

Preliminary communication

SOME CHEMISTRY OF MIXED LIGAND COMPLEXES OF PLATINUM

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Summary

Simple synthetic routes to the mixed ligand complexes $\text{PtLL}'\text{X}_2$ and $\text{PtLL}'\text{XY}$ ($\text{L}' = \text{PEt}_3$; $\text{L} =$ phosphine, arsine, etc.; $\text{X} = \text{Cl}$ and $\text{Y} = \text{Cl, H or Me}$) are described; unexpectedly, these display an extensive chemistry without disproportionation, although in some cases ligand scrambling does occur.

The preparation of metal complexes of low symmetry containing readily available ligands can greatly benefit studies of (a) asymmetric synthesis catalyzed by metal complexes, and (b) electronic and steric effects of ligands on the catalytic activity of metal complexes. Particularly for those species containing monodentate ligands, the tendency towards disproportionation to more symmetrical complexes, has obviously deterred investigation, e.g. for platinum(II)



However, in a low symmetry species such as *trans*- $\text{PtLL}'\text{XY}$, the ability to vary systematically, just one ligand L' , would open a unique method to study steric and electronic ligand effects, especially for those complexes which catalyze organic transformations.

There have been only a few scattered reports [1,2] of such platinum(II) complexes, most of which have been dichlorides*. Hitherto, the extent to which their full chemistry can be developed without the occurrence of extensive disproportionation** has not been determined. We now describe a simple route to such low symmetry platinum(II) complexes containing readily available monodentate ligands, and demonstrate the extent of their potentially interesting chemistry.

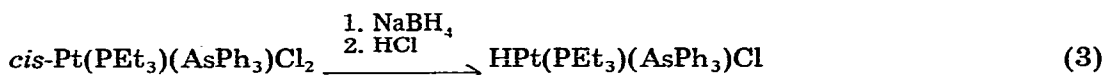
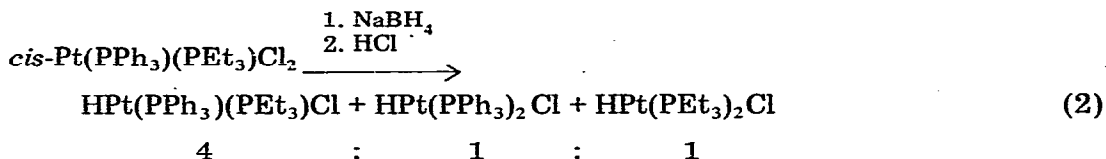
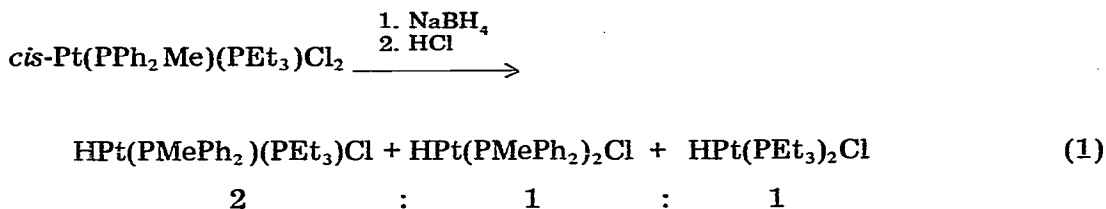
Dropwise addition of a solution of L ($\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{P-}i\text{-Pr}_3, \text{PCy}_3, \text{AsPh}_3$ or SbPh_3) to a dichloromethane solution of $[\text{PtL}'\text{Cl}_2]_2$ ($\text{L}' = \text{PEt}_3$) resulted in the formation of the lemon-yellow crystalline *trans*- $\text{PtLL}'\text{Cl}_2$, except for $\text{L} =$

*Preparation of $\text{PtRCILL}'$ ($\text{R} =$ phenyl) has been described recently [3].

