

## Multiple Methylene Insertion Reactions: the Crystal Structure of a Complex formed by Insertion of Methylene into a Pt–P Bond

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Up to three methylene groups from diazomethane may be incorporated into hydridodiplatinum(II) complexes by insertion into Pt–Pt, Pt–H and, in one case, a Pt–P bond; X-ray structure determination establishes the existence of an ylide-( $\mu$ -methylene) complex of platinum, and the first details of the geometry of an  $M_2(\mu\text{-CH}_2)$  group with no M–M bond are reported.

Interest in methylene complexes of transition elements has grown rapidly since the suggestion that the Fischer–Tropsch synthesis involves  $\mu$ -methylene complexes, with chain growth occurring by sequential alkyl migratory-insertion reactions

with  $\mu\text{-CH}_2$  groups.<sup>1</sup> Diazomethane is often used to prepare  $\mu$ -methylene complexes but usually only a single methylene group is added, even in reactions with metal clusters and complexes with metal-metal multiple bonds.<sup>2–6</sup> We now report

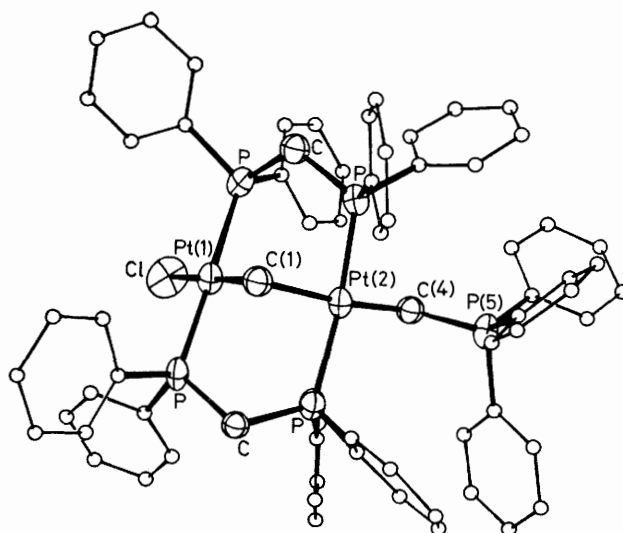
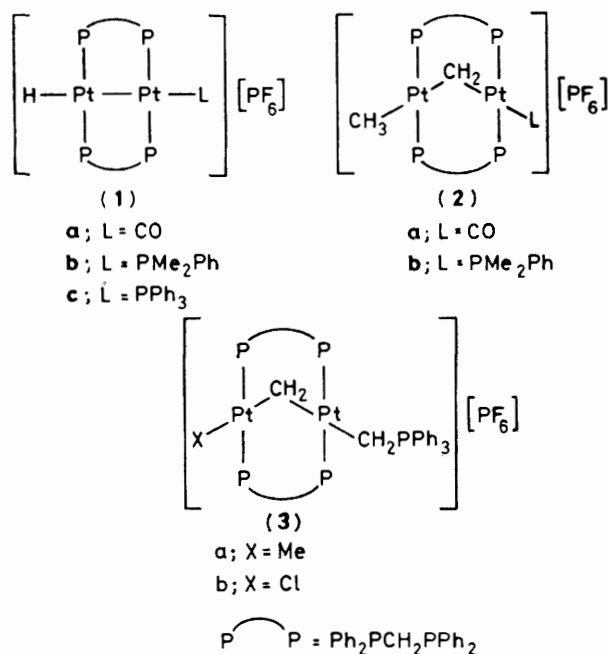


Figure 1. The structure of  $[\text{Pt}_2\text{Cl}(\text{CH}_2\text{PPh}_3)(\mu\text{-CH}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^+$ . Selected bond lengths are: Pt–P 2.263(6)–2.302(6) and P–C 1.77(3)–1.89(2) Å; the P–C–P bond angles are equal at  $116(1)^\circ$  and those involving the Pt(1) and Pt(2) atoms deviate from  $90$  and  $180^\circ$  by as much as  $9.4$  and  $12.3^\circ$ , respectively.

reactions in which up to three methylene groups can be added to diplatinum(i) complexes, including the first example of methylene insertion into a Pt–P bond, using diazomethane as the source of methylene groups.

