Formation and Isomerisation of *cis*-Bis(phenylethynyl)bis(tertiary phosphine)platinum Complexes

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cis-[Pt(C≡CPh)$_2$L$_2$] (L = PPh$_3$ or PMePh$_2$) have been isolated from the reactions of PhC≡CH and *cis*-[PtCl$_2$L$_2$] with Na(OEt), from ligand displacement by L from [Pt(C≡CPh)$_2$(cod)] (cod = cyclo-octa-1,5-diene) {itself made from [PtCl$_2$(cod)], PhC≡CH, and Na(OEt)}, and from CO displacement by L from *cis*-[Pt(C≡CPh)$_2$(CO)L]. Failures were encountered with some other ethynyls and phosphines, and none of these routes may be generally applicable to the preparation of *cis* bis-ethynyls. The *cis* complexes formed, though not affected by the usual nucleophilic isomerisation catalysts, were readily converted to the *trans* isomers by traces of HgCl$_2$, HgBr$_2$, HgI$_2$, HgCl(C≡CPh), HgClPh, CuI, [CuCl(PPh$_3$)], or SnCl$_2$. The mechanism proposed to account for these observations involves reversible ethynyl transfers between platinum and mercury, copper, or tin, and ready isomerisation of the intermediates *cis*-[PtX(C≡CPh)L$_2$] (X = Cl, Br, or I).

Platinum(II) ethynyl complexes, [Pt(C≡CR)$_2$L$_2$] and [PtX(C≡CR)L$_2$] (L = tertiary phosphine, R = alkyl or aryl, X = halide), have been prepared by an unrivalled variety of methods. These include the use of Grignard,[1] organolithium,[2] and organosodium [1a,3] reagents, and ethynyl transfer from less reactive species such as ethynyls of tin,[4] mercury,[5] and gold.[6] The slight acidity of the terminal protons of ethynes has allowed applications of several routes promoted by bases such as Ag$_2$O,[7] NaOH,[8] KOH,[9] NH$_3$,[3b,8,10] and NHEt$_2$.[11] (This last method, probably the most popular of all the preparative methods employed, invariably uses CuI as a catalyst. Copper ethynyls are likely intermediates, and they have been used independently to prepare platinum ethynyls.[11a,12a]) In addition, platinum ethynyls have been made by oxidative additions[12] to Pt^0 and by HX elimination from platinum halogenoalkenyls.[2b] They have been modified by ligand replacements [11e] and by reactions of co-ordinated ligands.[2d]

Unless chelating diphosphines are used for L$_2$, the bis-ethynyls formed by nearly all these methods are mostly of *trans* configuration, even from *cis* starting materials. A few papers report *cis* complexes [11a,12a] or mixtures,[10] but isomerisations to the *trans* forms have been noted,[11a,b] and it is clear that for these bis-ethynyls, unlike most diaryl and dialkyl complexes of platinum,[13] the *trans* form is thermodynamically favoured. The mono-ethynyls, in keeping with other mono-organoplatinum compounds of this type, are usually *trans*.

Recently we have used a simple elimination route to prepare [Au(C≡CR)L] from [AuClL] and HC≡CR by treatment with Na(OEt).[6] We report here the application of this method, and other reactions, to prepare *cis*-[Pt(C≡CR)$_2$L$_2$], and examine the catalysed *cis* to *trans* conversions of these compounds. A preliminary communication has been published.[14]

Results and Discussion

Suspensions of *cis*-[PtCl$_2$(PMePh$_2$)$_2$] in ethanol react at 0 °C with PhC≡CH and sodium ethoxide to produce *cis*-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] as a white crystalline solid [equation (1)].

$$cis\text{-[PtCl}_2\text{(PMePh}_2)_2] + 2\text{PhC≡CH} + 2\text{Na(OEt)} \xrightarrow{\text{EtOH}} cis\text{-[Pt(C≡CPh)}_2\text{(PMePh}_2)_2] \quad (1)$$

Spectroscopic parameters are listed in Table 1. When only half the amount of PhC≡CH and Na(OEt) are used, a mixture of *cis*-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] and unreacted dichloride results, rather than a mono-ethynyl complex. This indicates that the second replacement of Cl by PhC≡C must be rapid in comparison to the dissolution time of unreacted [PtCl$_2$(PMePh$_2$)$_2$]. Also, any disproportionation between *cis*-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] and *cis*-[PtCl$_2$(PMePh$_2$)$_2$] must be slow.

