A Study of the Generality of the Reaction of Diazomethane with Halogenoplatinum(II) Complexes in the Preparation of (Halogenomethyl)platinum(II) Complexes

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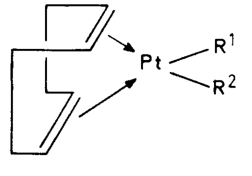
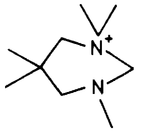
Treatment of a range of platinum(II) halide (mainly chloride) complexes with diazomethane has been examined. Formation of both mono- and bis-halogenomethyl products has been observed. With one exception, methylene insertion appears to occur only when the metal–halogen bond is *trans* to a group of high *trans* influence (olefin, phosphine, isocyanide, alkyl, or hydride). With the *trans*-chlorohydrido derivatives investigated, the initially formed *trans*-(chloromethyl)hydrido products rearranged into the *trans*-(chloro)methyl species. Mechanisms of the methylene insertion and rearrangement processes are discussed.

We have reported recently that diazomethane reacts with certain complexes of palladium(II)[1] and platinum(II)[2,3] halides giving, by carbene insertion into metal–halogen bonds, halogenomethylmetal complexes. This type of insertion is well known[4] for main-group halides but has been found[5–10] only rarely for the transition-metal analogues. The palladium and platinum complexes used in our initial studies[1,3] all contained either an olefinic sulphide or an olefinic amine as chelating ligands and gave, in general, products derived from insertion of a methylene group into one metal–halogen bond. The present paper deals with some aspects of the scope of the reaction of diazomethane with complexes of platinum(II) halides by summarising the results obtained when a wider variety of such compounds was treated with this reagent. A future paper will describe a similar study for palladium(II) complexes.



(1) $R^1 = R^2 = Cl$
(2) $R^1 = Cl$, $R^2 = CH_2Cl$
(3) $R^1 = R^2 = CH_2Cl$
(4) $R^1 = R^2 = I$
(5) $R^1 = R^2 = CH_2I$
(6) $R^1 = CH_2Cl$, $R^2 = CH_2OMe$
(7) $R^1 = R^2 = CH_2OMe$
(8) $R^1 = Cl$, $R^2 = CH_2OMe$



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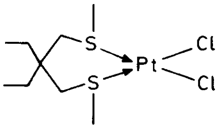

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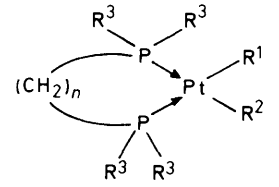
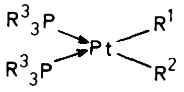
Results

Reactions with Symmetrical cis-*Bis(olefin), -Bis(amine), and -Bis(sulphide) Complexes.*—The reaction of diazomethane with dichloro- and with di-iodo-(1,5-cyclo-octadiene)platinum(II) was studied first.[2] When a solution of [$PtCl_2$(cod)] (**1**) in dichloromethane was treated with small aliquots of diazomethane in diethyl ether, the build-up of two products was detected by t.l.c. After the addition of sufficient diazomethane to result in consumption of all the starting material, these products were separated by preparative t.l.c. and purified by crystallisation. The more polar was identified as the chloromethyl complex (**2**) and the less polar as its bis(chloromethyl) analogue (**3**) on the basis of their elemental analyses and ^1H and ^{13}C n.m.r. spectra. For example, the ^1H n.m.r. spectrum of the former, (**2**), contains resonances attributable to the $PtCH_2Cl$ group and two sets of magnetically non-equivalent olefinic and allylic protons, while that of the latter, (**3**), reveals only three resonances, one each for the chloromethyl, olefinic, and allylic protons. Compound (**3**) was the only product formed when an excess of diazomethane was used. Both (**2**) and (**3**) are stable at room temperature as solids or in solution in the absence of acids. However, when complex (**3**) in methylene chloride is shaken with dilute hydrochloric acid it is readily converted into (**2**). The compound [PtI_2(cod)] (**4**) reacts in a similar fashion with an excess of diazomethane to give the bis(iodomethyl) complex (**5**), which was detected by t.l.c. Attempted purification of (**5**) by preparative t.l.c. led to extensive decomposition. Accordingly, it was purified by chromatography through a short column of silica gel and then by crystallisation. The structure of the resulting colourless, air-stable solid was again readily assigned on the basis of its elemental analysis and ^1H and ^{13}C n.m.r. spectra. When the reaction of [$PtCl_2$(cod)] with an excess of diazomethane was carried out in dichloromethane–methanol solution the major products (^1H n.m.r., deuteriochloroform) were (chloromethyl)(methoxymethyl)- and bis(methoxymethyl)-platinum(II) derivatives (**6**) and (**7**). The bis(chloromethyl) derivative (**3**) was a minor component in the product mixture. After the ^1H n.m.r. spectrum had been obtained, the deuteriochloroform was evaporated to give a residue which was stored in a refrigerator for 8 weeks. When the ^1H n.m.r. spectrum was rerun after this time the peaks due to (**3**), (**6**), and (**7**) had largely disappeared, and were replaced by resonances ascribable mainly to a single product, chloro(1,5-cyclo-octadiene)(methoxymethyl)platinum(II) (**8**).

