An Unexpected Dinuclear Zwitterionic Pt^{II} Cation $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\}_2I_4]^{2+}$ and Alcohols from the Reaction of an Aryl(diamine)(aquo)Pt^{II} Complex with Alkyl Iodides; *X*-Ray and N.M.R. Studies

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The unusual dinuclear zwitterionic platinum(II) complex $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2I_4][CF_3SO_3]_2$ (**3**), characterized by *X*-ray crystallographic methods and ^1H n.m.r. spectroscopy, is formed together with ROH from the addition of an alkyl iodide RI (R = Et, Pr^i, $PhCH_2$, allyl; but not Me) to $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}(H_2O)][CF_3SO_3]$ in wet acetone; when R = Me the known arenonium complex $[Pt\{MeC_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}I]^+$ results.

The oxidative addition reaction of substrates to d^8 metal centres is still far from completely understood and is a topic of much current theoretical[1] and experimental[2] interest. Recent results, such as the isolation of organometallic Pd^{IV} species[3] and of a trapped $\eta^1\text{-}I_2$ addition product of Pt^{II},[4] indicate that metal species with N-donor instead of P-donor ligands can provide new and unexpected insights into this fundamental reaction.

We have investigated several aspects of the co-ordination chemistry of the tridentate monoanionic ligand $C_6H_3(CH_2NMe_2)_2\text{-}2,6$ that readily forms square planar d^8 metal species having a *trans* N-donor arrangement.[5] In particular we were intrigued by the fact that $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}(H_2O)]^+$ (**1**) with MeI affords a highly unusual addition product $[Pt\{MeC_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}I]^+$ (**2**);[6] in this metal stabilized arenonium ion the methyl group of the incoming alkyl iodide has become bonded (possibly after migration from the metal centre) to the aryl nucleus.[7] The results of our studies of (**1**) with other alkyl halides now show the domination of a completely different, and to our knowledge unprecedented, reaction pathway that leads to the formation of a unique dinuclear zwitterionic complex (**3**) and the corresponding alkyl alcohol; the characterization of this complex (*X*-ray and n.m.r. spectral studies) and some reactions that it undergoes with nucleophiles are described here.

When an excess of an alkyl halide RI (R = Et, Pr^i, benzyl, allyl) is added to a solution of (**1**) in acetone at room temp. a slow reaction occurs (virtually complete in ≤10 days) to afford specifically the poorly soluble, air-stable, orange complex $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2I_4][CF_3SO_3]_2$ (**3**); PhI does not react under the same conditions. Quantitative and qualitative product analysis of the organic solution (g.c.m.s.) shows that formation of (**3**) is accompanied by the conversion per platinum atom of 2 equiv. of the alkyl iodide to 2 equiv. of the alkyl alcohol. The overall reaction is summarised in equation (1).

$$2[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}(H_2O)][CF_3SO_3] + 4\,RI \xrightarrow{\text{acetone}/H_2O,\ \text{room temp.}} [Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2I_4][CF_3SO_3]_2 + 4\,ROH \quad (1)$$

The ^1H n.m.r. spectrum of (**3**) (200 MHz, $[^2H_6]$acetone) is characteristic. Compared to the starting material (**1**) the signals for the aryl nucleus are similar but those of the *ortho* substituents [δ 4.98 (d, CH_2) and 3.14 (d, NMe_2)] lack the ^{195}Pt satellites invariably found when CH_2NMe_2 groups chelate through nitrogen to a platinum centre.[5] Together with a broad resonance at *ca.* 9.0 p.p.m. (removed upon addition of D_2O), these data for (**3**) are consistent with the presence of the $[C_6H_3(CH_2NHMe_2)_2\text{-}2,6]$ ligand in which the amine functions

