Synthesis and Characterization of New Complexes of *cis*-[$PtCl_2(PR_3)(PhCN)$] and *cis*-[$PtCl_2(PR_3)$(amine)]

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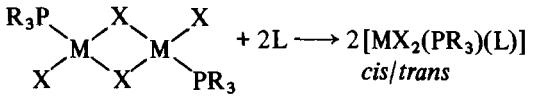
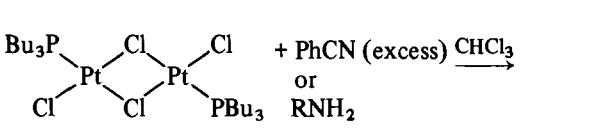
The halogen bridged phosphine complexes [$M_2X_4(PR_3)_2$], where M = Pt or Pd, PR_3 = tertiary phosphine and X = halogen, all have the *trans*-halogen bridged structure [1]. However, recently, we report the formation of a variety of unsym. *cis*/sym. *trans* halogen bridged complexes [2]. Halogen bridged complexes are very useful in reactions in which the bridge is cleaved to give monomeric complexes [3, 4]. Bridge-cleavage by monodentate ligands of sym. *trans*-[$Pt_2(\mu\text{-}X)_2X_2L_2$] (where L are neutral ligands) produces two isomers. The bond broken is generally found to be that opposite the terminal ligand of higher *trans* effect [5]. This is illustrated by eqn. (1).



When the ligand L is an amine the product is invariably the *trans*-isomer [3, 4] whereas with carbon monoxide or olefin it is the *cis*-isomer [6]. Treatment of halogen bridged tertiary phosphine with 2 mole (or excess) of benzonitrile yields *trans*-[$MX_2(PhCN)(PR_3)$], as expected. Benzonitrile ligand behaves like amines in the reaction with the dimer (eqn. (2)).



cis-[$PtCl_2(PhCN)(PBu_3)$]
or
cis-[$PtCl_2(RNH_2)(PBu_3)$] (2)

Benzonitrile possesses a weak *trans* effect compared with olefin, phosphine and carbon monoxide ligands [7, 8]. There is no reported result on the possibility of formation of *cis*-[$MX_2(PR_3)(L)$], where M = Pt or Pd and L = PhCN or amines, and all trials made have failed because theoretically and experimentally the final product will be the *trans* monomer.

We present here the results of the reaction of sym. *trans*-[$Pt_2(\mu\text{-}Cl)_2(Cl)_2(PR_3)_2$] ($PR_3$ = PBu_3 and PPh_3) (I) with benzonitrile, primary and secondary amines which lead to the formation of new *cis*-[$PtCl_2(PR_3)(PhCN)$] and *cis*-[$PtCl_2(PBu_3)$(primary amine)] complexes.

Experimental

Preparation of cis-[$PtCl_2(PBu_3)(PhCN)$] (II)

A mixture of PhCN (3–5 ml) and sym. *trans*-[$Pt_2Cl_4(PBu_3)_2$] (0.5 g) in chloroform solution (30–50 ml) was stirred and left overnight at room temperature. The reaction mixture was evaporated *in vacuo* to a yellow solution (*ca.* 2 ml). Addition of light-petroleum (30–40°) to the concentrated solution gave a white precipitate, which was collected, washed with petroleum ether (30–40°) and dried in air (total yield 80%). *Anal.* Calc. for $C_{19}H_{32}Cl_2NPPt$: C, 39.93; H, 5.61; N, 2.45. Found: C, 40.33; H, 5.30; N, 2.56%.

[It is worth noting that the *cis*-monomer product was precipitated only when the final yellow solution (after evaporation) contains some free benzonitrile solution (*ca.* 1–2 ml), *i.e.* the $CHCl_3$ solution was evaporated completely in addition to some of the PhCN solution. Further concentration of the petroleum ether filtrate to 1–2 ml, and addition of more petroleum ether (30–40°), and cooling of the mixture, led to the formation of more *cis*-monomer.]

Preparation of cis-[$PtCl_2(PBu_3)$(prim. amine)] (III)

Treatment of sym. *trans*-[$Pt_2Cl_4(PBu_3)^2$] with excess primary amine in chloroform (as above), led to the formation of *cis*-[$PtCl_2(PBu_3)$(prim. amine)] (Table I) in quantitative yield. *Anal.* Calc. for $C_{16}H_{38}Cl_2NPPt$: C, 35.49; H, 7.02; N, 2.59. Found: C, 34.05; H, 7.22; N, 2.40%.

Preparation of cis-[$PtCl_2(PRh_3)(PhCN)$] (IV)

Treatment of sym. *trans*-[$Pt_2Cl_4(PPh_3)_2$] with excess PhCN (as above), led to the formation of IV quantitatively.

