Reactions of Halogeno(phenyl)alkynes with Complexes of Platinum(0), Palladium(0), Rhodium(I), and Iridium(I). The Preparation of [1—2-η-Chloro(phenyl)ethyne]bis(triphenylphosphine)platinum(0) and Chloro-[1—2-η-chloro(phenyl)ethyne]bis(triphenylphosphine)rhodium(I) and the Kinetics of Isomerisation of the Former to an Alkynyl Complex

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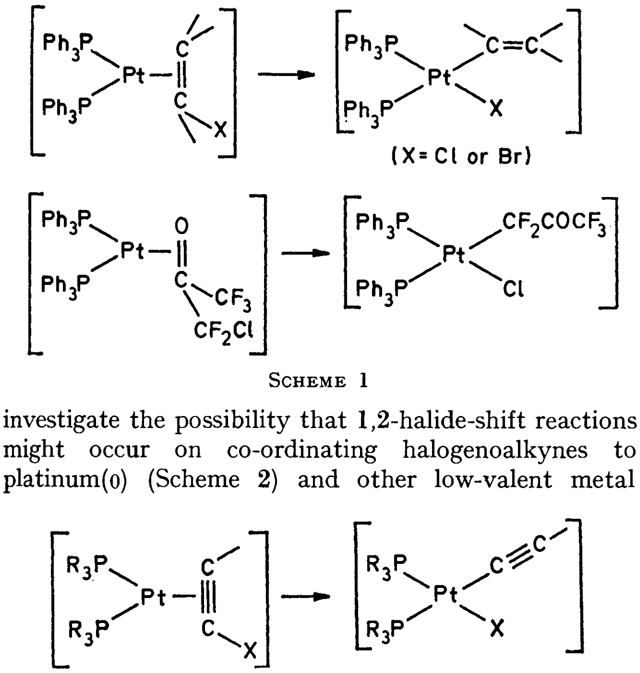
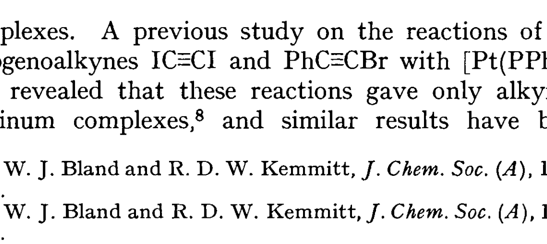
Hydrazine hydrate reduction of *cis*-$[PtCl_2(PPh_3)_2]$ in the presence of PhC≡CCl gives the 1—2-η-halogenoalkyne complex $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$. Similar reactions with PhC≡CX (X = Br or I) give the alkynyls *trans*-$[PtX(C{\equiv}CPh)(PPh_3)_2]$. Treatment of $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ with $Na[BH_4]$ in the presence of PhC≡CCl gives $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(Ph_2PCH_2CH_2PPh_2)]$. The reactions of PhC≡CX (X = Cl, Br, or I) with [Pt(*trans*-PhHC=CHPh)-$(PPh_3)_2]$ in diethyl ether give *cis*-$[PtX(C{\equiv}CPh)(PPh_3)_2]$ which isomerise to the *trans* complexes in benzene solution. The complex $[RhCl(PPh_3)_3]$ reacts with PhC≡CCl to give $[RhCl(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$, and the reaction of PhC≡CCl with *trans*-$[IrCl(CO)(PPh_3)_2]$ affords a mixture containing the complexes $[IrCl(\eta^2\text{-}PhC{\equiv}CCl)(CO)\text{-}(PPh_3)_2]$ and $[IrCl_2(C{\equiv}CPh)(CO)(PPh_3)_2]$, but other alkynes PhC≡CX (X = Br or I) give only alkynyl complexes of iridium. The alkynyl complexes *trans*-$[PdX(C{\equiv}CPh)(PPh_3)_2]$ are formed in reactions of $[Pd(PPh_3)_4]$ with PhC≡CX. The kinetics and mechanism of isomerisation of $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ to $[PtCl(C{\equiv}CPh)(PPh_3)_2]$ in a range of monohydroxylic alcohols are reported and discussed.

OUR interest in 1,2- and 1,3-halide-shift reactions from carbon to platinum (Scheme 1)[1–7] prompted us to investigate the possibility that 1,2-halide-shift reactions might occur on co-ordinating halogenoalkynes to platinum(0) (Scheme 2) and other low-valent metal complexes. A previous study on the reactions of the halogenoalkynes IC≡CI and PhC≡CBr with $[Pt(PPh_3)_4]$ had revealed that these reactions gave only alkynylplatinum complexes,[8] and similar results have been observed in reactions with $PhC{\equiv}CSnMe_3$.[9] However, in view of our previous experience on the reactions of halogenoalkenes with platinum(0) complexes, we reasoned that the reactions of halogenoalkynes might proceed *via* intermediate (halogenoalkyne)platinum complexes which could isomerise under the reaction conditions. A photochemical isomerisation of $[Pt(\eta^2\text{-}NCC{\equiv}CCN)(PPh_3)_2]$ has indeed been reported.[10] In this paper we now describe the preparations of $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ and $[RhCl(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ and the kinetics of isomerisation of the platinum complex to an alkynyl complex, together with the reactions of the halogenoalkynes PhC≡CX (X = Cl, Br, or I) with complexes of Pt^0, Pd^0, and Ir^I.



