

Preliminary communication

OXIDATIVE ADDITION WITH METHYL GROUP TRANSFER IN DIPLATINUM COMPLEXES: CRYSTAL STRUCTURE OF A BRIDGED PLATINUM(IV)-PLATINUM(II) COMPLEX

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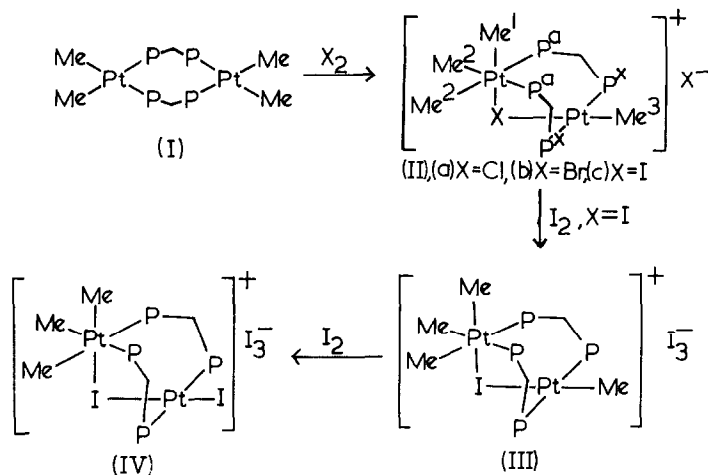
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Summary

Reactions of $[\text{Me}_2\text{Pt}(\mu\text{-dmpm})_2\text{PtMe}_2]$, ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$) with halogens, (X_2) or methyl iodide give the platinum(IV)-platinum(II) complexes $[\text{Me}_3\text{Pt}(\mu\text{-X})(\mu\text{-dmpm})_2\text{PtMe}]X$ or $[\text{Me}_3\text{IPt}(\mu\text{-dmpm})_2\text{PtMe}_2]$ respectively, and the former reactions involve methyl group transfer between the platinum atoms of the binuclear complex; one of the derivatives ($[\text{Me}_3\text{Pt}(\mu\text{-I})(\mu\text{-dmpm})_2\text{PtL}]I_3$, $L = 1/2 I + 1/2 \text{Me}$) is characterized by an X-ray crystal structure determination.

We wish to report a new type of reaction in which oxidative addition to a binuclear methylplatinum complex is accompanied by methyl group transfer between the platinum atoms [1]. The reactions are summarised in Scheme 1 ($\text{P-P} = \text{Me}_2\text{PCH}_2\text{PMe}_2 = \text{dmpm}$). Complexes II were formed as white solids by addition of 1 mol. equivalent of halogen to the dimer (I) [2] at low temperature. They were characterised by ^1H , $^1\text{H}\{^{31}\text{P}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy* and by elemental analysis. The ionic nature of IIc was confirmed by conversion of the iodide to the hexafluorophosphate salt on reaction with $\text{NH}_4[\text{PF}_6]$. Reaction of I with 2 mol. equivalents of iodine gave a mixture

*NMR data for IIc (δ in ppm, J in Hz): $\delta(^1\text{H})$ 0.86 (t, $^3J(\text{PH})$ 7, $^2J(\text{PtH})$ 83, Me^3), 0.94 (m, $^3J(\text{P}^a\text{H}) + ^3J(\text{P}^a\text{H})$ 4, $^2J(\text{PtH})$ 54.5, Me^2), 0.96 (t, $^3J(\text{PH})$ 9, $^2J(\text{PtH})$ 71, Me^1), 1.50 and 1.93 (d, MeP^a), 1.68 and 1.87 (t, MeP^x), 2.98 and 3.94 (m, $^2J(\text{H}^a\text{H}^b)$ 14, $\text{CH}^a\text{H}^b\text{P}_2$), $\delta(^{31}\text{P})$ -13.9 (t, $^2J(\text{P}^a\text{P}^x) + ^4J(\text{P}^a\text{P}^x)$) 16, $^1J(\text{PtP})$ 2621, P^x, P^x), -41.7 (t, $^1J(\text{PtP})$ 1216, $^2J(\text{PtP})$ 129, P^a, P^a). Data for IIa and IIb were similar. Satisfactory elemental analyses were obtained for all complexes isolated.



