Stereospecific Transfer of Ethynyl Groups between Platinum(II) and Mercury(II)

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Reactions between *cis*-$[PtCl_2(CO)L]$ (L = $PMePh_2$) and $Hg(C{\equiv}CR)_2$ (R = Me or Ph) lead first to $[PtCl(C{\equiv}CR)(CO)L]$ [isomer (I); L *trans* to C≡CR] and Hg(C≡CR)Cl, then to *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgCl_2$, and finally to $[PtCl(C{\equiv}CR)(CO)L]$ [isomer (II); L *trans* to Cl] and Hg(C≡CR)Cl. The reactions of (II) with $Hg(C{\equiv}CR)_2$ quantitatively form *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$, and (II) with $Hg(C{\equiv}R')_2$(R′ = Me or Ph; R ≠ R′) produce single isomers of $[Pt(C{\equiv}CR)(C{\equiv}CR')(CO)L]$. Treatment of these bis(ethynyl)platinum complexes with $HgCl_2$ specifically removes the ethynyl *trans* to L, reforming (II) and the ethynylmercury(II) chloride. Reactions of the bis(ethynyl)mercurials can be advantageously carried out in the presence of $[NEt_4]Cl$, which symmetrises the Hg(C≡CR)Cl by-product to $Hg(C{\equiv}CR)_2$ (thus making both ethynyls available for transfer to platinum) and $[NEt_4]_2[Hg_2Cl_6]$ (which, being insoluble in organic solvents, is easily separated from the desired product).

We have previously shown that a wide variety of organomercurials, HgR_2 (R = alkyl or aryl) react with *cis*-$[PtCl_2(CO)L]$ (L = tertiary phosphine or arsine) to produce quantitatively the isomer of [PtClR(CO)L] with L *trans* to R, (I).[1-4] The other two isomers, with CO *trans* to R, (II), and Cl *trans* to R, (III), were produced by CO cleavage of the halide-bridged dimers $[Pt_2(\mu\text{-}Cl)_2R_2L_2]$. The reaction between *cis*-$[PtCl_2(CO)L]$ and phenyl-lithium led to several products including some isomer (II) of [PtClPh(CO)L], but none of the isomer (I).

This variation in products was rationalised in terms of different reaction mechanisms. It seemed likely that organolithium reagents would react *via* carbanion attack at platinum, a view supported by recent mechanistic studies of organopalladium complexes.[5] Thus displacement of the chloride *trans* to carbon monoxide, the resident group of highest *trans* effect,[6] to yield isomer (II) would be expected.[1] The reaction between HgR_2 and *cis*-$[PtCl_2(CO)L]$, on the other hand, seemed likely to proceed *via* an S_E2(cyclic) mechanism. Such reactions are well documented for organic group transfers between mercury atoms,[7] and such a route can explain the high stereospecificity of the platinum reactions. The chloride replaced to give isomer (I) is opposite tertiary phosphine, a group of high *trans* influence [6] which would selectively weaken and polarise the Pt–Cl bond *trans* to it, rendering it more liable to participate in S_E2(cyclic) exchange processes.[1]

We report here the reactions of bis(ethynyl)mercury compounds with *cis*-$[PtCl_2(CO)L]$. These lead to the production of isomer (II) and provide evidence for the operation of a more complicated series of reactions than has been observed with other organomercurials.

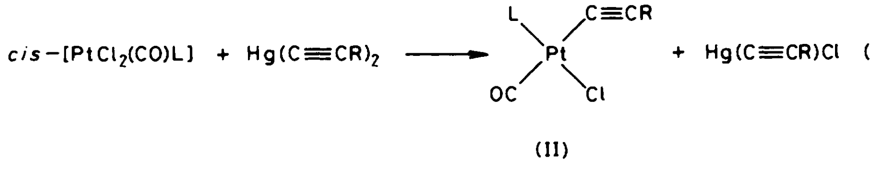
Results and Discussion

cis-$[PtCl_2(CO)L]$ (L = $PMePh_2$) reacts rapidly at room temperature with chloroform solutions of $Hg(C{\equiv}CR)_2$ (R = Me or Ph) to produce the isomers (II) of [PtCl(C≡CR)(CO)L], with C≡CR *trans* to CO [equation (1)]. The n.m.r. parameters of (II) leave no doubts about their geometry. Values of $^1J_{PPt}$ are 3 231 (R = Me) and 3 190 Hz (R = Ph), typical of phosphine *trans* to Cl, but too large for phosphine *trans* to organic groups.[1-4] Values of $^2J_{^{13}CP}$, from reactions performed using ^{13}CO labelled material, are 7.5 (R = Me) and 6.0 Hz (R = Ph). These are typical of phosphine *cis* to CO.[8]