Reaction of the hydridodiplatinum(i) complexes (1a) and (1b)<sup>7</sup> with an excess of diazomethane occurred cleanly to give (2a) and (2b), respectively, with insertion of methylene groups into both the Pt–H and Pt–Pt bonds. The compounds are readily characterised by elemental analysis and by  $^1\text{H}$  (and  $^1\text{H}\{^{31}\text{P}\}$ ) and  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectroscopy,<sup>8</sup> and are unusual in having both methyl and  $\mu$ -methylene groups in the same molecule.<sup>9</sup> However, the methyl and methylene groups are mutually *trans* and pyrolysis of (2a) does not give coupling of these groups,<sup>9,10</sup> but only methane and carbon monoxide are evolved. Reduction of (2a) with  $\text{NaBH}_4$  gave evolution of CO (and  $\text{CH}_4$ ) and formation of  $[\text{Pt}_2\text{Me}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6]^8$  (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), but the carbonyl group of (2a) is tightly bound and is not displaced by triphenylphosphine in refluxing dichloromethane solution. It has been shown that the first reaction of (1a) with diazomethane gives insertion into the Pt–Pt bond but, in the absence of excess of diazomethane, a further reaction with solvent dichloromethane probably gives  $[\text{Pt}_2\text{Cl}(\mu\text{-CH}_2)(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]$  (*vide infra*).

A surprising reaction occurred with an excess of diazomethane and (1c) to give (3a), which then underwent reaction with solvent  $\text{CH}_2\text{Cl}_2$  to give (3b) by cleavage of the methylplatinum group. The formation of (3a) involves insertion of three methylene groups, the surprising feature being the insertion into the Pt– $\text{PPh}_3$  bond to give a triphenylphosphineylidene complex. This reaction appears to be unique although it may be related mechanistically to reactions involving nucleophilic attack by phosphines on metal–carbene complexes.<sup>11</sup> The new

complexes were characterised by n.m.r. spectroscopy,<sup>†12</sup> (3a), and X-ray crystallography, (3b).

The compound (3b) crystallizes with one molecule of solvent. Crystal data:  $\text{C}_{70}\text{H}_{63}\text{ClP}_5\text{Pt}_2\text{F}_6\text{P}\cdot\text{CH}_2\text{Cl}_2$ ,  $M = 1714.7$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.184(2)$ ,  $b = 17.822(5)$ ,  $c = 30.011(5)$  Å,  $\beta = 91.25(1)^\circ$ ,  $U = 7049.9$  Å<sup>3</sup>,  $F(000) = 3368$ ,  $Z = 4$ ,  $D_c = 1.616$  g cm<sup>-3</sup> (Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å).

The intensities of 6782 independent reflections, with  $I \geq 2.5\sigma(I)$  and  $2 < \theta < 22^\circ$ , were measured on a CAD-4F diffractometer. The crystal structure was solved by the heavy atom method and refined by a full-matrix least-squares procedure to a current  $R$  value of 0.086.§

The structure of the cation is shown in Figure 1 together with selected bond lengths and angles. It confirms insertion of the methylene groups into the Pt–Pt bond and also into the Pt–P bond to yield a co-ordinated ylide molecule,  $\text{CH}_2\text{PPh}_3$ . The V-shaped Cl–Pt–C(1)–Pt–C(4)–P(5) fragment is planar and gives dihedral angles of *ca.*  $79$  and  $100^\circ$  with the co-ordination planes of the Pt(1) and Pt(2) atoms, respectively. The Pt–P bond lengths are as expected,<sup>8</sup> the Pt–Cl distance [2.424(8) Å] indicates a relatively high *trans*-influence of the bridging methylene and the three Pt–C distances are 2.10(2)–2.12(2) Å. Hence, the metal centres are symmetrically bridged by the  $\mu\text{-CH}_2$  group, but their separation of 3.115(1) Å suggests no significant bonding interaction. This structural feature is in contrast with the dimetallacyclopropane ring, MCM, observed in other  $\text{R}_2\text{C}$ -bridged binuclear complexes.<sup>13</sup>

