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Amido-Complexes of Platinum(II). An X-Ray Crystal Structure Determination of *cis*-[PtCl(NPh$_2$)(PEt$_3$)$_2$]

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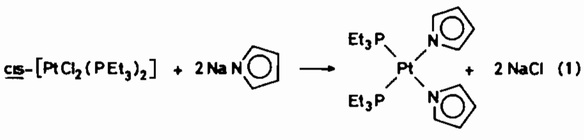
Attention has recently been drawn to the fact that few diorgano-amido complexes of the late transition metals are known [1]. This contrasts with the abundance of such complexes of the earlier transition metals, and with the isoelectronic alkyl complexes, which for Pt and Au are of considerable thermal stability and were among the earliest known organo-transition metal compounds [2]. Several amido complexes of Group VIII metals have been made by oxidative addition reactions or other indirect methods, and complexes of N(SiMe$_3$)$_2$ have been obtained from the lithium amide [1, 3]. These complexes may derive some stability from the presence of electron withdrawing substituents on N or from the absence of facile decomposition pathways *via* β-elimination. It has been shown [4] that reactions directed towards the formation of (dimethylamido)(phosphine) complexes of Ru, Rh or Pd lead in high yield to known hydrido-complexes as a result of a β-elimination analogous to that identified in the decomposition of metal alkyls and alkoxides.

We find that the reaction between LiNPh$_2$ and an equimolar proportion of *cis*-[PtCl$_2$(PEt$_3$)$_2$] in THF (at room temperature for 1 h) affords [PtCl(NPh$_2$)(PEt$_3$)$_2$] as bright yellow crystals (60–80% yield. *Anal.* Found: C, 45.0; H, 6.3; N, 2.2; Cl, 5.3. C$_{24}$H$_{40}$ClNP$_2$ calcd.: C, 45.4; H, 6.3; N, 2.2; Cl, 5.61%). The solid product is stable in the absence of air but is air-sensitive in THF solution. The complex has a *cis*-geometry in the solid state (*vide infra*) and the ^{31}P{^{1}H} NMR spectrum (in CD$_2$Cl$_2$: δ** −134.7 ppm, ^{1}J(PtP) 3867 Hz; δ −138.8 ppm, ^{1}J(PtP) 2720 Hz, ^{2}J(PP) 22 Hz) shows that the same configuration persists in solution.

The complex *cis*-[PtCl(NPh$_2$)(PMe$_2$Ph)$_2$] has been obtained in a similar manner, but reactions using a larger molar proportion of LiNPh$_2$ failed to give a corresponding bis(diphenyl-amido)platinum(II) complex. A bis(amido) complex has, however, been obtained from the pyrollyl anion, as represented in eqn. (1). The white, air-stable product (*Anal.* Found: C, 41.8; H, 6.8; N, 5.0. C$_{20}$H$_{38}$N$_2$Pt calcd.: C, 42.6; H, 6.8; N, 5.0%) gives a ^{31}P{^{1}H} NMR spectrum (δ −138.5 ppm, ^{1}J(PtP) 2883 Hz) with somewhat broadened lines, possibly due to unresolved coupling to ^{14}N. The complex is probably of *cis*-configuration. Although the magnitude of ^{1}J(PtP) is close to one of the values for *cis*-[PtCl(NPh$_2$)(PEt$_3$)$_2$] (2720 Hz), suggesting that both are associated with P *trans* to N, the coupling for the pyrollyl complex is within the range found for some *trans*-bis(phosphine) complexes [5]. However, the ^{1}H NMR spectrum of pyrollyl complexes does not show a 'virtually coupled' spectrum for the PEt$_3$ ligands which is a characteristic of *trans*-bis(phosphine) complexes.



Crystals of *cis*-[PtCl(NPh$_2$)(PEt$_3$)$_2$] are orthorhombic, *Pca2$_1$*, a = 15.614(10), b = 10.217(8), c = 16.391(3) Å, MoK$_{\alpha'}$ radiation, λ = 0.71069; $F(000)$ = 1264, μ = 53.65 cm^{-1}, D_c = 1.612 g cm^{-3}, Z = 4. A total of 1892 unique reflections were measured of which 1550 had $I > 3\sigma(I)$. With anisotropic temperature factors on all atoms, the structure was refined to R = 0.044 (R = 0.057 on full data); hydrogen atoms were not included. The molecular structure is depicted in Fig. 1. The central Pt atom and the skeleton of the diphenylamido ligand lie close to a plane which is tilted through 77° from the plane of the square arrangement around the metal. Bond lengths (Å) aare Pt–N = 2.09(2), Pt–P = 2.277(4) (*trans* to N) and 2.235(6) (*trans* to Cl), and Pt–Cl = 2.392(5).

Comparison with results for the closely related complexes *cis*-[PtClL(PEt$_3$)$_2$]$^+$(BF$_4$)$^-$ (L = phenanthroline, naphthiridine) [6, 7] shows that the sp^2-hybridized N-atom in the diphenylamido-ligand has a greater *trans* influence than the heterocyclic N-atoms, this although the Pt–N lengths are not significantly different. Thus, in the complexes of the

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**From external (MeO)$_3$P; positive shifts are to high frequency.

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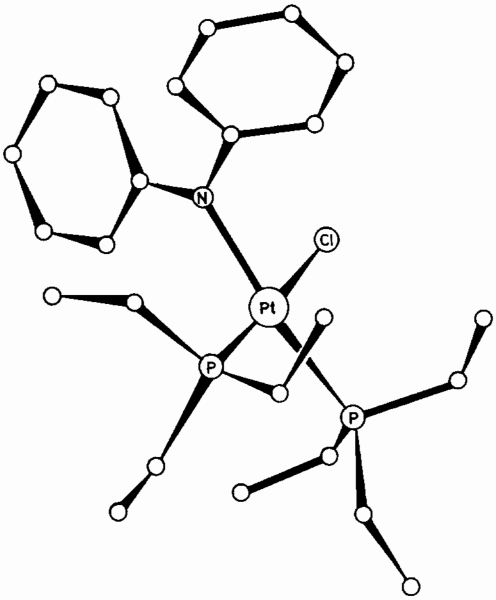

Fig. 1. Molecular Structure of *cis*-[PtCl(NPh$_2$)(PEt$_3$)$_2$].

heterocyclic N-donors the non-equivalent Pt–P bonds do not differ significantly in length [6], and the coupling constants ^1J(PtP) differ [7] by only *ca.* 300 Hz; by contrast, the Pt–P bond *trans* to the diphenylamido group is longer by *ca.* 0.04 Å than that *trans* to Cl, and this is paralleled by a difference in the coupling constants ^1J(Pt–P) of *ca.* 1150 Hz. It is noteworthy in this respect (and also in relation to the planarity at the amido-N atom) that any Pt–N d_π–p_π interaction in the amido-complex must be antibonding, since the d_π orbitals of Pt and the p_π orbital of nitrogen are fully occupied.

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