Phosphine Exchange in *trans*-Chlorobis(methyldiphenylphosphine)[2-(phenylazo)phenyl]platinum(II) promoted by Intramolecular Nucleophilic Attack

By **Ronald J. Cross** * and **Norman H. Tennent**, Chemistry Department, University of Glasgow, Glasgow G12 8QQ

Temperature variations in ^{1}H n.m.r. spectra of the title compound, (I), in CDCl$_3$ or nitrobenzene solutions are interpreted in terms of facile exchange of phosphine. Chemical evidence supporting ready loss of Ph$_2$MeP from compound (I), together with the failure to observe phosphine exchange in [(Ph$_2$MeP)$_2$PtX$_2$] (X = Cl, Br, or I) except when excess of phosphine is present, suggest that an S_Ni mechanism operates in (I) to eliminate Ph$_2$MeP, which could then participate in S_N2 exchange reactions.

SEVERAL phosphine complexes have been reported to undergo rapid phosphine exchange in solution at room temperature. Exchange is usually observed by broadening and decoupling of ^{1}H n.m.r. signals, most often of alkyl groups attached to phosphorus, but occasionally of similar groups or hydrogen atoms bonded directly to the metal atom. Most examples involve metals of the Group VIII triad. 18-Electron molecules such as [RhH(PPh$_3$)$_4$] [1] and Pt(PMePh$_2$)$_4$ [2] undergo phosphine

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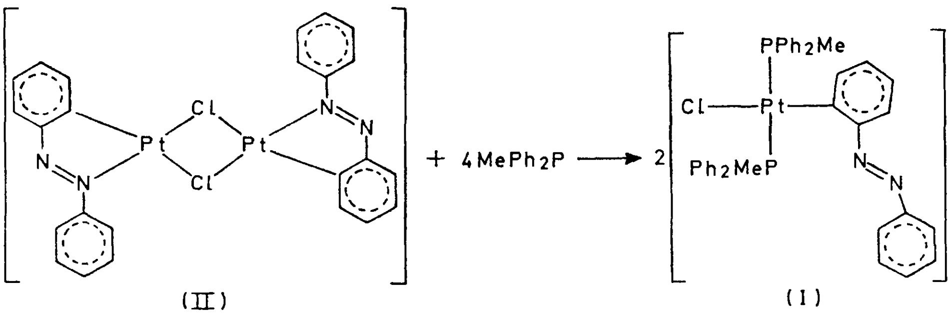
[1] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

[2] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

exchange by an S_N1 mechanism, spontaneously losing a ligand, whereas 16-electron molecules such as $[PdCl_2(PMePh_2)_2]$ [3] and $[PtI_2(PMe_2Ph)_2]$ [4] usually require the presence of excess of phosphine in solution, and presumably exchange *via* an S_N2 process. Fackler *et al.*[3] have considered theoretically the effect of phosphine exchange on n.m.r. spectra of virtually coupled systems. He summarised their conclusions[5] in relation to the rapid exchange observed by Deeming and Shaw[6] between excess of dimethylphenylphosphine and the compound *trans*-$[RhCl(CO)(PMe_2Ph)_2]$.

We report here results of a variable temperature n.m.r. examination of the compound $[(Ph_2MeP)_2PtCl(C_6H_4{\cdot}N_2{\cdot}Ph)]$, (I), and the effects of adding excess of phosphines to $[(Ph_2MeP)_2PtX_2]$ (X = Cl, Br, or I).