A more convenient synthesis can be carried out using half the amount of diorganomercurial and $[NEt_4]Cl$. The chloride ions symmetrise the organomercuric halide by-product, reforming diorganomercury. This not only makes available both of the organic groups for transfer to platinum [equation (2)], but removes any separation problems of the organomercuric halide, which can have similar solubility characteristics to the platinum product. The by-product from the chloride-symmetrised reactions, $[NEt_4]_2[Hg_2Cl_6]$,[9] is insoluble and readily removed by filtration. By this method, isomer (II) can be obtained in solution in 100% yield. The solutions are stable at room temperature for several hours, after which decomposition to a variety of compounds, including *trans*-$[PtCl(C{\equiv}CR)L_2]$ and *cis*-$[PtCl_2(CO)L]$ as major components, becomes apparent. Isomer (II; R = Ph) was also prepared by CO cleavage of $[Pt_2(C{\equiv}CPh)_2(\mu\text{-}Cl)_2L_2]$ (L = $PMePh_2$) {prepared from *cis*-$[PtCl_2(C_2H_4)(PMePh_2)]$ and $Hg(C{\equiv}CPh)_2$} along with another complex having ^{31}P n.m.r. parameters δ 4.4 p.p.m. and J_{PPt} 3 460 Hz, presumably isomer (III) [1] of $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ with CO *trans* to $PMePh_2$.

$$2\ cis\text{-}[PtCl_2(CO)L] + Hg(C{\equiv}CR)_2 \xrightarrow{Cl^-} 2\,(II) + \tfrac{1}{2}\,[Hg_2Cl_6]^{2-} \quad (2)$$

The production of isomers (II) of [PtCl(C≡CR)(CO)L] from the reactions of *cis*-$[PtCl_2(CO)L]$ with $Hg(C{\equiv}CR)_2$ was surprising, since previous reactions using phenyl, alkyl,[1-3] or substituted aryl [4] mercurials appeared to produce only isomer (I) (Cl *trans* to CO). It was soon apparent that the reaction sequences were not simple, however. When followed at low temperature by ^{31}P n.m.r. spectroscopy, the formation of intermediate species was observed which then decayed to (II) and Hg(C≡CR)Cl. Moreover, these intermediates were not

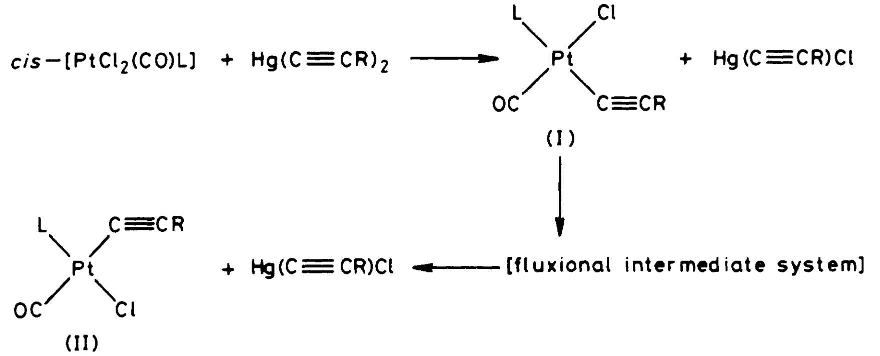


(1)

(II)

simple compounds. At −60 °C their ^{31}P n.m.r. signals were slightly broad, and the parameters varied (from δ −3.2, J_{PPt} = 2 117 to δ −4.1 p.p.m., J_{PPt} = 2 166 Hz for the phenylethynyl case) as the reaction proceeded. Such behaviour is characteristic of two or more platinum phosphine complexes in rapid (n.m.r. time-scale) equilibria. Reactions of the methylethynyl complexes were faster and the parameters of the intermediate (δ −5.6 p.p.m., J_{PPt} = 2 226 Hz) did not vary so much, possibly a reflection of the shorter time that they were available for examination.

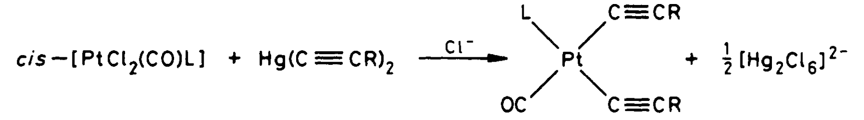
When the reactions were performed in more polar solvents at low temperature [dry tetrahydrofuran (thf) or Me_2SO–$CDCl_3$ (1 : 1)] they proceeded more slowly than in chloroform and resonances due to a new species could be observed to grow between those of *cis*-$[PtCl_2(CO)L]$ and the fluxional intermediate. The new species had parameters δ 2.7 p.p.m., J_{PPt} = 1 964 Hz ($C\equiv CPh$), typical for an ethynyl group *trans* to tertiary phosphine (see below), and we assign this as isomer (I) of $[PtCl(C\equiv CPh)(CO)L]$. A weaker transient signal at δ 2.7 p.p.m. could also be observed in the absence of thf or Me_2SO. Equation (3) summarises the reaction sequence. The n.m.r. signals of *cis*-$[PtCl_2(CO)L]$, (I), and (II) were not broadened, and were independent of the fluxional intermediate. Those species are not involved, therefore, in the exchange process.



(3)

The reactions of *cis*-$[PtCl_2(CO)L]$ with one equivalent of $Hg(C\equiv CR)_2$ in the presence of chloride ions as symmetrising agent lead to the transfer of two ethynyl groups to platinum, equation (4). The same products were formed from the reactions of isomers (II) of $[PtCl(C\equiv CR)(CO)L]$ with the bis(ethynyl)mercurials. They can be isolated as pale yellow crystalline solids. Their ^{31}P n.m.r. spectra reveal values of $^1J_{PPt}$ = *ca.* 2 100 Hz as typical of tertiary phosphine *trans* to ethynyl groups.

