Novel Mono- and Bis-metallated Complexes of Dialkyldiaziridines; X-Ray Diffraction Structures of Three Platinum Complexes

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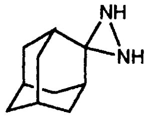
The preparation, characterization and structures of three new platinum complexes of dialkyldiaziridines are presented; both mono- and bis-platinated derivatives can be isolated under appropriate conditions.

The coordination chemistry of diaziridines has been little investigated, and only one metal diaziridine complex has been previously structurally characterised.[1] We now report the preparation and characterisation of mono- and bis-platinated derivatives of two diaziridines, and their further characterisation by multinuclear NMR spectroscopy.

The diaziridines **1** and **2** were prepared by the standard methods of reaction of the ketone with liquid ammonia and hydroxylamine-*O*-sulfonic acid.[2] Reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$[3] with **1** or **2** (CH_2Cl_2, 25 °C, 3 h) in a diaziridine : Pt ratio of 1 : 1 unexpectedly yielded the bis-platinated species **3** and **4**, respectively,† isolated as pale-yellow crystals by recrystallisation from dichloromethane–light petroleum. The structures of the complexes were established in diffraction studies‡ and are shown in Figs. 1 and 2. Interestingly the structure of the cyclohexyldiaziridine derived complex is chiral, and we assume that the complex has undergone spontaneous resolution during crystallisation. In both cases the arrangement of the platinum atoms is *trans* with respect to the diaziridine rings, although the hydrogen atoms could not be located directly. We were surprised to discover that it was easier to isolate the bis- than the mono-metallated species. We have since studied the equilibrium between the species in solution, and have found that this is a genuine effect of the equilibrium rather than an artefact of isolation procedures reflecting differential solubility. The monoplatinated complex **5** could be isolated from solutions containing a large excess of the diaziridine, **1**, as an impure material contaminated with free diaziridine. However, a few single crystals were isolated by slow diffusion of diethyl ether into a dichloromethane solution of the impure complex, and the structure is shown in Fig. 3.§ In this case the hydrogen atoms bound to nitrogen could be directly located, and are clearly *trans*, as expected.



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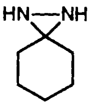

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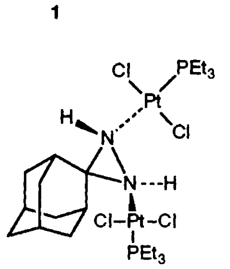

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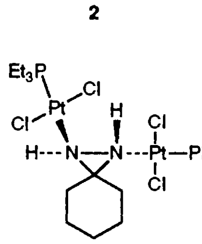

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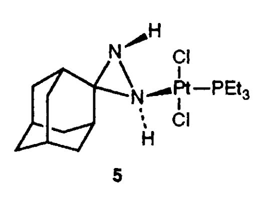

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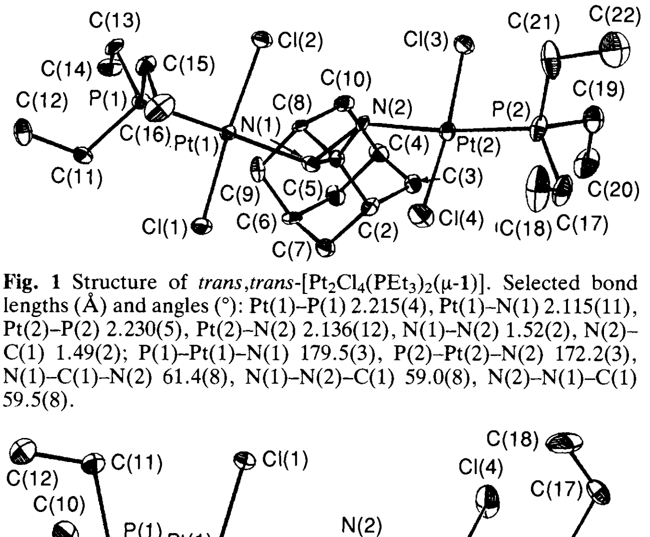

Fig. 1 Structure of *trans,trans*-$[Pt_2Cl_4(PEt_3)_2(\mu\text{-}\mathbf{1})]$. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.215(4), Pt(1)–N(1) 2.115(11), Pt(2)–P(2) 2.230(5), Pt(2)–N(2) 2.136(12), N(1)–N(2) 1.52(2), N(2)–C(1) 1.49(2); P(1)–Pt(1)–N(1) 179.5(3), P(2)–Pt(2)–N(2) 172.2(3), N(1)–C(1)–N(2) 61.4(8), N(1)–N(2)–C(1) 59.0(8), N(2)–N(1)–C(1) 59.5(8).

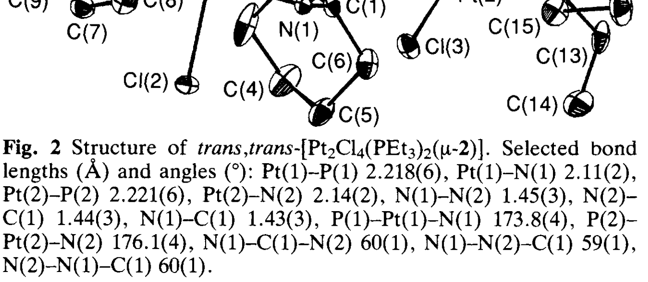

Fig. 2 Structure of *trans,trans*-$[Pt_2Cl_4(PEt_3)_2(\mu\text{-}\mathbf{2})]$. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.218(6), Pt(1)–N(1) 2.11(2), Pt(2)–P(2) 2.221(6), Pt(2)–N(2) 2.14(2), N(1)–N(2) 1.45(3), N(2)–C(1) 1.44(3), N(1)–C(1) 1.43(3), P(1)–Pt(1)–N(1) 173.8(4), P(2)–Pt(2)–N(2) 176.1(4), N(1)–C(1)–N(2) 60(1), N(1)–N(2)–C(1) 59(1), N(2)–N(1)–C(1) 60(1).