SCHEME 1



SCHEME 2

RESULTS AND DISCUSSION

Hydrazine hydrate reduction of *cis*-$[PtCl_2(PPh_3)_2]$ followed by addition of PhC≡CCl gives the η-bonded halogenoalkyne complex $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ (1). The i.r. spectrum of (1) exhibits a band at 1 698 cm^{-1} characteristic of an alkyne η^2-bonded to Pt^0. In benzene solution or warm methanol, (1) isomerises to *trans*-$[PtCl(C{\equiv}CPh)(PPh_3)_2]$ (3). However, in the solvents chloroform or dichloromethane no isomerisation of (1) takes place. Similar results have been found[2] in studies on the isomerisation of $[Pt(\eta^2\text{-}Cl_2C{=}CCl_2)(PPh_3)_2]$ to *cis*-$[PtCl(ClC{=}CCl_2)(PPh_3)_2]$. Surprisingly, addition of PhC≡CCl to a suspension of [Pt(*trans*-PhHC=CHPh)-$(PPh_3)_2]$ in diethyl ether gives *cis*-$[PtCl(C{\equiv}CPh)(PPh_3)_2]$ (2), and we have not been able to obtain (1) using this method. It is possible that the reaction of PhC≡CCl with the *trans*-stilbene complex proceeds *via* the formation of (1) followed by isomerisation to the *cis* complex

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[1] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

[2] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1969, 2062.

[3] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **14**, 201.

[4] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **15**, 217.

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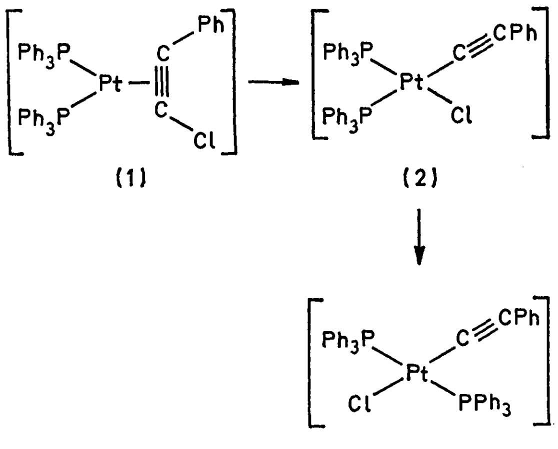
[7] J. Burgess, J. G. Chambers, D. A. Clarke, and R. D. W. Kemmitt, *J.C.S. Dalton*, 1977, 1906.

[8] C. D. Cook and G. S. Jauhal, *Canad. J. Chem.*, 1967, **45**, 301.

[9] B. Çetinkaya, M. F. Lappert, J. McMeeking, and D. E. Palmer, *J.C.S. Dalton*, 1973, 1202.

[10] W. H. Baddley, G. Bandoli, U. Belluco, D. A. Clemente, and C. Panattoni, *J. Amer. Chem. Soc.*, 1971, **93**, 5590.

(2), but an alternative mechanism involving direct attack of Pt^0 at the carbon–chlorine bond of PhC≡CCl followed by C–Cl bond cleavage cannot be ruled out.



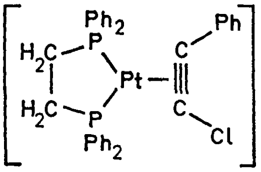
(1) (2) (3)

Such a mechanism has been proposed in reactions of *trans*-$(F_3C)(NC)C$=$C(CN)(CF_3)$ with [Pt(*trans*-PhHC=CHPh)-$(PPh_3)_2$].[11]

Complex (2) has not previously been reported. It exhibits a band at 2 125 cm^{-1} typical of an alkynyl ligand and a strong band at 544 cm^{-1} which is indicative of a *cis* arrangement of triphenylphosphine ligands.[12] In benzene solution (2) isomerises to (3), and addition of PhC≡CCl to [Pt(*trans*-PhHC=CHPh)$(PPh_3)_2$] in benzene solution also affords (3). This *trans* complex has previously been isolated either by the reaction of hydrogen chloride with *trans*-[Pt(C≡CPh)$_2(PPh_3)_2$] or by the reaction of Na[C≡CPh] with *cis*-[$PtCl_2(PPh_3)_2$].[13] The platinum–chlorine i.r. stretching frequency for (2) occurs at 306 cm^{-1}, whereas for (3) ν(Pt–Cl) is observed at 320 cm^{-1} signifying a stronger Pt–Cl bond in the *trans* than the *cis* complex and a greater *trans* influence for PPh_3 than C≡CPh.[14]