Suspensions of the relatively insoluble complexes dichloro-(*N,N,N′,N′*-tetramethylethylenediamine)platinum(II) and (2,2′-bipyridine)dichloroplatinum(II) in dichloromethane gave no evidence of the formation of insertion products which in other cases are generally much more soluble than the substrate. Attempts to prepare the complex of 2,2,*N,N,N′,N′*-hexamethyl-1,3-propanediamine, which was expected to be more soluble, resulted in the deposition of platinum metal and oxidation of



(**11**) $R^1 = R^2 = Cl$, $R^3 = Ph$, $n = 3$
(**12**) $R^1 = Cl$, $R^2 = CH_2Cl$, $R^3 = Ph$, $n = 3$
(**13**) $R^1 = R^2 = CH_2Cl$, $R^3 = Ph$, $n = 3$
(**20**) $R^1 = R^2 = Cl$, $R^3 = C_6H_{11}$, $n = 2$
(**21**) $R^1 = R^2 = CH_2Cl$, $R^3 = C_6H_{11}$, $n = 2$
(**22**) $R^1 = R^2 = Cl$, $R^3 = C_6H_{11}$, $n = 3$
(**23**) $R^1 = R^2 = Cl$, $R^3 = C_6H_{11}$, $n = 4$



(**14**) $R^1 = R^2 = Cl$, $R^3 = Ph$
(**15**) $R^1 = R^2 = CH_2Cl$, $R^3 = Ph$
(**16**) $R^1 = Cl$, $R^2 = CH_2Cl$, $R^3 = Ph$
(**17**) $R^1 = R^2 = Cl$, $R^3 = Et$
(**18**) $R^1 = R^2 = CH_2Cl$, $R^3 = Et$
(**19**) $R^1 = Cl$, $R^2 = CH_2Cl$, $R^3 = Et$
(**24**) $R^1 = R^2 = Cl$, $R^3 = C_6H_{11}$

the potential ligand to a product containing a cation which is tentatively formulated as (**9**).*

The relatively soluble dichloro(4,4-diethyl-2,6-dithiaheptane)-platinum(II) (**10**) was recovered unchanged from exposure to an excess of diazomethane. The chelating ligand was prepared in two steps from 2,2-diethyl-1,3-propanediol. The ^1H n.m.r. spectrum of complex (**10**) (see Experimental section) shows that it consists mainly of a single isomer, probably with both S-methyl groups equatorial in a chair chelate ring, and having fortuitously n.m.r.-equivalent ethyl groups. The spectrum does, however, show an additional signal (at δ 1.46), which suggests that a small quantity of another isomer is present. In an experiment related to the immediately previous one, only substrate was detected after *cis*-dichlorobis(diethyl sulphide)-platinum(II) had been treated with diazomethane.

