

Ethynyl-group Transfers between Platinum(II) Atoms or between Platinum(II) and Mercury(II) *via cis*-Oxidative Addition–Reductive Elimination Sequences

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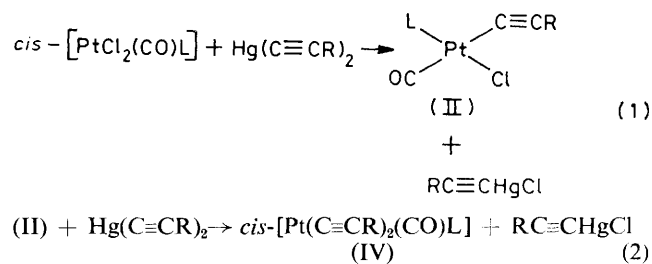
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Site migrations of resident ethynyl groups during formation and exchange reactions of $[\text{Pt}(\text{C}\equiv\text{CMe})(\text{C}\equiv\text{CPh})(\text{CO})\text{PMePh}_2]$ provide evidence for the operation of oxidative addition–reductive elimination sequences.

Much interest has recently centred on the mechanisms of formation of organoplatinum(II) compounds. Amongst those proposed have been nucleophilic attack of carbanions,¹ electrophilic substitution at organomercury² or organotin³ derivatives, and oxidative addition–reductive elimination sequences.⁴ It has proved very difficult to assign any mechanism positively to most organic-group transfer reactions, though wide variations in rate⁵ or product geometry⁶ have been taken as indications that different mechanisms operate for reactions under comparison. Thus although it has been postulated that methyl groups are transferred from $[\text{PtMePhL}_2]$ to other metals by oxidative addition–reductive elimination mechanisms whereas phenyl group transfer is by electrophilic substitution,⁵ it has not been possible to prove this unambiguously. We report here some formation and transfer reactions of mixed bisethynylplatinum(II) complexes, where definite indications of an oxidative addition–reductive elimination sequence are apparent.

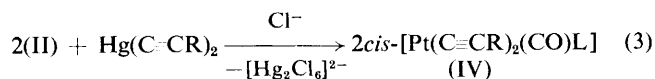
Previously we have found that a wide range of organomercurials, R_2Hg , react with *cis*- $[\text{PtCl}_2(\text{CO})\text{L}]$ (L is tertiary phosphine) to produce the isomer of $[\text{PtClR}(\text{CO})\text{L}]$ with L

trans to R (I).^{6,7} We now find that the compounds $\text{Hg}(\text{C}\equiv\text{CR})_2$ (R = Me or Ph) react with *cis*- $[\text{PtCl}_2(\text{CO})\text{L}]$ to form specifically the isomer with CO *trans* to R (II, equation 1).[†] These ethynylplatinum complexes readily react further with $\text{Hg}(\text{C}\equiv\text{CR})_2$ to produce *cis*-bisethynyl complexes, (IV) (equation 2).



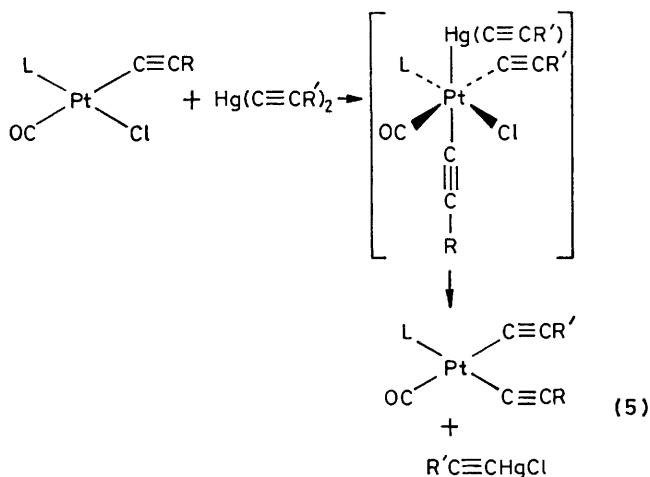
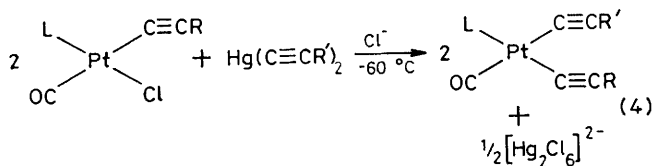
[†] $[\text{PtCl}(\text{C}\equiv\text{CMe})(^{13}\text{CO})(\text{PMePh}_2)]$; $^1J_{\text{PtP}}$ 3231 Hz, $^2J_{\text{PC}}$ 7.5 Hz; $[\text{PtCl}(\text{C}\equiv\text{CPh})(^{13}\text{CO})(\text{PMePh}_2)]$; $^1J_{\text{PtP}}$ 3190 Hz, $^2J_{\text{PC}}$ 6.0 Hz. Isomers (II) and (III) (L *trans* to CO) can also be made by CO cleavage of $[\text{Pt}_2(\text{C}\equiv\text{CR})_2(\mu\text{-Cl})_2\text{L}_2]$.