The reactions of both PhC≡CBr and PhC≡CI with *cis*-[$PtCl_2(PPh_3)_2$] in the presence of hydrazine hydrate give *trans*-[PtX(C≡CPh)$(PPh_3)_2$] (X = Br or I) and we have not been able to prepare η^2-bonded alkyne complexes of Pt^0 with these compounds. For X = Br the complex has previously been prepared by reaction of PhC≡CBr with a benzene solution of [$Pt(PPh_3)_4$], although no stereochemistry was specified.[8] It can now be concluded that the geometry is *trans*, since the melting points of the complex prepared from [$Pt(PPh_3)_4$], and the complex prepared from *cis*-[$PtCl_2(PPh_3)_2$], are in agreement, and the i.r. spectrum shows no absorptions in the 540—560 cm^{-1} region. The addition of PhC≡CX to [Pt(*trans*-PhHC=CHPh)$(PPh_3)_2$] in benzene solution similarly gives the *trans*-alkynyl complexes but in diethyl ether these reactions give *cis*-[PtX(C≡CPh)-$(PPh_3)_2$] (X = Br or I).

The reduction of [$PtCl_2(Ph_2PCH_2CH_2PPh_2)$] with Na[$BH_4$] in the presence of chloro(phenyl)ethyne gives the η^2-bonded alkyne complex (4) which exhibits a band in its i.r. spectrum at 1 667 cm^{-1}. In contrast to (1) this complex shows no tendency to isomerise to an alkynyl complex in methanol. Recently it has been observed that *cis*-[PtCl(FC=CF_2)$(CNBu^t)_2$] reverts to the 1—2-η-chlorotrifluoroethylene complex [Pt(η^2-F_2C=CFCl)$(CNBu^t)_2$] in solution,[15] and the observation that (4) shows no tendency to isomerise to an alkynyl complex may be a consequence of the inability of the resulting alkynyl to achieve a *trans* stereochemistry.



(4)

Treatment of diethyl ether suspensions of [$Pd(PPh_3)_4$] with the alkynes PhC≡CX (X = Cl or Br) gives complexes having i.r. bands at 2 125 (X = Cl) and 2 120 cm^{-1} (X = Br) indicative of alkynyl complexes, [PdX-(C≡CPh)$(PPh_3)_2$]. In these reactions we have obtained no evidence for η^2-bonded alkyne complexes. Experiments involving the reactions of halogenoalkenes with [$Pd(PPh_3)_4$] have shown that only alkenyl complexes are formed[16] and it appears that Pd^0 in contrast to Pt^0 has little tendency to form η^2-bonded halogenoalkene complexes. Halogenoalkynes appear to behave in a similar fashion. The alkynyl complexes obtained, [PdX(C≡CPh)$(PPh_3)_2$] (X = Cl or Br), most probably have a *trans* configuration since they can be recovered unchanged after several days in benzene solution and their i.r. spectra exhibit no bands in the 540—560 cm^{-1} region which is known to indicate a *trans* geometry for bis(triphenylphosphine)platinum(II) complexes of this type. The alkyne PhC≡CI does not give an alkynyl complex with [$Pd(PPh_3)_4$] in diethyl ether, and *trans*-[$PdI_2(PPh_3)_2$] is formed.

The reaction of a benzene solution of [$RhCl(PPh_3)_3$] with PhC≡CCl results in a change in colour of the solution from deep red to bright orange over 1 h. An orange solid can be isolated from this solution which shows a medium band at 1 883 cm^{-1} in its i.r. spectrum, in the region associated with η^2-bonded alkyne ligands. It was found, however, that the complex could be obtained in a purer form by stirring the reactants in the dark, in diethyl ether suspension, for *ca.* 24 h. Analytical and i.r. data are consistent with the formulation of the complex as (5), a *trans* geometry being proposed by analogy with other alkyne and alkene complexes of

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[11] J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1970, 1847.

[12] S. H. Mastin, *Inorg. Chem.*, 1974, **13**, 1003.

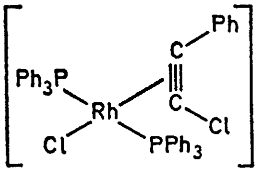
[13] I. Collamati and A. Furlani, *J. Organometallic Chem.*, 1969, **17**, 457.

[14] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

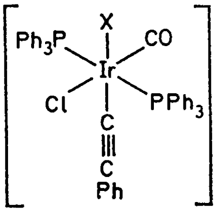
[15] J. Forniés, M. Green, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1515.

