Cis to *Trans* Isomerisation of $[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ Catalysed by Mercury(II) Halides

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The relative unreactivity of platinum alkynyls has ensured that many complexes of the type $[Pt(C{\equiv}CR)_2L_2]$ or $[PtX(C{\equiv}CR)L_2]$ (L is tertiary phosphine) are known. Examples have been prepared by the usual routes from Grignard [1], organolithium [2], organo-sodium [1a, 3], organomercury [4] or organo-tin [5] reagents, but the acidity of terminal alkynes has allowed a variety of mild-condition HX elimination pathways to be used, and several have recently been exploited. These include reactions promoted by bases such as NaOH [6], NH_3 [3b, 6], Ag_2O [7], and $NHEt_2$ (with CuI catalyst) [8], of which the latter method is perhaps the most popular.

The *trans* isomers of $[Pt(C{\equiv}CR)_2L_2]$ seem to be thermodynamically favoured, and unless chelating diphosphine ligands are employed for L_2 *trans* complexes are nearly always formed. We report here two routes to *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (and some related *cis* compounds) and a new isomerisation route which can affect the preparation of such complexes.

Results and Discussion

The reaction between *cis*-$[PtCl_2(PMePh_2)_2]$, NaOEt, and PhC≡CH in ethanol at room temperature produced *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (eqn. 1, L = $PMePh_2$) as a white crystalline solid. Its spectro-

$$cis\text{-}[PtCl_2L_2] + 2PhC{\equiv}CH + 2NaOEt \longrightarrow cis\text{-}[Pt(C{\equiv}CPh)_2L_2] \quad (1)$$

scopic characteristics (δP, −2.0 ppm; $^1J_{PtP}$ 2298 Hz; δH(CH_3), 1.91 ppm (triplet of doublets); $^2J_{PH}$ 9.0 Hz; $^3J_{PtH}$ 27.3 Hz) are those expected for a *cis* complex, and different from the (known [9]) *trans* isomer. We [10] and others [11] have recently used this sodium alkoxide route to prepare gold ethynyls, and it appears to be a very versatile preparative method [12].

We have also prepared *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ from *cis*-$[Pt(C{\equiv}CPh)_2(CO)PMePh_2]$. This latter compound can be made readily from $Hg(C{\equiv}CPh)_2$ [4], and the CO replaced by $PMePh_2$ (eqn. 2). *Cis*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ was similarly prepared.

$$cis\text{-}[PtCl_2(CO)L] \xrightarrow[-\frac{1}{2}[Hg_2Cl_6]^{2-}]{Hg(C{\equiv}CPh)_2,\ Cl^-} cis\text{-}[Pt(C{\equiv}CPh)_2(CO)L] \xrightarrow[-CO]{L} cis\text{-}[Pt(C{\equiv}CPh)_2L_2] \quad (2)$$

In contrast, when *cis*-$[PtCl_2(PMePh_2)_2]$ was treated with PhC≡CH in $NHEt_2$, with CuI as catalyst according to literature methods [8], the *trans* isomer was produced (eqn. 3, L = $PMePh_2$). Also,

$$cis\text{-}[PtCl_2L_2] + 2PhC{\equiv}CH \xrightarrow[CuI]{NHEt_2} trans\text{-}[Pt(C{\equiv}CPh)_2L_2] \quad (3)$$

treatment of *cis*-$[PtCl_2L_2]$ by $Hg(C{\equiv}CPh)_2$ or $Ph_3PAuC{\equiv}CPh$ [10] led only to *trans*-$[Pt(C{\equiv}CPh)_2L_2]$, via *trans*-$[PtCl(C{\equiv}CPh)L_2]$ as intermediate.

Cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ remained unchanged in organic solvents over 24 h at room temperature, and retained its structural identity in solution even in the presence of free $PMePh_2$ or iodide (as $[Bu_4N]I$), both of which catalyse isomerisations of many square-planar platinum complexes [13]. Treatment of solutions by catalytic amounts of $HgCl_2$, however, steadily converted the material to the *trans* isomer, the process being complete after a few hours at room temperature in $CHCl_3$, or toluene, but more quickly (*ca.* 40 min) in thf.

