

X-Ray Crystal Structure of μ -5-Cyclopentadienylcyclopentadiene-bis-(π -cyclopentadienylplatinum)-Pt-Pt

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Summary The product of the reaction between C_5H_5Na and $PtCl_2$ is shown by X-ray crystal structure analysis to consist of two π -cyclopentadienylplatinum units joined by a Pt-Pt bond and a bridging 5-cyclopentadienylcyclopentadiene unit.

platinum atom from the carbon atoms of their π -cyclopentadienyl rings is *ca.* 2.3 Å. The corresponding distance in $[(\pi-C_5H_5)PtMe_3]$, the only other cyclopentadienylplatinum complex of known structure,⁴ is 2.2 Å.

THE green, diamagnetic complex $[(C_{20}H_{20})Pt_2]$, prepared by treating $PtCl_2$ with C_5H_5Na in hexane, has been reported¹ and assigned the structure $[(C_5H_5)_4Pt_2]$ with a Pt-Pt bond and π - and σ -bonded cyclopentadienyl rings in rapid, valence-tautomeric equilibria. We questioned this structure on two counts. First, such a structure would place a formal valency of three on each platinum atom making the diamagnetism of the complex difficult to explain. Secondly we did not observe the expected change² in the n.m.r. spectrum of a $[^2H_8]$ toluene solution of the complex on cooling to $-95^\circ C$.

Crystals of $[(C_{20}H_{20})Pt_2]$ were prepared for X-ray study as previously described.¹ The crystals are monoclinic, $a = 16.43$, $b = 5.64$, $c = 17.11$ Å, $\beta = 92.7^\circ$, $D_m = 2.71$, $Z = 4$, $D_c = 2.728$, space group, $P2_1/c$. Cu- K_α radiation and equi-inclination Weissenberg methods were used with a small crystal sealed in a capillary tube rotating about b . The structure was determined by the heavy-atom method. Based on 1332 independent reflections, the structure was refined by least-squares, and $R = 14.0\%$ at present. The structure is shown (Figure) and the Pt-C distances in the π -bonded systems are listed (Table). The e.s.d. of the

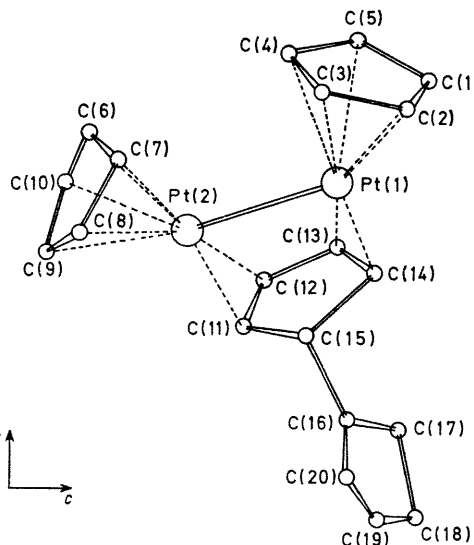


FIGURE. Arrangement of molecules in $[(C_{20}H_{20})Pt_2]$ viewed along the b -axis.

The most interesting feature of the structure is the presence of the hitherto unsuspected 5-cyclopentadienylcyclopentadiene unit bridging the two metal atoms. Each platinum atom bonds to one of the olefinic links of one of the C_5 rings, and the Pt-C distances are *ca.* 2.05 Å, comparable to those in Zeisé's salt and related compounds. The second ring of the $C_{10}H_{10}$ group is directed away from the platinum atoms and is uncomplexed. The only comparable structures are those reported for the dimers $[Rh_2-C_{20}H_{20}]$ and $[Ir_2C_{20}H_{20}]$.⁵ Here, two π -cyclopentadienylmetal units are believed to be bridged by 5-cyclopentadienylcyclopentadiene, but no metal-metal bonds are present and all the olefinic links are co-ordinated to the metals.

We thank Johnson, Matthey, and Co. for a loan of platinum chloride, and one of us (R.W.) thanks the Carnegie Trust for Scotland for a maintenance grant.

(Received, May 3rd, 1971; Com. 673.)

TABLE

Bond lengths (Å)

Pt(1)-C(1)	..	2.33	Pt(2)-C(6)	..	2.36
Pt(1)-C(2)	..	2.36	Pt(2)-C(7)	..	2.09
Pt(1)-C(3)	..	2.24	Pt(2)-C(8)	..	2.33
Pt(1)-C(4)	..	2.21	Pt(2)-C(9)	..	2.39
Pt(1)-C(5)	..	2.32	Pt(2)-C(10)	..	2.22
Pt(1)-C(13)	..	2.03	Pt(2)-C(11)	..	2.00
Pt(1)-C(14)	..	2.03	Pt(2)-C(12)	..	2.12

Pt-Pt bond is 0.004 and those involving carbon atoms are 0.08–0.09 Å at this stage.

The complex contains a platinum-platinum bond, with a π -cyclopentadienyl ring bound to each metal atom. The Pt-Pt distance is 2.581 Å, slightly less than the value of 2.65 Å obtained for the single covalent Pt-Pt bond in $[Pt_2S(CO)(PPh_3)_3]$, the only compound containing a Pt-Pt bond previously examined.³ The average distance of each

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