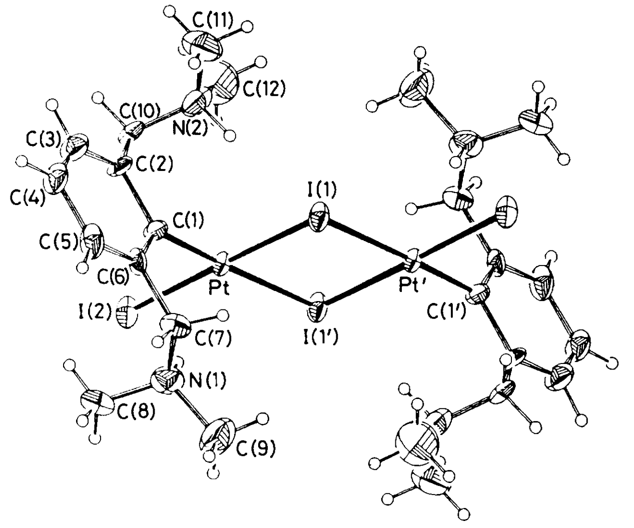
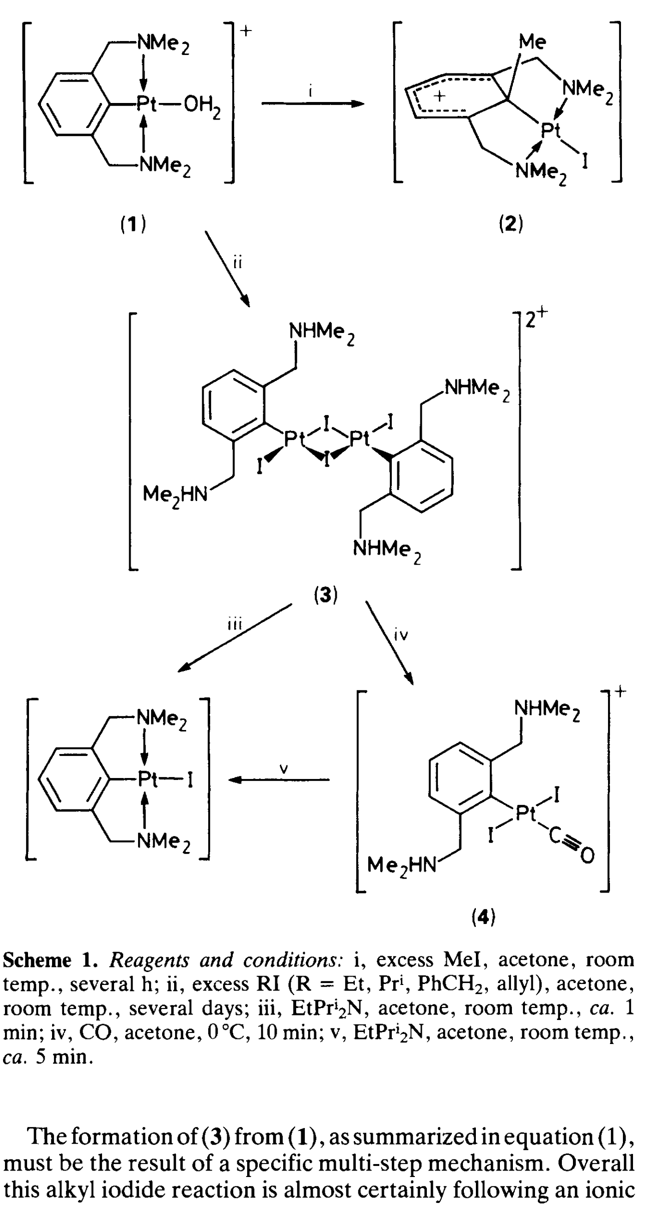


Figure 1. Thermal ellipsoid plot (30% probability level) for the $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2I_4]$ dication of (**3**). Atoms marked ' are related by crystallographic inversion symmetry. Selected bond lengths (Å) and angles (°): Pt–C(1) 1.99(3), Pt–I(1) 2.603(2), Pt–I(1') 2.708(2), Pt–I(2) 2.590(2); C(1)–Pt–I(1') 176.6(7), I(1)–Pt–I(2) 178.67(8), I(1)–Pt–I(1') 85.85(6), I(2)–Pt–C(1) 90.5(7).

initially co-ordinated to platinum in (**1**) are now protonated. An *X*-ray crystallographic study of (**3**) has been undertaken† and the resultant molecular structure shows it to be a most interesting dinuclear ionic organometallic species $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2I_4][CF_3SO_3]_2$; this is the first structurally characterized halide-bridged dinuclear aryl platinum species.

