Cleavage of the P–C Bond in $[PtCl_2(Ph_2PCH_2PPh_2\text{-}P,P')]$ under Mild Conditions

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Treatment of $[PtCl_2(Ph_2PCH_2PPh_2\text{-}P,P')]$ with an excess of NaOH in NH_3 at −50 °C gives, in >80% yield, the *cis* and *trans* isomers of $[(Ph_2MeP)(Ph_2PO)Pt(\mu\text{-}NH_2)_2Pt(POPh_2)(PMePh_2)]$, the structure of the *trans* form being confirmed by *X*-ray crystallography; both the structure and the proposed mechanism display highly novel features.

The complex $[PtCl_2(dppm\text{-}P,P')]$ (dppm = $Ph_2PCH_2PPh_2$) is the starting material for much Pt–dppm chemistry.[1] The reactions of this complex include (i) metathesis of the chloro ligands to give other four-membered chelate complexes,[2] (ii) cleavage of the Pt–P bond to give dppm-*P* or μ-dppm complexes,[3,4] (iii) deprotonation of the CH_2 group,[5] and (iv) reduction of the platinum(II) to platinum(I).[2] In each of these classes of reaction the integrity of the dppm ligand is maintained. We now describe a specific reaction cleaving one P–C bond in a Pt–dppm complex which takes place under mild conditions (−50 °C, liquid ammonia).

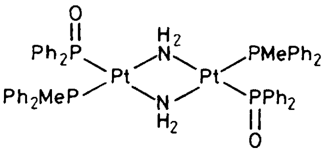
Treatment of $[PtCl_2(dppm\text{-}P,P')]$ with an excess of NaOH in liquid ammonia gave an off-white solid which, from ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy,† appeared to be a mixture of two similar species. However we were unable to assign a structure without the aid of *X*-ray crystallography.‡ The crystal structure revealed (Figure 1) that one of the products has the structure (**1a**). The n.m.r. spectra and elemental analysis (C, H, N) are consistent with the reaction products being a 1 : 1 mixture of *trans* (**1a**) and *cis* (**1b**) isomers.

Hence (**1a**,**b**) are rare examples[6] of the diphenylphosphine oxide anion, platinum(II) complexes of which have been shown recently to be useful hydroformylation catalysts.[7]

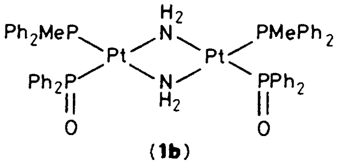
The compounds (**1a**,**b**) are unaffected by air and their $CDCl_3$ solutions are stable for at least one week. Moreover the NH_2 bridges are not hydrolysed under neutral or basic conditions but the complexes do react rapidly with aqueous HCl. In view of this stability and the great interest in platinum(II)–ammine chemistry,[8] it is surprising that, to our knowledge, only one other $Pt_2{}^{II}(\mu\text{-}NH_2)_2$ complex is known, the cationic species (**2**).[9]

No deuterium incorporation into the NH_2 groups of (**1**) was observed upon shaking $CDCl_3$ solutions of (**1a**,**b**) with D_2O for 5 min which indicates that the hydrogens are not protonic and consistent with this observation is the unexpectedly high field ^1H resonance for the NH_2 hydrogens (−0.3 to −1.6).

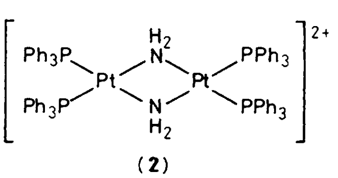
The reaction of $[PtCl_2(dppm\text{-}P,P')]$ to give (**1a**,**b**) is highly specific: they are the only platinum-containing products detected by ^{31}P n.m.r. spectroscopy and yields of isolated product are high (>80%). Scheme 1 shows a possible mechanism for the formation of (**1a**,**b**). The cationic intermediate (**3**) is the dppm analogue of the known complex (**2**).



(**1a**)



(**1b**)



(**2**)