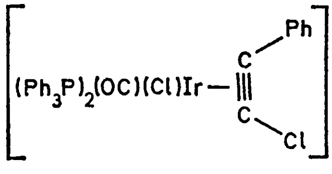
[16] P. Fitton and J. E. McKeon, *Chem. Comm.*, 1968, 4.

this type.[17,18] Complex (5) is stable in air but undergoes decomposition in light to give a brownish product having i.r. bands at 1 883, 1 968, and 2 125 cm^{-1} suggesting partial isomerisation to an alkynyl complex. On warming a suspension of (5) in methanol at 40 °C for 12 h in the dark a dark orange solid was produced. The i.r. spectrum of the product exhibited a weak band at 2 125 cm^{-1} characteristic of an alkynyl group, the band due to the η^2-bonded alkyne at 1 883 cm^{-1} was absent, and a Rh–Cl stretching frequency appeared at 309 cm^{-1} some 20 cm^{-1} higher than that found for (5), consistent with a change in oxidation state from Rh^{I} to Rh^{III}. It appears, therefore, that the complex has undergone isomerisation to an alkynyl complex, possibly $[RhCl_2(C{\equiv}CPh)(PPh_3)_2]$, but consistent analytical data for this complex could not be obtained. Difficulty in obtaining analytically pure samples of both rhodium(I) and rhodium(III) alkynyl complexes has been noted previously.[9]


(5)

On stirring a solution of *trans*-$[IrCl(CO)(PPh_3)_2]$ with $PhC{\equiv}CCl$ in benzene solution for 4 d the complex (6a) is obtained. The i.r. spectrum of (6a) exhibits a strong band at 2 070 cm^{-1} which can be assigned to ν(CO) of an octahedral iridium(III) complex and a medium-intensity band at 2 142 cm^{-1} which can be assigned to ν(C≡C) of an alkynyl ligand. In addition, two iridium–chlorine stretching frequencies are observed at 312 and 285 cm^{-1}. By comparison with values obtained previously for octahedral iridium(III) complexes,[19,20] the band at 312 cm^{-1} may be assigned to chlorine *trans* to carbon monoxide and the band at 285 cm^{-1} to chlorine *trans* to the alkynyl ligand. Thus if the phosphines remain *trans* during the oxidative-addition reaction[20] the structure (6a) can be drawn for this complex. Complexes (6b) and (6c) can similarly be obtained using the appropriate halogeno(phenyl)alkyne. As in the reactions of $PhC{\equiv}CCl$ with platinum(0) and rhodium(I) complexes, the reaction of $PhC{\equiv}CCl$ with *trans*-$[IrCl(CO)(PPh_3)_2]$ appears to proceed *via* an intermediate η^2-bonded halogenoalkyne complex (7). Thus if the reaction of $PhC{\equiv}CCl$ with Vaska's complex is stopped after 12 h a yellow solid can be isolated which exhibits strong i.r. absorptions at 1 964 and 1 700 cm^{-1} in addition to bands due to (6a) at 2 142 and 2 070 cm^{-1}. The band at 1 964 cm^{-1} can be assigned to a carbonyl group co-ordinated to Ir^{I}, whilst the band at 1 700 cm^{-1} is a typical value for a triple bond of an alkyne η^2-bonded to Ir^{I}. However, attempts to obtain a pure sample of (7) by crystallisation or chromatographic separation on an alumina column resulted in complete isomerisation to (6a).


(6a) X = Cl
(6b) X = Br
(6c) X = I


(7)

Isomerisation Kinetics.—Spectroscopic monitoring of the product(s) of isomerisation of $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ at low concentration (*i.e.* under kinetic conditions, u.v. monitoring; see Experimental section) indicates that in different solvents there is differing conversion of the starting complex into the *cis* and *trans* isomers of $[PtCl(C{\equiv}CPh)(PPh_3)_2]$. Although first-order kinetics are observed over three or more half-lives, the resulting rate constants are composite quantities. We have therefore only been able to estimate initial rates for the isomerisation of $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$. These are reported in Table 1. The striking feature is the insensitivity of the rate constant to the nature of the solvent. In accordance with our previous practice, we have plotted logarithms of rate constants against Grunwald–Winstein solvent *Y* values[21] and Brownstein solvent *S* values.[22] Gradients of these graphs, *m* and *R* respectively, are reported in Table 2. Gradients of analogous plots for isomerisations of halogenoalkene complexes are included in Table 2 for comparison. High values of *m* and *R* (*cf.* 1.00 and 36 for t-butyl chloride solvolysis, Table 2) suggest an intermolecular isomerisation mechanism in which the rate-determining step is cleavage of a C–Cl bond in the halogenoalkene (halogenoalkyne) ligand, as in the isomerisation of $[Pt(\eta^2\text{-}Cl_2C{=}CCl_2)(PPh_3)_2]$.[4] Low values

TABLE 1

Rate constants for the isomerisation of $[Pt(\eta^2\text{-}PhC{\equiv}CCl)(PPh_3)_2]$ to the alkynyl complex in alcohols at 308.2 K

Solvent	S^{a}	Y^{b}	$10^4k_{obs.}{}^{c}/s^{-1}$
MeOH	0.05	−1.09	2.0
EtOH	0	−2.03	1.9
Pr^nOH	−0.016	-2.30^{d}	1.6
Pr^iOH	−0.041	−2.73	1.8
Bu^nOH	−0.024	-2.42^{d}	0.95
Bu^tOH	−0.105	−3.26	0.80

[a] Brownstein's solvent parameter (*cf.* text). [b] Grunwald–Winstein solvent parameter (*cf.* text). [c] From initial rates. [d] Estimated from solvent E_T and *Z* values (see C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29).