By contrast, the reaction between *cis*-[PtCl$_2$(PMePh$_2$)$_2$] and PhC≡CH (1:2) in NHEt$_2$ with copper(I) iodide catalyst yielded only the (known[2d]) *trans* isomer [equation (2)], in keeping with

$$cis\text{-[PtCl}_2\text{(PMePh}_2)_2] + 2\text{PhC≡CH} \xrightarrow[\text{CuI}]{\text{NHEt}_2} trans\text{-[Pt(C≡CPh)}_2\text{(PMePh}_2)_2] \quad (2)$$

the majority of literature reports on the use of this method.[11] Interestingly, if half the amount of phenylacetylene was employed here, a 1:1 mixture of starting material and the *trans* isomer of [Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] resulted, with only a trace of *trans*-[PtCl(C≡CPh)(PMePh$_2$)$_2$] detectable by ^{31}P n.m.r. spectroscopy. Again, the second displacement step must be more rapid than dissolution and reaction of *cis*-[PtCl$_2$(PMePh$_2$)$_2$], and no rapid disproportionation can take place between *trans*-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] and *cis*-[PtCl$_2$(PMePh$_2$)$_2$] either. The reaction between *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] and C$_2$H$_2$, performed by bubbling the gas through the diethylamine solution containing CuI catalyst, similarly resulted in the (known[2b]) *trans* complex [equation (3)].

$$cis\text{-[PtCl}_2\text{(PMe}_2\text{Ph)}_2] + 2\text{C}_2\text{H}_2 \xrightarrow[\text{NHEt}_2]{\text{CuI}} trans\text{-[Pt(C≡CH)}_2\text{(PMe}_2\text{Ph)}_2] \quad (3)$$

The reactions of *cis*-[PtCl$_2$(PMePh$_2$)$_2$] with [Au(C≡CPh)(PPh$_3$)] have already been reported,[6] and they usually also lead to *trans* products. In rare cases, *cis*-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] was detected, however,[6] and the main product of the reaction between *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] and [Au(C≡CPh)(PPh$_3$)] (1:2) was *cis*-[Pt(C≡CPh)$_2$(PMe$_2$Ph)$_2$], although this slowly isomerised (4 d) to the known[2b] *trans* complex. This is the only time we have obtained a *cis* product for this phosphine, but its isomerisation prevented isolation.

Reactions of *cis*-[PtCl$_2$(PMePh$_2$)$_2$] with Hg(C≡CPh)$_2$ (1:2) {or with one mol Hg(C≡CPh)$_2$ and [NEt$_4$]Cl symmetrising

Table 1. N.m.r. spectra of ethynyl complexes

Compound	δ(P)/p.p.m.	J_{PtP}/Hz	δ(H)/p.p.m.[a]	J_{PH}/Hz[a,b]	J_{PtH}/Hz[a]
cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$	16.7	2 328			
trans-$[Pt(C\equiv CPh)_2(PPh_3)_2]$	18.6	2 649			
cis-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$	−2.0	2 298	1.91	9.0	27.3
trans-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$	1.4	2 536	2.42	7.4	33.3
cis-$[Pt(C\equiv CMe)_2(PMePh_2)_2]$	−2.1	2 315			
trans-$[Pt(C\equiv CMe)_2(PMePh_2)_2]$[c]	1.2	2 588	2.28	7.3	33.0
cis-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$	−17.8	2 254	1.70	9.3	26.7
trans-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$	−12.4	2 418	2.08	7.3	32.3
trans-$[Pt(C\equiv CH)_2(PMe_2Ph)_2]$[d]			2.03	7.5	32.2
cis-$[Pt(C\equiv CPh)_2(PPh_3)(PMePh_2)]$[e]	16.8 −3.2	2 333 2 252			
$[Pt(C\equiv CPh)_2(dtpe)]$	39.6	2 288			
$[PtCl(C\equiv CPh)(dtpe)]$[f]	41.9 36.4	2 334 3 638			
cis-$[PtCl(C\equiv CPh)(PPh_3)_2]$[g]	14.9 18.6	4 441 1 755			
trans-$[PtCl(C\equiv CPh)(PPh_3)_2]$	21.5	2 661			
cis-$[PtBr(C\equiv CPh)(PPh_3)_2]$[h]	16.1 15.3	1 782 4 423			
trans-$[PtBr(C\equiv CPh)(PPh_3)_2]$	20.7	2 623			
trans-$[PtI(C\equiv CPh)(PPh_3)_2]$	18.2	2 556			
cis-$[PtCl(C\equiv CPh)(PMePh_2)_2]$[i]	−4.8 3.6	3 672 2 325			
trans-$[PtCl(C\equiv CPh)(PMePh_2)_2]$	5.1	2 547	2.22	7.4	30.3
trans-$[PtBr(C\equiv CPh)(PMePh_2)_2]$	3.2	2 606			
trans-$[PtI(C\equiv CPh)(PMePh_2)_2]$	5.2	2 539			
trans-$[PtCl(C\equiv CMe)(PMePh_2)_2]$	5.0	2 580	2.22	7.7	30.0
trans-$[PtCl(C\equiv CPh)(PMe_2Ph)_2]$	−7.5	2 439			