The *cis*-bis(ethynyl)platinum complexes react readily with mercury(II) chloride to produce $[PtCl(C\equiv CR)(CO)L]$ [isomer (II)], and it is apparent that these two materials are part of the fluxional intermediate system *en route* to isomers (II) from *cis*-$[PtCl_2(CO)L]$, equation (5). The reaction between *cis*-$[Pt(C\equiv CPh)_2(CO)L]$ and $HgCl_2$ in $CDCl_3$ produces the same fluxional signals observed in the intermediate from *cis*-$[PtCl_2(CO)L]$ and $Hg(C\equiv CPh)_2$. Also, when *cis*-$[Pt(C\equiv CPh)_2(CO)L]$ was added to the reaction mixture of *cis*-$[PtCl_2(CO)L]$ and $Hg(C\equiv CPh)_2$ at the time when only the fluxional intermediate system was visible by ^{31}P n.m.r. spectroscopy, no separate signals for the bis(ethynyl)platinum complex could be distinguished from the slightly broadened resonances of the fluxional intermediate, and when the reaction was complete, the *cis*-$[Pt(C\equiv CPh)_2(CO)L]$ was seen to remain, accompanying isomer (II) of $[PtCl(C\equiv CPh)(CO)L]$. Moreover, when one equivalent of $[NEt_4]Cl$ or $HgPh_2$ was added to the fluxional intermediate system (to remove $HgCl_2$ by precipitation as $[NEt_4]_2[Hg_2Cl_6]$ or HgPhCl, respectively) *cis*-$[Pt(C\equiv CPh)_2(CO)L]$ was left and could be isolated.



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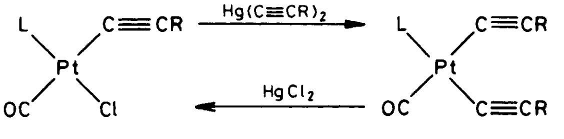

(5)

Details of the n.m.r. spectra of *cis*-$[Pt(C\equiv CMe)_2(CO)L]$ and other complexes are shown in Tables 1 (^1H and ^{31}P) and 2 (^{13}C). The value of the $^5J_{HP}$ coupling of the methyl(ethynyl) protons of isomer (II) of $[PtCl(C\equiv CMe)(CO)L]$ (1.5 Hz) is similar to the analogous values for *trans*-$[Pt(C\equiv CMe)_2(PMe_2Ph)_2]$ (1.9 Hz)[10] and *trans*-$[PtCl(C\equiv CMe)(PMe_2Ph)_2]$ (2.3 Hz),[10] all with propynyl groups *cis* to tertiary phosphine. Comparison with the two $^5J_{HP}$ values of *cis*-$[Pt(C\equiv CMe)_2(CO)(PMePh_2)]$ (1.95 and 3.3 Hz) would thus indicate that the former, smaller, value originated from the propynyl *cis* to $PMePh_2$, and the larger coupling from that *trans* to $PMePh_2$, but selective proton decoupling of the ^{13}C n.m.r. spectrum of this compound revealed that the correct assignments are in fact the other way around. The strikingly large value of one of the $^2J_{CP}$ couplings (Table 2, 144.9 Hz) clearly identifies this α-carbon atom as the propynyl *trans* to phosphine. [Markedly larger values of ^2J couplings to *trans* phosphines appear to be quite general: *e.g.* to ^{13}C (ref. 8) and ^{31}P (ref. 11).] Irradiation of the methyl(ethynyl) signals at δ 1.98 ($^5J_{HP}$ = 1.95) and 1.79 p.p.m. ($^5J_{HP}$ = 3.3 Hz), respectively, demonstrated that the former signal, with the smaller value of $^5J_{HP}$, was associated with the α-carbon atom at δ 78.8 p.p.m. ($^2J_{CP}$ = 144.9 Hz). Sign reversals of the coupling constants along carbon chains to *cis* and *trans* substituents of platinum have been observed.[12]

Mixed Bis(ethynyl)platinum Complexes.—*cis*-Carbonyl(methyldiphenylphosphine)bis(phenylethynyl)platinum and bis(methylethynyl)mercury reacted readily in solution at

Table 1. Phosphorus-31 and ^{1}H n.m.r. parameters [a]

Compound ($L = PMePh_2$)	δ (P)/ p.p.m.	$^1J_{PPt}$/Hz	$CH_3C{\equiv}C{-}Pt$ δ/p.p.m.	$CH_3C{\equiv}C{-}Pt$ $^5J_{HP}$/Hz	$CH_3C{\equiv}C{-}Pt$ $^4J_{PtH}$/Hz	$C_6H_5C{\equiv}C$ δ/p.p.m.	C_6H_5P δ/p.p.m.	CH_3P δ/p.p.m.	CH_3P $^2J_{HP}$/Hz	CH_3P $^3J_{PtH}$/Hz
$[PtCl(C{\equiv}CMe)(CO)L]$, (II)	−4.7	3 231	1.79	1.5	14.0	—	7.50	2.46	11.6	44.6
$[PtCl(C{\equiv}CPh)(CO)L]$, (II)	−4.7	3 190	—	—	—	7.05	7.45	2.50	11.0	46.0
cis-$[Pt(C{\equiv}CMe)_2(CO)L]$	−3.2	2 104	1.98 1.79	1.95 3.30	15.5 15.8	—	7.46	2.26	10.6	29.3
cis-$[Pt(C{\equiv}CPh)_2(CO)L]$	−3.2	2 096	—	—	—	7.12	7.46	2.40	10.0	30.0
(IV)	−3.0	2 070	2.06	1.5	*b*	7.10	7.45	2.36	10.6	29.0
(V)	−2.9	2 104	1.87	2.8	16.5	7.16	7.46	2.32	10.9	30.0

[a] In $CDCl_3$. ^{31}P N.m.r. spectra were recorded at −60 °C on a Varian XL100 spectrometer operating in the Fourier-transform mode. Chemical shifts are positive downfield of external H_3PO_4. ^{1}H N.m.r. spectra were recorded at ambient temperatures on a Perkin-Elmer R32 spectrometer at 90 MHz. [b] Unresolved.