SCHEME 1

of III and IV, which crystallised as brown crystals, while a large excess of iodine gave IV* as a black solid. The mixture of III and IV was identified by X-ray crystal structure analysis** as $[Me_3Pt(\mu-I)(\mu-dmpm)_2PtL]I_3$, where $L = 1/2(I + Me)$.

The structure of the $[Me_3Pt(\mu-I)(\mu-dmpm)_2PtL]^+$, shown in Fig. 1, reveals the presence of the platinum(IV) and platinum(II) metal centres, which are characterised by octahedral and square planar coordination geometries. The metal atoms are spanned by two bridging dmpm and one bridging iodide ligand, to form an L-shaped $MePt(\mu-I)PtL$ fragment ($Pt-I-Pt$ $91.2(1)^\circ$) perpendicular to the $Pt(2)P_2C(2)C(3)$ and $Pt(1)P_2L(\mu-I)$ coordination planes. The bond lengths and angles involving the metal atoms are as expected for platinum(IV) and platinum(II) complexes. The overall geometry of the cation approximates to C_s symmetry, the plane of symmetry passing through the $MePt(\mu-I)PtL$ fragment.

*NMR data for IV (δ in ppm, J in Hz): $\delta(^1H)$ 1.02 (m, $^3J(P^aH) + ^3J(P^a'H)$ 2, $^2J(PtH)$ 53.5, Me^2), 1.20 (t, $^3J(PH)$ 9, $^2J(PtH)$ 73, Me^1), 1.56–2.28 (complex, MeP), 3.43 and 4.09 (m, $^2J(H^aH^b)$ 14.5, $CH^aH^bP_2$, $\delta(^{31}P)$ -23.7 (t, $^2J(P^aP^x) + ^4J(P^aP^x')$ 15, $^1J(PtP)$ 2152, P^x, P^x'), -37.6 (t, $^1J(PtP)$ 1241, $^3J(PtP)$ 112, P^a, P^a').

**Crystallographic data for $[Me_3Pt(\mu-I)(\mu-dmpm)_2PtL]I_3$, ($L = 1/2(I + Me)$). $[C_{13.5}H_{38.5}I_4.5P_4Pt_2]I_3$, $M = 1286.1$, triclinic, space group $P\bar{1}$, a 9.240(2), b 9.328(4), c 18.044(7) Å, α 102.39(4), β 94.63(3), γ 96.93(3)°. U 1499 Å³, D_c 2.850 g cm⁻³, $Z = 2$. Mo- K_α X-radiation (graphite monochromator), λ 0.71069 Å, $\mu(Mo-K_\alpha)$ 142.2 cm⁻¹.

Intensities of 5045 reflections with $I > 3\sigma(I)$ were measured on a CAD4F diffractometer and were corrected for Lorentz, polarisation, crystal decomposition, and absorption effects. The structure was solved by the heavy atom method and refined to R 0.048 by full-matrix least-squares. The occupancies of I and Me were refined and integration of the $^{31}P\{^1H\}$ NMR spectrum confirmed the presence of III and IV in approximately equal amounts.

