

## Novel Cyclobutadiene-Platinum(II) and Alkoxy-carbene-Platinum(IV) Cations

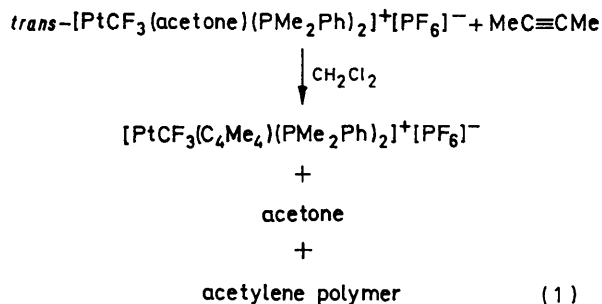
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**Summary** The novel tetramethylcyclobutadiene complex  $[\text{PtCF}_3(\text{C}_4\text{Me}_4)(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  and the first platinum(IV)-alkoxy-carbene complex  $[\text{PtMe}_2(\text{CF}_3)(\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}\cdot\text{CH}_2)(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  have been prepared from cationic acetylenic intermediates.

CATIONIC methylplatinum acetylenic complexes  $\text{trans-}[\text{PtMe}(\text{R}^1\text{C}\equiv\text{CR}^2)\text{Q}_2]^+[\text{PF}_6]^-$  (I) (Q = a tertiary phosphine or arsine ligand, show reactivity characteristic of carbonium ions and are the reactive intermediates in the formation of acetylide, acyl, alkoxy-carbene, vinyl, and vinyl ether complexes.<sup>1,2</sup> The products derived from (I) are dependent on (i) the substituents R<sup>1</sup> and R<sup>2</sup>; (ii) the ligands on the platinum, and (iii) the availability and nature of a nucleophile.

We now find that replacement of the platinum-methyl group by the more electron-withdrawing trifluoromethyl group increases the electrophilicity of the platinum-induced carbonium ion. Indeed, we have been unable to isolate simple dialkyl acetylenic complexes analogous to (I), even by the reaction of  $\text{trans-}[\text{PtCF}_3(\text{acetone})(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  with  $\text{RC}\equiv\text{CR}$  in a non-nucleophilic solvent such as dichloromethane. Polymerization of acetylenes occurs much faster than for (I), and the formation of the tetramethylcyclobutadiene complex  $[\text{PtCF}_3(\text{C}_4\text{Me}_4)(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  (II) from reaction (1) is considered to arise from cyclization of a single *trans*-addition of another acetylene.

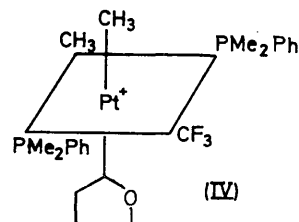


The ready formation of the cyclobutadiene ligand by reaction (1) (room temperature, 60% based on Pt after purification) contrasts dramatically with the only previous report of the preparation of cyclobutadiene complexes of platinum  $[\text{Pt}(\text{C}_4\text{Ph}_4)\text{X}_2]_2$  (X = Cl, Br, or I).<sup>3</sup>

$\text{trans-PtCF}_3\text{I}(\text{PMe}_2\text{Ph})_2$  reacts with  $\text{RC}\equiv\text{CH}$  and silver hexafluorophosphate in MeOH to give alkoxy-carbene complexes  $\text{trans-}[\text{PtCF}_3(\text{RCH}_2\text{COMe})(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  (III) and in this respect parallels the reactions of (I) in alcohols (R = H or alkyl).