The stoichiometry of the complexes was established by elemental analysis and IR data. Further evidence was obtained from ^{31}P NMR spectra. Support for the existence of four coordinate species formed is provided by the δ ^{31}P NMR value of a well-resolved signal which is flanked by platinum-195 satellites (33%) ($^1J(^{195}Pt-^{31}P)$ see Table I), compared with the *trans* monomer.

On the basis of infrared spectroscopy these complexes have been assigned *cis* configurations. The main evidence for these assignements is provided by the ν(Pt–Cl) regions in the far infrared spectra. On symmetry grounds *cis* complexes should have two

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TABLE I. $^{31}P[^{1}H]$ NMR Spectral Data of *cis*-$[PtCl_2(PR_3)(L)]$ and Related Complexes

Complexes	$^{31}P[^{1}H]$[a] δ (ppm)	$^{1}J(^{195}Pt-^{31}P)$ (Hz)	Reference
cis-$[PtCl_2(PhCN)(PBu_3)]$	−0.19	3318	this work
cis-$[PtCl_2(PhCN)(PPh_3)]$	+5.09	3560	this work
cis-$[PtCl_2(BuNH_2)(PBu_3)]$	−6.90	3364	this work
sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$	+2.2	3820	this work, 10
sym. *trans*-$[Pt_2Cl_4(PPh_3)_2]$	+5.3	4100	this work, 10
trans-$[PtCl_2(PhCN)(PBu_3)]$	−6.30	3760	this work
trans-$[PtCl_2(BuNH_2)(PBu_3)]$	−7.08	3374	this work
trans-$[PtCl_2(PBu_3)(Me_2NH)]$	−7.27	3300	this work, 10
trans-$[PtCl_2(PPh_3)(^{t}BuNH_2)]$	−3.15	3628	this work

[a] In $CDCl_3$ solution; δ values relative to 85% H_3PO_4 (external), positive shifts representing deshielding.

ν(Pt–Cl) absorption bands (symmetry A_1 and B_2) whereas *trans* complexes should only have one (symmetry B_{2u}) [9]. The ν(Pt–Cl) regions in the spectra conform to the *cis* isomer.

When the above experiments were repeated in $CDCl_3$ solution in the NMR tube and the reactions were followed by ^{31}P NMR, we found that when 1 mole equivalent of PhCN was added to **I**, a new signal appeared at δ −6.30 ppm, $^{1}J(^{195}Pt-^{31}P)$ 3760 Hz, and assigned for *trans*-$[PtCl_2(PhCN)(PBu_3)]$ compared with the authentic sample, Table I. Addition of 2 mole equivalents of PhCN (or excess), led to the formation of the *trans* monomer complex, which is the only phosphine containing species. This product was expected. When the above solution was left for several days at room temperature, there was no change in the spectrum. The same behaviour was observed when **I** was treated with primary amines in $CDCl_3$ solution followed by ^{31}P NMR. The complex obtained was the *trans*-$[PtCl_2(amine)(PBu_3)]$, as expected.

Interestingly, a different behaviour was observed with secondary amines; when dimer **I** was treated with secondary amines the only products isolated were the *trans*-$[PtCl_2(amine)(PBu_3)]$. This result suggests that the steric effect of the secondary amine prevents the formation of the *cis* monomer (compared with PhCN and primary amines).

However, bis (benzonitrile) complexes $[M(PhCN)_2X_2]$, where X is a halogen, have been widely used as starting materials for the preparation of organometallic complexes of platinum and palladium because of the weak donor and ease of the displacement of the benzonitrile ligand [7, 8]. Thus the new complexes (**II**, **III** and **IV**) are very useful starting materials and can be used for ligand substitution reaction mechanisms. A detailed study of the mechanism of autocatalysis *cis*/*trans* isomerization and ligand substitution reactions is now in progress.

Another interesting point which was investigated is the coupling constant (^{1}J); for the *trans* isomer (*trans*-$[PtCl_2(PhCN)(PBu_3)]$) ^{1}J = 3760 Hz which is greater than that of *cis*-form (*cis*-$[PtCl_2(PhCN)(PBu_3)]$), ^{1}J = 3318 Hz. This result indicates that the chlorine atom *trans* to the phosphine ligand (in the *cis* isomer) shows a strong *trans* effect, which leads to a weakening of the metal–phosphine bond more than when the benzonitrile ligand is *trans* to the phosphine (in the *trans* isomer). However, in amine complexes there is a small difference in ^{1}J values (*cis*, 3364 Hz; *trans*, 3374 Hz), which indicates a similar *trans* influence of the chlorine and the amine. Thus PhCN ligand show a weaker *trans* effect compared with chlorine and an amine ligand.

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