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

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cis-[Pt(C=CPh)₂L₂] (L = PPh₃ or PMePh₂) have been isolated from the reactions of PhC=CH and *cis*-[PtCl₂L₂] with Na(OEt), from ligand displacement by L from [Pt(C=CPh)₂(cod)] (cod = cyclo-octa-1,5-diene) {itself made from [PtCl₂(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 HgCl₂, HgBr₂, Hgl₂, HgCl(C=CPh), HgClPh, Cul, [CuCl(PPh₃)], or SnCl₂. 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)L₂] (X = Cl, Br, or I).

Platinum(11) ethynyl complexes, $[Pt(C=CR)_2L_2]$ and [PtX(C=(L = tertiary phosphine, R = alkyl or aryl, $CR)L_2$] 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_2O ,⁷ NaOH,⁸ KOH,⁹ NH₃,^{3b,8,10} and NHEt₂.¹¹ (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 Pt⁰ and by HX elimination from platinum halogenoalkenyls.^{2b} They have been modified by ligand replacements ^{11e} and by reactions of co-ordinated ligands.²⁴

Unless chelating diphosphines are used for L_2 , the bisethynyls 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)₂L₂], and examine the catalysed *cis* to *trans* conversions of these compounds. A preliminary communication has been published.¹⁴

Results and Discussion

Suspensions of cis-[PtCl₂(PMePh₂)₂] in ethanol react at 0 °C with PhC=CH and sodium ethoxide to produce cis-[Pt(C= CPh)₂(PMePh₂)₂] as a white crystalline solid [equation (1)].

$$cis-[PtCl_2(PMePh_2)_2] + 2PhC \equiv CH + 2Na(OEt) \xrightarrow{EtOH} cis-[Pt(C \equiv CPh)_2(PMePh_2)_2] \quad (1)$$

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(PMePh₂)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 [PtCl₂(PMePh₂)₂]. Also, any disproportionation between cis-[Pt(C=CPh)₂(PMe-Ph₂)₂] and cis-[PtCl₂(PMePh₂)₂] must be slow.

By contrast, the reaction between cis-[PtCl₂(PMePh₂)₂] and PhC=CH (1:2) in NHEt₂ with copper(1) iodide catalyst yielded only the (known^{2d}) trans isomer [equation (2)], in keeping with

$$cis-[PtCl_{2}(PMePh_{2})_{2}] + 2PhC \equiv CH \xrightarrow{NHEt_{2}} trans-[Pt(C \equiv CPh)_{2}(PMePh_{2})_{2}]$$
(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(PMePh₂)₂] resulted, with only a trace of trans-[PtCl(C=CPh)(PMePh₂)₂] detectable by ³¹P n.m.r. spectroscopy. Again, the second displacement step must be more rapid than dissolution and reaction of cis-[PtCl₂(PMePh₂)₂], and no rapid disproportionation can take between trans-[Pt(C=CPh)₂(PMePh₂)₂] and place cis- $[PtCl_2(PMePh_2)_2]$ either. The reaction between cis- $[PtCl_2(PMe_2Ph)_2]$ and C_2H_2 , performed by bubbling the gas through the diethylamine solution containing CuI catalyst, similarly resulted in the (known^{2b}) trans complex [equation (3)].

$$cis-[PtCl_2(PMe_2Ph)_2] + 2C_2H_2 \xrightarrow{Cul}_{NHEt_2} trans-[Pt(C=CH)_2(PMe_2Ph)_2] \quad (3)$$