Table 2. ^{13}C-{^{1}H} n.m.r. parameters [a]

Compound ($L = PMePh_2$)		δ (C_α)/ p.p.m.	δ (C_β)/ p.p.m.	$^1J_{CPt}$/Hz	$^2J_{CPt}$/Hz	$^2J_{CP}$/Hz	$^3J_{CP}$/Hz
cis-$[Pt(C{\equiv}CMe)_2(CO)L]$	ethynyl *trans* to CO	84.4	107.5	1 161.8	335.8	18.9	3.6
	ethynyl *trans* to L	78.8	103.0	1 066.5	299.7	144.9	32.8
	CO	171.4		1 146.8		7.5	
(IV)	ethynyl *trans* to CO	97.0	111.6	*b*	*b*	18.5	2.9
	ethynyl *trans* to L	78.3 [c]	103.9	*b*	*b*	144 [c]	32.3
	CO	170.9		1 162.6		8.0	
(V)	ethynyl *trans* to CO	82.7	108.3	*b*	*b*	18.7	<5
	ethynyl *trans* to L	93.3	108.0	*b*	*b*	143.4	30.6
	CO	170.7		1 162.6		7.9	

[a] In $CDCl_3$ at −60 °C on a Bruker WP200SY spectrometer operating in the Fourier-transform mode. Chemical shifts are relative to $CDCl_3$ at 77.0 p.p.m. [b] Unresolved. [c] Estimated values: one half of the doublet partially obscured by $CDCl_3$.

ambient temperatures. Phosphorus-31 n.m.r. investigations indicated the initial formation of a single *cis*-like isomer of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]$, (IV), and ^{1}H n.m.r. spectroscopy revealed, in addition, the presence of $Hg(C{\equiv}CMe)(C{\equiv}CPh)$. The analogous reaction between *cis*-$[Pt(C{\equiv}CMe)_2(CO)L]$ and $Hg(C{\equiv}CPh)_2$ produced the other *cis*-like mixed bis(ethynyl)platinum product, (V), showing that the products were the kinetic ones. On standing for 15 min or more at ambient temperatures, further reactions took place leading to an intractable mixture of all possible bis(ethynyl) compounds of platinum and mercury. The isomers (IV) and (V) can also be prepared from the reactions of $[PtCl(C{\equiv}CR)(CO)L]$ [isomer (II)] with bis(ethynyl)mercurials, and when the chloride symmetrisation route is employed they can be obtained pure in solution. As such they are stable at room temperature for several hours.

The geometry of the mixed ethynylplatinum complexes, (IV) and (V), can be determined from their ^{13}C n.m.r. spectra (Table 2) by comparison with that of *cis*-$[Pt(C{\equiv}CMe)_2(CO)L]$. In each case the α-carbon of the ethynyl *trans* to $PMePh_2$ can be identified by its large value of $^2J_{CP}$. In compound (V) this signal (δ 93.3 p.p.m.) is unaffected in the proton coupled spectrum, and is therefore that of phenylethynyl. The other ethynyl (α-carbon at δ 82.7, *cis* to $PMePh_2$) collapses to a quartet ($^5J_{HP}$ = 2.8 Hz at −60 °C) in the proton coupled spectrum, and is due to $C{\equiv}CMe$. In compound (IV), propynyl is *trans* to $PMePh_2$. Its ^{13}C n.m.r. parameters closely resemble those for the same group in *cis*-$[Pt(C{\equiv}CMe)_2(CO)L]$. Equations (6)—(9) thus illustrate the formation of (IV) and (V).*

The remarkable specificity of these steps is equalled by the reaction of mercury(II) chloride with (IV) or (V). This leads to formation of isomers (II) as the only platinum-containing products [equations (10) and (11)].

In each of the reactions (6)—(11), the group *trans* to $PMePh_2$ is substituted with 100% specificity. This would be quite in keeping with the operations of an S_E2(cyclic) reaction path, proceeding *via* a transition state such as (VI) [for reaction (11)]. Oxidative addition of $HgCl_2$ to (IV) could result in intermediate (VII), which could lead to the observed products by reductive elimination of $Hg(C{\equiv}CMe)Cl$, and these two processes might be regarded as extremes of a single substitution pathway.[14] Other oxidative addition intermediates, (VIII) and (IX), can be ruled out. Reductive elimination of $Hg(C{\equiv}CMe)Cl$ from (VIII) would result in migration of $C{\equiv}CPh$ to produce isomer (I) of $[PtCl(C{\equiv}CPh)(CO)L]$, and the same elimination from (IX) is symmetry restricted [15] to produce isomer (III) of $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$, with CO and $PMePh_2$ mutually *trans*. We have not observed those materials.