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† All new complexes gave satisfactory microanalytical and spectroscopic data.

‡ *Crystal data* for **3**: $C_{22}H_{46}Cl_4N_2P_2Pt_2$, M_r = 932.5, monoclinic, $P2_1/n$, a = 14.841(4), b = 12.663(3), c = 16.925(5) Å, β = 101.81(2)°, U = 3113.3 Å^3, Z = 4, D_c = 1.97 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 95.3 cm^{-1}, F(000) = 1784, T = 295 K. Final R = 0.050 for 3882 observed reflections. Crystal dimensions 0.35 × 0.35 × 0.07 mm. S = 1.85, 289 variables. $(\Delta/\sigma)_{max}$ = 0.01, $(\Delta\rho)_{max,min}$ = +1.7, −1.2 e Å^3 near Pt atoms on a final difference map.

For **4**: $C_{18}H_{42}Cl_4N_2P_2Pt_2$, M_r = 880.5, monoclinic, $P2_1$ (No. 4), a = 11.660(3), b = 11.621(9), c = 11.814(5) Å, β = 114.56(3)°, U = 1459.4 Å^3, Z = 2, D_c = 2.00, λ(Mo-Kα) = 0.71069 Å, μ = 101.6 cm^{-1}, F(000) = 836, T = 295 K. Final R = 0.044 for 2471 observed reflections. Crystal dimensions 0.4 × 0.4 × 0.2 mm. S = 1.9, 252 variables. $(\Delta/\sigma)_{max}$ = 0.03, $(\Delta\rho)_{max,min}$ = +1.68, −1.77 e Å^3 near Pt atoms on a final difference map. The opposite absolute structure refined to higher R value (R = 0.048).

§ *Crystal data* for **5**: $C_{16}H_{31}Cl_2N_2PPt$, M_r = 548.4, orthorhombic, $Pbca$, a = 13.327(4), b = 18.982(7), c = 15.573(6) Å^3, U = 3939.5 Å^3, Z = 8, D_c = 1.85 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 75.5 cm^{-1}, F(000) = 2144, T = 295 K. Final R = 0.031 for 2482 observed reflections. Crystal dimensions 0.25 × 0.25 × 0.08 mm. S = 1.85, 205 variables. $(\Delta/\sigma)_{max}$ = 0.01, $(\Delta\rho)_{max,min}$ = +0.72, −0.76 e Å^3 near Pt atoms on a final difference map.

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **3**–**5** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

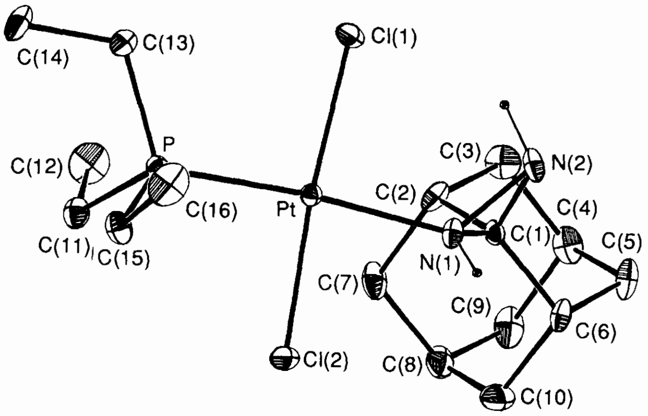

Fig. 3 Structure of *trans,trans*-[PtCl$_2$(PEt$_3$)(**1**)]. Selected bond lengths (Å) and angles (°): Pt–P 2.238(2), Pt–N(1) 2.115(6), N(1)–N(2) 1.513(8), N(2)–C(1) 1.465(9); P–Pt–N(1) 175.0(2), N(1)–C(1)–N(2) 62.1(4), N(2)–N(1)–C(1) 58.8(4), N(1)–N(2)–C(1) 59.1(4), C(1)–N(1)–HN(1) 110(7), C(1)–N(2)–HN(2) 105(5).

^{15}N NMR spectroscopy was also used to characterise the complexes, using the INEPT (insensitive nuclei enhanced by polarization transfer) technique. For the free ligands (**1**, δ −319.3,¶ J_{NH} 58.5 Hz; **2** −302.8, J_{NH} 56.6 Hz), $^1J_{\mathrm{NH}}$ is considerably lower than observed for aliphatic amines.[4] On complexation (**3** δ −314.2, J_{NH} 78.5, J_{NP} 55.5 Hz; **4** δ −315.8, J_{NH} 79 Hz, J_{NP} 56 Hz), it is clear that a substantial rehybridisation takes place at the coordinated nitrogen atom, resulting in an apparent shift of s-electron character from the lone pair to the N–H bond. The complexation shifts are not large, but the change in J_{NH} is very characteristic of complexation. In **5**, free (δ −298.7, J_{NH} 58 Hz) and coordinated (δ −315.4, J_{NH} 78, J_{NP} 57 Hz) nitrogen atoms can be clearly distinguished in this way. Theoretical studies on the bonding in these systems are underway.

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¶ Chemical shifts are recorded relative to external nitromethane.