Reactions with Symmetrical cis-*Bis(phosphine) Complexes.*—When a suspension of [1,3-bis(diphenylphosphino)propane]-dichloroplatinum(II) (**11**) in dichloromethane was stirred with diazomethane in diethyl ether the solid dissolved and gave initially a mixture of the chloromethyl derivative (**12**) and its bis(chloromethyl) analogue (**13**). In the presence of an excess of diazomethane only the latter was isolated. The structures of these two products were readily assigned on the basis of microanalyses and their n.m.r. spectra. Thus, for example, the ^{31}P n.m.r. spectrum of (**13**) contains a singlet at δ 0.99 p.p.m. with platinum satellites while the spectrum of (**12**) contains two doublets (at δ 1.69 and −1.13 p.p.m.) each with platinum satellites.† Both of these compounds are stable as solids or in acid-free solvents. A stable bis(chloromethyl) product was also obtained as a colourless solid when *cis*-dichlorobis(triphenyl-phosphine)platinum(II) (**14**) was treated with an excess of diazomethane. The ^1H, ^{13}C, and ^{31}P n.m.r. spectra are consistent with the structure (**15**) drawn. The observation that the methylene protons give rise to a clean doublet, with platinum satellites, presumably indicates that the magnitudes of both *cis* $^3J(PPtCH)$ and $^2J(PPtP)$ are quite small. Treatment of (**14**) with a limited quantity of diazomethane gave a mixture of unreacted substrate, the mono(chloromethyl) derivative (**16**), and (**15**) as judged by the ^1H and ^{31}P n.m.r. spectra of the mixture. An integration of the proton spectrum indicated that (**15**) and (**16**) were formed in an approximate ratio of 4:1 and thus the second methylene insertion is more favourable than the first. The ^{31}P n.m.r. spectrum of (**16**) shows that the two phosphines are magnetically non-equivalent as expected for the *cis* geometry. Again, the methylene group gives rise to a doublet in the ^1H n.m.r. spectrum rather than a doublet of doublets. The most obvious explanation for this is that the magnitude of *cis* $^3J(P\text{–}H)$ must be near zero while, for the ^{31}P resonances, $|\delta(P_{cis}) - \delta(P_{trans})|$ must be significantly larger than $^2J(P\text{–}P)$. Indeed, the latter coupling is 15 Hz and the shift separation is 1.2 p.p.m.

Our attention was next directed to the reaction of diazomethane with *cis* complexes of platinum(II) chloride in which both phosphines bear only alkyl groups. Here, when methylene insertion into the metal–halogen bonds was observed, the instability of the products prevented their isolation. Thus treatment of *cis*-dichlorobis(triethylphosphine)platinum(II) (**17**) with an excess of diazomethane gave a product for which the ^1H and ^{31}P n.m.r. spectra were consonant with structure (**18**). No attempt was made to isolate (**18**), since significant decomposition took place in solution over a few hours at ambient temperature. Monitoring with ^{31}P n.m.r. spectroscopy indicated that upon reaction of (**17**) with limited amounts of reagent a mixture of (**18**) and the *cis*-monoinsertion product (**19**) is formed. In this case, when about one half of the substrate had reacted the ratio of (**18**):(**19**) was approximately 1:1, indicating that the second insertion is marginally more favourable than the first. On treatment with an excess of diazomethane, [1,2-bis(dicyclo-hexylphosphino)ethane]dichloroplatinum(II) (**20**) gave the bis insertion product (**21**), whereas the higher homologues (**22**) and (**23**) were recovered unchanged from such treatment. Substrate was also recovered when *cis*-dichlorobis(tricyclohexyl-phosphine)platinum(II) (**24**) was exposed to an excess of diazomethane. However, when this reaction was repeated in the presence of an excess of tricyclohexylphosphine and monitored by ^{31}P n.m.r. spectroscopy, signals ascribable to a small amount of *trans*-chloro(chloromethyl)bis(tricyclohexylphosphine)-platinum(II) (**25**) were detected.