A *trans* oxidative addition or reductive elimination could only operate *via* an ionic mechanism.[16] Whilst such an addition may be plausible for $HgCl_2$, it seems unlikely for $Hg(C{\equiv}CR)_2$.

Nature of the Fluxional Intermediate.—There are three reasonable possibilities to account for the fluxional nature of the reaction between *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgCl_2$. The first involves rapid and reversible co-ordination of the chloride (of $HgCl_2$) to platinum. As the reaction proceeds, $RC{\equiv}CHgCl$ is produced, and this could likewise co-ordinate *via* a π-bonded ethynyl group. There is no evidence for such associations with this or with other square planar complexes, even

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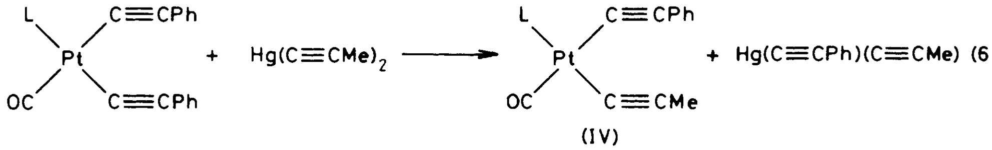
* A preliminary account of this work included an incorrect assignment of the geometries of (IV) and (V).[13] This led to the erroneous conclusion that the formation and reactions of these compounds proceeded by specific oxidative addition/reductive elimination sequences. The correct geometries shown here preclude the operation of such a reaction pathway.



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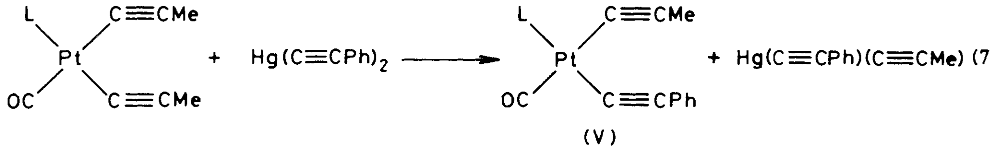

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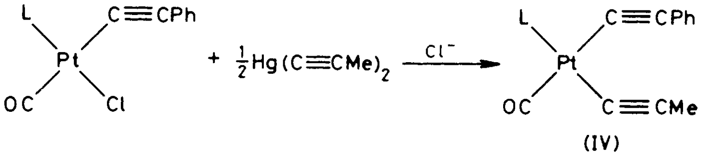

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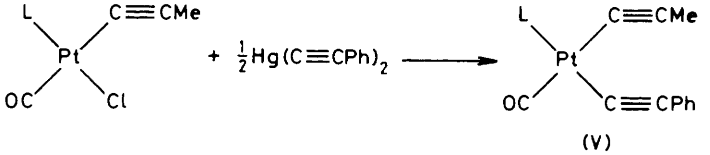

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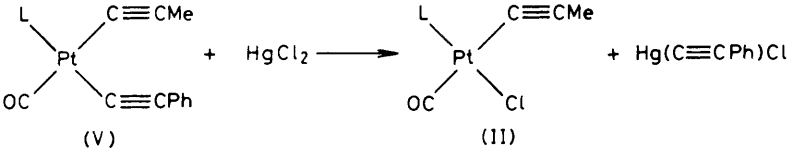

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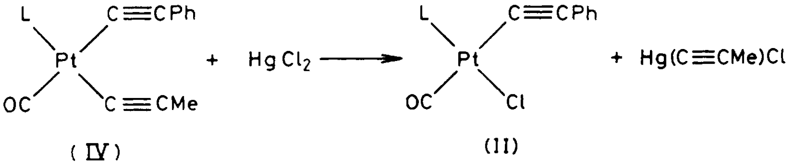

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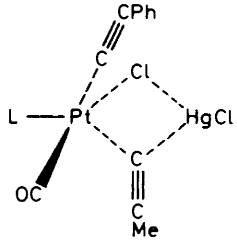

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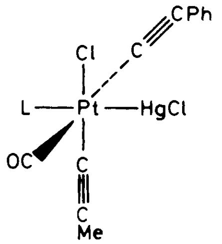

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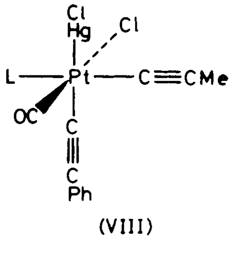

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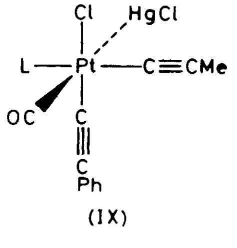

(IX)

with more electron-withdrawing substituents. The n.m.r. parameters of *cis*-[$PtCl_2(CO)L$] were not affected by addition of PhC≡CPh or PhC≡CH to the solution.

A second possibility involves co-ordination of the ethynyls (on platinum) to mercury. Examples of σ : η^2-bridging ethynyls with two platinum atoms are known,[17] but none bridging Pt to Hg. Also, our monoethynylplatinum complexes do not exhibit such behaviour with $HgCl_2$, although the chelating effect of the two ethynyls could be important.