[a] CH_3 on phosphines. [b] $|{}^2J_{PH} + {}^4J_{PH}|$ for *trans* compounds. [c] CH_3 of propynyl: δ 1.49 p.p.m., $J_{PtH} = 14.7$ Hz. [d] H of ethynyl: δ 2.14 p.p.m., ${}^4J_{PH} = 2.3$, ${}^3J_{PtH} = 44$ Hz. [e] ${}^2J_{PP} = 21$ Hz. [f] ${}^2J_{PP} = 6.3$ Hz. [g] ${}^2J_{PP} = 17.5$ Hz. [h] ${}^2J_{PP} = 17.8$ Hz. [i] ${}^2J_{PP} = 18.0$ Hz.

agent}[5] generally resemble the reactions with gold ethynyls and produce *trans* materials [equation (4); L = $PMePh_2$]. Followed

$$cis\text{-}[PtCl_2L_2] + 2Hg(C\equiv CPh)_2 \longrightarrow trans\text{-}[Pt(C\equiv CPh)_2L_2] + 2HgCl(C\equiv CPh) \quad (4)$$

in $CDCl_3$ by ^{31}P n.m.r. spectroscopy, the transient appearance of pairs of doublets (δ 3.6, ${}^1J_{PtP}$ 2 325; δ −4.8 p.p.m., ${}^1J_{PtP}$ 3 672; ${}^2J_{PP}$ 18 Hz) suggests the intermediacy of *cis*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$. Transient signals for *trans*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$ were also detected, and in some cases traces of *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ were observed. The final products, however, were always *trans*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ {or *trans*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$ if insufficient $Hg(C\equiv CPh)_2$ was used}. Similarly, the reactions between *cis*-$[PtCl_2(PMe_2Ph)_2]$ and $Hg(C\equiv CPh)_2$, and *cis*-$[PtCl_2(PMePh_2)_2]$ and $Hg(C\equiv CMe)_2$ produced *trans*-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$ and *trans*-$[Pt(C\equiv CMe)_2(PMePh_2)_2]$, respectively.

The isomerisations leading to *trans* products in all of these reactions probably take place between the first and second replacements. Although CuI and mercury halides (see later) do catalyse *cis* to *trans* isomerisations of $[Pt(C\equiv CR)_2L_2]$, it seems unlikely that these reactions could proceed fast enough to account for the *trans* products.* *cis* Mono-ethynyls, on the other hand, do readily convert to the *trans* isomers under these reaction conditions.

With copper(I) ethynyls being likely intermediates in the CuI catalysed route, a common factor in these reactions which produce *trans* compounds is ethynyl for chloride exchange between the two metals. This may be significantly slower at the second step than reactions involving the strong base Na(OEt) in EtOH, thus allowing the isomerisation step to compete at this stage (Scheme), in the methyldiphenylphosphine complexes at least.

The reaction between $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) and phenylacetylene with sodium ethoxide in ethanol also produces the bis(phenylethynyl)platinum complex, constrained in the *cis* position by the chelating diolefin ligand [equation (5)]. The compound proved difficult to purify,

$$[PtCl_2(cod)] + 2PhC\equiv CH \xrightarrow[EtOH]{Na(OEt)} [Pt(C\equiv CPh)_2(cod)] \quad (5)$$

decomposing during attempted crystallisation from chloroform. It was finally recrystallised at a lower temperature using CH_2Cl_2. $[Pt(C\equiv CPh)_2(cod)]$ was also prepared from the reaction of two equivalents of $Hg(C\equiv CPh)_2$ with $[PtCl_2(cod)]$, but purification in this case proved impossible, decomposition accompanying the formation reaction. All attempts to isolate the propynyl analogue, $[Pt(C\equiv CMe)_2(cod)]$, led to failure. We have previously noted that platinum propynyls are more prone to decomposition than their phenylethynyl analogues.[5]