Reactions with Unsymmetrical cis-*Dichloro Complexes.*—*cis*-Dichloro(diethyl sulphide)(quinuclidine)platinum(II) (**26**) was recovered unchanged from treatment with an excess of diazomethane.

Under similar reaction conditions, dichloro(*N*,*N*-dimethyl-3-diphenylphosphinopropylamine)platinum(II) (**27**) afforded the monoinsertion product (**28**). Upon standing at ambient temperature for several hours in deuteriochloroform (**28**) was converted into the isomeric (**29**) in which the chloromethyl group is *trans* to the amino ligand. This product, in turn, decomposes in solution to give the original reactant (**27**). While some 2:1

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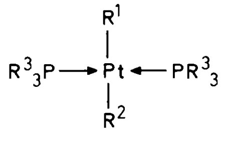
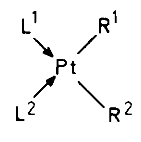
* It appears likely that this oxidation is similar to that found[11] for a series of tertiary amines on exposure to Pd^{II}. Indeed $NEtPr^i{}_2$, which is readily oxidised by Pd^{II}, reacts rapidly with aqueous K_2PtCl_4 to give a deposit of Pt^0.

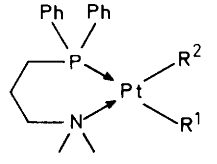
† The magnitudes of the various coupling constants for this and other products accord well with those reported in the literature for related compounds (see, for example, ref. 12).



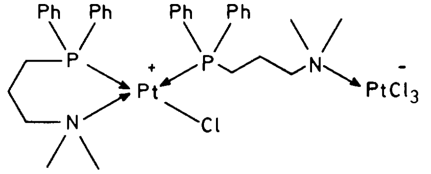
(25) $R^1=Cl, R^2=CH_2Cl, R^3=C_6H_{11}$
(36) $R^1=R^2=Cl, R^3=Pr^i$
(37) $R^1=R^2=Cl, R^3=C_6H_{11}$
(45) $R^1=H, R^2=Cl, R^3=Et$
(54) $R^1=H, R^2=CH_2Cl, R^3=Et$
(55) $R^1=Me, R^2=CH_2Cl, R^3=Et$
(56) $R^1=Cl, R^2=Me, R^3=Et$
(57) $R^1=R^2=Cl, R^3=Et$



(26) $R^1=R^2=Cl, L^1=Et_2S, L^2=$quinuclidine
(31) $R^1=R^2=Cl, L^1=PEt_3, L^2=Bu^tNC$
(32) $R^1=R^2=CH_2Cl, L^1=PEt_3, L^2=Bu^tNC$
(33) $R^1=Cl, R^2=CH_2Cl, L^1=PEt_3, L^2=Bu^tNC$



(27) $R^1=R^2=Cl$
(28) $R^1=CH_2Cl, R^2=Cl$
(29) $R^1=Cl, R^2=CH_2Cl$



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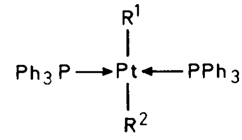
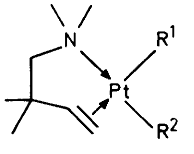




(34) $R^1=R^2=Cl$
(35) $R^1=Cl, R^2=CH_2Cl$
(38) $R^1=Cl, R^2=Me$
(39) $R^1=CH_2Cl, R^2=Me$
(40) $R^1=Cl, R^2=CF_3$
(41) $R^1=I, R^2=CF_3$
(42) $R^1=CH_2I, R^2=CF_3$
(43) $R^1=Cl, R^2=H$
(44) $R^1=CH_2Cl, R^2=H$