The reactions of cis-[PtCl₂(PMePh₂)₂] with [Au(C=CPh)-(PPh₃)] have already been reported,⁶ and they usually also lead to *trans* products. In rare cases, cis-[Pt(C=CPh)₂-(PMePh₂)₂] was detected, however,⁶ and the main product of the reaction between cis-[PtCl₂(PMe₂Ph)₂] and [Au(C=CPh)(PPh₃)] (1:2) was cis-[Pt(C=CPh)₂(PMe₂Ph)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-[PtCl₂(PMePh₂)₂] with Hg(C=CPh)₂ (1:2) for with one mol Hg(C=CPh)₂ and [NEt₄]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. ^{<i>a</i>}	J _{PH} /Hz ^{a,b}	J _{PtH} /Hz ^a
cis-[Pt(C=CPh) ₂ (PPh ₃) ₂]	16.7	2 328			
trans-[Pt(C=CPh),(PPh)]	18.6	2 649			
cis-[Pt(C=CPh) ₂ (PMePh ₂) ₂]	-2.0	2 298	1.91	9.0	27.3
trans-[Pt(C=CPh),(PMePh)]	1.4	2 536	2.42	7.4	33.3
cis-[Pt(C=CMe),(PMePh))]	-2.1	2 315			
trans-[Pt(C=CMe),(PMePh_),]°	1.2	2 588	2.28	7.3	33.0
cis-[Pt(C=CPh),(PMe,Ph),]	-17.8	2 254	1.70	9.3	26.7
trans-[Pt(C=CPh),(PMe,Ph)]	-12.4	2 418	2.08	7.3	32.3
trans-[Pt(C=CH)2(PMe2Ph)2]			2.03	7.5	32.2
$cis-[Pt(C=CPh)_2(PPh_3)(PMePh_2)]^e$	ſ 16.8	2 333			
	1 - 3.2	2 252			
[Pt(C=CPh) ₂ (dtpe)]	39.6	2 288			
	€ 41.9	2 334			
[PtCl(C=CPh)(dtpe)]	ັ <u>ງ</u> 36.4	3 638			
	∤ 14.9	4 441			
cis-[PtCl(C=CPh)(PPh ₃) ₂]"	້ 18.6	1 755			
trans-[PtCl(C=CPh)(PPh3)2]	21.5	2 661			
$= (C - CD^{1})(DD^{1}) $	∫ 16.1	1 782			
cis-[PtBr(C=CPn)(PPh ₃) ₂]"	15.3	4 423			
trans-[PtBr(C=CPh)(PPh_3)2]	20.7	2 623			
trans-[PtI(C=CPh)(PPh ₃) ₂]	18.2	2 556			
cis-[PtCl(C=CPh)(PMePh ₂) ₂] ⁱ	$\int -4.8$	3 672			
	3.6	2 325			
trans-[PtCl(C=CPh)(PMePh ₂) ₂]	5.1	2 547	2.22	7.4	30.3
trans-[PtBr(C=CPh)(PMePh ₂) ₂]	3.2	2 606			
trans-[PtI(C=CPh)(PMePh ₂) ₂]	5.2	2 539			
trans-[PtCl(C=CMe)(PMePh_),]	5.0	2 580	2.22	7.7	30.0
trans-[PtCl(C=CPh)(PMe2Ph)2]	-7.5	2 439			

^{*a*}CH₃ on phosphines. ${}^{b}|^{2}J_{PH} + {}^{4}J_{PH}|$ for *trans* compounds. ^{*c*}CH₃ of propynyl: δ 1.49 p.p.m., $J_{PH} = 14.7$ Hz. ^{*d*} H of ethynyl: δ 2.14 p.p.m., ${}^{4}J_{PH} = 2.3$, ${}^{3}J_{PH} = 44$ Hz. ${}^{e}J_{PP} = 21$ Hz. ${}^{f}J_{PP} = 6.3$ Hz. ${}^{g}J_{PP} = 17.5$ Hz. ${}^{h}J_{PP} = 17.8$ Hz. ${}^{i}J_{PP} = 18.0$ Hz.

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

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

in CDCl₃ by ³¹P 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= CPh)(PMePh₂)₂]. Transient signals for *trans*-[PtCl(C= CPh)(PMePh₂)₂] were also detected, and in some cases traces of *cis*-[Pt(C=CPh)₂(PMePh₂)₂] were observed. The final products, however, were always *trans*-[Pt(C=CPh)₂(PMePh₂)₂] {or *trans*-[PtCl(C=CPh)(PMePh₂)₂] if insufficient Hg(C=CPh)₂ was used}. Similarly, the reactions between *cis*-[PtCl₂-(PMe₂Ph)₂] and Hg(C=CPh)₂, and *cis*-[PtCl₂(PMePh₂)₂] and Hg(C=CMe)₂ produced *trans*-[Pt(C=CPh)₂(PMe₂Ph)₂] and *trans*-[Pt(C=CMe)₂(PMePh₂)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 $[Pt(C=CR)_2L_2]$, 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(1) 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-1,5diene) 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=CPh)₂(cod)] was also prepared from the reaction of two equivalents of $Hg(C=CPh)_2$ with [PtCl₂(cod)], but purification in this case proved impossible, decomposition accompanying the formation reaction. All attempts to isolate the propynyl analogue, [Pt(C=CMe)₂(cod)], led to failure. We have previously noted that platinum propynyls are more prone to decomposition than their phenylethynyl analogue.⁵

