

Preliminary communication

THE STRUCTURE OF THE PYRIDINE COMPLEX OF DICYCLOPENTADIENYLCADMIUM

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Summary

The structure of the pyridine complex of dicyclopentadienylcadmium is described; the two cyclopentadienyl rings are both monohapto-bonded to cadmium.

In the course of our investigations on reactions of cyclopentadienylzinc compounds with nickel(0) complexes [1–3] we prepared dicyclopentadienylcadmium (Cp_2Cd) in order to compare its reactivity with that of dicyclopentadienylzinc (Cp_2Zn).

Although the synthesis of Cp_2Cd had been reported by Lorberth [4], very little was known of its properties. Cp_2Cd appears to be a colourless solid which is even less soluble than Cp_2Zn in weakly polar solvents such as hydrocarbons and ethers. It dissolves only in donor solvents such as DMSO and pyridine. From the latter solvent, colourless crystals of the bis-pyridine complex were obtained [5]. This is remarkable since very few stable coordination complexes of diorganocadmium compounds have been reported [6]. The complex is more soluble than Cp_2Cd itself in solvents such as THF. These properties indicate a polymeric structure for Cp_2Cd in the solid state, as was found in dicyclopentadienylzinc [7].

In view of the paucity of structural information on organocadmium compounds, we decided to carry out a crystal structure investigation on Cp_2Cd or its pyridine complex. However, all attempts to obtain crystals of Cp_2Cd itself, either by sublimation or crystallisation, were unsuccessful. Crystals of the pyridine complex suitable for X-ray crystal structure determination were obtained by slow crystallisation from pyridine [8].

In the solid state the compound **1** consists of $\text{Cp}_2\text{Cd} \cdot 2\text{py}$ units in which the cadmium atom is in a pseudotetrahedral environment (cf. Fig. 1); angles

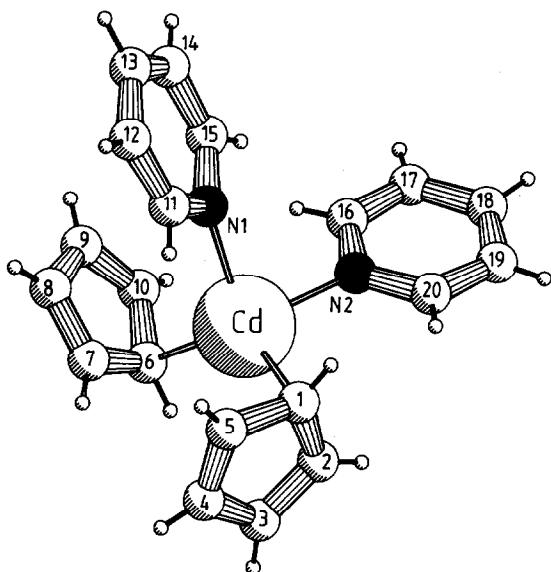


Fig. 1. X-Ray structure of dicyclopentadienylcadmium·2(pyridine). Selected bond distances: Cd–C(1) 2.353(5), Cd–C(6) 2.307(5) Å, Cd–N(1) 2.309(3), Cd–N(2) 2.360(3) Å.

N(1)–Cd–N(2) $96.4(1)^\circ$, C(1)–Cd–C(6) $129.1(2)^\circ$. The deviations from purely tetrahedral coordination show the same features as observed in ω -functionally substituted organozinc compounds [9], i.e. these metals have a tendency to conserve their sp -hybridisation upon complex formation [10].

The cadmium–nitrogen distance, 2.360(3) Å, is smaller than that in the only other known organocadmium complex with a nitrogen base, namely $[\text{Cd}(\text{bpy})(\text{CH}_2\text{SiMe}_3)_2] \cdot 0.5\text{bpy}$ [11] 2.55 Å. Both cyclopentadienyl rings are monohapto-bound to cadmium and possess partial diene character with alternating bond lengths. The bonding mode of the cyclopentadienyl ring is similar to that of the monohapto-bound ring in $(\text{C}_5\text{Me}_5)_2\text{Zn}$ [12]. In both compounds the angle between the ring plane and the η^1 -carbon–metal bond is close to 90° : $80.1(1)^\circ$ and $80.9(3)^\circ$ for **1** and $84(4)^\circ$ for $(\text{C}_5\text{Me}_5)_2\text{Zn}$. In the case of predominantly covalent bond character of the metal–carbon bond a much smaller angle of ca. 54° would be expected as a result of the sp^3 hybridisation of the bonding ring carbon atom. In $\text{H}_3\text{SiC}_5\text{H}_5$, where the cyclopentadienyl ring is covalently bound to silicon, this is indeed the case, and the angle between the ring plane and the silicon–carbon bond is 65.5° [13].

