

## A Novel Type of Pt–C Interaction and a Model for the Final Stage in Reductive Elimination Processes Involving C–C Coupling at Pt; Synthesis and Molecular Geometry of [1,N,N'– $\eta$ -2,6-Bis{(dimethylamino)methyl}-toluene]iodoplatinum(II) Tetrafluoroborate

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**Summary** Square-planar complexes of the type  $R_2\overset{\ominus}{M}X$  (M = Pt or Pd), containing the terdentate ligand 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, undergo with MeI (M = Pt, X = BF<sub>4</sub>) oxidative addition and consecutive reductive elimination resulting in the formation of the complex  $BF_4^- [IPt\overset{\oplus}{\leftarrow}R-Me]^+$  in which the C-aryl centre, at which C–C coupling has occurred, is bonded to the cationic Pt-centre by a novel Pt-to-C-interaction.

the pentaco-ordinate triorganotin cations are blocked. This is reasonable because then high energy conformers with (I) in  $eq_N-eg_C-ax_N$  positions have to be traversed.

We now report results of a study concerning the influence of the geometric constraint of the terdentate ligand (I) on processes which involve a change of the geometry around a transition metal centre from square-planar to trigonal bipyramidal. These results and those recently reported by Shaw *et al.*<sup>3</sup> show that the use of polydentate ligands which, as a result of their specific attachment to the metal, force specific carbon sites into the co-ordination sphere of the metal, gives rise to intriguing transition metal chemistry.

Two different types of Pd and Pt compounds containing (I) have been prepared (*cf.* Scheme); the halogen complexes (III) and (IV) for which oxidative addition should lead to hexaco-ordinate Pt<sup>IV</sup> complexes and the BF<sub>4</sub> complexes (V) and (VI) which might yield pentaco-ordinate oxidative addition products. The square-planar structures, in which the N-ligands occupy *trans* positions,<sup>†</sup> are confirmed by

THE C-1 and N atoms of the terdentate monoanionic ligand 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (I) show a distinct site-preference when bonded to XR<sub>2</sub>Sn species. Thus, in trigonal bipyra-

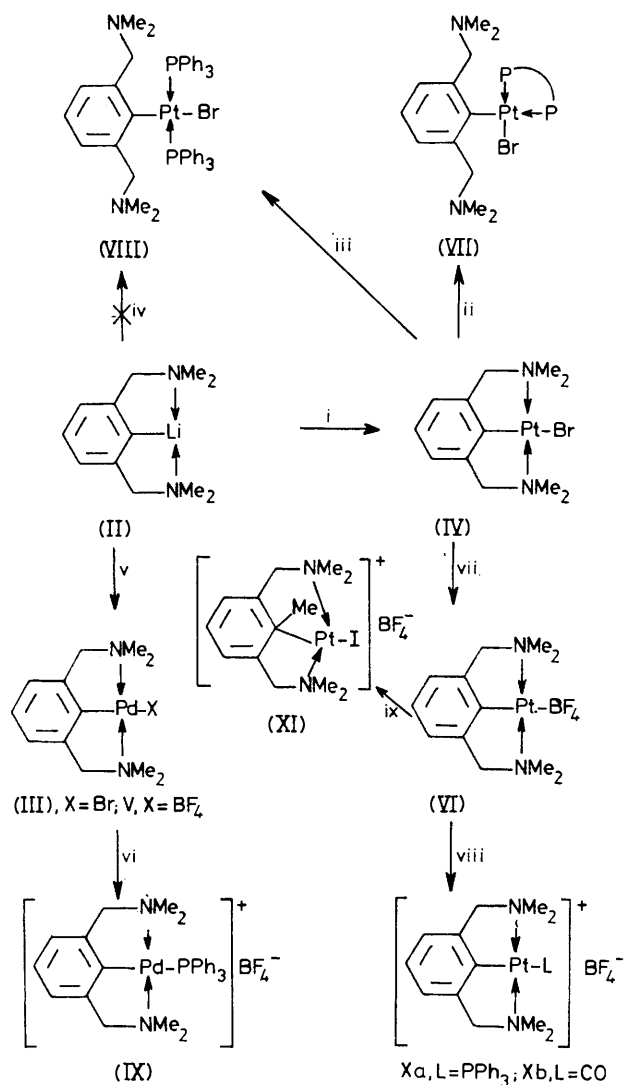
midal 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SnR<sub>2</sub><sup>+</sup>X<sup>−</sup>, (I) occupies  $ax_N-eg_C-$