Despite its success in preparing cis-[Pt(C=CPh)₂(PMe-Ph₂)₂] and [Pt(C=CPh)₂(cod)], the sodium ethoxide route has its problems and has proved less versatile than in preparing gold ethynyls.⁶ The reaction between [PtCl₂(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=CPh)₂(dtpe)], and several attempts to produce [Pt(C=CMe)₂(PMePh₂)₂] by prolonged bubbling of propyne into ethanolic suspensions of *cis*-[PtCl₂(PMePh₂)₂] in the presence of Na(OEt) resulted in no reactions. {The reaction of [PtCl₂(dtpe)] with Hg(C=CPh)₂ in CDCl₃ readily produced

^{*} 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 (CDCl₃) differs from that of the preparations (NHEt₂).



trans - [Pt(C=CPh)2(PMePh2)2]

Scheme. (i) Na(OEt), EtOH, PhC=CH; (ii) Hg(C=CPh)2; (iii) PhC=CH, CuI, NHEt2

[Pt(C=CPh)₂(dtpe)] or [PtCl(C=CPh)(dtpe)], depending on the ratio of reactants, identified from their ³¹P n.m.r. parameters (Table 1).}

Failure was also encountered in reactions of cis-[PtCl₂-(PMe₂Ph)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 ³¹P n.m.r. spectroscopy revealed the presence of several compounds. These included *trans*-[PtCl(C=CPh)(PMe₂Ph)₂], *trans*-[Pt(C=CPh)₂(PMe₂Ph)₂], and an unidentified material with δ (P) at -21.7 p.p.m., J_{PIP} 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 $[Pt(C=CPh)_2(cod)]$ by PMePh₂ or PPh₃ led smoothly to the *cis* bis-phosphine complexes *cis*- $[Pt(C=CPh)_2(PMePh_2)_2]$ and *cis*- $[Pt(C=CPh)_2(PPh_3)_2]$ respectively [equation (6)]. Surprisingly, however, use of dimethylphenyl-

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

phosphine produced the *trans* isomer of $[Pt(C=CPh)_2-(PMe_2Ph)_2]$. 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.

A third method of synthesis of *cis* bis-ethynyl complexes met the same limited success. *cis*-[Pt(C=CPh)₂(CO)(PMePh₂)], synthesised from *cis*-[PtCl₂(CO)(PMePh₂)], Hg(C=CPh)₂, and [NEt₄]Cl,⁵ when treated with PMePh₂ readily produced the bis-phosphine complex [equation (7)]. The triphenylphosphine $cis-[Pt(C=CPh)_2(CO)(PMePh_2)] + PMePh_2 \longrightarrow$ $cis-[Pt(C=CPh)_2(PMePh_2)_2] + CO \quad (7)$

analogue was similarly prepared from $cis-[Pt(C=CPh)_2-(CO)(PPh_3)]$ and PPh₃, and the mixed-phosphine complex $cis-[Pt(C=CPh)_2(PPh_3)(PMePh_2)]$ was produced by treating $cis-[Pt(C=CPh)_2(CO)(PMePh_2)]$ with PPh₃ (though this reaction was accompanied by phosphine exchange and the two symmetrical cis bis-phosphine complexes were also formed).

The propynyl complex cis-[Pt(C=CMe)₂(CO)(PMePh₂)] 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 PMePh₂ to cis-[Pt(C=CMe)₂(CO)(PMePh₂)] in CDCl₃ produced cis-[Pt(C=CMe)₂(PMePh₂)₂], observed by ³¹P 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=CMe)₂(PMePh₂)₂]. An attempt to produce cis-[Pt(C=CPh)₂(PMePh₂)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 PPh₃ or PMePh₂ 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 PMe₂Ph, 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=CPh)₂-(PMePh₂)₂] is configurationally stable in organic solvents at room temperature, and was unaffected by refluxing CHCl₃. Moreover, treatment in solution by free PMePh₂ or iodide (as [NBu₄]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 ³¹P n.m.r. spectroscopy in CDCl₃, addition of *ca*. 10% of HgCl₂, HgBr₂, or HgI₂ caused complete conversion over *ca*. 3 h at ambient temperature. The growth of signals from *cis*-[PtX(C=CPh)(PMePh₂)₂] (X = Cl) then *trans*-[PtX(C=CPh)(PMePh₂)₂] was detected before any *trans*-

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

Ethynyl complex	Salt	Ratio	δ(P)/ p.p.m.	J _{PtP} / Hz
cis-[Pt(C=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=CPh)2(PPh3)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.				

