Nucleophilic Attack by O or N upon Reaction of Chloromethylplatinum(II) Phosphine Complexes with MeOH–$Me_2NCH(OMe)_2$; X-Ray Structure of $[(Ph_2PCH_2CH_2PPh_2)Pt(CH_2)_2NMe_2]^+PF_6^-$

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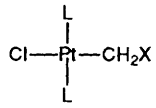
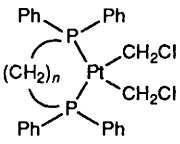
MeOH–$Me_2NCH(OMe)_2$ reacts with *trans*-$(R_3P)_2Pt(CH_2Cl)Cl$ (R = c-C_6H_{11} or Et) to give the methoxymethyl complexes *trans*-$(R_3P)_2Pt(CH_2OMe)Cl$, and with $Ph_2P(CH_2)_nPPh_2Pt(CH_2Cl)_2$ (n = 2, 3 or 4) to give the 3-platina-azetidinium salts $[Ph_2P(CH_2)_nPPh_2Pt(CH_2)_2NMe_2]^+Cl^-$ (n = 2, 3 or 4); reaction of $Ph_2P(CH_2)_2PPh_2Pt(CH_2Cl)_2$ with isopropylamine gives the 3-platina-azetidine.

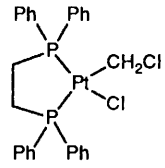
In previous publications[1] we have described the preparation and characterisation of a variety of halomethyl Pd^{II} and Pt^{II} derivatives. Such complexes are potentially valuable precursors[2,3] of reactive carbenoid species and of α-functionalised alkyl derivatives of these metals. More recently we have investigated the stability and some reactions of chloromethyl derivatives of Pd^{II} and Pt^{II}. In the course of these investigations we have found[4] that upon standing in deuteriochloroform the platinum complexes *trans*-$L_2Pt(CH_2Cl)Cl$ [**1a**, L = PCy_3 (Cy = c-C_6H_{11}); **1b**, L = PEt_3; **1c**, L = PPh_3] gradually form first the corresponding hydride, *trans*-$L_2Pt(H)Cl$, and then L_2PtCl_2 (*cis* and *trans*). This transformation depends upon the presence of water in the solvent and is promoted by acid.[4] Since a likely intermediate in this conversion is a hydroxymethyl complex, we attempted to generate *trans*-$(PEt_3)_2Pt(CH_2OMe)Cl$ **2b** by exposing **1b** to methanol in deuteriochloroform. However, decomposition to first hydride and then dichloride proceeded as before and **2b** was not detected upon monitoring the reaction by ^1H and ^{31}P NMR spectroscopy. Reasoning[4] that HCl and adventitious H_2O were responsible for this outcome, we repeated this reaction in the presence of dimethylformamide dimethylacetal. This



1a L = PCy_3, X = Cl
1b L = PEt_3, X = Cl
1c L = PPh_3, X = Cl
2a L = PCy_3, X = OMe
2b L = PEt_3, X = OMe



3a *n* = 2
3b *n* = 3
3c *n* = 4



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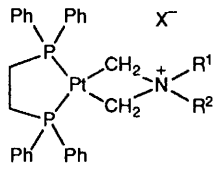
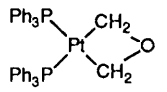


5a $R^1 = R^2$ = Me, X = Cl
5b R^1 = Pr^i, R^2 = CH_2Cl, X = Cl
5c $R^1 = R^2$ = Me, X = PF_6



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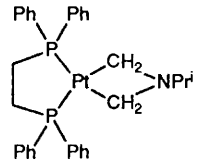


7

resulted in quantitative conversion of **1b** into **2b**. Similarly the Cy_3P complex **1a** gave **2a**† m.p. 220–223 °C.‡