In the dinuclear dication of (**3**) (Figure 1) two bridging iodo atoms link two square planar Pt^{II} centres whose coplanar co-ordination spheres are completed by a terminal iodo atom and a monodentate C-bonded aryl system. Overall the $[Pt_2(\mu\text{-}I)_2(aryl)_2I_2]^{2+}$ ion has a *trans* geometry and the rings of the aryl groups lie, presumably for steric reasons, almost perpendicular to the $Pt_2(\mu\text{-}I)_2I_2$ plane. The four $-CH_2NHMe_2^+$ substituents of the two aryl rings together with the double negative charge of the 'central' $(aryl)_2Pt_2I_4$ system, *cf.* $[Pt_2I_6]^{2-}$,[8] make this a zwitterionic cation with a very distinctive charge distribution. In this complex ion there appears to be some weak attraction between the 'central' anionic moiety and the four $-CH_2NHMe_2^+$ units that occupy pseudo-octahedral positions above and below the Pt^{II} co-ordination planes [Pt· · ·N = 3.20(2) and 3.31(2) Å].



Scheme 1. *Reagents and conditions:* i, excess MeI, acetone, room temp., several h; ii, excess RI (R = Et, Pr^i, PhCH$_2$, allyl), acetone, room temp., several days; iii, EtPr$^i_2$N, acetone, room temp., *ca.* 1 min; iv, CO, acetone, 0 °C, 10 min; v, EtPr$^i_2$N, acetone, room temp., *ca.* 5 min.

The formation of (**3**) from (**1**), as summarized in equation (1), must be the result of a specific multi-step mechanism. Overall this alkyl iodide reaction is almost certainly following an ionic route, since Pr^{i}Br (whose reactions exclusively follow ionic pathways) also reacts with (**1**) to produce in this case Pr^{i}OH, $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}Br]$ and most probably CF_3SO_3H. This result would thus also appear to exclude the possibility of a route to complexes like (**3**) that involves transient formation of neutral $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}X]$ and subsequent protonation by either the alcohol or free acid. It is noteworthy in this context that the attempted direct protonation of (**1**) using HI does not afford (**3**) but, unexpectedly, neutral $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}I(\eta^1\text{-}I_2)]$.[4]

Our understanding of the mechanism for the reaction of (**1**) with alkyl iodides, that must be able to account for the formation of arenonium complex (**2**) when using MeI, is far from complete, although we can deduce some of the more likely steps. Firstly, there needs to be co-ordination and activation of the alkyl iodide substrate at the transition metal centre[9] and for (**1**) we can envisage a transition state in which the I–C$_{alkyl}$ bond is either η^1-C,[9] η^1-I,[6] or even asymmetrically side-on bonded; *cf.* the bonding of the Sn–Br bond in $[Ir\{C_6H_4(CH_2NMe_2)\text{-}2\}(cyclo\text{-}octa\text{-}1,5\text{-}diene)(Br\text{-}SnMe_2Br)]$.[10] With methyl iodide oxidative addition, *via* an S_N2-type pathway,[6] and subsequent migration of the methyl group from