(52) $R^1=CH_2Cl, R^2=Cl$
(53) $R^1=Cl, R^2=CH_2Cl$

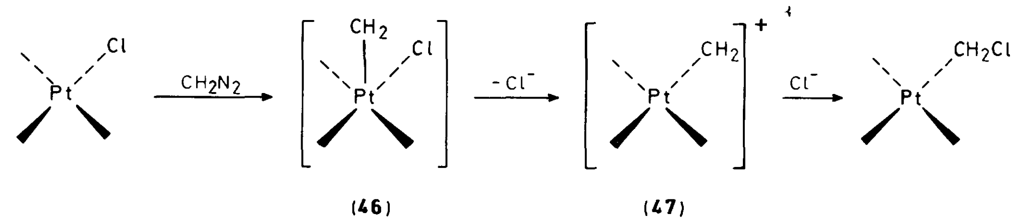
(ligand : metal) complexes of platinum(II) with *N,N*-dimethyl-3-diphenylphosphinopropylamine have been reported,[13] the simple chelate, (**27**), is apparently new. This complex was prepared by reaction of *cis*-dichlorobis(diethyl sulphide)platinum(II) with the stoicheiometric quantity of the ligand in deuteriochloroform. Monitoring by ^1H n.m.r. spectroscopy revealed that displacement of the first equivalent of sulphide, by the phosphine end of the ligand, occurred rapidly at ambient temperature while amine co-ordination took place slowly at 50 °C and was incomplete even after 2 weeks. An attempt to prepare (**27**) by stirring 1 equivalent of the ligand in dichloromethane with platinum(II) chloride led to the isolation of a 1 : 1 adduct which we suggest is the bridged species (**30**).

Reaction of *cis*-dichloro(t-butyl isocyanide)(triethylphosphine)platinum(II) (**31**) with an excess of diazomethane gave the bis insertion product (**32**). With smaller amounts, mixtures of (**32**) and the monoinsertion product (**33**) were obtained. The configuration of the latter is assigned on the basis of the magnitude[14] of ^1J(Pt–P). Neither product was sufficiently stable to permit purification.

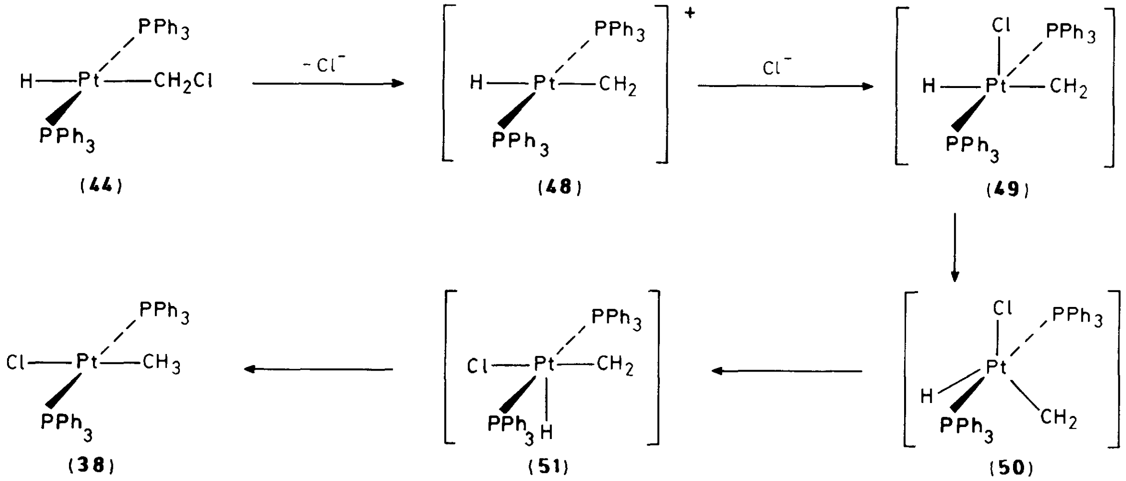
Reactions with trans-*Diphosphine Complexes*.—On treatment with an excess of diazomethane *trans*-dichlorobis(triphenylphosphine)platinum(II) (**34**) reacted to give mainly the *cis*-bis(chloromethyl) derivative (**15**) along with some *trans*-chloro(chloromethyl)bis(triphenylphosphine)platinum(II) (**35**). The latter, which was identified by ^1H and ^{31}P n.m.r. spectroscopy, was converted into (**15**) by further treatment with diazomethane. The *trans*-bis(tri-isopropyl- and -bis(tricyclohexyl-phosphine) complexes, (**36**) and (**37**), were both recovered from treatment with an excess of diazomethane.