The organomercury(II) chloride by-product proved difficult to separate from the ethynylplatinum products, but it was readily symmetrised (symmetrise = conproportionate) by tetraethylammonium chloride. Thus, by halving the amount of $\text{Hg}(\text{C}\equiv\text{CR})_2$, and performing the reaction in the presence of $[\text{Et}_4\text{N}]\text{Cl}$, the by-product was the insoluble $[\text{Et}_4\text{N}]_2[\text{Hg}_2\text{Cl}_6]$, which was readily separated. Using this technique,[‡] complexes (IV) were isolated as yellow-orange solids (equation 3).



The complexes $[\text{PtCl}(\text{C}\equiv\text{CR})(\text{CO})\text{L}]$ (II, $\text{L} = \text{PPh}_2\text{Me}$) react readily with the alternative organomercurial, $\text{Hg}(\text{C}\equiv\text{CR}')_2$, to produce specific isomers of the mixed bisethynyl complexes (equation 4). The geometry of the mixed-substituent bisethynyls is readily determined from their n.m.r. spectra,[§] and it is clearly evident that although it is the chloride ion which is displaced from platinum, a resident ethynyl group finally occupies the position *trans* to L from which the chloride ion came.

The only simple mechanism which will produce this geometry change is by a *cis*-oxidative addition displacing the resident organic group and with mercury occupying the site *trans* to it. *cis*-Reductive elimination then leads to the products (equation 5). An S_N2 (cyclic) mechanism, or a *cis*-oxidative addition with mercury in the plane of L and CO,[¶] would



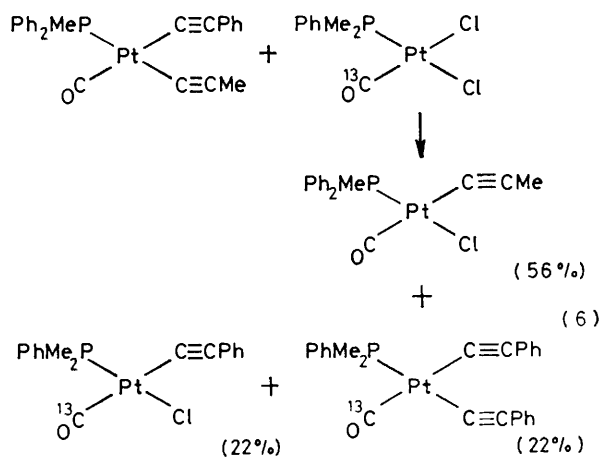
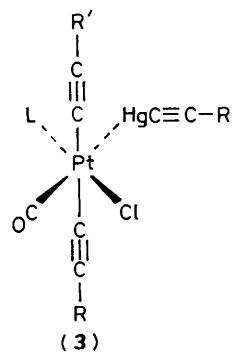
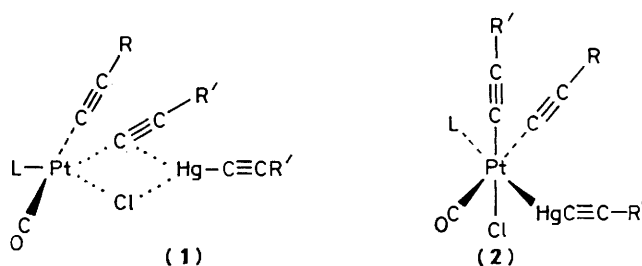
[‡] This appears to be a general way of making available for transfer both R groups of HgR_2 , as well as generally simplifying purification procedures. We have now adopted this technique as the preferred route to isomers (I),^{6,7} as well as for reactions of $\text{Hg}(\text{C}\equiv\text{CR})_2$ described herein.

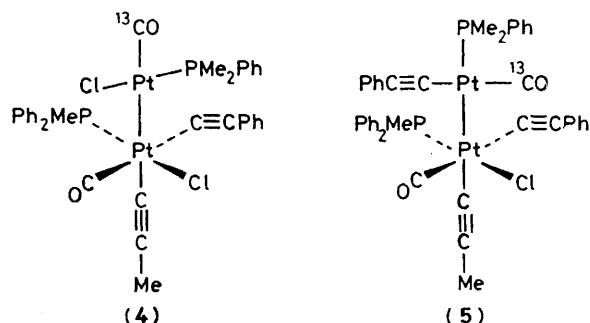
[§] Of greatest value are the $^5J_{\text{PH}}$ parameters of the methylethynyl groups. Values of 3.5 Hz are typical when $\text{MeC}\equiv\text{C}$ is *trans* to PR_3 , but values of 1.5 Hz only are found when these ligands are mutually *cis*.