$ax_N$  positions, an arrangement imposed by the small angles at Sn in the five-membered chelate rings.<sup>1,2</sup> As shown by dynamic n.m.r. spectroscopy, pseudorotation processes in

<sup>†</sup> Pt–N interaction was confirmed by the observation of <sup>3</sup>J(Pt–NMe) and <sup>3</sup>J(Pt–NCH<sub>2</sub>–) in (IV) (39 and 46 Hz), (VI) (43 and 54 Hz), (Xa) (43 and 54 Hz), and (Xb) (45 and 51 Hz). These couplings are absent in the phosphine complexes (VII) [*cis*-diphosphine, <sup>31</sup>P n.m.r.  $\delta$  –3.469 {J(P-1–P-2) 17.2, J(P-1–Pt) 4277 Hz} and –0.045 {J(P-2–Pt) 1638 Hz} p.p.m.] and (VIII) [*trans*-diphosphine, 18.95 {J(Pt–P) 3088 and <sup>4</sup>J(Pt–CCCH<sub>2</sub>N) 11 Hz} p.p.m.].

their n.m.r. resonance pattern and multiplicity as well as by molecular weight data.

Reactions of these compounds with phosphines indicate that the intramolecular N-ligands in (III) cannot be substituted by phosphines whereas similar reactions with (IV) afford the novel phosphine complexes (VII) and (VIII).



SCHEME. i, in the presence of LiBr, (Pr<sub>2</sub>S)<sub>2</sub>PtCl<sub>2</sub>, Et<sub>2</sub>O, room temp.; ii, L(-)-diop [2,2-dimethyl-1,3-dioxolan-4,5-bis(methylene)bis(diphenylphosphine)], Et<sub>2</sub>O, room temp.; iii, 2 equiv. of PPh<sub>3</sub>; iv, (PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>, no reaction; v, for X = Br, Br<sub>2</sub>Pd(cod), Et<sub>2</sub>O room temp. and for X = BF<sub>4</sub>, Br<sub>2</sub>Pd(cod), Et<sub>2</sub>O, room temp., followed by AgBF<sub>4</sub> in acetone; vi, PPh<sub>3</sub>, acetone; vii, AgBF<sub>4</sub>, acetone, room temp.; viii, PPh<sub>3</sub> or CO; ix, MeI, acetone, room temp. Correct elemental data were obtained for all complexes.

The BF<sub>4</sub> complexes (V) and (VI), however, react with PPh<sub>3</sub> to give the tetraco-ordinate Pd and Pt cationic complexes (IX) and (XI) in which strong interaction of the metal with the intramolecular N-ligands still exists.

Whereas the compounds (III), (IV), and (V) fail to react, complex (VI) undergoes oxidative addition with MeI under mild conditions (in acetone at room temperature) to give a

ruby-red product (XI) which analyses for 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>PtMeIBF<sub>4</sub> and decomposes slowly at 175 °C while fast decomposition occurs at 233–235 °C [*M* (cryometry in H<sub>2</sub>O) found 312, calc. 615].

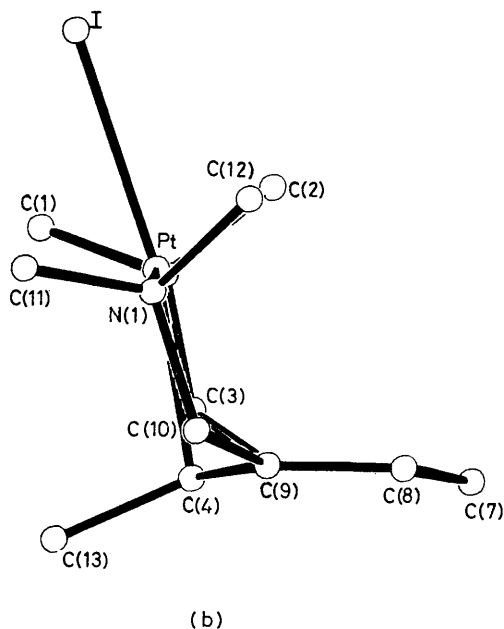
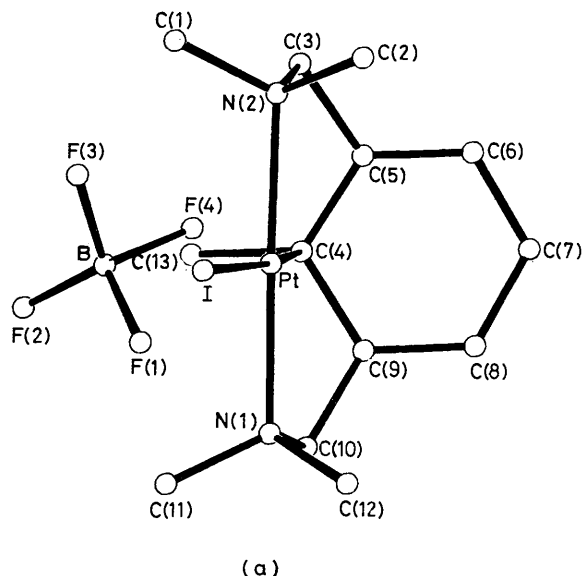