The reaction of *trans*-chloro(methyl)bis(triphenylphosphine)platinum(II) (**38**) proceeded slowly with an excess of diazomethane to give mixtures containing substrate and the methylene-insertion product (**39**). The latter decomposed when attempts were made to purify it by chromatography. The trifluoromethyl analogue (**40**) of (**38**) reacted rapidly with diazomethane to give a myriad of products (^{31}P n.m.r.). The corresponding iodide (**41**) also reacted readily with diazomethane, but, in this case, when only a small excess of the reagent was used the iodomethyl derivative (**42**) was detected as the predominant product and it was isolated by preparative t.l.c. When (**41**) was treated with a large excess of diazomethane for several hours at room temperature, comparable amounts of two major products were detected by ^1H and ^{31}P n.m.r. spectroscopy. One of these was (**42**); the other appears to be the corresponding *cis* isomer, which was unstable in solution and decomposed during attempted purification.

Finally, when *trans*-chlorohydridobis(triphenylphosphine)platinum(II) (**43**) was treated with diazomethane the initial product was identified by ^1H and ^{31}P n.m.r. spectroscopy as the *trans*-(chloromethyl)hydrido complex (**44**), which gradually rearranged into the *trans*-chloro(methyl) complex (**38**). An appreciable amount of rearrangement is observed in solution



Scheme 1. Proposed mechanism for the insertion of the methylene moiety into the Pt–Cl bond



Scheme 2. Proposed mechanism for the rearrangement of (**44**) into (**38**)

within 4 h and thus if (**43**) is allowed to stand with an excess of diazomethane for several hours a mixture of (**38**), (**39**), and (**44**) is produced. Similar results were obtained with the analogous bis(triethylphosphine) complex (**45**).

Discussion

The above results indicate that, in general, insertion of a methylene unit into a platinum(II)–halogen bond is observed only if a ligand of high *trans* effect (alkene, phosphine, alkyl, or hydride) occupies the co-ordination site *trans* to the halogen. These results are also consistent with the isolation[3] of only monoinsertion products from reaction of an excess of diazomethane with chelating olefinic amine and olefinic sulphide complexes of $PtCl_2$. For the latter reactions, a mechanism for the inserton process (see Scheme 1) involving nucleophilic attack of diazomethane at platinum (with concomitant, or subsequent, loss of nitrogen) to give a five-co-ordinate intermediate (**46**), displacement of chloride ion to give a square-planar cationic platinum carbene intermediate (**47**), and finally combination of chloride ion with this carbene, was proposed.[3] A similar mechanism appears reasonable for the other derivatives described in the Results section above. Support for the proposed involvement of a cationic carbene species is provided by the formation of methoxymethyl products (**6**) and (**7**) which is observed when the reaction of (**1**) is carried out in the presence of methanol. Related cationic carbene species have been suggested to be intermediates in carbene-insertion reactions of rhodium(III) derivatives[10] and in various reactions involving hydroxymethyl, alkoxymethyl, and halogenomethyl derivatives of osmium and iridium.[15]