[¶] These two routes can be viewed as extremes of a single displacement mechanism, and the choice of description will depend on the degree of platinum-mercury interaction.

replace the halide directly and not lead to group site-migration. (1) or (2) depict the transition-state or intermediate for these processes. A *cis*-oxidative addition with mercury displacing the resident organic group (3) is also incapable of leading to the observed products, since reductive elimination of $\text{R}'\text{C}\equiv\text{CHgCl}$ to bring $\text{C}\equiv\text{CR}$ and $\text{C}\equiv\text{CR}'$ into a mutual *cis*-arrangement involves a twist mechanism which is symmetry forbidden,⁸ so L and CO would need to adopt a *trans*-configuration. This geometry has not appeared in any of our reactions. Moreover there is much evidence from the literature that carbonyls and tertiary phosphines are not displaced in oxidative addition reactions.⁹ *trans*-Oxidative additions or reductive eliminations could only operate by ionic routes,¹⁰ and are highly improbable under our conditions and with these compounds.

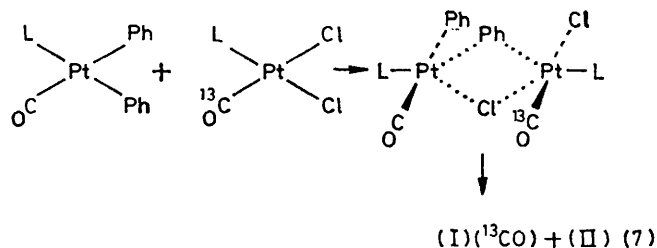
The reactions between *cis*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{CO})\text{L}]$ and *cis*- $[\text{PtCl}_2(\text{CO})\text{L}]$ produced only isomer (II) of $[\text{PtCl}(\text{C}\equiv\text{CR})(\text{CO})\text{L}]$, an unusual reaction at first sight in that the substitution sites on each platinum must be different. In order to examine which groups moved in this process, the reaction between $[\text{Pt}(\text{C}\equiv\text{CMe})(\text{C}\equiv\text{CPh})(\text{CO})\text{PMePh}_2]$ and *cis*- $[\text{PtCl}_2(^{13}\text{CO})\text{PMe}_2\text{Ph}]$ was examined in CDCl_3 by ^{31}P n.m.r. spectroscopy. Equation 6 shows the initial (and major)





products.** Again the structural integrity of L and CO is retained, the ethynyl *trans* to CO is transferred, and the other one migrates to its site. Only *cis*-oxidative addition of the Pt-Cl bond *trans* to ^{13}CO , and with the entering Pt in an axial site (4), can produce this geometry change and account for the observed isomers (II) by reductive elimination. The transfer of two phenylethynyl groups to produce *cis*-[Pt(C≡CPh)₂(^{13}CO)PMe₂Ph] was unexpected but the product can be explained by other, specific oxidative addition-reductive elimination sequences such as between [PtCl(C≡CPh)(^{13}CO)PMe₂Ph] (II) and the mixed bisethynyl starting material *via* intermediate (5). [Compounds (II) do not themselves disproportionate.] After about 75% of the starting materials had reacted, several other ethynylplatinum complexes became apparent as minor products. These were presumably formed by further reactions of the initial products.

Whilst there is no doubt that many other reactions may proceed by this type of mechanism, it may well be that the ethynyl substituents have a particular propensity for it. Thus we find that the reaction between *cis*-[PtPh₂(CO)PMePh₂] and *cis*-[PtCl₂(CO)PMePh₂] produces equal amounts of (I) (Ph *trans* to L) and (II), where the analogous reaction of the bis-



ethynyl derivative led only to (II). Although an oxidative addition-reductive elimination sequence is probably involved here also, other routes cannot yet be ruled out. One such possibility is the $S_{\text{E}}2$ (cyclic) route shown in equation 7. A similar mechanism has been postulated for the formation of (I) from Ph₂Hg and *cis*-[PtCl₂(CO)L].⁶ Final confirmation must await the results of experiments with more complete labelling of substituents.

Received, 5th August 1982; Com. 929

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** The identities of the new compounds were confirmed by independent preparations: [PtCl(C≡CPh)(^{13}CO)PMe₂Ph] $\delta(\text{P})$ -14.9 p.p.m., $^1J_{\text{Pt}}$ 3097 Hz, $^2J_{\text{PC}}$ 6.2 Hz; *cis*-[Pt(C≡CPh)₂(^{13}CO)PMe₂Ph] $\delta(\text{P})$ -15.4 p.p.m., $^1J_{\text{Pt}}$ 2054 Hz, $^2J_{\text{PC}}$ 6.5 Hz.