Another measure of covalency of the metal–ligand bond is the diene character of the cyclopentadienyl ring. In the covalent $\text{H}_3\text{SiC}_5\text{H}_5$ the bond lengths are similar to those in cyclopentadiene [14], while in the ionic $\text{CpNa} \cdot \text{TMEDA}$ [15] the difference in the alternating bond lengths is much smaller (cf. Table 1). The bond lengths of **1** are in the same range as those for $\text{CpNa} \cdot \text{TMEDA}$, and similar correlations are found between the angles within the cyclopentadienyl rings (cf. Table 1).

Cadmium in R_2Cd compounds is usually a very weak acceptor as shown by the fact that only very few stable coordination complexes of the type $\text{R}_2\text{Cd} \cdot 2\text{L}$ are known. In $\text{Cp}_2\text{Cd} \cdot 2\text{py}$, however, the Cd–N bonds are sufficiently strong to permit isolation of the complex. Moreover, there was no evidence for dissociation in

TABLE 1

STRUCTURAL PARAMETERS FOR CYCLOPENTADIENYLMETAL (Cp) COMPOUNDS

Compounds	Angle C ₅ /M(°) ^a	C-C distances(Å)				
		C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(5)-C(1)
CpH	(54) ^d	1.506	1.352	1.474	(1.352)	(1.506)
CpSiH ₃	65.6	1.500	1.389	1.43	(1.389)	(1.500)
Zn(C ₅ Me ₅) ₂	84.4	1.54	1.37	1.50	(1.37)	(1.54)
CpNa · TMEDA	88	1.387	1.375	1.402	1.366	1.376
Cp ₂ Cd · 2py	80.1(1) ^b	1.408(6)	1.371(6)	1.382(7)	1.365(7)	1.407(6)
	80.9(3) ^c	1.373(8)	1.341(8)	1.356(8)	1.331(8)	1.387(7)

Ring bond angles (°)					
C(1)-C(2)-C(3)	C(2)-C(3)-C(4)	C(3)-C(4)-C(5)	C(4)-C(5)-C(1)	C(5)-C(1)-C(2)	
CpH	109.3	109.3	109.3	102.8	
CpSiH ₃	112.0	107.9	107.9	100.3	
Zn(C ₅ Me ₅) ₂	—	—	—	—	
CpNa · TMEDA	107.3	108.5	108.2	106.8	109.1
Cp ₂ Cd · 2py	108.8(4)	107.7(4)	109.3(4)	108.1(4)	106.1(4)
	108.8(4)	107.8(5)	109.3(5)	108.0(5)	106.1(4)

^a Angle between the least-squares-plane of the cyclopentadienyl group and the metal to carbon bond vector. ^b Values belong to C(1)-C(5). ^c Values belong to C(6)-C(10). ^d Calculated.

solution. These facts indicate that the Cp groups have a relatively strong electron-withdrawing character, thus enhancing the acceptor character of the Cd. When this argument is considered along the close similarity of the ring geometries of Cp₂Cd · 2py and CpNa · TMEDA, it seems reasonable to conclude that the Cp-Cd bonds in this complex have a largely ionic character. Of course, this conclusion may not be extended to Cp₂Cd itself.

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- 5 ¹H NMR data

Compound	Solvent	C ₅ H ₅ (ppm)	Pyridine(ppm)
Cp ₂ Cd	DMSO- <i>d</i> ₆	5.8	
	Pyridine- <i>d</i> ₅	6.6	
	Pyridine- <i>d</i> ₅ (lit.[4])	5.6	
Cp ₂ Cd · 2py	DMSO- <i>d</i> ₆	5.7(10H)	8.5-8.3 7.9-7.1(10H)
	THF	5.8(10H)	8.4-8.2 7.6-6.8(10H)

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- 8 Crystal structure determination data: CAD4F, Mo- K_{α} -radiation (Zr, filtered); $P2_1/n$, a 12.79(1), b 10.093(4), c 14.38(1) Å, β 107.20(8)°, V 1773(2) Å³, $Z = 4$, D_{calc} 1.501 g cm⁻³; 2407 reflections with $I > 2\sigma(I)$, θ_{max} 27.5°. Non hydrogen atoms refined with anisotropic thermal parameters and hydrogen atoms with one overall isotropic parameter $R = 0.0326$; $R_w = 0.0185$, $w = 1/\sigma^2(F)$, 269 parameters. Full details will be published elsewhere.
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