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† Crystals grown with difficulty from acetone–chloroform solution by slow solvent evaporation. *Crystal data* for (**3**): $C_{24}H_{42}I_4N_4Pt_2 \cdot 2\,SO_3CF_3$, brownish plate, $M = 1582.53$; monoclinic; space group $P2_1/a$, $a = 13.126(3)$, $b = 14.176(2)$, $c = 13.006(2)$ Å, $\beta = 117.81(1)°$, $U = 2140.6(7)$ Å^3, $D_c = 2.455$ g cm^{-3}, $Z = 2$, $F(000) = 1456$, Zr filtered Mo-K_α radiation ($\lambda = 0.71073$ Å) μ(Mo-K_α) = 96.1 cm^{-1}. Intensities of 5316 reflections were collected [CAD-4F; $\theta_{max.} = 27.5°$, $\omega/2\theta$-scan] of which 3672 with $I > 3\sigma(I)$ were used in the refinement. The data were corrected for absorption (gaussian integration). The structure was solved with standard Patterson and Fourier techniques (SHELXS-86), and refined by full matrix least squares techniques (SHELX-76) to $R = 0.074$. Hydrogen atoms were introduced at calculated positions. The trifluoromethane sulphonate anions were refined with bond distance restraints in view of some orientational disorder that was indicated by high thermal motion. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

platinum to C_{ipso}, affording (**2**) would appear to be a facile process.[7] However, with the other alkyl iodides this process, if it occurs at all, must be reversible and non-productive so that a second pathway, in which dissociation of a Pt–N bond could be rate determining, becomes dominant. Since no organometallic intermediates were observed when the slow conversion of (**1**) to (**2**) was followed by ^{1}H n.m.r. spectroscopy, this step, in which the amine lone pair becomes accessible for protonation, is most likely coupled with nucleophilic attack of OH^- at the activated alkyl iodide to generate the alcohol. Although addition of CF_3SO_3H does not affect the reaction rate, protonation of the amine is an important component of the reaction since (**1**) and Pr^iI do not react to form (**3**) in the presence of a strong base such as $EtPr^i_2N$. The role of non-co-ordinated but close, intramolecularly bound, Lewis bases (such as amines) in assisting nucleophilic substitutions is now becoming recognised and has already found application in homogeneous catalysis.[11]

Reactions of dinuclear (**3**) with nucleophiles (Scheme 1) afford complexes of various types. With (**3**) the strong, non-nucleophilic, base $EtPr^i_2N$ reacts rapidly (<1 min) to form $[EtPr^i_2NH]^+$ and monomeric $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}I]$. In contrast, halide ions do not disrupt the iodide bridges of (**3**) and NaX (X = Cl, Br, I) in H_2O–acetone forms the highly insoluble anion exchange product $[Pt_2\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}_2(I)_2(\mu\text{-}I)_2](X)_2$. Carbon monoxide reacts rapidly with (**3**) to give mononuclear $[Pt\{C_6H_3(CH_2NHMe_2)_2\text{-}2,6\text{-}C\}(I)_2(CO)]^+$ (**4**).‡ The $^{13}C\{^1H\}$ n.m.r. spectral data are consistent with the carbonyl group being *trans* to the aryl ring; the low bond coupling constant of 1029 Hz between platinum and the carbonyl carbon (δ 175.9) being typical for a carbonyl *trans* to a ligand of high *trans* influence. Complex (**4**) can also be obtained in good yield from the reaction of HI with $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}CO]^+$; the reason why protonation occurs with this complex but not with cationic (**1**), *vide supra*, is under study.

In conclusion, the reactions of alkyl iodides with $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}(H_2O)]^+$ do not lead to oxidative addition products. Those iodides studied, other than MeI, generate an unusual zwitterionic dinuclear platinum complex and in the operative ionic reaction pathway the amine bearing substitutent of the aryl ligand plays an important role in the formation of the alkyl alcohol as the only organic product.

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‡ *Selected spectroscopic data* for (**4**): ^{1}H n.m.r. (200 MHz, [$^2H_6$]acetone): δ 4.82 [d, NCH_2, $^3J_{(HH)}$ 6 Hz], 3.00 [d, NCH_3, $^3J_{(HH)}$ 5 Hz], 10.0 [br. s, NH].