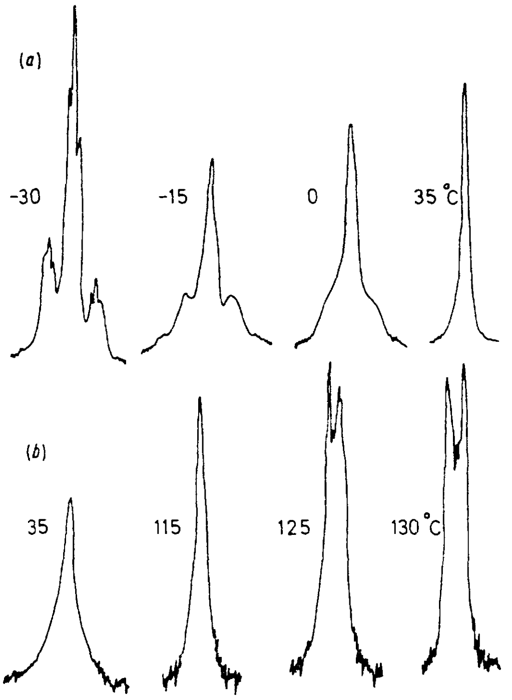
(1)

RESULTS AND DISCUSSION

Chlorobis(methyldiphenylphosphine)[2-(phenylazo)-phenyl]platinum(II), (I), was prepared by bridge cleavage of di-μ-chloro-bis{[2-(phenylazo)phenyl-C^2N']platinum(II)}, (II) [equation (1)].[7] Platinum and palladium analogues of compound (I) with other phosphines are well known,[7] and a crystal-structure analysis of a triethylphosphine derivative confirmed the *trans*-configuration of the phosphines.[8]

Temperature variations of ^{1}H n.m.r. spectra of compound (I) are shown in the Figure. Only at −30 °C were the three triplets expected for methyl signals of virtually coupled *trans*-phosphines at platinum resolved. At room temperature they collapsed to a broad singlet, which sharpened by 60 °C and was converted to a doublet at 125 °C. These changes were reversible, though above 140 °C decomposition occurred. These observations are consistent with predictions made by Fackler *et al.*[3,5] for the appearance of exchange spectra in virtually coupled systems at different rates of exchange. Thus we ascribe the broad singlet observed for the methyl signals at room temperature to rapid phosphine exchange, leading to relaxation decoupling of ^{31}P–H and ^{195}Pt–H. The appearance of the high-temperature doublet has been observed in only one other case.[5,6]

In contrast to the behaviour of compound (I), n.m.r. spectra of chloro(methyldiphenylphosphine)[2-(phenylazo)phenyl-C^2N']platinum(II), (III) [prepared by adding two equivalents of phosphine to (II)[7]], showed no evidence of phosphine exchange. Furthermore, no exchange of ligands was apparent from ^{1}H n.m.r. spectra of the compounds $[(MePh_2P)_2PtX_2]$ (X = Cl, Br, or I) in $CDCl_3$. We therefore propose a mechanism for exchange whereby internal nucleophilic attack of a nitrogen atom promotes loss of phosphine ligand [equation (3)]; the latter can then undertake intermolecular nucleophilic substitutions. Associative (S_N2) mechanisms are well established for square-planar platinum(II) complexes,[9] and are undoubtedly involved



Variable-temperature ^{1}H n.m.r. spectra of the methyl signals of *trans*-chlorobis(methyldiphenylphosphine)[2-(phenylazo)-phenyl]platinum(II), (I): (*a*) in $CDCl_3$ solution at 100 MHz, τ 1·74 (Varian HA100); (*b*) in $PhNO_2$ solution at 60 MHz, τ 1·84 (Jeol C-60H)

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[3] J. P. Fackler, jun., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 1969, **91**, 1941.

[4] D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

[5] J. P. Fackler, jun., *Inorg. Chem.*, 1970, **9**, 2625.

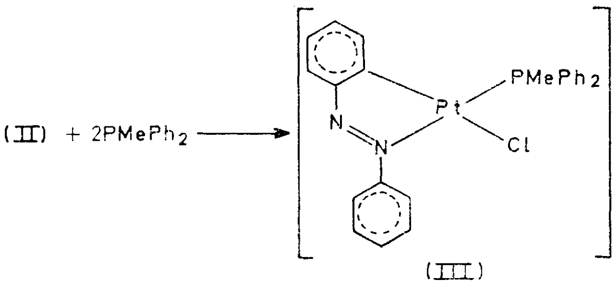
[6] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.