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[17] M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.

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[19] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789.

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[22] S. Brownstein, *Canad. J. Chem.*, 1960, **38**, 1590.

of *m* and *R* suggest an intramolecular isomerisation mechanism, as in the case of $[\mathrm{Pt}(\eta^2\text{-BrFC=CF}_2)(\mathrm{AsPh}_3)_2]$.[6]

TABLE 2

Dependence of isomerisation rates of halogenoalkene and halogenoalkyne complexes on solvent, expressed as Grunwald–Winstein *m* and Brownstein *R* values (*cf.* text)

Substrate	*m*	*R*	Ref.
$[\mathrm{Pt}(\eta^2\text{-PhC}\equiv\mathrm{CCl})(\mathrm{PPh}_3)_2]$	0.16 ± 0.08	2.5 ± 1.0	*
$[\mathrm{Pt}(\eta^2\text{-BrFC=CF}_2)(\mathrm{AsPh}_3)_2]$	0.32 ± 0.12	4.9 ± 1.2	6
$[\mathrm{Pt}(\eta^2\text{-ClHC=CCl}_2)(\mathrm{PPh}_3)_2]$	0.54 ± 0.07	10.2 ± 0.5	5
$[\mathrm{Pt}(\eta^2\text{-Cl}_2\mathrm{C=CCl}_2)(\mathrm{PPh}_3)_2]$	0.86 ± 0.07	18.0 ± 1.0	4
$\mathrm{Bu^tCl}$	1.00	36	

* This work.

By these criteria we can assign an intramolecular mechanism to the isomerisation of $[\mathrm{Pt}(\eta^2\text{-PhC}\equiv\mathrm{CCl})(\mathrm{PPh}_3)_2]$. The rate constant for isomerisation of $[\mathrm{Pt}(\eta^2\text{-PhC}\equiv\mathrm{CCl})(\mathrm{PPh}_3)_2]$ in methanol (2×10^{-4} s^{-1} at 308.2 K) is slightly smaller than that for isomerisation of $[\mathrm{Pt}(\eta^2\text{-Cl}_2\mathrm{C=CCl}_2)(\mathrm{PPh}_3)_2]$. Therefore any intermolecular contribution to isomerisation of the chloroalkyne complex must be very much slower than the intermolecular isomerisation of the tetrachloroalkene complex. This difference in reactivity with respect to $S_\mathrm{N}1$ carbon–chlorine dissociation of the platinum(0) complexes parallels the behaviour of the respective organic ligands.

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls, using CsI plates, on a Perkin-Elmer 580 spectrophotometer, and were calibrated using a polystyrene film. Melting points were determined on a Reichart hot-stage apparatus and are uncorrected. Microanalytical data were obtained by the Butterworth Microanalytical Consultancy Ltd. or by CHN Analyses Ltd. All the reactions were carried out in an atmosphere of dry nitrogen.

The complexes *cis*-$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2]$,[23] $[\mathrm{Pt}(\textit{trans}\text{-PhHC=CHPh})(\mathrm{PPh}_3)_2]$,[24] $[\mathrm{Pd}(\mathrm{PPh}_3)_4]$,[25] *trans*-$[\mathrm{IrCl(CO)}(\mathrm{PPh}_3)_2]$,[26] $[\mathrm{RhCl}(\mathrm{PPh}_3)_3]$,[27] $[\mathrm{PtCl}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{CH}_2\mathrm{PPh}_2)]$,[28] and the alkynes $\mathrm{PhC}\equiv\mathrm{CCl}$,[29] $\mathrm{PhC}\equiv\mathrm{CBr}$,[30] and $\mathrm{PhC}\equiv\mathrm{CI}$ [31] were prepared as described in the literature.