 $[Pt(C=CPh)_2(PMePh_2)_2]$ appeared, and *trans*- $[PtX-(C=CPh)(PMePh_2)_2]$ in an amount equivalent to the HgX₂ added remained at the end of the reaction, presumably along with a similar amount of HgX(C=CPh). A separate experiment confirmed that HgCl(C=CPh) was as effective as HgX₂ 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=CPh)(PMePh₂)₂]. This occurs very readily for other organoplatinum halides,¹³ and has been observed for *cis*-[PtCl(C=CPh)(PPh₃)₂].^{12b} We find that *cis*-[Pt(C=CPh)₂-(PPh₃)₂] is also isomerised readily by HgCl₂, HgBr₂, or HgI₂ in CDCl₃ 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

$$cis-[Pt(C=CPh)_{2}(PMePh_{2})_{2}] + HgX_{2} \longrightarrow cis-[PtX(C=CPh)(PMePh_{2})_{2}] + HgX(C=CPh)$$
(8)

$$cis-[Pt(C=CPh)_2(PMePh_2)_2] + HgX(C=CPh) \Longrightarrow$$
$$cis-[PtX(C=CPh)(PMePh_2)_2] + Hg(C=CPh)_2 \quad (9)$$

$$cis-[PtX(C=CPh)(PMePh_2)_2] \longrightarrow trans-[PtX(C=CPh)(PMePh_2)_2]$$
(10)

$$trans-[PtX(C=CPh)(PMePh_2)_2] + Hg(C=CPh)_2 \Longrightarrow trans-[Pt(C=CPh)_2(PMePh_2)_2] + HgX(C=CPh) (11)$$

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 $[Pt(C=CPh)_2(PMePh_2)_2]$. These included HgClPh and $[NEt_4]_2[Hg_2Cl_6]$, though both act much more slowly than the other mercury compounds listed above. Copper(1) iodide, when added to *cis*- $[Pt(C=CPh)_2(PMePh_2)_2]$ in CDCl₃ also caused isomerisation, and the presence of *trans*- $[PtI(C=CPh)(PMePh_2)_2]$ was detected by ³¹P 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*- $[PtCl(C=CPh)(PMePh_2)_2]$ 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=CPh)(PPh_3)], compared to [Cu(C=CPh)] (from CuI) or Hg(C=CPh)_2 (from mercury halides).

Neither CuCl nor $[AuCl{P(C_6H_4Me-p)_3}]$ had any catalytic effect on cis-[Pt(C=CPh)₂(PMePh₂)₂] in CDCl₃. 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=CPh)₂(PMe₂Ph)₂], prepared from [Au(C=CPh)(PPh₃)], may well be catalysed by the [AuCl(PPh₃)] by-product. Indeed *trans*-[PtCl(C=CPh)-(PMe₂Ph)₂] was detected by ³¹P n.m.r. spectroscopy as an intermediate during the change. The apparent greater readiness of PMe₂Ph 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=CPh)₂(PMePh₂)₂] irreversibly, leaving *trans*-[PtCl(C=CPh)(PMePh₂)₂] and *cis*-[PtCl₂(PMePh₂)₂]. Finally, it can be noted that *cis*-[Pt(C=CPh)₂(PMePh₂)₂] has been obtained and kept in solution in the presence of *trans*-[PtCl(C=CPh)(PMePh₂)₂] and/or *cis*-[PtCl₂(PMePh₂)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, ${}^{1}J_{PtP}$ of the phosphorus *trans* to Cl or Br in cis-[PtX(C=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 PMePh₂ 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 v(Pt-Cl) in the i.r. spectrum of cis-[PtCl(C=CPh)- $(PPh_3)_2].$

The second observation concerns the ³¹P 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

³¹P N.m.r. and ¹H n.m.r. spectra were recorded in CDCl₃ 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: [PtCl₂(CO)(PMePh₂)], *cis*-[Pt(C=CPh₂(CO)(PMePh₂)],⁵ [PtCl₂(cod)],²⁰ [Au(C= CPh)(PPh₃)],⁶ [CuCl(PPh₃)],²¹ and Hg(C=CPh)₂.²²

