon triple bond. The length of this bond is significantly longer than that observed for normal C=C double bonds and is close to the length of a typical C–C single bond (1.54). The bending angle through the alkyne in **3** is 107°.

We have characterized the interaction of the furfuryne ligand with the $\text{Cp}_3\text{Co}_3(\text{CO})$ framework in **2** through a comparison of several spectroscopic and electronic properties with those exhibited by the analogous, noncyclic dimethoxybutyne adduct

(15) Crystal data for **3** at 25 °C: black rectangular, $a = 8.564(2)$ Å, $b = 16.720(4)$ Å, $c = 14.290(4)$ Å, $\beta = 98.13(2)^\circ$, $V = 2025.5(9)$ Å³, monoclinic, $P2_1/n$, $Z = 4$, $D_{\text{calc}} = 1.850$ g cm⁻³. Of the 2836 independent reflections collected, 2436 with $F_o^2 > 4\sigma(F_o^2)$ were used and gave a final $R = 0.0309$ and $R_w = 0.0393$.

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(17) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612. The unsaturated C–C bond distance in the carbonyl-based cluster $\text{Co}_4(\text{CO})_{10}(\text{HC}_2\text{H})$ is considerably shorter (1.399(7) Å) than the distance observed in **3**.

$\text{Cp}_3\text{Co}_3(\text{CO})(\text{RCH}_2\text{CCCH}_2\text{R})$ ($\text{R} = \text{OMe}$) (**4**). The alkyne ligands in both complexes are fluxional in solution, undergoing rapid *helicopter* rotation over the Cp_3Co_3 plane at room and low (–100 °C) temperature. The ¹³C NMR shifts of the alkyne carbons of **2** and **4** (153.5 and 157.0 ppm, respectively) are quite similar, as are the CO stretching frequencies in the IR ($\nu(\text{CO})$ (CH_2Cl_2) 1680 (**2**), 1679 cm⁻¹ (**4**)). Chemically reversible, reductive, and oxidative features are observed in cyclic voltammograms of both **2** and **4**. The E_o values for both couples are again quite similar: 0.221 and –1.488 V for **2** versus 0.211 and –1.525 V for **4** (Pt electrode; 0.1 M TBAP in CH_2Cl_2 ; $\text{Fc}/\text{Fc}^+ = 0.274$ V). From the above data, formation of the five-membered furfuryne ring does not appear to alter the metal–alkyne interactions significantly in $\text{Cp}_3\text{Co}_3(\text{CO})$ –alkyne complexes.

Aside from the tremendous stabilization experienced by such a strained hydrocarbon ring, the chemical and physical properties of the ring itself and the attendant trinuclear cluster in **2** appear not to differ significantly from those exhibited by noncyclic analogues. The lack of suitable tetranuclear complexes for comparison makes it more difficult to characterize the interaction between the butterfly metal core and the furfuryne ring in **3**. However, the robust nature of the complex and the tremendous elongation of the alkyne bond observed in the furfuryne ring provide strong testimony to the importance of the interaction between the metal skeleton and this ligand in **3**. Current work on these novel complexes is proceeding in two directions. The addition of the butynediol ligand to a variety of mixed metal trinuclear complexes¹⁸ yields the desired precursors for further investigations of the ring-forming, dehydration reaction. Finally, a number of other suitably functionalized alkynes $\text{X}(\text{CH}_2)_n\text{C}\equiv\text{C}(\text{CH}_2)_m\text{Y}$ are available, the properties of which are being investigated as precursors to new ring systems in these cluster systems.

Supplementary Material Available: Listing of details of data collection and refinement of the structure determinations of **2** and **3** and full tables of atomic coordinates, anisotropic displacement factors, and bond lengths and bond angles for **2** and **3** (18 pages); structure factor tables for complexes **2** and **3** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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