When the isomerisations were followed by ^{31}P NMR spectroscopy in $CDCl_3$, small doublets at δ −4.8 and +3.6 ppm, $^2J_{PP}$ = 17.7 Hz, which we assign to *cis*-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$, were produced within 5 min, followed by signals from *trans*-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$ (δ 5.2 ppm; J_{PtP} 2543 Hz). *Trans*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (δ 0.9 ppm; J_{PtP} 2534 Hz).

Some *trans*-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$ remained, equivalent to the $HgCl_2$ originally added. We propose reactions (4–6) (L = $PMePh_2$) to account for these observations and the isomerisation.

$$cis\text{-}[Pt(C{\equiv}CPh)_2L_2] + HgCl_2 \rightleftharpoons cis\text{-}[PtCl(C{\equiv}CPh)L_2] + PhC{\equiv}CHgCl \quad (4)$$

$$cis\text{-}[PtCl(C{\equiv}CPh)L_2] \longrightarrow trans\text{-}[PtCl(C{\equiv}CPh)L_2] \quad (5)$$

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$$trans\text{-}[PtCl(C{\equiv}CPh)L_2] + PhC{\equiv}CHgCl \rightleftharpoons$$

$$trans\text{-}[Pt(C{\equiv}CPh)_2L_2] + HgCl_2 \qquad (6)$$

Key steps are the rapid reversible exchange reactions of ethynyl for chloride between Hg and Pt, and the *cis* to *trans* isomerisation of $[PtCl(C{\equiv}CPh)L_2]$. Such isomerisations of mono-organo complexes are well know [13], and that of $[PtCl(C{\equiv}CPh)(PPh_3)_2]$ has been demonstrated [14].

The isomerisation of *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ is also catalysed by PhHgCl, HgI_2, and CuI, and it seems likely that a similar mechanism operates in each case. Isomerisations of $[Pt(C{\equiv}CR)_2L_2]$ (L = PEt_3 or PBu_3) catalysed by copper(I) halides have previously been noted [8a]. Interestingly, $(tol)_3PAuCl$ did not catalyse the isomerisation of *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ over 24 h, though the reaction of $Ph_3PAuC{\equiv}CPh$ with *cis*-$[PtCl_2L_2]$ leads readily to *trans*-$[Pt(C{\equiv}CPh)_2L_2]$. We believe this failure to be the result of adverse equilibrium positions in the reactions analogous to (4) and (6), and have already established that equilibria involving gold complexes lie well to the side of platinum bis-alkynyls [10].

Ethynyls are unusual amongst bis-organoplatinum compounds in that the *trans* isomers of $[PtR_2L_2]$ are preferred to the *cis*. This, coupled with the general greater stability of the *trans* isomers of $[PtXRL_2]$, probably means that applications of this new isomerisation route will be limited. The operation of this mechanism does, however, serve to limit the value of some preparative routes to *cis* bis-alkynyls. The rapid operation of reaction (5) probably explains why the $NHEt_2$/CuI method usually produces *trans*-$[Pt(C{\equiv}CR)_2L_2]$, even from *cis*-$[PtCl_2L_2]$ (note, however, that some *cis*-$[Pt(C{\equiv}CR)_2(PEt_3)_2]$ and *cis*-$[Pt(C{\equiv}CR)_2(PBu_3)_2]$ have been made this way under carefully controlled conditions [8g]). Presumably the second step (eqn. 7) of our alkoxide route is faster than reaction (5) in ethanol, thus accounting for the stereo-specificity of reaction (1).

$$cis\text{-}[PtCl(C{\equiv}CPh)L_2] \xrightarrow[NaOEt]{PhC{\equiv}CH} cis\text{-}[Pt(C{\equiv}CPh)_2L_2] \qquad (7)$$

The ability of halomercury(II) derivatives to cleave organic groups from platinum and effect isomerisation means that it is essential to remove all traces of such by-products in attempting to prepare *cis* bis-ethynyl complexes. We have ourselves encountered complications and failures in some attempts to convert *e.g.* *cis*-$[Pt(C{\equiv}CMe)_2(CO)PMePh_2]$ to the bis-phosphine compound, which we assign to this cause.

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