Reactions of cis-$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2]$ + *Hydrazine Hydrate*.—(*a*) *With chloro*(*phenyl*)*ethyne*. The complex *cis*-$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2]$ (0.25 g, 0.28 mmol) was suspended in ethanol (5 cm^3) and was treated with hydrazine hydrate (0.25 cm^3). After stirring for 4 min the yellow solution was filtered and chloro(phenyl)ethyne (0.06 g, 0.56 mmol) was added to the filtrate. On warming to 60 °C for 5 min crystals began to appear, and the mixture was then cooled to 0 °C. The pale yellow crystalline product was filtered off, washed with water, ethanol, and diethyl ether, and dried *in vacuo* to afford [1—2-η-chloro(phenyl)ethynyl]bis(triphenylphosphine)platinum(0) (1) (0.16 g, 65%), m.p. 225—227 °C (decomp.) (Found: C, 61.5; H, 4.1; Cl, 4.1. $\mathrm{C_{44}H_{35}ClP_2Pt}$ requires C, 61.8; H, 4.1; Cl, 4.3%); $\nu_\mathrm{max.}$ at 1 698m, 1 592m, 1 572w, 1 479s, 1 437s, 1 310w, 1 207w, 1 173vw, 1 168vw, 1 158w, 1 100s, 1 073s, 1 030m, 1 002m, 974w, 852vw, 754m (sh), 746s, 725w, 694s, 676w, 621vw, 555vw, 543s, 526s, 512s, 503s, 461w, 441w, and 426w cm^{-1}.

(*b*) *With bromo*(*phenyl*)*ethyne*. As above, *cis*-$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2]$ (0.2 g, 0.25 mmol), hydrazine hydrate (0.2 cm^3), and bromo(phenyl)ethyne (0.08 g, 0.50 mmol) gave, after warming to 60 °C for 15 min followed by cooling to 0 °C, pale yellow crystals of *trans*-bromo(phenylethynyl)bis(triphenylphosphine)platinum(II) (0.13 g, 64%), m.p. 225 °C (decomp.) [lit.,[8] 225 °C (decomp.)]; $\nu_\mathrm{max.}$ at 2 130w, 2 125w, 1 591w, 1 572vw, 1 566vw, 1 471m, 1 434s, 1 314w,br, 1 272w, 1 265vw, 1 212vw, 1 171w, 1 159w, 1 099m, 1 072w, 1 028w, 999w, 920vw, 757m, 746s, 732m, 709m, 692s, 667vw, 524s, 512m, 500m, 461w, 437w, and 427w cm^{-1}.

(*c*) *With iodo*(*phenyl*)*ethyne*. As above, *cis*-$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2]$ (0.25 g, 0.28 mmol), hydrazine hydrate (0.25 cm^3), and iodo(phenyl)ethyne (0.12 g, 0.56 mmol) gave, after warming to 60 °C for 5 min followed by cooling to 0 °C, pale yellow crystals of *trans*-iodo(phenylethynyl)bis(triphenylphosphine)platinum(II) (0.19 g, 71%), m.p. 214—220 °C (decomp.) (Found: C, 55.8; H, 4.0. $\mathrm{C_{44}H_{35}IP_2Pt}$ requires C, 55.8; H, 3.7%); $\nu_\mathrm{max.}$ at 2 125w, 1 587w, 1 573w, 1 566w, 1 469s, 1 433s, 1 209vw, 1 161w, 1 155w, 1 095m, 1 070w, 1 063vw, 1 028w, 996w, 972w,br, 842vw, 769vw, 755m, 743s, 722w, 705m, 688s, 665w, 616w, 522s, 510s, 499s, 457m, and 425m cm^{-1}.

Reactions of $[\mathrm{Pt}\{\textit{trans}\text{-PhHC=CHPh})(\mathrm{PPh}_3)_2]$.—(*a*) *With chloro*(*phenyl*)*ethyne in benzene*. The complex $[\mathrm{Pt}(\textit{trans}\text{-PhHC=CHPh})(\mathrm{PPh}_3)_2]$ (0.3 g, 0.33 mmol) and $\mathrm{PhC}\equiv\mathrm{CCl}$ (0.05 g, 0.36 mmol) were stirred in benzene solution for 24 h at room temperature. The solution was evaporated to small volume under reduced pressure and diethyl ether was added. The resulting pale yellow solid was collected and dried *in vacuo* to afford *trans*-$[\mathrm{PtCl}(\mathrm{C}\equiv\mathrm{CPh})(\mathrm{PPh}_3)_2]$ (3) (0.15 g, 53%), m.p. 228—232 °C (decomp.) [lit.,[13] 212—214 °C (decomp.)]; $\nu_\mathrm{max.}$ at 2 125s, 1 593m, 1 572w, 1 569w, 1 480s, 1 434s, 1 315m, 1 286w, 1 218w, 1 193w, 1 185w, 1 161w, 1 119w, 1 101s, 1 095s, 1 069w, 1 031m, 1 004m, 1 000m, 972vw, 922w, 906w, 849w, 755s, 745s, 708s, 693vs, 619w, 571w, 549w, 541w, 525s, 514s, 508s (sh), 501s, 493m (sh), 444vw, 428m, and 320m cm^{-1}.