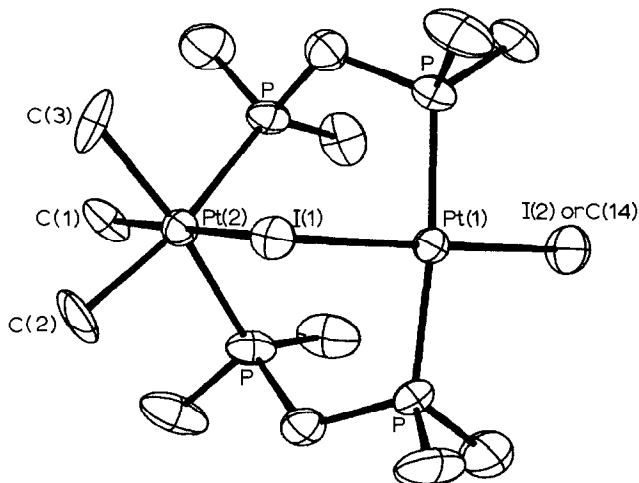
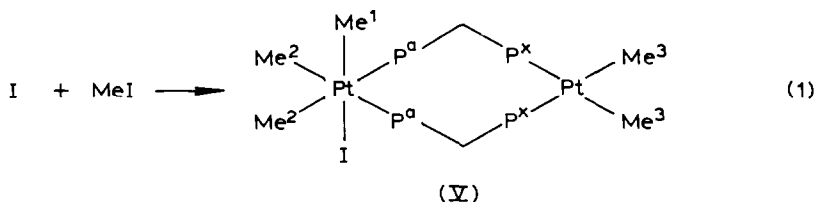


Fig. 1. The structure of $[\text{Pt}_2\text{Me}_3\text{L}(\mu\text{-I})(\mu\text{-dmpm})_2]_1^+$, $\text{L} = 1/2(\text{I} + \text{Me})$. Selected bond lengths and angles are: Pt(1)—I(2) 2.529(3), Pt(1)—C(14) 1.99(4), Pt(1)—I(1) 2.652(1), Pt(2)—I(1) 2.756(2), Pt(2)—C 2.14(1)—2.19(2) Å, I(2)—Pt(1)—I(1) 179.0(1), C(14)—Pt(1)—I(1) 170(1) and I(1)—Pt(2)—C(1) 174.7(4)°.

Another example of a bridged platinum(IV)-platinum(II) species is formed by the rapid reaction of methyl iodide with I, eq. 1*.



In this case no methyl transfer occurs. Reaction of I with CD_3I gave partial CD_3 group incorporation in the Me^1 and Me^2 positions of V but no CD_3 groups in the Me^3 position as shown by both ^1H and ^2H NMR studies**. Complex V reacted more slowly with excess methyl iodide to give oxidative addition at the second platinum(II) centre.

The most interesting feature of the reactions in Scheme 1 is the rapid inter-nuclear transfer of a methyl group as a result of oxidative addition. In a similar mononuclear system, oxidative addition of iodine to *cis*- $[\text{PtMe}_2\text{L}_2]$, ($\text{L} = \text{PMe}_2\text{Ph}$) gives $[\text{PtI}_2\text{Me}_2\text{L}_2]$ and this reacts only very slowly and incompletely with *cis*- $[\text{PtMe}_2\text{L}_2]$, [3]. In the present system, it is probable that the methyl group transfer occurs at an intermediate stage of oxidative addition, with an intermediate such as $[\text{IME}_2\text{Pt}(\mu\text{-dmpm})_2\text{PtMe}_2]^+ \Gamma^-$, to account for

*NMR data for V (δ in ppm, J in Hz): $\delta(^1\text{H})$ 0.52 (m, $^2J(\text{PtH})$ 66, Me^3), 0.87 (t, $^3J(\text{PH})$ 7, $^2J(\text{PtH})$ 73, Me^1), 1.10 (m, $^2J(\text{PtH})$ 57, Me^2), 1.56—1.78 (overlapping m, MeP), $\delta(^{31}\text{P})$ -52.1 ($^1J(\text{PtP})$ 1160, $^3J(\text{PtP})$ 11 P^a), -22.6 ($^1J(\text{PtP})$ 1688, P^x).

**This scrambling of label between the Me^1 and Me^2 positions was not expected by analogy with chemistry of mononuclear complexes, which gave only *trans* addition.

unique reactivity of the binuclear system [4,5]. Although bridged platinum(II)-platinum(II) and platinum(IV)-platinum(IV) complexes are known [6,7], the complexes II–V appear to be the first bridged platinum(II)-platinum(IV) mixed oxidation state complexes to have been characterized.

References

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