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Crystal and molecular structure of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$

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Abstract

The structure of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ has been determined by a single crystal X-ray diffraction study at −120°C. There are differences in the C–C bond lengths within the cyclopentadienyl ring that are in agreement with theoretical predictions.

Introduction

It is well known that the replacement of all the hydrogen atoms by methyl groups alters both the steric and electronic influence of the η^5-cyclopentadienyl ring, resulting in different reactivities, stabilities, solubilities, and spectroscopic properties of (η^5-pentamethylcyclopentadienyl)metal complex compared with those of their (η^5-cyclopentadienyl)metal counterparts [1]. This prompted us to investigate the molecular structure of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ (**I**), which is a liquid at ambient temperatures, and to compare it with that determined previously for $[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$ (**II**), [2]. Furthermore, it was of interest to determine the extent of localized distortion within the cyclopentadienyl ring arising from its coordination to a transition metal in order to allow comparison with that observed for **II**.

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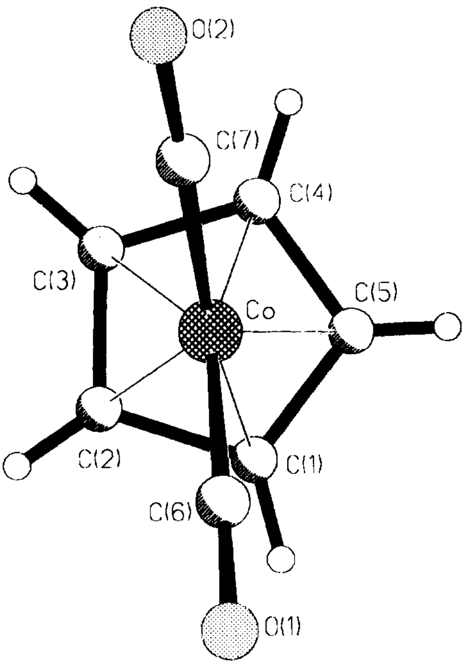


Fig. 1. View of **I**, showing atom numbering system.

Results and discussion

Crystals of complex **I** consist of discrete molecules, separated by normal van der Waals distances. The general view of the molecule **I** projected on the cyclopentadienyl plane, is shown, with the atom numbering, in Fig. 1: Bond lengths and bond angles are given in Table 1. The cyclopentadienyl-ring is planar within 0.014 Å, and the average displacement of the H atoms from the plane towards the metal atom is 0.09 Å, which is characteristic of this type of π-complex. The atoms

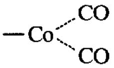
Table 1

Bond distances (Å) and angles (deg.) in **I**

Co–C(1)	2.057(3)	C(6)–Co–C(7)	94.3(1)
Co–C(2)	2.086(3)	C(2)–C(1)–C(5)	108.7(3)
Co–C(3)	2.090(3)	C(1)–C(2)–C(3)	107.6(3)
Co–C(4)	2.065(3)	C(2)–C(3)–C(4)	107.7(3)
Co–C(5)	2.109(3)	C(3)–C(4)–C(5)	109.2(3)
Co–C(6)	1.732(3)	C(1)–C(5)–C(4)	106.7(3)
Co–C(7)	1.742(3)	Co–C(6)–O(1)	179.0(3)
O(1)–C(6)	1.153(4)	Co–C(7)–O(2)	178.6(3)
O(2)–C(7)	1.132(5)		
C(1)–C(2)	1.429(5)		
C(1)–C(5)	1.411(5)		
C(2)–C(3)	1.393(5)		
C(3)–C(4)	1.424(5)		
C(4)–C(5)	1.402(5)		

Table 2

Comparison of the main geometrical parameters I–IV



N	R	Bond lengths (Å)					Bond angles (deg)		Refs.
		Co–C_{carb}	Co–Cp	O–C	C–C (eclipsed)	C–C (non-eclipsed)	C_{carb}–Co–C_{carb}	Co–C_{carb}–O	
I	H	1.732(3) 1.742(3) Avg. 1.737	1.700	1.153(4) 1.132(5) Avg. 1.143	1.429(5) 1.424(5)	1.411(5) 1.393(5) 1.402(5)	94.3(1)	179.0(3) 178.6(3)	Present work
II	Me	1.724(5) 1.732(5) Avg. 1.728	1.703	1.137(6) 1.134(6) Avg. 1.136	1.445(6) 1.447(6)	1.414(6) 1.407(6) 1.392(6)	93.7(2)	179.3(5) 179.4(5)	2
III	Bz	1.705(7) 1.644(7) Avg. 1.674	1.686	1.156(7) 1.185(7) Avg. 1.170	1.463(6) 1.460(7)	1.386(7) 1.407(7) 1.407(7)	96.0(3)	178.5(6) 176.2(7)	1
IV	Ph	1.71(1) 1.70(1) Avg. 1.705	1.70	1.15(1) 1.14(1) Avg. 1.145	1.45(1)	1.43(1) 1.44(1) 1.41(1) 1.44(1)	89.5(5)	177(1) 177(1)	1