(*b*) *With bromo*(*phenyl*)*ethyne in benzene*. As above to give *trans*-$[\mathrm{PtBr}(\mathrm{C}\equiv\mathrm{CPh})(\mathrm{PPh}_3)_2]$ (58%), m.p. 225 °C (decomp.).[8]

(*c*) *With iodo*(*phenyl*)*ethyne in benzene*. As above to give *trans*-$[\mathrm{PtI}(\mathrm{C}\equiv\mathrm{CPh})(\mathrm{PPh}_3)_2]$ (42%), m.p. 214—220 °C (decomp.).

(*d*) *With chloro*(*phenyl*)*ethyne in diethyl ether*. The complex $[\mathrm{Pt}(\textit{trans}\text{-PhHC=CHPh})(\mathrm{PPh}_3)_2]$ (0.3 g, 0.33 mmol) and $\mathrm{PhC}\equiv\mathrm{CCl}$ (0.05 g, 0.36 mmol) were stirred together as a suspension in diethyl ether for 30 h at room temperature. The resulting white precipitate was washed with diethyl ether and dried *in vacuo* to afford cis-*chloro*(*phenylethynyl*)-*bis*(*triphenylphosphine*)*platinum*(II) (2) (0.24 g, 84%) (Found: C, 61.8; H, 4.2%); $\nu_\mathrm{max.}$ at 2 125m, 1 596w, 1 587w, 1 437w, 1 432w, 1 311w, 1 218w, 1 186w, 1 158w, 1 098s, 1 091m (sh), 1 071w, 1 026m, 1 000m, 850w, 802vw, 763m, 755s, 741s, 725w, 706m (sh), 689s, 666vw, 617w, 564w,

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544s, 526s, 513m (sh), 510s, 496s, 467m, 439w, 426m, and 306m cm^{-1}.

(*e*) *With bromo(phenyl)ethyne in diethyl ether*. As above (except the reaction time was 4 h) to give a white precipitate of cis-*bromo(phenylethynyl)bis(triphenylphosphine)platinum*(II) (0.21 g, 71%), m.p. 223—224 °C (decomp.) (Found: C, 58.7; H, 3.9%); $\nu_{max.}$ at 2 125m, 1 595w, 1 586w, 1 570w,br, 1 485s, 1 480s, 1 432s, 1 312w, 1 217w, 1 186w, 1 158w, 1 098s, 1 091s, 1 069w, 1 026m, 997m, 970vw, 920vw, 904vw, 848vw, 843w, 801vw, 761m (sh), 753s, 740s, 704s, 690vs, 617w, 561w, 541s, 523vs, 511s, 496s, 465w, 456w, 439w, and 425m cm^{-1}.

(*f*) *With iodo(phenyl)ethyne in diethyl ether*. As above (except the reaction time was 24 h) to give a pale yellow precipitate of *cis*-iodo(phenylethynyl)bis(triphenylphosphine)platinum(II) (0.21 g, 67%), m.p. 224—229 °C (decomp.) (Found: C, 55.7; H, 3.8%); $\nu_{max.}$ at 2 125m, 1 594w, 1 586w, 1 571w, 1 469s, 1 432s, 1 210vw, 1 185vw, 1 176vw, 1 161vw, 1 155w, 1 120vw, 1 099m, 1 095m (sh), 1 070vw, 1 028vw, 997w, 844vw, 756m, 743s, 705m, 690s, 617vw, 540m, 524s, 513s, 498m, 460w, and 426w cm^{-1}.

On stirring the complexes *cis*-[PtX(C≡CPh)(PPh$_3$)$_2$] (X = Cl, Br, or I) in benzene solution for 48 h at room temperature the complexes *trans*-[PtX(C≡CPh)(PPh$_3$)$_2$] were isolated from the solution.

[1,2-*Bis(diphenylphosphino)ethane*][1—2-η-*chloro(phenyl)ethyne*]*platinum*(0) (4).—The complex [PtCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] (0.33 g, 0.5 mmol) was suspended in ethanol with chloro(phenyl)ethyne (0.14 g, 1.0 mmol). Sodium tetrahydroborate (0.13 g, 3.4 mmol) dissolved in ethanol was added with stirring and the mixture was stirred for 20 h at room temperature. After filtration and washing the cream residue with water and ethanol, the solid was recrystallised from CH$_2$Cl$_2$–MeOH to give the grey-white product (0.24 g, 66%), m.p. 148—153 °C (decomp.) (Found: C, 55.8; H, 4.0. $C_{34}H_{25}ClP_2Pt$ requires C, 55.9; H, 4.0%); ν(C≡C) at 1 667m cm^{-1}.

Heating a suspension of (4) in methanol at 35 °C for 16 h resulted only in the recovery of the unchanged complex.

