Preparation and Crystal Structure of Bis(triphenylphosphine)-(1,2-dimethylcyclopropene)platinum

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Summary The formation and crystal structure are reported of a thermally stable 1,2-dimethylcyclopropene–platinum(0) complex.

CYCLOPROPENES are usually highly reactive and thermally unstable hydrocarbons.[1] It was felt that this thermal stability might be improved by co-ordination with a transition metal.

The title compound can be prepared by replacement of ethylene in bis(triphenylphosphine)(ethylene)platinum[2] by 1,2-dimethylcyclopropene (I).† The reaction in $CDCl_3$ or C_6H_6 is complete in a few minutes. After addition of ethanol an off-white, crystalline compound precipitates (II; m.p. 141—144°) which gives a satisfactory elemental analysis. 1,2-Dimethylcyclopropene can be set free quantitatively by addition of triphenylphosphine or carbon disulphide to the complex.

Comparison of the n.m.r. spectra of unco-ordinated‡ and co-ordinated 1,2-dimethylcyclopropene shows that co-ordination results in an upfield shift for the methyl hydrogens and a downfield shift for the methylene hydrogens. One of the methylene hydrogens appears as a pseudo-quartet at 2·13 p.p.m.; integration indicates that the other is situated under the complex methyl signal. This means that the ^{195}Pt coupling of the latter is less than the width of the methyl signal (about 41 Hz).

It is reasonable to assume that the methylene hydrogen in the *syn*-position with respect to platinum is at higher field than the *anti*-proton. This assignment is consistent with the relative ^{195}Pt coupling of these hydrogens. We hope to substantiate these assignments in the future by comparison with other complexed cyclopropenes.

We have also investigated the crystal structure of this cyclopropene complex. Crystals of (II) are monoclinic, space group $P2_1/c$, with $a = 12{\cdot}49(1)$, $b = 17{\cdot}77(2)$, $c = 16{\cdot}38(2)$ Å, $\beta = 109{\cdot}44(5)°$, $Z = 4$. Data were collected on a Nonius automatic three-circle diffractometer, using Zr-filtered Mo-K radiation. The structure was solved by conventional Patterson and Fourier techniques, using 2390 independent reflections, and by means of least squares using anisotropic vibration parameters for the platinum and phosphorus atoms, it was refined to a current R factor, based on F, of 3·2%. The results are shown in the Figure.

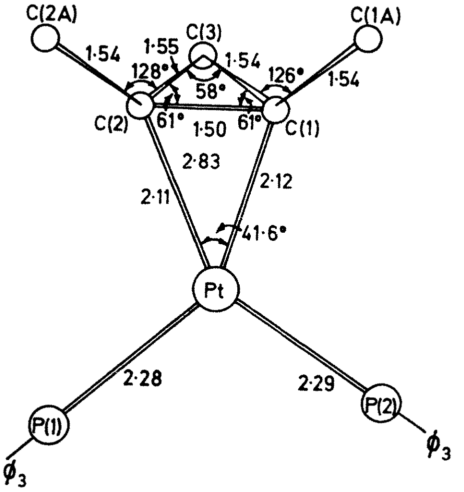

FIGURE. *Bis(triphenylphosphine)-(1,2-dimethylcyclopropene)-platinum co-ordination. Bond lengths in* Å.

One of the most important features of the structure is that the cyclopropene ring remains intact on complexing. This contrasts with the case of cyclopropane[4] in $PtCl_2(C_3H_6)(NC_5H_5)_2$, where the metal is inserted into the ring. The phosphine ligands and atoms 1 and 2 of the 1,2-dimethylcyclopropene make up a distorted square-planar configura-

N.m.r. data for bis(triphenylphosphine)-(1,2-dimethylcyclopropene)platinum

	CH_3	H_{syn}[a]	H_{anti}[a]
Chemical shifts, in $CDCl_3$ downfield from $SiMe_4$ external, p.p.m.	1·80	*ca.* 1·8	2·13
Coupling constants (Hz)	$J(H_{syn}–H_{anti})$	2	
	$\vert J(P\text{-}CH_3)\vert + \vert J(P'\text{-}CH_3)\vert$	8[b]	
	$J(Pt\text{-}CH_3)$	33[c]	
	$J(Pt\text{-}H_{anti})$	98[c]	
	$J(P\text{-}H_{anti})$	2	

[a] *syn* and *anti* with respect to the platinum atom.
[b] This is an example of an $A_3XX'A_3'$ system.[7]
[c] ^{195}Pt in 33·8% natural abundance.

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† Prepared by dimethylation of the cyclopropenyl anion.[3]

‡ The chemical shifts for (I) are 2·50 p.p.m. for the methyl group and 1·25 p.p.m. for the methylene group under the conditions mentioned in the Table.

tion about the platinum atom in which the co-ordinated carbon atoms are at 2·11(1) Å from the metal. The third ring-atom lies at 2·83(1) Å from the Pt atom and therefore does not participate in the ring–metal bonding. The angle between the cyclopropene ring and the plane defined by Pt, P(1), and P(2) is 116(1)°. The methyl groups are bent out of the plane of the ring, away from the metal, such that the angles between the plane of the ring and the best plane through the C(1), C(2), C(1A), C(2A) grouping is 112(1)°. This distortion is consistent with a high degree of σ-character in the metal–olefin bonding, as is the lengthening of the C–C double bond from 1·30 Å reported for the free ligand[5] to 1·50(2) Å in the complex. The latter distance is in good agreement with the 1·52 Å found for the corresponding distance in bis(triphenylphosphine)(tetracyanoethylene)-platinum.[6]

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