

(η^5 -Bicyclo[3.2.0]hepta-1,3-dienyl)-(η^4 -cyclo-octa-1,5-diene)cobalt(i)

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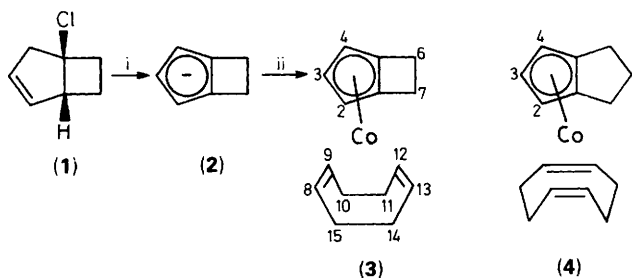
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The synthesis of the title compound is presented, and its unusual ^1H NMR data are interpreted by means of an X-ray crystal structure analysis.

Metal complexes of arene or cyclopentadienyl ligands with conformationally flexible annelated five- or six-membered rings are well known.¹ However, there are only few reports dealing with complexes of conformationally rigid small-ring-annelated arene or cyclopentadienyl ligands.^{2,3} These are of interest with regard to the influence of the co-ordination of the cyclic π system to a metal on ring opening and other reactions. Here, the synthesis and characterization of the first cobalt(i) complex of the η^5 -bicyclo[3.2.0]hepta-1,3-dienyl ligand (**2**), a cyclopentadienyl ligand with an annelated four-membered ring, are presented. Cyclopentadienyl cobalt complexes have attracted considerable interest as catalysts, e.g., for the synthesis of pyridines.⁴

A route to the title compound (**3**) was finally found by the reaction of the bicyclo[3.2.0]hepta-1,3-dienyl anion (**2**), which had first been prepared by Breslow and Oda³ from 5-chlorobicyclo[3.2.0]hept-2-ene (**1**), with a halogenated cobalt complex. While experiments with $\text{ClCo}(\text{PPh}_3)_3$ and $\text{BrCo}[\text{P}(\text{OMe})_3]_3$ failed, the preparation of the cyclo-octa-1,5-diene complex (**3**) was successful if (**2**) reacted with the sterically more demanding $\text{ClCo}[\text{P}(\text{OPri})_3]_3$ ⁵ followed by treatment with cyclo-octa-1,5-diene (cod) (Scheme 1). Purification by column chromatography and crystallization from ether gave (**3**) as brick-red slightly air-sensitive crystals (m.p. 112 °C). Complex (**3**) was identified by its spectroscopic data, and its molecular structure was determined by an X-ray crystal structure analysis.

A comparison of the ^1H NMR data† of (**3**) with those of the next higher homologue, the bicyclo[3.3.0]octa-1,3-dienyl complex (**4**),⁶ indicates that the difference between the chemical shifts of 2(4)-H and 3-H in (**3**) ($\Delta\delta$ 1.67 ppm) is more than ten times larger than the corresponding difference in (**4**) ($\Delta\delta$ 0.14 ppm). In addition, the chemical shifts of 2(4)-H and 3-H of (**3**) are unusually temperature dependent: $\Delta\delta$ becomes smaller with rising temperature ($\Delta\delta$ 1.15 ppm at 170 °C). That



Scheme 1. Reagents: i, LiNPr_2 , tetrahydrofuran (THF), -20°C ;³ ii, $\text{ClCo}[\text{P}(\text{OPri})_3]_3$, THF, -20 to 25°C , 16 h, then cod, 100°C , 4 h, 49%.

† ^1H NMR (200 MHz, C_6D_6): δ 1.7 (m, 4H, 10-, 11-, 14-, 15-H), 1.98 + 2.36 (AA'BB', $2 \times 2\text{H}$, 6-, 7-H), 2.5 (m, 4H, 10-, 11-, 14-, 15-H), 3.1 (m, 4H, 8-, 9-, 12-, 13-H), 3.16 (t, 1H, $^3J_{2(4),3}$ 2.2 Hz, 3-H), and 4.83 (d, 2H, 2-, 4-H). All other spectroscopic data and the elemental analysis are consistent with the structure assigned.

other bicyclo[3.2.0]hepta-1,3-dienyl cobalt complexes⁷ do not show similarly large $\Delta\delta$ values implies that this is not a typical feature of the bicyclic ligand, but is most likely the result of an anisotropy effect associated with the cod ligand. Apparently at higher temperatures conformations other than the energetically most favourable are increasingly populated, thus reducing the effect.