Reactions of [Pd(PPh$_3$)$_4$].—(*a*) *With chloro(phenyl)ethyne*. The complex [Pd(PPh$_3$)$_4$] (0.38 g, 0.33 mmol) and an excess of chloro(phenyl)ethyne were stirred as a suspension in diethyl ether at room temperature. After 24 h a pale yellow solid was filtered off, washed with diethyl ether, and dried *in vacuo* to give pale yellow *trans*-[PdCl(C≡CPh)(PPh$_3$)$_2$] (0.2 g, 80%), m.p. 149—157 °C (decomp.) (Found: C, 68.5; H, 4.7. $C_{44}H_{35}ClP_2Pd$ requires C, 68.8; H, 4.6%); ν(C≡C) at 2 125m, ν(Pd–Cl) at 331m cm^{-1}.

(*b*) *With bromo(phenyl)ethyne*. As above to give yellow *trans*-[PdBr(C≡CPh)(PPh$_3$)$_2$] (85%), m.p. 157—162 °C (decomp.) (Found: C, 64.7; H, 4.4. $C_{44}H_{34}BrP_2Pd$ requires C, 65.1; H, 4.3%); ν(C≡C) at 2 120 cm^{-1}.

(*c*) *With iodophenylethyne*. As above to give *trans*-[PdI$_2$(PPh$_3$)$_2$] (90%).

Reactions of [RhCl(PPh$_3$)$_3$].—(*a*) *With chloro(phenyl)ethyne*. The complex [RhCl(PPh$_3$)$_3$] (0.46 g, 0.5 mmol) and an excess of chloro(phenyl)ethyne were stirred together in diethyl ether in the dark for 24 h. The resulting bright orange product was filtered off, washed with diethyl ether, and dried *in vacuo* to give [RhCl(η^2-PhC≡CCl)(PPh$_3$)$_2$] (5) (0.37 g, 93%), m.p. 149—154 °C (decomp.) (Found: C, 66.1; H, 4.6. $C_{44}H_{35}Cl_2P_2Rh$ requires C, 66.0; H, 4.4%); ν(C≡C) 1 883, ν(Rh–Cl) 289 cm^{-1}. The complex is sensitive to light, but even in the dark decomposition starts to occur after 7 d.

On heating a suspension of (5) in methanol at 40 °C for 12 h in the dark the solution darkened considerably, and the solid changed from bright to dark orange. The solid was filtered off, washed with diethyl ether, and dried *in vacuo*, m.p. 99—102 °C (decomp.). The i.r. spectrum exhibits a band at 2 125vw cm^{-1}, suggesting that the product may be an alkynyl complex, but satisfactory analytical data could not be obtained.

Reactions of trans-[IrCl(CO)(PPh$_3$)$_2$].—(*a*) *With chloro(phenyl)ethyne*. The complex *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.26 g, 0.33 mmol) and chloro(phenyl)ethyne (0.05 g, 0.36 mmol) were stirred in benzene at room temperature for several days, whereupon a white precipitate started to appear. After 4 d the solid was collected, washed with benzene, and recrystallised from dichloromethane–benzene to give grey-white *crystals* of [IrCl$_2$(C≡CPh)(CO)(PPh$_3$)$_2$] (6a) (0.18 g, 59%), m.p. 252—255 °C (decomp.) (Found: C, 59.3; H, 3.9. $C_{45}H_{35}Cl_2IrOP_2$ requires C, 59.3; H, 3.9%); ν(C≡C) 2 142m, ν(CO) 2 070s cm^{-1}.

On repeating the above reaction for 12 h followed by removal of the benzene a yellow solid was obtained. The i.r. spectrum of the solid exhibited bands at 2 142m, 2 070s, 1 964s, and 1 700s cm^{-1}, suggesting that the solid is probably a mixture of [IrCl(η^2-PhC≡CCl)(CO)(PPh$_3$)$_2$] and (6a). Attempts to separate the mixture either by recrystallisation or chromatography on an alumina column gave only the alkynyl complex.

(*b*) *With bromo(phenyl)ethyne*. As above to give white *crystals* of [IrBr(Cl)(C≡CPh)(CO)(PPh$_3$)$_2$] (6b) (51%), m.p. 243—246 °C (decomp.) (Found: C, 56.3; H, 3.9. $C_{45}H_{35}BrClIrOP_2$ requires C, 56.2; H, 3.7%); ν(C≡C) at 2 140m, ν(CO) at 2 070s cm^{-1}.

(*c*) *With iodo(phenyl)ethyne*. As above to give grey-white *crystals* of [IrCl(I)(C≡CPh)(CO)(PPh$_3$)$_2$] (69%), m.p. 158—160 °C (decomp.) (Found: C, 52.2; H, 3.4. $C_{45}H_{35}ClIIrOP_2$ requires C, 53.5; H, 3.6%); ν(C≡C) at 2 140m, ν(CO) at 2 070s cm^{-1}.

Kinetic runs were carried out in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Optical densities were monitored at 295 nm; this wavelength corresponds to maximum optical-density change consequent on isomerisation.

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