We favour a third possibility: nucleophilic attack of platinum(II) on mercury(II) of $HgCl_2$. A variety of adducts involving bonds between platinum and mercury, palladium, thallium, or silver have recently been described by van Koten and co-workers.[18-20] Electrochemical, u.v.-visible spectroscopic, INEPT ^{109}Ag n.m.r. spectroscopic, and crystallographic investigations support the formulation of the complexes as platinum to metal donor links. Many similar adducts of mercury(II) chloride and other transition metals are also known. These include [(η-C_5H_5)$(CO)_2Co \rightarrow HgCl_2$],[21] [{RhCl(cod)}$_2$($HgCl_2$)$_2$] (cod = cyclo-octa-1,5-diene),[22] and [$L'_2(CO)_3Fe{\cdot}HgCl_2$] (L′ = PPh_3, $AsPh_3$, or $SbPh_3$) [23] some of which are also fluxional in solution. The variations in the parameters observed in our *cis*-[Pt(C≡CR)$_2$(CO)L]–$HgCl_2$ system would be dependent on the concentrations of the reactants, and the very low solubility of $HgCl_2$ in chloroform would influence these.

Experimental

The platinum [24] and mercury [25] starting materials were prepared by published methods. Phosphorus-31 n.m.r.

spectra were recorded in CDCl$_3$ solution using a Varian XL-100 spectrometer in the Fourier-transform mode; ^{1}H n.m.r. spectra were recorded in CDCl$_3$ solution on a Perkin-Elmer R32 90 MHz spectrometer; ^{13}C n.m.r. spectra were recorded in CDCl$_3$ on a Bruker WP200SY spectrometer operating at 50.32 MHz.

cis-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)].—*cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.2 g, 0.405 mmol), [NEt$_4$]Cl (0.067 g, 0.405 mmol), and Hg(C≡CPh)$_2$ (0.163 g, 0.405 mmol) were mixed in CH$_2$Cl$_2$ (5 cm^3). A clear yellow solution formed along with a silver-grey precipitate. The precipitate was filtered off to yield [NEt$_4$]$_2$[Hg$_2$Cl$_6$] (0.14 g, 80%) identified by comparison of its i.r. spectrum with that of an authentic sample. The solution was reduced in volume and hexane added until a fine light yellow precipitate formed. The solvent was decanted off and the solid was dried to give [Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] (yield 0.063 g, 25%) (Found: C, 57.6; H, 3.7. C$_{30}$H$_{23}$OPPt requires C, 57.7; H, 3.9%). Its i.r. spectrum revealed bands at 2 130w and 2 090s cm^{-1}.

Samples of *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] used subsequently in reactions were prepared similarly *in situ*, and filtered to remove [NEt$_4$]$_2$[Hg$_2$Cl$_6$].

cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)].—*cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.2 g, 0.405 mmol), [NEt$_4$]Cl (0.067 g, 0.405 mmol), and Hg(C≡CMe)$_2$ (0.113 g, 0.405 mmol) were mixed in CH$_2$Cl$_2$ (5 cm^3). A clear yellow solution formed along with a silver-grey precipitate of [NEt$_4$]$_2$[Hg$_2$Cl$_6$] which was filtered off (0.13 g, 75%). The volume of solution was reduced by half using a rotary evaporator. It turned dark brown, and a black precipitate began to form. The mixture was treated with activated charcoal and filtered to give a pale orange solution. Hexane was added until a light orange-yellow precipitate formed. The solvent was decanted off to give the *product* (yield 0.003 g, 15%) (Found: C, 47.8; H, 3.8. C$_{20}$H$_{19}$OPPt requires C, 46.35; H, 3.8%). Samples subsequently used in reactions were similarly prepared *in situ* and [NEt$_4$]$_2$[Hg$_2$Cl$_6$] filtered off before use.

[PtCl(C≡CR)(CO)(PMePh$_2$)] [*Isomers* (II)].—*cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.0405 mmol), [NEt$_4$]Cl (0.0033 g, 0.020 24 mmol), and Hg(C≡CPh)$_2$ (0.008 15 g, 0.020 24 mmol) were dissolved together in CDCl$_3$ (0.5 cm^3). A clear yellow solution and a silver-grey precipitate formed. The precipitate, [NEt$_4$]$_2$[Hg$_2$Cl$_6$], was filtered off. The ^{31}P n.m.r. spectrum of the solution showed the presence of a single *product* (δ −4.7 p.p.m., $^1J_{\mathrm{PtP}}$ = 3 190 Hz). N.m.r. parameters are presented in Tables 1 and 2. The solution of [PtCl(C≡CPh)(CO)(PMePh$_2$)] remained unchanged for several hours, after which signals from decomposition products were observed in the n.m.r. spectra.

Similarly, *cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.040 48 mmol), [NEt$_4$]Cl (0.0033 g, 0.020 24 mmol), and Hg(C≡CMe)$_2$ (0.0056 g, 0.020 24 mmol) mixed in CDCl$_3$ (0.5 cm^3) produced a clear yellow solution and a silver-grey precipitate of [NEt$_4$]$_2$[Hg$_2$Cl$_6$]. The precipitate was removed by filtration through glass filter paper. A ^{31}P n.m.r. spectrum of the solution showed only one *species* present (δ −4.7 p.p.m., $^1J_{\mathrm{PtP}}$ = 3 231 Hz). N.m.r. spectroscopic parameters are reported in Tables 1 and 2. The solution of [PtCl(C≡CMe)(CO)(PMePh$_2$)] was indefinitely stable at −60 °C, but darkened on standing at room temperature.