Despite its success in preparing *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ and $[Pt(C\equiv CPh)_2(cod)]$, the sodium ethoxide route has its problems and has proved less versatile than in preparing gold ethynyls.[6] The reaction between $[PtCl_2(dtpe)]$ [dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane] and PhC≡CH in ethanolic sodium ethoxide under identical conditions to those employed for equation (1) led to production of only a small percentage of $[Pt(C\equiv CPh)_2(dtpe)]$, and several attempts to produce $[Pt(C\equiv CMe)_2(PMePh_2)_2]$ by prolonged bubbling of propyne into ethanolic suspensions of *cis*-$[PtCl_2(PMePh_2)_2]$ in the presence of Na(OEt) resulted in no reactions. {The reaction of $[PtCl_2(dtpe)]$ with $Hg(C\equiv CPh)_2$ in $CDCl_3$ readily produced

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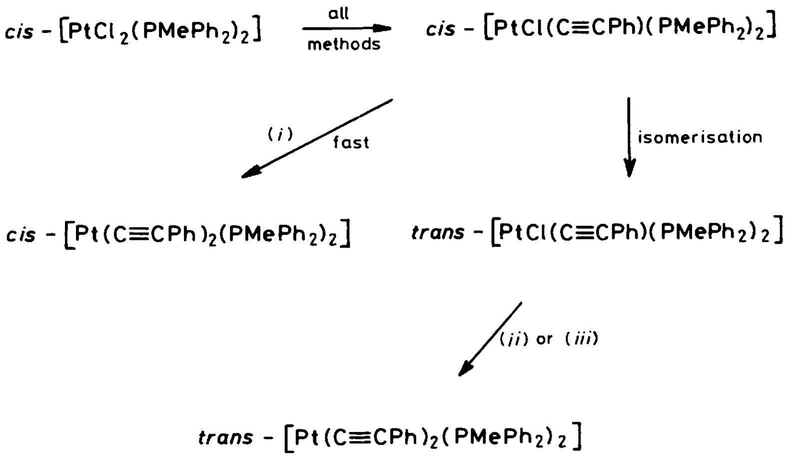
* This is certainly true for the mercury compounds, where we have followed catalysed isomerisations under the same conditions as the preparative reactions described. The CuI cases are less certain in that the solvent used by us for the isomerisations ($CDCl_3$) differs from that of the preparations ($NHEt_2$).



Scheme. (*i*) Na(OEt), EtOH, PhC≡CH; (*ii*) $Hg(C{\equiv}CPh)_2$; (*iii*) PhC≡CH, CuI, $NHEt_2$

$[Pt(C{\equiv}CPh)_2(dtpe)]$ or $[PtCl(C{\equiv}CPh)(dtpe)]$, depending on the ratio of reactants, identified from their ^{31}P n.m.r. parameters (Table 1).}

Failure was also encountered in reactions of *cis*-$[PtCl_2(PMe_2Ph)_2]$ and PhC≡CH with Na(OEt). At 0 °C for 2 h, room temperature overnight, or 60 °C for 2 h, the reactions were complex, and examinations by ^{31}P n.m.r. spectroscopy revealed the presence of several compounds. These included *trans*-$[PtCl(C{\equiv}CPh)(PMe_2Ph)_2]$, *trans*-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$, and an unidentified material with δ(P) at −21.7 p.p.m., J_{PtP} 3 510 Hz, but no *cis* ethynyls. The reactions were slow, some starting complex persisting in the low-temperature reactions, even after stirring overnight, and the *trans* mono-ethynyl compound was still the major product after 2 h at 60 °C.

The failure of some reactions with sodium ethoxide presumably means that the mechanism does not involve attack of ethoxide at platinum, since the formation of platinum hydrides would almost certainly result.[15] It was similarly determined that the related reactions of gold halide complexes do not proceed in this manner,[6] and the most likely routes involve formation of ethynyl anions or prior co-ordination of ethyne to the metal.

Treatment of $[Pt(C{\equiv}CPh)_2(cod)]$ by $PMePh_2$ or PPh_3 led smoothly to the *cis* bis-phosphine complexes *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ and *cis*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ respectively [equation (6)]. Surprisingly, however, use of dimethylphenylphosphine produced the *trans* isomer of $[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$. We have consistently failed to isolate the *cis* isomer of this compound, and its propensity to obtain or retain the *trans* geometry seems greater than for the other complexes. Nevertheless none of the agents which cause *cis* to *trans* isomerisations of these compounds (see later) was, to our knowledge, present, and we are unable to explain the *trans* geometry found in this case. This, and the problems in obtaining other cod complexes, means that this method also cannot be claimed to be of general application in the production of those *cis* bis-ethynyl complexes.

$$[Pt(C{\equiv}CPh)_2(cod)] + 2PPh_3 \longrightarrow cis\text{-}[Pt(C{\equiv}CPh)_2(PPh_3)_2] \quad (6)$$