† Spectral data for complexes (2): (2a)  $\delta$   $-0.08$  [t,  $^3J(\text{PH})$  6,  $^2J(\text{PtH})$  59 Hz, MePt], 2.71 [ $^3J(\text{PH})$  5,  $^2J(\text{PtH})$  34 Hz,  $\text{CH}_2\text{Pt}_2$ ], 3.68 [ $^2J(\text{PH})$  3.6,  $^3J(\text{PtH})$  49,  $^2J(\text{H}^A\text{H}^B)$  14 Hz,  $\text{CH}^A\text{H}^B\text{P}_2$ ], and 4.16 p.p.m.;  $\delta(^{31}\text{P})$  7.65 [ $^1J(\text{PtP})$  3162 Hz] and 17.53 p.p.m. [ $^1J(\text{PtP})$  3055 Hz]. (2b)  $\delta$   $-0.85$  [ $^3J(\text{PH})$  6,  $^2J(\text{PH})$  3,  $^2J(\text{PtH})$  59 Hz, MePt], 1.45 (m,  $\text{CH}_2\text{Pt}_2$ ), 3.60 [ $^2J(\text{PH})$  3,  $^3J(\text{PtH})$  51,  $^2J(\text{H}^A\text{H}^B)$  14 Hz,  $\text{CH}^A\text{H}^B\text{P}_2$ ] and 4.15 p.p.m.;  $\delta(^{31}\text{P})$  13.09 [ $^1J(\text{PtP})$  3320 Hz, dppm], 18.91 [ $^1J(\text{PtP})$  3080 Hz, dppm], and  $-22.94$  p.p.m. [ $^1J(\text{PtP})$  1972 Hz,  $\text{PMe}_2\text{Ph}$ ].

‡ Spectral data for (3a):  $\delta$   $-0.40$  [ $^3J(\text{PH})$  5,  $^2J(\text{PtH})$  56 Hz, MePt], 1.50 [ $^3J(\text{PH})$  9,  $^2J(\text{PtH})$  50 Hz,  $\text{CH}_2\text{Pt}_2$ ], 1.77 [ $^2J(\text{PH})$  18,  $^2J(\text{PtH})$  68 Hz,  $\text{CH}_2\text{PPh}_3$ ], 2.99 and 3.93 p.p.m. [ $^2J(\text{HH})$  14 Hz,  $\text{CH}^A\text{H}^B\text{P}_2$ ];  $\delta(^{31}\text{P})$  11.48 [ $^1J(\text{PtP})$  3330 Hz, dppm], 13.28 [ $^1J(\text{PtP})$  3325 Hz, dppm], and 29.75 p.p.m. [ $^2J(\text{PtP})$  45,  $^4J(\text{PtP})$  27 Hz,  $\text{CH}_2\text{PPh}_3$ ].

§ The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The Pt–C(1)–Pt angle is  $95.1(9)^\circ$ . In the monodentate  $\text{CH}_2\text{PPh}_3$  ligand the P–C( $sp^3$ ) distance is  $1.84(2) \text{ \AA}$ , thus suggesting that in this complex the co-ordinated triphenylphosphineylide can best be represented by the zwitterionic canonical formula  $\text{H}_2\text{C}^-\text{PPh}_3^+$ .<sup>14</sup> The Pt–C(4)–P bond angle [ $129(1)^\circ$ ] is much larger than the tetrahedral value. This probably reflects considerable steric strain in this highly crowded cation, which is also evident from the substantial distortions of the bond angles subtended at the metal centres (Figure 1).

We thank the University of Glasgow for a studentship (to A. A. F.) and NSERC and Imperial Oil Limited for financial support (to R. J. P.).

Received, 16th March 1982; Com. 305

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