(Cyclo-octa-1,5-diene)bis(phenylethynyl)platinum.—A suspension of [PtCl₂(cod)] (0.5 g, 1.34 mmol) in ethanol (30 cm³) was maintained at 0 °C under nitrogen, and a freshly prepared mixture of PhC=CH (0.27 g, 2.7 mmol) and sodium ethoxide (prepared from 61.5 mg sodium) in ethanol (10 cm³) 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=CPh)₂(cod)] (0.7 g, 103%). Three recrystallisations from CH₂Cl₂ finally yielded the pure complex [m.p. 178—197 °C (decomp.); v(C=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 [PtCl₂(PMePh₂)₂]. To a suspension of [PtCl₂(PMePh₂)₂] (0.5 g, 0.75 mmol) in ethanol (20 cm³) at 0 °C was added PhC=CH (153 mg, 1.5 mmol), rapidly followed by sodium ethoxide [prepared from sodium (34.5 mg, 1.5 mmol) in ethanol (5 cm³)]. The solid remained during 2 h stirring, after which filtration yielded the solid product (440 mg, 74%). Recrystallisation from CHCl₃-pentane afforded the pure material [m.p. 172–173 °C; v(C=C) 2 120w, 2 130 (sh) cm⁻¹. Found: C, 62.4; H, 4.6. Calc. for C₄₂H₃₆P₂Pt: 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 cm³) at 0 °C under N₂ was added Hg(C=CPh)₂ (163 mg, 0.4 mmol) in CHCl_3 (5 cm³). 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=CPh)₂(CO)(PMePh_2)] in the orange solution (confirmed by ³¹P n.m.r. spectroscopy). PMePh₂ (87 µl, 0.4 mmol) was immediately added to the solution which was stirred for 5 min. Removal of solvent yielded cis-[Pt(C=CPh)₂(PMePh_2)_2] (303 mg, 94%).

(c) From [Pt($\subseteq CPh$)₂(cod)]. To a solution of [Pt($\subseteq CPh$)₂(cod)] (500 mg, 0.99 mmol) in CH₂Cl₂ (30 cm³) under N₂ was added a solution of PMePh₂ (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 CHCl₃-light petroleum (314 mg, 40%).

cis-Bis(phenylethynyl)bis(triphenylphosphine)platinum.—To a solution of $[Pt(C=CPh)_2(cod)]$ (185 mg, 0.37 mmol) in CH₂Cl₂ (20 cm³) at 0 °C under N₂ was added PPh₃ (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 CH₂Cl₂-pentane [m.p. 210—211 °C (lit.,^{3a} 206—208 °C); v(C=C) 2 110 cm⁻¹].

trans-Chlorobis(methyldiphenylphosphine)(phenylethynyl)platinum.—To a suspension of cis-[PtCl₂(PMePh₂)₂] (0.5 g, 0.75 mmol) in CHCl₃ (25 cm³) was added Hg(C=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 CHCl₃-pentane gave the pure compound as white crystals (352 mg, 64%) [m.p. 213—214 °C; v(C=C) 2 130 cm⁻¹, v(Pt-Cl) 315 cm⁻¹. Found: C, 55.4; H, 4.1; P, 8.8. Calc. for C₃₄H₃₁ClP₂Pt: C, 55.8; H, 4.3; P, 8.5%].

trans-Bis(methyldiphenylphosphine)bis(propynyl)platinum.— To a solution of cis-[PtCl₂(CO)(PMePh₂)] (0.5 g, 1.01 mmol) in CHCl₃ (50 cm³) under a nitrogen atmosphere was added Hg(C=CMe)₂ (281 mg, 1.01 mmol), followed by [NEt₄]Cl (165.5 mg, 1.01 mmol). After stirring for 5 min, rapid filtrations left an orange solution, to which was added PMePh₂ (188 µl, 1.01 mmol) by syringe. Solvent was removed and the resulting solid recrystallised from acetone to yield *trans*-[Pt(C=CMe)₂-(PMePh₂)₂] (0.5 g, 73%) [m.p. 176—178 °C; v(C=C) 2 130 cm⁻¹. Found: C, 56.8; H, 4.6; P, 9.25. Calc. for C₃₂H₃₂P₂Pt: C, 57.1; H, 4.8; P, 9.2%].

trans-Bis(methyldiphenylphosphine)bis(phenylethynyl)-

platinum.—To a suspension of *cis*-[PtCl₂(PMePh₂)₂] (0.2 g, 0.3 mmol) in NHEt₂ (25 cm³) were added PhC=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=CPh)₂(PMePh₂)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(PMePh₂)₂] by bubbling C₂H₂ through the suspension of *cis*-[PtCl₂(PMe₂Ph)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 CDCl₃ (0.5 cm³), and followed by ³¹P n.m.r. spectroscopy at ambient temperature. Catalysts were added either as solids (HgCl₂, HgClPh, CuI, or SnCl₂) or as standard solutions [HgBr₂ in ethanol (10 μ l), HgCl(C=CPh) in CDCl₃ (10 μ l)] by syringe.

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