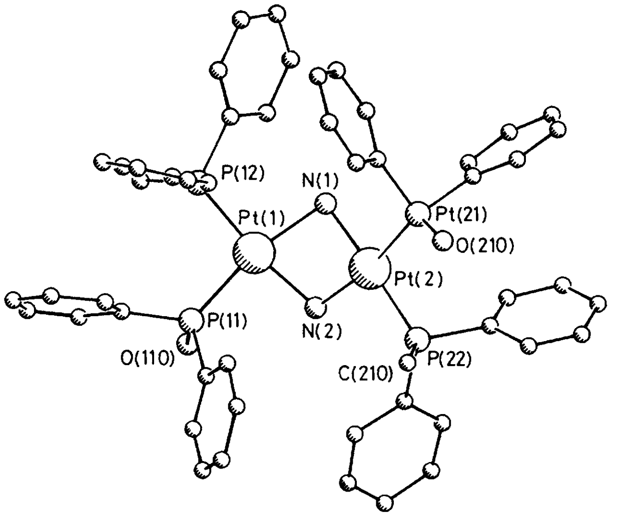


Figure 1. View of complex (**1a**) (omitting H-atoms). The Pt_2N_2 plane has a butterfly form with an angle of 44° between Pt(1)N(1)N(2) and Pt(2)N(1)N(2). Principal dimensions are: Pt–Pt 3.087(1), Pt–N 2.107(13)—2.127(14), Pt–P 2.252(5)—2.256(4) [for P=O containing groups], 2.239(4)—2.241(4) [for P–CH_3 containing groups], P–O 1.526(11) Å; Pt–N–Pt 93.8(4)°. *Crystal data:* $C_{50}H_{48}N_2O_2P_4\text{-}Pt_2{\cdot}C_2H_5OH$, monoclinic, space group $C2/c$, a = 25.576(10), b = 14.609(4), c = 26.988(10) Å, β = 102.73(4)°, U = 9835(8) Å^3, M = 1223.0, Z = 8, D_c = 1.65 g cm^{-3}, Mo-K_α radiation, α = 0.71069 Å, μ(Mo-K_α) = 58.8 cm^{-1}. $F(000)$ = 4752. Data were collected with a Syntex $P2_1$ four circle diffractometer. Maximum 2θ was 40°. R = 0.045 for 3478 unique observed reflections [$I/\sigma(I) \geq 3.0$]. The heavy atoms were located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were given fixed isotropic temperature factors. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl hydrogen atoms were omitted. One disordered EtOH solvent molecule was located. Computing was with the SHELXTL[6] system on a Data General DG30.‡

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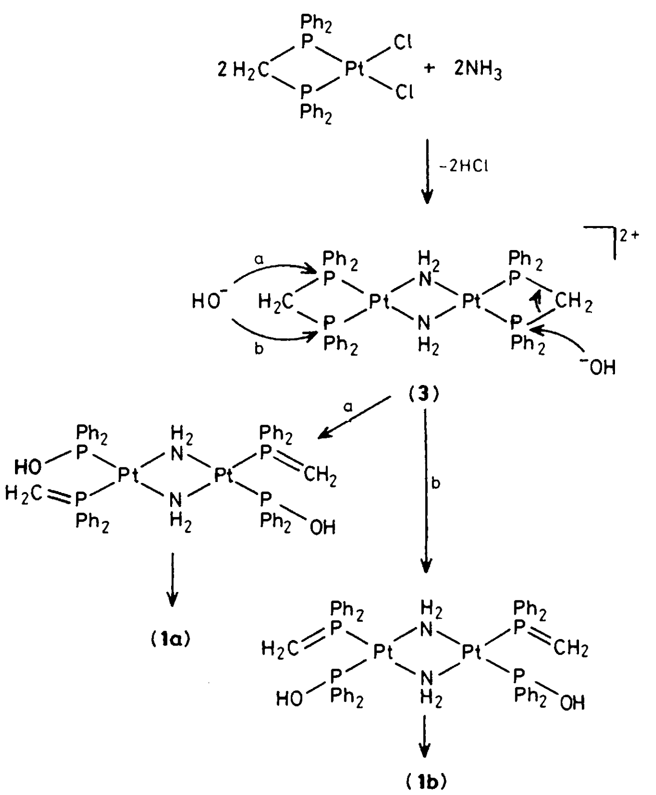
† ^1H N.m.r. ($CDCl_3$) (**1a**): δ −0.87 (NH_2, br.), 1.94 [PCH_3, J(PH) 8 Hz]. (**1b**): δ −0.34, −1.62 (NH_2, br.), 2.09 [PCH_3, J(PH) 10 Hz]; $^{31}P\text{-}\{^1H\}$ n.m.r. ($CDCl_3$): (**1a**): δ 3.1 [P_A, $^1J(PtP_A)$ 3306 Hz], 39.8 [P_X, $^1J(PtP_X)$ 3170 Hz, $|^2J(P_AP_X) + {}^4J(P_AP_X)|$ 19.7 Hz]; (**1b**): δ 1.3, [P_A, $^1J(PtP_A)$ 3308 Hz], 39.6 [P_X, $^1J(PtP_X)$ 3230 Hz, $|^2J(P_AP_X) + {}^4J(P_AP_X)|$ 29.7 Hz].

‡ 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.



Scheme 1

Nucleophilic attack by OH^- at P by paths a and b, followed by proton transfer from O to C, would lead to the observed products (**1a**) and (**1b**) respectively.

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