of the $[Co(CO)_2]$ moiety are almost ideally coplanar (within 0.007 Å), and their plane forms a dihedral angle of 92.9° with the cyclopentadienyl ring plane.

The main geometrical parameters for **I** and related compounds, **II–IV** are listed in Table 2, and it is evident that the displacement of the Co atom from the cyclopentadienyl mean plane is almost the same for all the complexes **I–IV**, and thus is independent of the volume of the R substituents. Although the Co–C(CO) distances in **I** and **II** are the same within experimental error, there is apparently a slight shortening of these bonds in the series **I–II–III–IV**, probably reflecting differences in electronic properties of the cyclopentadienyl rings bearing different substituents [1]. At the same time the experimental uncertainty in the experimental data for **I–IV** precludes attempts to seek a correlation between the relative electron-withdrawing properties of the ligands R and the carbonyl C≡O bond distances.

In all the complexes **I–IV** there are distinct variations in the C–C bond lengths in the cyclopentadienyl rings. The bonds eclipsed by the carbonyl groups C(1)–C(2) and C(3)–C(4) in **I** are significantly longer than the other C–C bonds. Such C–C bond length alternation is caused by a non-cyclindrical field produced by the planar $[Co(CO)_2]$ moiety [1,2] and is in agreement with theoretical calculations [3]. It is noteworthy that similar variations in the C–C bond lengths within the cyclopentadienyl ring were observed in other complexes, *e.g.* $[Co(\eta^5\text{-}C_5H_5)(PEt_3)_2]$ [4] and $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$ [5].

Experimental

The single crystal of **I**, suitable for X-ray study, was grown from the melt in a thin-walled capillary (approx. 0.4 mm diameter) by very slow cooling of the melt

Table 3

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U
Co	1943(1)	4165(1)	1119(1)	26(1) [a]
O(1)	5300(3)	5162(3)	921(2)	45(1)
O(2)	2062(4)	2488(3)	-233(2)	57(1)
C(1)	1407(4)	5086(4)	2154(2)	41(1)
C(2)	408(5)	5669(3)	1557(2)	38(1)
C(3)	-581(4)	4660(4)	1243(2)	36(1)
C(4)	-200(4)	3456(3)	1644(2)	38(1)
C(5)	973(5)	3726(4)	2227(2)	40(1)
C(6)	3964(4)	4754(3)	1003(2)	32(1)
C(7)	2023(4)	3136(3)	305(2)	36(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

near the m.p. of -30 to -35°C. The resulting crystal was slowly cooled to -120°C and the X-ray diffraction experiment was carried out at this temperature. Crystals of **I** are orthorhombic, space group *Pbca*, $a = 7.997(2)$, $b = 10.017(2)$, $c = 17.253(3)$ Å, $V = 1382.1(9)$ Å^3, $Z = 8$; 2876 reflections were measured with a Syntex P2_1 diffractometer at -120°C (Mo-K_α radiation, θ–2θ scan, graphite monochromator, $2\theta < 54°$); 1271 of them with $F^2 > 8\sigma$ were then used in the structure solution and refinement. The structure was solved by direct methods, and refined anisotropically by least-squares techniques. In the final refinement cycles, the Seiler–Dunitz type weighting scheme with $w = (\sigma^2 F + 0.0323F^2)^{-1}$ was used; H atoms were included in fixed positions. Final R values were $R = 0.044$, $R_w = 0.046$, GOF = 1.33. Atomic coordinates and relevant thermal parameters are listed in Table 3. All calculations were performed with the PC/AT computer using the SHELXTL PC program. The general view of complex **I** with the atom numbering in the projection on the plane of the cyclopentadienyl ring is shown in Fig. 1. A table of hydrogen atom coordinates and a list of observed and calculated structure factors are available from Yu.T.S.

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