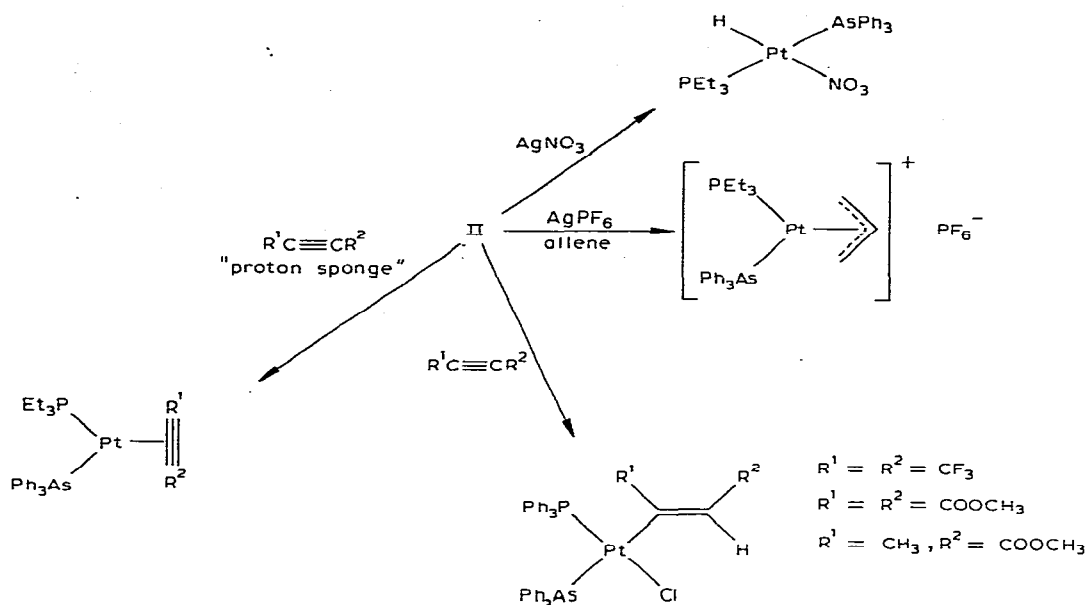
**For example, the preparation of $\text{Pt}(\text{P-}n\text{-Bu}_3)(\text{PEt}_3)\text{Cl}_2$ [2] leads to impure products.

SbPh_3 in which case the *cis* isomer is obtained. *trans*- $\text{Pt}(\text{PEt}_3)\text{LCl}_2$ ($\text{L} = \text{PPh}_3$, PMePh_2 , AsPh_3), when suspended in a small amount of dichloromethane in the presence of a catalytic amount of L , isomerized to the *cis* isomer. Isomerization is usually complete in 2–3 h to give the *cis* isomer in excellent yield (95–100%). The ^{31}P NMR spectrum showed that no observable disproportionation had occurred.

Hydrazine reduction of *cis*- $\text{PtLL}'\text{Cl}_2$ ($\text{L}' = \text{PEt}_3$, $\text{L} = \text{PPh}_3$, PMePh_2 or AsPh_3) in refluxing ethanol led to extensive disproportionation. However, reduction with NaBH_4 [4] at 0°C followed by acidification with HCl afforded the mixed-ligand hydrides (equations 1–3).



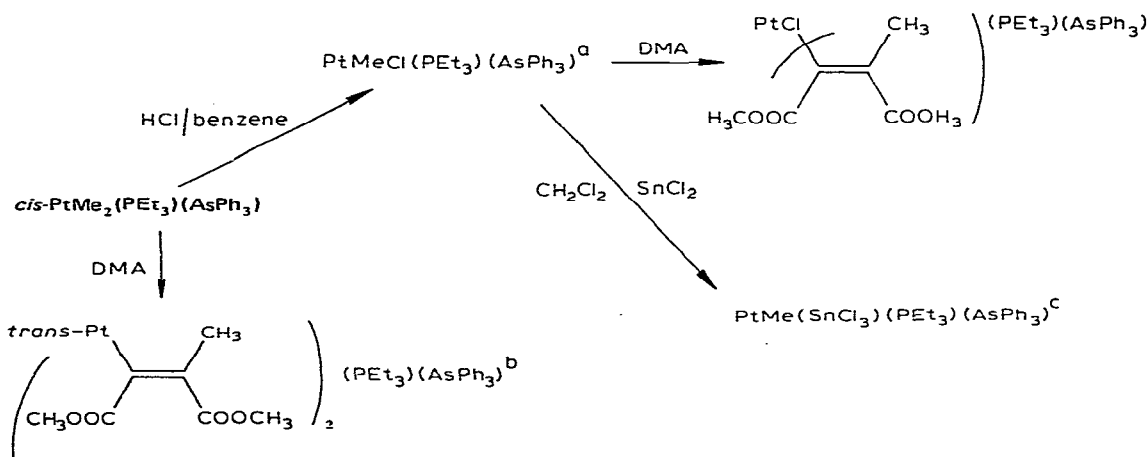
Some ligand scrambling occurs, the extent of which depends on the nature of the ligands L and L' . The less alike the two ligands are, the smaller is the extent of disproportionation. Thus, for $\text{L}' = \text{PEt}_3$ and $\text{L} = \text{PMePh}_2$, there is about 50% disproportionation, about 34% for $\text{L}' = \text{PEt}_3$ and $\text{L} = \text{PPh}_3$, and 0% for $\text{L}' = \text{PEt}_3$ and $\text{L} = \text{AsPh}_3$ (77% yield of hydrido-chloride). Both $\text{HPt}(\text{PPh}_3)(\text{PEt}_3)\text{Cl}$ (I) (^1H NMR $\delta(\text{PtH})$ -17.1 triplet, $J(\text{PH})$ 14.0 , $J(\text{PtH})$ 1271.4 Hz; ^{31}P NMR δ 24.4 , $J(\text{PtP})$ 2852 Hz, δ 25.3 , $J(\text{PtP})$ 2825 Hz) and $\text{HPt}(\text{PEt}_3)(\text{AsPh}_3)\text{Cl}$ (II) (^1H NMR $\delta(\text{PtH})$ -18.4 ppm doublet, $J(\text{PtH})$ 1016 Hz, $J(\text{PH})$ 12.5 Hz; ^{31}P NMR δ 19.00 , $J(\text{PtP})$ 3530.3 Hz) are fairly stable towards disproportionation in solution; I disproportionates only slightly ($< 5\%$) in CDCl_3 over a period of 3 days, while II shows no signs of disproportionation over the same time. Both I and II undergo the usual type of hydride reactions. Thus, metathetical displacement occurs in the reaction of II with AgNO_3 to give $\text{HPt}(\text{PEt}_3)(\text{AsPh}_3)(\text{NO}_3)$ (Pt-H δ -24.6 , $J(\text{PtH})$ 1260 , $J(\text{PH})$ 14 Hz; ^{31}P NMR, $\delta(\text{P})$ 21.61 , $J(\text{PtP})$ 3415 .) Also, in the presence of AgPF_6 , allene reacts with II to give a static π -allyl complex at room temperature, and activated acetylenes insert into the Pt-H bond of II forming σ -alkenyl products. Although, in the latter type of reaction, a large number of isomeric products is possible, only one isomer is formed (Scheme 1) e.g. for $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{COOCH}_3$, ^1H NMR gives R^1 δ 2.17 , $^3J(\text{PtH})$ 48 Hz, $^4J(\text{HH})$ 1.4 Hz, and R^2 δ 3.52 ; ^{31}P NMR, δ 10.76 , $J(\text{PtP})$ 3727 Hz.