No  $\pi$ -co-ordinated acetylenic complexes of tetravalent platinum are known, presumably owing to the inadequacy of platinum(IV) *d*-acetylene  $\pi^*$  bonding.<sup>4</sup> Although we would not expect to be able to isolate stable cationic acetylenic complexes of platinum(IV) we expect that if formed they would be reactive carbonium ion intermediates. We find that the cation  $[\text{PtMe}_2(\text{CF}_3)(\text{PMe}_2\text{Ph})_2]^+$  [formed by the reaction of  $\text{PtMe}_2(\text{CF}_3)\text{I}(\text{PMe}_2\text{Ph})_2$  with  $\text{AgPF}_6$ ] readily polymerizes acetylenes and, in acetone solution reacts with the acetylene  $\text{CH}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  to give the alkoxy-carbene complex  $[\text{PtMe}_2(\text{CF}_3)(\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}\cdot\text{CH}_2)(\text{PMe}_2\text{Ph})_2]^+[\text{PF}_6]^-$  (IV). The isolation of (IV) provides evidence for the transient existence of a  $\pi$ -bonded acetylenic complex of tetravalent platinum and furthermore provides the first example of a carbene ligand co-ordinated to a metal in a higher valency state than two. Its isolation also demonstrates further the strong nucleophilic character of the alkoxy-carbene ligand and the relative insignificance of platinum *d* to carbene  $p_3\pi$  bonding.<sup>2</sup>

Compounds (II), (III), and (IV) were characterized by analysis, vibrational spectroscopy (i.r. and Raman) and n.m.r. spectroscopy (<sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, and <sup>13</sup>C). Evidence for the tetramethylcyclobutadiene ligand in (II) is found in the <sup>1</sup>H n.m.r. spectrum, which shows the chemical equivalence of the four methyl groups:  $\delta(\text{Me}) -1.52$  p.p.m. from Me<sub>4</sub>Si,  $J(\text{Pt-H}) 12.7$  Hz and  $J(\text{FH}) 0.8$  Hz, and in the i.r. spectrum (KBr disc), which shows bands at 1540 (m), 1445 (vs), 1360 (m), 1070 (s), and 1000 (vs).<sup>5</sup> The non-planar stereochemistry about platinum (pseudotetrahedral—required to allow stable bonding between platinum and the cyclobutadiene ligand)<sup>6</sup> is indicated by the absence of virtual coupling between the two phosphorus nuclei and by the absence of phosphorus coupling to the trifluoromethyl fluorine atoms:  $\delta(\text{PMe}) -1.90$  p.p.m. from Me<sub>4</sub>Si,  $^3J(\text{Pt-H}) 20.0$  Hz,  $^2J(\text{P-H}) 10.0$  Hz and  $\delta(\text{CF}_3) + 9.86$  p.p.m. from  $\text{CFCl}_3$ ,  $^2J(\text{Pt-F}) 496$  Hz.



The <sup>1</sup>H n.m.r. spectra of the alkoxy-carbene ligands in (III) and (IV) are similar to those previously reported.<sup>1b</sup> The stereochemistry of (IV) follows from the phosphine-methyl proton resonances which appear as two sets of 1:2:1 triplets and thus indicates the presence of mutually *trans*-phosphine ligands and the absence of a plane of symmetry containing the P-Pt-P axis<sup>7</sup> [ $\text{PMeMe}'\text{Ph}$ ,  $\delta(\text{Me})$ , (Me') 1.78 and  $-2.03$  p.p.m. from Me<sub>4</sub>Si,  $^3J(\text{Pt-H}) 20.5$

Hz,  ${}^2J + {}^4J(\text{P-H})^8$  8.0 Hz.] This stereochemistry is further substantiated by the platinum-methyl proton resonances which also appear as two sets of 1:2:1 triplets and therefore show that they are inequivalent (*i.e.* mutually *cis*) and that they are flanked by mutually *trans*-phosphine ligands.

(Received, August 17th, 1971; Com. 1450.)

<sup>1</sup> (a) M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Comm.*, 1971, 809; (b) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 1711.

<sup>2</sup> M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, in the press.

<sup>3</sup> F. Canziani, P. Chini, A. Quarta, and A. Dimartino, *J. Organometallic Chem.*, 1971, **26**, 285.

<sup>4</sup> *E.g.* see E. O. Greaves, C. J. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879 (cases D and E).

<sup>5</sup> Compare assignments for  $[\text{C}_4\text{Me}_4\text{NiCl}_2]_2$ : H. P. Fritz, *Adv. Organometallic Chem.*, 1964, **1**, 260

<sup>6</sup> F. A. Cotton in 'Chemical Applications of Group Theory,' Interscience, New York, 1964, p. 180.

<sup>7</sup> J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2801.

<sup>8</sup>  ${}^2J + {}^4J(\text{P-H})$  is quoted: R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.