[PtCl(C≡CPh)(CO)(PMePh$_2$)] [*Isomer* (II)] *and* Hg(C≡CMe)$_2$.—[PtCl(C≡CPh)(CO)(PMePh$_2$)] (0.0405 mmol) was prepared *in situ* as above in CDCl$_3$ (0.5 cm^3). To this was added Hg(C≡CMe)$_2$ (0.005 g, 0.020 24 mmol) and [NEt$_4$]Cl (0.033 g, 0.020 24 mmol) in CDCl$_3$ (0.5 cm^3) at room temperature. A clear yellow solution and a silver-grey precipitate formed. The precipitate was filtered off. The ^{31}P n.m.r. spectrum of the solution showed a single *species* (δ −3.0 p.p.m., $^1J_{\mathrm{PtP}}$ = 2 070 Hz). Its n.m.r. spectra (Tables 1 and 2) revealed it to be the isomer of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] with C≡CMe *trans* to PMePh$_2$, (IV).

[PtCl(C≡CMe)(CO)(PMePh$_2$)] [*Isomer* (II)] *and* Hg(C≡CPh)$_2$.—Similarly, [Pt(C≡CMe)Cl(CO)(PMePh$_2$)] (0.0405 mmol) was prepared *in situ* and to it was added a CDCl$_3$ solution (0.5 cm^3) containing Hg(C≡CPh)$_2$ (0.008 g, 0.020 24 mmol) and [NEt$_4$]Cl (0.0033 g, 0.020 24 mmol). The ^{31}P n.m.r. spectrum of the resulting clear yellow solution after filtration showed only one *species* with room-temperature parameters δ −2.9 p.p.m., $^1J_{\mathrm{PtP}}$ = 2 104 Hz. Its n.m.r. spectra (Tables 1 and 2) showed it to be (V), with C≡CMe *trans* to CO.

The solutions of (IV) and (V) remained unchanged for several hours at room temperature. Samples of (IV) and (V) prepared from Hg(C≡CR)$_2$ alone (in the absence of [NEt$_4$]Cl symmetrising agent) were contaminated in solution by Hg(C≡CR)Cl, which accelerated decomposition.

cis-[Pt(C≡CR)$_2$(CO)(PMePh$_2$)] *and* Hg(C≡CR′)$_2$.—*cis*-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] (0.0405 mmol in 0.5 cm^3 CDCl$_3$), prepared *in situ*, was treated with Hg(C≡CPh)$_2$ (0.0163 g, 0.0405 mmol). A dark yellow solution formed. A ^{1}H n.m.r. spectrum run immediately showed only (V) and Hg(C≡CMe)(C≡CPh) [δ (CH$_3$) 1.91 p.p.m., $J_{\mathrm{H}^{199}\mathrm{Hg}}$ not resolved]. After 15 min, the solution darkened, and ^{31}P and ^{1}H n.m.r. spectra revealed a complex mixture of species.

Similarly, when *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] (0.0405 mmol), prepared *in situ*, was treated with Hg(C≡CMe)$_2$ (0.0113 g, 0.0405 mmol) at room temperature, the ^{1}H n.m.r. spectrum revealed only (IV) and Hg(C≡CMe)(C≡CPh). Decomposition resulted after 15 min at room temperature.

[Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] [*Isomers* (IV) *and* (V)] *and* HgCl$_2$.—The isomer of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] with C≡CMe *trans* to CO, (V), was prepared *in situ* from (II; R = Me), and its identity confirmed by ^{31}P and ^{1}H n.m.r. spectroscopy. The sample was cooled to −60 °C and excess solid HgCl$_2$ was added to the n.m.r. tube. The first species to appear was [PtCl(C≡CMe)(CO)(PMePh$_2$)] [isomer (II); δ (^{31}P) −3.9 p.p.m., $^1J_{\mathrm{PtP}}$ = 3 239 Hz]. As the reaction proceeded the ^{31}P n.m.r. parameters of the bis(ethynyl) species (V) changed to δ −3.1 p.p.m., ^1J = 2 131 Hz. After 30 min signals due to some [PtCl(C≡CPh)(CO)(PMePh$_2$)] [isomer (II)] were also present.

When the isomer of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] with C≡CMe *cis* to CO, (IV), was prepared *in situ* and treated with excess HgCl$_2$ at room temperature the ^{31}P n.m.r. spectrum (run immediately) showed [PtCl(C≡CPh)(CO)(PMePh$_2$)] as the only product. After 1 h at room temperature, *cis*-[PtCl$_2$(CO)(PMePh$_2$)] was observed.

cis-[PtCl$_2$(CO)(PMePh$_2$)] *and* Hg(C≡CPh)$_2$.—*cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.0405 mmol) and Hg(C≡CPh)$_2$ (0.0163 g, 0.0405 mmol) were mixed in CDCl$_3$ (0.5 cm^3) in an n.m.r. tube. The reaction was followed by ^{31}P n.m.r. spectroscopy. After 2 min at ambient temperature, [PtCl(C≡CPh)(CO)(PMePh$_2$)] [isomer (II)] and one other species (δ −4.1 p.p.m., $^1J_{\mathrm{PPt}}$ = 2 156 Hz) was observed. This latter species was no longer evident after 30 min, and a fine precipitate of Hg(C≡CPh)Cl [ν(C≡C) = 2 200 cm^{-1}] was removed by filtration. The reaction was repeated at −60 °C. A species (A) with a slightly broadened signal (δ −3.2 p.p.m., $^1J_{\mathrm{PPt}}$ = 2 117 Hz) grew in intensity, and its parameters steadily changed to δ −4.1 p.p.m., $^1J_{PPt}$ 2 166 Hz, at which stage it was the only phosphorus-containing species observed. This species then began to diminish in intensity, and [PtCl(C≡CPh)(CO)(PMePh$_2$)] [isomer (II)] replaced it. The solution slowly darkened and a precipitate formed. The parameters of the intermediate species now changed to δ −3.7 p.p.m., $^1J_{PPt}$ − 2 141 Hz. Repetition of the experiment using *cis*-[PtCl$_2$(^{13}CO)(PMePh$_2$)] revealed the intermediate (A) to have $^2J_{PC}$ = 7.4 Hz.