A third method of synthesis of *cis* bis-ethynyl complexes met the same limited success. *cis*-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$, synthesised from *cis*-$[PtCl_2(CO)(PMePh_2)]$, $Hg(C{\equiv}CPh)_2$, and $[NEt_4]Cl$,[5] when treated with $PMePh_2$ readily produced the bis-phosphine complex [equation (7)]. The triphenylphosphine analogue was similarly prepared from *cis*-$[Pt(C{\equiv}CPh)_2(CO)(PPh_3)]$ and PPh_3, and the mixed-phosphine complex *cis*-$[Pt(C{\equiv}CPh)_2(PPh_3)(PMePh_2)]$ was produced by treating *cis*-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ with PPh_3 (though this reaction was accompanied by phosphine exchange and the two symmetrical *cis* bis-phosphine complexes were also formed).

$$cis\text{-}[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)] + PMePh_2 \longrightarrow cis\text{-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] + CO \quad (7)$$

The propynyl complex *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ is more difficult to isolate,[5] but it was used in an attempt to obtain *cis* bis-propynyl bis-phosphine complexes. Careful addition of portions of $PMePh_2$ to *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ in $CDCl_3$ produced *cis*-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$, observed by ^{31}P n.m.r. spectroscopy. This rapidly isomerised to the *trans* form, however, and a larger scale reaction led to the isolation only of *trans*-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$. An attempt to produce *cis*-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ by this route also produced the *trans* isomer. In these instances it is possible that traces of mercury compounds, which catalyse the *cis* to *trans* isomerisation, could have been present from the synthesis of the carbonyl intermediates. Spectroscopic parameters for all the complexes are listed in Table 1.

To summarise, *cis* complexes with C≡CPh and PPh_3 or $PMePh_2$ can be made by all three routes described, the most expedient being the sodium ethoxide route. Attempts to isolate *cis* propynyl or ethynyl complexes, or complexes with the phosphine PMe_2Ph, consistently failed, however, so none of the routes tested can be claimed as general. Whilst we cannot account for the limitations, it can be noted that this situation is not uncommon with other synthetic routes to ethynyl complexes, and others have reported a dependence on ethynyl or phosphorus substituents.[11b]

Isomerisations of cis *Bis-ethynyls.*—*cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ is configurationally stable in organic solvents at room temperature, and was unaffected by refluxing $CHCl_3$. Moreover, treatment in solution by free $PMePh_2$ or iodide (as $[NBu_4]I$), both catalysts for nucleophile-assisted isomerisations of square-planar complexes,[13] had no effect on this complex.

Small amounts of mercury(II) halides catalysed immediate isomerisation. Followed by ^{31}P n.m.r. spectroscopy in $CDCl_3$, addition of *ca.* 10% of $HgCl_2$, $HgBr_2$, or HgI_2 caused complete conversion over *ca.* 3 h at ambient temperature. The growth of signals from *cis*-$[PtX(C{\equiv}CPh)(PMePh_2)_2]$ (X = Cl) then *trans*-$[PtX(C{\equiv}CPh)(PMePh_2)_2]$ was detected before any *trans*-

Table 2. Effects of metal salts on ^{31}P n.m.r. parameters

Ethynyl complex	Salt	Ratio	δ(P)/ p.p.m.	J_{PtP}/ Hz
cis-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$	$HgCl_2$	10:1	−2.9	2 378
	$HgCl_2$	2:1	−3.3*	2 420
	$HgBr_2$	10:1	−2.4	2 318
	$HgBr_2$	1:1	−2.6	2 336
	HgI_2	10:1	−3.1	2 375
	HgI_2	5:1	−4.2	2 450
	CuI	10:1	−2.0	2 308
	$[CuCl(PPh_3)]$	10:1	−2.2	2 316
cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$	$HgCl_2$	5:1	16.7*	2 359
	$HgCl_2$	2:1	16.5	2 337
	$HgCl_2$	1:1	13.4	2 491

* Peaks broad.

$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ appeared, and *trans*-$[PtX(C\equiv CPh)(PMePh_2)_2]$ in an amount equivalent to the HgX_2 added remained at the end of the reaction, presumably along with a similar amount of $HgX(C\equiv CPh)$. A separate experiment confirmed that $HgCl(C\equiv CPh)$ was as effective as HgX_2 in catalysing the isomerisation.