SCHEME 1

Again reaction of II with an activated acetylene such as dimethylacetylenedicarboxylate (DMA) in the presence of proton sponge, gives the acetylene-platinum(0) complex with mixed ligands.

Similarly, the *cis* mixed-ligand dichlorides react with excess methyllithium in ether to afford the complexes $\text{PtMe}_2\text{LL}'$ ($\text{L}' = \text{PET}_3$, $\text{L} = \text{PPh}_3$, ~ 50% disproportion-



SCHEME 2.

(a) ^1H NMR: $\delta(\text{CH}_3)$ 0.35, $^2J(\text{PtH})$ 80 Hz, $^3J(\text{PH})$ 4.5 Hz; (in CD_2Cl_2)

^{31}P NMR: $\delta(\text{PET}_3)$ 13.07, $J(\text{PtP})$ 3738 Hz.

(b) ^1H NMR: $\delta(\text{C}(\text{CH}_3))$ 1.86, $\delta(\text{COOCH}_3)$ 3.24, 3.47;

^{31}P NMR: $\delta(\text{PET}_3)$ 4.32, $J(\text{PtP})$ 3462 Hz.

(c) ^1H NMR: δ 0.67, $J(\text{PH})$ 5.5 Hz.

tionation, *cis*, ^1H NMR $\delta(\text{CH}_3^1)$ 0.12, $J(\text{PH})$ 7 Hz, $J(\text{PtH})$ 67 Hz; $\delta(\text{CH}_3^2)$ 0.28, $J(\text{PH})$, 7 Hz, $J(\text{PtH})$ 67 Hz; ^{31}P NMR $\delta(\text{PEt}_3)$ 4.87, $J(\text{PtP})$ 1848 Hz; $\delta(\text{PPh}_3)$ 24.78, $J(\text{PtP})$ 1919 Hz, $J(\text{PP})$ 12.2 Hz; for $\text{L}' = \text{PEt}_3$, $\text{L} = \text{AsPh}_3$ no disproportionation, *cis*, ^1H NMR $\delta(\text{CH}_3)$ 0.28, $J(\text{PH})$ 7 Hz, $J(\text{PtH})$ 64 Hz; ^{31}P NMR δ 7.34, $J(\text{PtP})$ 1941 Hz; for $\text{L}' = \text{PEt}_3$, $\text{L} = \text{SbPh}_3$, no disproportionation, *cis*). The dimethyl complexes are stable and do not disproportionate in CDCl_3 over a period of 3 days. Some reactions of *cis*- $\text{PtMe}_2(\text{PEt}_3)(\text{AsPh}_3)$ are summarized in Scheme 2.

We have thus demonstrated that the low symmetry of mixed ligand complexes of platinum(II) can be preserved and even enhanced through a wide variety of reactions. The stability of the species such as $\text{PtRCl}(\text{PEt}_3)(\text{AsPh}_3)$ ($\text{R} = \text{H}$ or CH_3) containing four different ligands on platinum, and the fact that its five coordinate olefin complex, $\text{PtRCl}(\text{PEt}_3)(\text{AsPh}_3)(\text{olefin})$, either isolable or occurring only as a reaction intermediate, would totally lack symmetry, offers many interesting possibilities. Further investigations of such complexes, including their possible use as catalysts, are under way.

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