[7] R. J. Cross and N. H. Tennent, *J. Organometallic Chem.*, 1974, in the press.

[8] D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2250.

[9] A. Peloso, *Co-ordination Chem. Rev.*, 1973, **10**, 123.

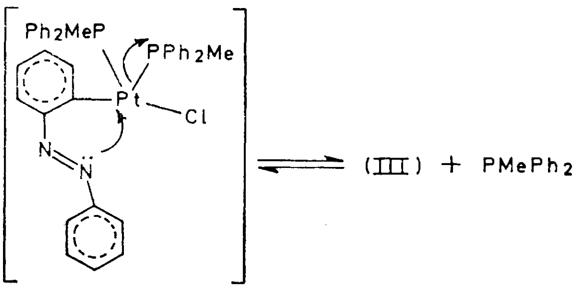
in some systems prone to rapid phosphine exchange where excess of ligand is necessary.[3-6,10,11] The present case is the only example where the complex itself has a free ligating group available to participate in intramolecular (S_Ni) displacement.



(2)

(III)

Facile loss of Ph_2MeP from compound (I) in perdeuteriochloroform was confirmed by addition of (II);



(3)

rapid transfer of phosphine took place to yield (III) [equation (4)]. Also, on heating nitrobenzene solutions

$$2(I) + (II) \longrightarrow 4(III) \qquad (4)$$

of compound (I) to temperatures in excess of 140 °C in the presence of air, decomposition to (III) and Ph_2MePO took place. This is unusual for bis(phosphine) complexes of platinum(II), even when the phosphine itself is more prone to oxidation than methyldiphenylphosphine. A separate experiment confirmed that free Ph_2MeP in nitrobenzene is oxidised under these conditions.

Although the compounds $[(Ph_2MeP)_2PtX_2]$ (X = Cl, Br, or I) do not exhibit exchange phenomena themselves in $CDCl_3$ solution, we observed that addition of Ph_3P, Ph_2MeP, or $PhMe_2P$ to their solutions caused immediate broadening and decoupling of the methyl ^1H n.m.r. resonances, typical of fast exchange. These observations are consistent with an S_N2 exchange process, of the type which may operate for compound (I) in conjunction with the S_Ni mechanism. The addition of triethylamine to the compound *cis*-$[(Ph_2MeP)_2PtCl_2]$ also produced exchange broadening, but, interestingly, free azobenzene did not, perhaps due to steric hindrance.

It is interesting to note that rapidly exchanging systems usually involve the less basic phosphines such as Ph_3P, Ph_2MeP, and $PhMe_2P$. Rapid exchange involving trialkylphosphines is rare.[12] We found that addition of free Ph_3P, Ph_2MeP, or $PhMe_2P$ caused exchange broadening in ^1H n.m.r. spectra of the compound $[(Ph_2MeP)_2PtCl_2]$, but not of $[(Et_3P)_2PtCl_2]$. In this latter case, spectra consistent with the formation of ionic species, $[(Et_3P)_2(L)PtCl]Cl$, were obtained.[13] Exchange broadening was also found in a detailed study of the addition of various phosphines to the compounds $[(Me_2PhP)_2PtX_2]$ (X = Cl or I).[4] Ionic species $[(PhMe_2P)_2(L)PtX]X$ were formed, and at room temperature S_N2 attack by both L and X^- promoted rapid exchange. Similar processes appear to operate in related palladium(II) complexes.[3,10,11]

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[10] S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 1970, **4**, 56.

[11] D. G. Cooper and J. Powell, *Canad. J. Chem.*, 1973, **51**, 1634.

[12] C. F. Shaw, J. W. Lundeen, and R. S. Tobias, *J. Organometallic Chem.*, 1973, **51**, 365.

[13] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074; H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.