The reaction clearly depends on the ready exchange of ethynyl for halide between mercury and platinum, and a key step is the isomerisation in solution of the intermediate *cis*-$[PtX(C\equiv CPh)(PMePh_2)_2]$. This occurs very readily for other organoplatinum halides,[13] and has been observed for *cis*-$[PtCl(C\equiv CPh)(PPh_3)_2]$.[12b] We find that *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ is also isomerised readily by $HgCl_2$, $HgBr_2$, or HgI_2 in $CDCl_3$ and follows the same reaction course as above though somewhat more slowly. The overall sequence is represented by equations (8)—(11), with (9)—(11) representing the catalytic

$$\textit{cis}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2] + HgX_2 \longrightarrow \textit{cis}\text{-}[PtX(C\equiv CPh)(PMePh_2)_2] + HgX(C\equiv CPh) \quad (8)$$

$$\textit{cis}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2] + HgX(C\equiv CPh) \rightleftharpoons \textit{cis}\text{-}[PtX(C\equiv CPh)(PMePh_2)_2] + Hg(C\equiv CPh)_2 \quad (9)$$

$$\textit{cis}\text{-}[PtX(C\equiv CPh)(PMePh_2)_2] \longrightarrow \textit{trans}\text{-}[PtX(C\equiv CPh)(PMePh_2)_2] \quad (10)$$

$$\textit{trans}\text{-}[PtX(C\equiv CPh)(PMePh_2)_2] + Hg(C\equiv CPh)_2 \rightleftharpoons \textit{trans}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2] + HgX(C\equiv CPh) \quad (11)$$

cycle. The isomerisations proceeded equally well in toluene, but much more rapidly in tetrahydrofuran (thf).

A number of other compounds also catalysed *cis* to *trans* isomerisation of $[Pt(C\equiv CPh)_2(PMePh_2)_2]$. These included HgClPh and $[NEt_4]_2[Hg_2Cl_6]$, though both act much more slowly than the other mercury compounds listed above. Copper(I) iodide, when added to *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ in $CDCl_3$ also caused isomerisation, and the presence of *trans*-$[PtI(C\equiv CPh)(PMePh_2)_2]$ was detected by ^{31}P n.m.r. during the reaction. This suggests that a mechanism analogous to that of equations (8)—(11) operates, and this is presumably also the case in the other reported[11a,b] examples of CuI catalysis. The complex $[CuCl(PPh_3)]$ catalyses the same isomerisation more slowly, *trans*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$ being detectable during the long (several days) reaction process. The slow reaction rate might well be due to low reactivity of the intermediate $[Cu(C\equiv CPh)(PPh_3)]$, compared to $[Cu(C\equiv CPh)]$ (from CuI) or $Hg(C\equiv CPh)_2$ (from mercury halides).

Neither CuCl nor $[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$ had any catalytic effect on *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ in $CDCl_3$. The former failure may be assigned to the very low solubility of CuCl, whereas the latter is probably due to the unfavourable equilibrium position of the step analogous to equation (8); ethynyl transfers from gold to platinum quantitatively in complexes of this type.[6] It should be noted, however, that the isomerisation of *cis*-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$, prepared from $[Au(C\equiv CPh)(PPh_3)]$, may well be catalysed by the $[AuCl(PPh_3)]$ by-product. Indeed *trans*-$[PtCl(C\equiv CPh)(PMe_2Ph)_2]$ was detected by ^{31}P n.m.r. spectroscopy as an intermediate during the change. The apparent greater readiness of PMe_2Ph complexes to isomerise probably contributes in this case, and the reaction is a slow one.

Anhydrous tin(II) chloride slowly causes isomerisation in these compounds, but tin(IV) chloride simply reacts with *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ irreversibly, leaving *trans*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$ and *cis*-$[PtCl_2(PMePh_2)_2]$. Finally, it can be noted that *cis*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ has been obtained and kept in solution in the presence of *trans*-$[PtCl(C\equiv CPh)(PMePh_2)_2]$ and/or *cis*-$[PtCl_2(PMePh_2)_2]$, indicating that neither of these complexes readily enters the halide–ethynyl exchange reactions necessary to cause isomerisation.

N.M.R. Parameters.—Two observations on the n.m.r. spectra of the ethynyl complexes (Table 1) are worth comment. The first is the large coupling constants, $^1J_{PtP}$ of the phosphorus *trans* to Cl or Br in *cis*-$[PtX(C\equiv CPh)(PPh_3)_2]$. At *ca.* 4 450 Hz, the values are notably greater than usual for phosphorus *trans* to these ligands. We have observed previously that when a phosphine is *cis* to an organic group of high *trans* influence, as well as *trans* to a group of low *trans* influence, this parameter can be exceptionally large,[16] but it is clear that these cannot be the only factors involved, since the corresponding values for the $PMePh_2$ analogues are in the 'normal' expected range (Table 1). The large values do not necessarily indicate that the group *trans* to phosphine is especially weakly held,[17,18] though it may be significant that Kemmitt and co-workers[12b] noted a very low value of ν(Pt–Cl) in the i.r. spectrum of *cis*-$[PtCl(C\equiv CPh)(PPh_3)_2]$.