A further repetition of the reaction in tetrahydrofuran at −60 °C revealed that a complex with n.m.r. parameters δ +2.7 p.p.m., $^1J_{PPt}$ = 1 964 Hz preceded the formation of the intermediate (A) observed above. This species was also apparent in Me$_2$SO–CDCl$_3$ (1 : 1) (δ +1.9 p.p.m., $^1J_{PPt}$ = 1 976 Hz). In both reactions this intermediate was replaced by the previously observed intermediate, (A) (δ −3.9 p.p.m., $^1J_{PPt}$ = 2 081 Hz; parameters are variable), then [PtCl(C≡CPh)(CO)(PMePh$_2$)] [isomer (II)]. The reactions in these solvents were considerably slower than in CDCl$_3$.

cis-[PtCl$_2$(CO)(PMePh$_2$)] *and* Hg(C≡CMe)$_2$.—This reaction followed a similar path to that with Hg(C≡CPh)$_2$, but proceeded more quickly. *cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.0405 mmol) and Hg(C≡CMe)$_2$ (0.0113 g, 0.0405 mmol) were mixed in CDCl$_3$ (0.5 cm^3) at room temperature. The solution darkened and a precipitate formed. Phosphorus-31 n.m.r. investigation revealed the presence of [PtCl(C≡CMe)(CO)(PMePh$_2$)] [isomer (II)]. When repeated at −60 °C, a species at δ +2.7 p.p.m. ($^1J_{PPt}$ unresolved) was initially observed, followed by the formation of an intermediate with parameters δ −5.6 p.p.m., $^1J_{PPt}$ = 2 226 Hz. This species was finally replaced by [PtCl(C≡CMe)(CO)(PMePh$_2$)] [isomer (II)] as the only phosphorus-containing product. The n.m.r. signals of the intermediate species were slightly broad, but the reaction proceeded too quickly to observe any changes in parameters. Unlike the reaction of the phenylethynyl complex, there was not a time when the intermediate was the only platinum–phosphine compound visible.

cis-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] *and* HgCl$_2$.–A solution of *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] was prepared *in situ* in CDCl$_3$ and to this excess solid HgCl$_2$ was added and the mixture briefly shaken. After 1 h at −60 °C a ^{31}P n.m.r. spectrum showed that *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] had disappeared and had been replaced by a species equivalent to (A) above, with parameters δ −4.16 p.p.m., $^1J_{PPt}$ = 2 167 Hz, and also by some isomer (II) (δ −3.9 p.p.m., $^1J_{PPt}$ = 3 187 Hz). Repeated brief warmings caused (A) to diminish and (II) to increase to become the only species present.

Species (A) *plus cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)].—*cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.0405 mmol) and Hg(C≡CPh)$_2$ (0.0163 g, 0.0405 mmol) were allowed to react in CDCl$_3$ at −60 °C as above until *only* the species with parameters δ −4.16 p.p.m., $^1J_{PPt}$ = 2 166 Hz was present. Then a solution of *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)], prepared *in situ* from *cis*-[PtCl$_2$(CO)(PMePh$_2$)] (0.02 g, 0.0405 mmol), Hg(C≡CPh)$_2$ (0.0163 g, 0.0405 mmol) and [NEt$_4$]Cl (0.0067 g, 0.0405 mmol) in CDCl$_3$ was added to it at −60 °C. The ^{31}P n.m.r. spectrum showed only one species present, with parameters δ −3.87 p.p.m., $^1J_{PPt}$ = 2 151 Hz. The solution remained clear and pale yellow. After standing for 1 h at room temperature the ^{31}P n.m.r. spectrum showed only *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] and [PtCl(C≡CPh)(CO)(PMePh$_2$)] [isomer (II)] to be present in equal quantities.

Similarly, a CDCl$_3$ solution containing only the species (A) (δ −4.16 p.p.m., $^1J_{PPt}$ = 2 166 Hz) was prepared as above, and to this at −60 °C was added HgPh$_2$ (0.0143 g, 0.0405 mmol). A white precipitate formed quickly and was filtered off and shown to be HgPhCl by i.r. examination. The ^{31}P n.m.r. spectrum of the clear yellow solution showed only *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] to be present (Table 1).

Similarly, addition of excess [NEt$_4$]Cl to another CDCl$_3$ solution of the species (A) (δ −4.16 p.p.m., $^1J_{PPt}$ = 2 166 Hz) at −60 °C produced a silver-grey precipitate. The ^{31}P n.m.r. spectrum showed *cis*-[Pt(C≡CPh)$_2$(CO)(PMePh$_2$)] as the only soluble product. I.r. examination identified the precipitate as [NEt$_4$]$_2$[Hg$_2$Cl$_6$].

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