Surprisingly, the relatively insoluble bischloromethyl complex **3a** under the same conditions (partly in suspension) was converted§ cleanly into the platina-azetidinium species **5a**† which was obtained as a hygroscopic solid, m.p. 90–100 °C.‡ Exchange with KPF_6 gave the corresponding hexafluorophosphate **5c** which formed crystals, m.p. 245–248 °C, suitable for X-ray analysis. The structure of the cation, shown in Fig. 1,¶ contains the first reported example of a 3-metalla-azetidinium moiety. Coordination about the platinum atom is distorted square planar and the four-membered ring is close to planar [the dihedral angle between C(3)–Pt–C(4) and C(3)–N(1)–C(4) is 3.0°]. This may be compared with the structure reported[2] for the platinaoxetane **6**, in which the four-membered ring is planar. The 1,3-bisdiphenylphosphinopropane and 1,4-bisdiphenylphosphinobutane adducts, **3b** and **3c**, appear to behave similarly upon treatment with MeOH–$Me_2NCH(OMe)_2$ in $CDCl_3$ (monitoring by ^{31}P NMR spectroscopy). The facile formation of the azetidinium moiety led us to attempt to generate a 3-platina-azetidine. Reaction of a solution of **3a** in CH_2Cl_2 with excess isopropylamine proceeded cleanly to give the *N*-chloromethylazetidinium salt **5b**†‡ rather than the azetidine **7** itself. The latter† was produced quantitatively when a suspension of **3a** in chlorobenzene was stirred with excess isopropylamine, the solid dissolving as the reaction proceeded. As anticipated, **7** is converted into **5b** upon standing in CH_2Cl_2, a process which is now well documented[5] for simple organic amines. Such azetidine and azetidinium complexes provide potential sources of intriguing reactive intermediates for condensation reactions.

The results reported above show that, in reactions with MeOH–$Me_2NCH(OMe)_2$, oxygen is the preferred nucleophile for the *trans*-monochloromethyl derivatives and nitrogen for the *cis*-bischloromethyl complexes. We do not yet have

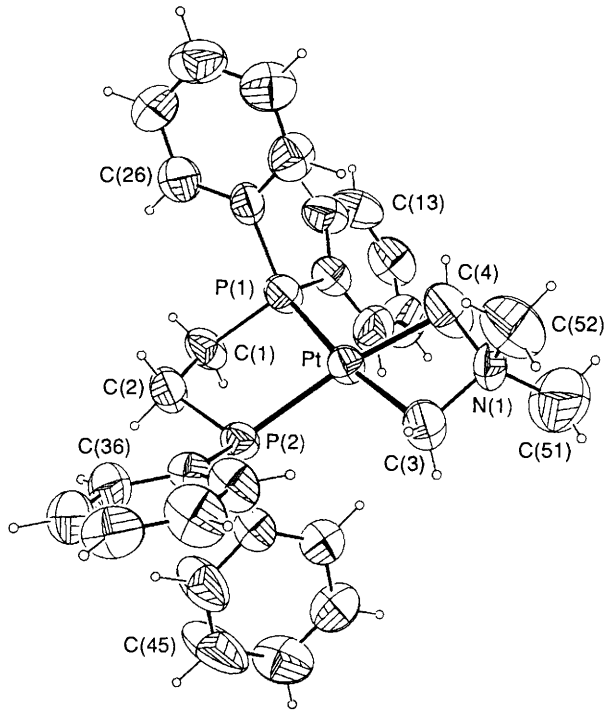
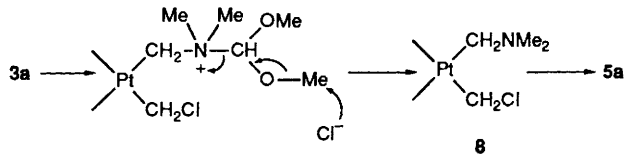


Fig. 1 An ORTEP projection of the cation of **5c**. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.278(2); Pt–P(2) 2.289(2); Pt–C(3) 2.067(8); Pt–C(4) 2.035(9); P(1)–C(1) 1.844(7); N(1)–C(3) 1.506(10); N(1)–C(4) 1.506(11); N(1)–C(51) 1.448(14): N(1)–C(52) 1.466(12); P(1)–Pt–P(2) 85.17(7); P(1)–Pt–C(3) 169.1(2); P(1)–Pt–C(4) 102.9(3); P(2)–Pt–C(3) 104.6(2); C(3)–Pt–C(4) 67.1(4); Pt–P(1)–C(1) 107.1(3); C(3)–N(1)–C(4) 97.8(6); C(3)–N(1)–C(52) 111.2(7); C(51)–N(1)–C(52) 108.1(8).