The second observation concerns the ^{31}P n.m.r. spectra of the ethynyl complexes when various metal halides are introduced into the solution. Significant changes in chemical shifts and coupling constants are concentration dependent, and in some cases the peaks are broadened (Table 2). Similar observations have been made before when mercury compounds are introduced into solutions of other platinum ethynyls.[5,19] A rapidly reversible exchange reaction or adduct formation is suspected as being the cause, but this remains speculative.

Experimental

^{31}P N.m.r. and ^1H n.m.r. spectra were recorded in $CDCl_3$ solutions on Varian XL100 and Perkin-Elmer R32 spectrometers, respectively. I.r. spectra were recorded as KBr discs on a Perkin-Elmer PE 580 spectrometer. The following compounds were prepared by literature methods: $[PtCl_2(CO)(PMePh_2)]$, *cis*-$[Pt(C\equiv CPh)_2(CO)(PMePh_2)]$,[5] $[PtCl_2(cod)]$,[20] $[Au(C\equiv CPh)(PPh_3)]$,[6] $[CuCl(PPh_3)]$,[21] and $Hg(C\equiv CPh)_2$.[22]

(Cyclo-octa-1,5-diene)bis(phenylethynyl)platinum.—A suspension of $[PtCl_2(cod)]$ (0.5 g, 1.34 mmol) in ethanol (30 cm^3) was maintained at 0 °C under nitrogen, and a freshly prepared mixture of $PhC\equiv CH$ (0.27 g, 2.7 mmol) and sodium ethoxide (prepared from 61.5 mg sodium) in ethanol (10 cm^3) was added dropwise with constant stirring. The white solid turned yellow after 50 min, at which stage it was filtered off, affording crude $[Pt(C\equiv CPh)_2(cod)]$ (0.7 g, 103%). Three recrystallisations from CH_2Cl_2 finally yielded the pure complex

[m.p. 178—197 °C (decomp.); ν(C$\equiv$C) 2 130w, 2 135(sh) cm^{-1}. Found: C, 57.3; H, 4.2. Calc. for $C_{24}H_{22}Pt$: C, 57.0; H, 4.4%].

cis-*Bis(methyldiphenylphosphine)bis(phenylethynyl)platinum.*—(*a*) *From* [$PtCl_2(PMePh_2)_2$]. To a suspension of [$PtCl_2(PMePh_2)_2$] (0.5 g, 0.75 mmol) in ethanol (20 cm^3) at 0 °C was added PhC$\equiv$CH (153 mg, 1.5 mmol), rapidly followed by sodium ethoxide [prepared from sodium (34.5 mg, 1.5 mmol) in ethanol (5 cm^3)]. The solid remained during 2 h stirring, after which filtration yielded the solid product (440 mg, 74%). Recrystallisation from $CHCl_3$–pentane afforded the pure material [m.p. 172—173 °C; ν(C$\equiv$C) 2 120w, 2 130 (sh) cm^{-1}. Found: C, 62.4; H, 4.6. Calc. for $C_{42}H_{36}P_2Pt$: C, 63.2; H, 4.55%].

(*b*) *From* [$PtCl_2(CO)(PMePh_2)$]. To a solution of *cis*-[$PtCl_2(CO)(PMePh_2)$] (0.2 g, 0.4 mmol) in $CHCl_3$ (10 cm^3) at 0 °C under N_2 was added Hg(C$\equiv$CPh)$_2$ (163 mg, 0.4 mmol) in $CHCl_3$ (5 cm^3). The mixture was stirred for 2 min, then [NEt_4]Cl (67 mg, 0.4 mmol) was added. Stirring was continued for 5 min, during which time a grey precipitate of [NEt_4]$_2$[Hg_2Cl_6] formed. This was rapidly removed by filtration leaving *cis*-[Pt(C$\equiv$CPh)$_2$(CO)($PMePh_2$)] in the orange solution (confirmed by ^{31}P n.m.r. spectroscopy). $PMePh_2$ (87 µl, 0.4 mmol) was immediately added to the solution which was stirred for 5 min. Removal of solvent yielded *cis*-[Pt(C$\equiv$CPh)$_2$($PMePh_2$)$_2$] (303 mg, 94%).