FIGURE. ORTEP drawing of the molecular structure of (XI). Important bond angles and distances are: Pt–N(1), 2.13; Pt–N(2), 2.15; Pt–I 2.58; Pt–C(4), 2.18; C(13)–C(4), 1.54; C(5)–C(4), 1.44; C(4)–C(9), 1.48; C(5)–C(6), 1.39; C(6)–C(7), 1.42; C(7)–C(8), 1.40; and C(8)–C(9), 1.41 Å; ∠Pt–C(4)–C(5), 93; ∠Pt–C(4)–C(9), 87; ∠Pt–C(4)–C(13), 104; ∠C(5)–C(4)–C(9), 114; ∠C(13)–C(4)–C(5) 124; and ∠C(13)–C(4)–C(9), 120°.

Crystal data: (XI), monoclinic, space group P2<sub>1</sub>/c; Z = 4; a = 11.033(2), b = 11.553(1); c = 13.915(3) Å; β = 98.34(1)°, U = 1755 Å<sup>3</sup>. The structure analysis was carried out using 4021 independent reflections of which 523 were < 2.5 σ(I). Intensities were collected on an ENRAF

NONIUS CAD 4 diffractometer using Zr-filtered Mo- $K_{\alpha}$  radiation. The structure was solved by direct methods and refined to a current  $R$ -factor of 0.11.†§

The structure (see Figure, a) shows that the methyl group is bonded to the aryl ring by a normal C-C single bond (1.54 Å) which establishes that (XI) represents the situation following the reductive elimination process, *i.e.* the situation before release of the C-C coupling product as the final step. Furthermore, this structure indicates that during the whole process the interaction of the intramolecular NMe<sub>2</sub> ligands with the Pt atom remains inert resulting in a glide of the Pt atom out of the plane of the aryl nucleus into a position above C(4) [Pt...C(4), 2.18 Å which is in the range found for Pt-C bonds<sup>4</sup>]. The Pt atom has an almost square-planar arrangement with N-Pt-N and I-Pt-C(4) angles of 172 and 171°, respectively. The BF<sub>4</sub> anion is located at independent sites in the unit cell at a distance of at least 4.5 Å from the Pt atom which reveals that the aryl nucleus indeed occupies the fourth co-ordination site at the IN<sub>2</sub>Pt-cation.

To our knowledge the observed aryl-to-Pt bonding is unprecedented. Although a detailed description of the

bonding scheme is not timely, it can be interpreted in terms of an overlap of a component of the  $e_{1g}, \pi_3$  orbital of the aryl nucleus (at C-1, C-2, and C-6) with an orbital of correct symmetry on Pt. This model explains the considerable bending of the aryl skeleton (see Figure, b) and the lengthening of the neighbouring C(4)-C(5) (1.44 Å) and C(4)-C(9) (1.48 Å) distances. The planar arrangement at C(4) (sum of angles 358°) remains unaffected. This model receives further support from the proton deshielding observed in the <sup>1</sup>H n.m.r. spectrum of (XI) in (CD<sub>3</sub>)<sub>2</sub>CO. As a result of release of electron density from the  $\pi$ -system of the aryl nucleus to the Pt cationic centre the aromatic protons shift to low field  $\delta$  8.47 [1H, t,  $J_{AB}$  7.2 Hz, C(7)-H] and 7.30 [2H, d, C(6)-H and C(8)-H]. That the structure of (XI) in solution is similar to that in the solid can be concluded from the observation of diastereotopic CH<sub>2</sub> protons ( $\delta$  3.80 and 4.90,  $J_{AB}$  13 Hz) and NMe<sub>2</sub> protons { $\delta$  2.53 [s,  $^3J(\text{Pt-H})$  29.5 Hz] and 3.00 [s,  $^3J(\text{Pt-H})$  31.5 Hz]} while the methyl group is found as a singlet at  $\delta$  3.10.

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† Both positional parameters and isotropic temperature factors for the non-hydrogen atoms were refined. Correction for absorption and further refinement are in progress.

§ The atomic co-ordinates for this work 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.

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