8

† *Spectroscopic data* (*J* in Hz) for **2a**: δ_H 3.20 (s, OMe), 3.68 (m, CH_2O, $^3J_{P-H}$ 6.8, $^2J_{Pt-H}$ 67); δ_P (external H_3PO_4) 21.6 ppm ($^1J_{Pt-P}$ 2933); **5a**: δ_H 3.29 (s, NMe_2), 3.51 (br. t, CH_2NCH_2, $^2J_{Pt-H}$ 66); δ_P 43.8 ppm ($^1J_{Pt-P}$ 2140); **5b**: δ_H 1.39 (d, CMe_2, $^3J_{H-H}$ 6.6), 3.41 and 3.45 (both m, 2H, CH_2NCH_2, $^2J_{H-H}$ 11.0, $^2J_{Pt-H}$ 67), 3.62 (septet, NCH, $^3J_{H-H}$ 6.6), 5.14 (s, CH_2Cl); δ_P 43.8 ppm ($^1J_{Pt-P}$ 2155); **7**: δ_H 1.32 (d, CMe_2, $^3J_{H-H}$ 6.2), 2.62 (septet, $^3J_{H-H}$ 6.2), 3.44 (br, t, CH_2NCH_2, $^2J_{Pt-H}$ 80); δ_P 44.2 ppm ($^1J_{Pt-P}$ 1841).

‡ Characterised by elemental analysis.

§ The reaction of MeOH–$Me_2NCH(OMe)_2$ with the monochloromethyl complex **4** ($CDCl_3$; NMR tube sealed under vacuum) proceeded extremely slowly (*ca.* 50% consumption of **4** over two months) to give (^{31}P NMR spectroscopy) mainly a single product of undetermined structure.

¶ *Crystal data* for **5c**: $C_{30}H_{34}F_6NP_3Pt$, M = 810.6, monoclinic, space group $P2_1/n$, a = 9.308(2), b = 12.585(2), c = 26.825(4) Å, β = 90.88(2)°, V = 3142(2) Å^3, Z = 4, D_c = 1.71 g cm^{-3}, μ(Mo-Kα) = 47.2 cm^{-1}. Intensity data were measured at 21 °C using an Enraf-Nonius CAD4 diffractometer. Lorentz, polarisation and absorption corrections were applied to the data. The structure was solved by the heavy-atom method and refined by full-matrix least-square calculations with hydrogens allowed for as riding atoms. At convergence R = 0.034, R_w = 0.041 for 3659 reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

sufficient information to allow us to suggest detailed mechanisms for these transformations. However, if these reactions involve simple nucleophilic substitutions, the contrasting behaviour of the two groups of compounds may be rationalised on the basis of steric effects. With the *trans* derivatives, approach of the nucleophile to the C atom of the chloromethyl moiety will be hindered, effectively blocking attack by the tertiary amino nitrogen. Attack therefore takes place exclusively by the smaller nucleophile, MeOH (or MeO^- generated with the participation[6] of the amide acetal). Approach to the analogous C atom in bischloromethyl derivatives is expected to be less hindered so that attack by the better nucleophile is now preferred (see Scheme 1). Since we have been unable to detect either the dimethylaminomethyl intermediate **8** or a bisdimethylaminomethyl product, ring closure of **8** to the azetidinium derivative must be relatively fast.

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References

1 R. McCrindle, G. J. Arsenault, R. Farwaha, A. J. McAlees and D. W. Sneddon, *J. Chem. Soc., Dalton Trans.*, 1989, 761; R. McCrindle, G. J. Arsenault, R. Farwaha, M. J. Hampden-Smith, R. E. Rice and A. J. McAlees, 1988, 1773.
2 J. F. Hoover and J. M. Stryker, *J. Am. Chem. Soc.*, 1989, **111**, 6466.
3 For further leading references see: M. Huser, M. T. Youinou and J. A. Osborn, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1386; G. B. Deacon, B. M. Gatehouse and S. C. Ney, *J. Organomet. Chem.*, 1988, **348**, 141; H. Werner, L. Hofmann, W. Paul and V. Schubert, *Organometallics*, 1988, **7**, 1106; T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543; J. L. Hubbard and W. K. McVicar, *J. Am. Chem. Soc.*, 1986, **108**, 6422.
4 R. McCrindle, G. J. Arsenault, A. Gupta, M. J. Hampden-Smith, R. E. Rice and A. J. McAlees, to be published.
5 For leading references see: H.-J. Federsel, E. Konberg, L. Lilljequist and B.-M. Swahn, *J. Org. Chem.*, 1990, **55**, 2254.
6 R. F. Abdulla and R. S. Brinkmeyer, *Tetrahedron*, 1979, **35**, 1675.