(*c*) *From* [Pt(C$\equiv$CPh)$_2$(cod)]. To a solution of [Pt(C$\equiv$CPh)$_2$(cod)] (500 mg, 0.99 mmol) in CH_2Cl_2 (30 cm^3) under N_2 was added a solution of $PMePh_2$ (350 µl, 1.38 mmol) over 5 min. After 15 min a clear brown solution resulted. Removal of the solvent left the crude product which was recrystallised from $CHCl_3$–light petroleum (314 mg, 40%).

cis-*Bis(phenylethynyl)bis(triphenylphosphine)platinum.*—To a solution of [Pt(C$\equiv$CPh)$_2$(cod)] (185 mg, 0.37 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C under N_2 was added PPh_3 (182 mg, 0.69 mmol). The solution was stirred for 15 min, during which time it turned brown. After filtration and concentration crystals of the product were formed (267 mg, 79%), which were purified by recrystallisation from CH_2Cl_2–pentane [m.p. 210—211 °C (lit.,[3a] 206—208 °C); ν(C$\equiv$C) 2 110 cm^{-1}].

trans-*Chlorobis(methyldiphenylphosphine)(phenylethynyl)platinum.*—To a suspension of *cis*-[$PtCl_2(PMePh_2)_2$] (0.5 g, 0.75 mmol) in $CHCl_3$ (25 cm^3) was added Hg(C$\equiv$CPh)$_2$ (0.3 g, 0.76 mmol), and the mixture was stirred at room temperature for 1 h. Filtration yielded an orange solution, removal of solvent from which gave the product. Two crystallisations from $CHCl_3$–pentane gave the pure compound as white crystals (352 mg, 64%) [m.p. 213—214 °C; ν(C$\equiv$C) 2 130 cm^{-1}, ν(Pt–Cl) 315 cm^{-1}. Found: C, 55.4; H, 4.1; P, 8.8. Calc. for $C_{34}H_{31}ClP_2Pt$: C, 55.8; H, 4.3; P, 8.5%].

trans-*Bis(methyldiphenylphosphine)bis(propynyl)platinum.*—To a solution of *cis*-[$PtCl_2(CO)(PMePh_2)$] (0.5 g, 1.01 mmol) in $CHCl_3$ (50 cm^3) under a nitrogen atmosphere was added Hg(C$\equiv$CMe)$_2$ (281 mg, 1.01 mmol), followed by [NEt_4]Cl (165.5 mg, 1.01 mmol). After stirring for 5 min, rapid filtrations left an orange solution, to which was added $PMePh_2$ (188 µl, 1.01 mmol) by syringe. Solvent was removed and the resulting solid recrystallised from acetone to yield *trans*-[Pt(C$\equiv$CMe)$_2$($PMePh_2$)$_2$] (0.5 g, 73%) [m.p. 176—178 °C; ν(C$\equiv$C) 2 130 cm^{-1}. Found: C, 56.8; H, 4.6; P, 9.25. Calc. for $C_{32}H_{32}P_2Pt$: C, 57.1; H, 4.8; P, 9.2%].

trans-*Bis(methyldiphenylphosphine)bis(phenylethynyl)platinum.*—To a suspension of *cis*-[$PtCl_2(PMePh_2)_2$] (0.2 g, 0.3 mmol) in $NHEt_2$ (25 cm^3) were added PhC$\equiv$CH (71.4 mg, 0.7 mmol) and CuI (11 mg). The mixture was refluxed for 10 min, and the solvent removed at low pressure. Recrystallisation of the white solid from $CHCl_3$–ethanol yielded *trans*-[Pt(C$\equiv$CPh)$_2$($PMePh_2$)$_2$] (136 mg, 57%) (i.r. and n.m.r. parameters consistent with literature values[2d]).

trans-*Bis(dimethylphenylphosphine)bis(ethynyl)platinum.*—This complex was prepared similarly to *trans*-[Pt(C$\equiv$CPh)$_2$($PMePh_2$)$_2$] by bubbling C_2H_2 through the suspension of *cis*-[$PtCl_2(PMe_2Ph)_2$] (250 mg), in diethylamine with CuI (10 mg) (i.r. and n.m.r. parameters of the product were identical to literature values[2b]).

Isomerisation Reactions.—These were performed on a small scale (20 mg samples of the platinum complex) in $CDCl_3$ (0.5 cm^3), and followed by ^{31}P n.m.r. spectroscopy at ambient temperature. Catalysts were added either as solids ($HgCl_2$, HgClPh, CuI, or $SnCl_2$) or as standard solutions [$HgBr_2$ in ethanol (10 µl), HgCl(C$\equiv$CPh) in $CDCl_3$ (10 µl)] by syringe.

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