The crystal structure of (**3**) (Figure 1) shows a distorted co-ordination of the bicyclic ligand.‡ In contrast to (**4**),⁸

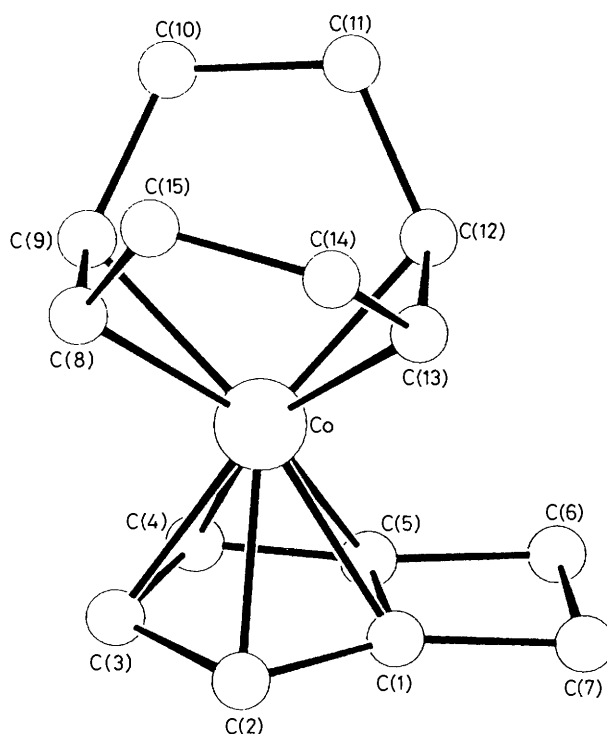


Figure 1. Crystal structure of (**3**). Selected distances (Å) and angles ($^\circ$): C(1)–C(2) 1.403(3), C(2)–C(3) 1.426(3), C(3)–C(4), 1.445(3), C(4)–C(5) 1.396(3), C(1)–C(5) 1.408(2), C(1)–C(7) 1.525(3), C(6)–C(7) 1.578(3), C(5)–C(6) 1.527(3), Co–C(1) 2.091(2), Co–C(2) 2.104(2), Co–C(3) 2.037(2), Co–C(4) 2.114(2), Co–C(5) 2.123(2), Co–C(8) 2.030(2), Co–C(9) 2.023(2), Co–C(12) 2.015(2), Co–C(13) 2.008(2); C(5)–C(1)–C(7) 93.2(1), C(1)–C(5)–C(6) 93.1(1), C(1)–C(7)–C(6) 86.9(1), C(5)–C(6)–C(7) 86.8(1).

‡ Crystal data of (**3**): $\text{C}_{15}\text{H}_{19}\text{Co}$, $M = 258.3$, monoclinic, space group $P2_1/a$, $a = 11.607(2)$, $b = 8.657(2)$, $c = 12.018(3)$ Å, $\beta = 102.04(1)^\circ$, $V = 1181.2$ Å³, $Z = 4$, $D_c = 1.45$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 14.17$ cm⁻¹; Enraf-Nonius CAD4 diffractometer, θ – 2θ scan technique; full-matrix least-squares refinement with FMLS, a highly modified version of W. R. Busing's and H. A. Levy's ORFLS, converged at $R = 0.023$, $R_w = 0.026$ [$w = 1/\sigma^2(F_o)$] for 2649 independent, 2167 observed [$I > 2\sigma(I)$] reflections and 221 refined parameters; maximum peak in final difference Fourier 0.29 e Å⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

differences in the bond lengths of the five-membered ring are observed for (3). In comparison with (4), bonds C(1)–C(2) [1.403(3) Å] and C(4)–C(5) [1.396(3) Å] are shortened by about 0.03 Å, while bond lengths C(2)–C(3) [1.426(3) Å], C(3)–C(4) [1.445(3) Å], and C(1)–C(5) [1.408(2) Å] are slightly increased. The bond C(3)–Co [2.037(2) Å] is significantly shorter than all other Co–C bonds in the system [2.091(2)–2.123(2) Å]; complex (4) does not show a similar effect.⁸ The geometry of the four-membered ring is similar to that observed in *exo*-1-methylcyclobutabenzenetricarbonylchromium(0).⁹

There is a striking difference between (3) and (4) with respect to the relative orientation of the cod ligand. Whereas in the preferred conformation of (4) the double bonds of the cod ligand are oriented nearly parallel to the bonds of the annelated ring starting from the bridgeheads,^{4,8} they are oriented nearly perpendicular to them in (3). In the preferred conformation of (3) this causes the double bond C(8)–C(9) of the cod ligand to be located relatively close to 3-H, and this may be regarded as the source of the anisochrony of 2(4)-H and 3-H.

The reactivity of the bicyclo[3.2.0]hepta-1,3-dienylcobalt complex (3) is similar to that of other cyclopentadienyl cobalt complexes.¹ Remarkably, the thermolysis of neat (3) at 260 °C yielded only cod and decomposition products. Thermolysis in tetrahydronaphthalene gave a mixture of 1-ethyl-¹⁰ and 1,2-dimethyl-cyclopentadienyl cobalt cod complexes (20%) in addition to decomposition products. The solvent presumably served as the hydrogen source. Derivatives with substituents at the four-membered ring appear to offer a more promising route to controlled ring-opening reactions. However, this calls for a new synthetic access to the corresponding anions, since the anion (2) is prepared from the symmetrical 7-methoxy-

cyclohepta-1,3,5-triene.³ Investigations are currently under way.

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