In two reactions, those of (**24**) in the presence of an excess of tricyclohexylphosphine and of (**34**), products having a chloromethyl ligand *trans* to chlorine were obtained. In the former case, no insertion product could be detected when (**24**) alone was subjected to the reaction conditions, but diazomethane was consumed at a rate comparable with that observed for complexes which give insertion. A preliminary investigation[16] has shown that diazomethane is converted into ethylene in the presence of (**24**), and further work is in progress to determine whether the failure to obtain insertion product(s), in this and other cases, is due to the instability of such products, and/or to the intervention of alternative reaction pathways. The isolation of (**25**) from reaction of (**24**) in the presence of an excess of phosphine may suggest that insertion does occur in this case, and that most of the anticipated *cis*-monoinsertion product reacts further to give ethylene while a minor portion undergoes isomerisation, promoted by the excess of phosphine, to (**25**). An alternative explanation is that insertion may proceed *via* the cationic intermediate $[PtCl\{P(C_6H_{11})_3\}_3]^+$ (C_6H_{11} = cyclohexyl). As for the formation of (**35**) from the *trans*-bis(triphenylphosphine) complex (**34**), this appears to be the only case where direct insertion into a Pt–Cl bond *trans* to a ligand (Cl) of relatively low *trans* effect may have taken place. An alternative pathway, involving two isomerisation steps, *viz.* (**34**) ⟶ (**14**) ⟶ (**16**) ⟶ (**35**), appears unlikely in view of the finding that (**16**), formed by reaction of *cis*-dichlorobis(triphenylphosphine)platinum(II) (**14**) with a limited amount of diazomethane, did not give detectable (^{31}P n.m.r.) quantities of the isomer (**35**) after standing for several hours in solution. This isomerisation, however, has been reported[17] to take place in dichloromethane solution at reflux.

Finally, the reaction sequence (**43**) ⟶ (**44**) ⟶ (**38**) is of particular interest since it indicates that where there is competition between insertion into a Pt–Cl and Pt–H bond, the former is preferred kinetically and the latter thermodynamically. The conversion of kinetic product (**44**) into thermodynamic product (**38**) may involve *e.g.* (Scheme 2) liberation of chloride ion from the chloromethyl group of (**44**), attack of the liberated chloride at platinum in the resulting cationic carbene intermediate (**48**) to give a five-co-ordinate square-pyramidal intermediate (**49**), rearrangement of (**49**) *via* trigonal-bypyramidal intermediate (**50**) to square-pyramidal intermediate (**51**), and finally hydride migration to generate (**38**). The intervention of similar types of intermediates has been proposed for certain carbonyl-insertion reactions of square-planar platinum(II) derivatives,[18] and for analogous isocyanide insertions.[19] In the latter,[19] the possible involvement of a neutral five-co-ordinate intermediate in the reaction *trans*-$[PtH(CNR)(PEt_3)_2]Cl \longrightarrow$ *trans*-$[PtCl(CHNR)(PEt_3)_2]$ (R = *p*-tolyl) is supported by the observation that the reaction proceeds faster in less-polar solvents (pentane–dichloromethane > dichloromethane > methanol), with no reaction being observed even after 3 d at 35 °C in methanol. We have observed that the reported[3] isomerisation of (**52**) to (**53**) also proceeds faster in chloroform than in methanol, lending further support to the analogy between reactions involving co-ordinated carbene and co-ordinated carbon monoxide or isocyanide. We have been able to find only two earlier reports[20,21] of reactions of diazomethane with terminal hydride derivatives of Pt^{II} and in both only the hydride-insertion product is mentioned. Thus *trans*-$[PtBrH(PEt_3)_2]$ and *trans*-$[PtClH(PEt_3)_2]$ (**45**) are reported to give *trans*-$[PtBrMe(PEt_3)_2]$ (in poor yield) and *trans*-$[PtClMe(PEt_3)_2]$ respectively. As mentioned in the Results section, we have reinvestigated the reaction of complex (**45**) and find (^{31}P n.m.r.) that like (**43**) it gives mainly insertion into the Pt–Cl bond initially, but that rearrangement to the methyl derivative takes place on standing.

Experimental

Melting points were determined on a Kofler hot-stage, and are uncorrected. Proton (internal tetramethylsilane reference), ^{31}P (external 85% H_3PO_4), and ^{13}C (internal tetramethylsilane) n.m.r. spectra were recorded for deuteriochloroform solutions on a Bruker WH-400 spectrometer (Southwestern Ontario NMR Centre). Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. Plates for thin-layer chromatography (Kieselgel G, Merck) were developed in dichloromethane–methanol (49:1 or 99:1 v/v) and extraction of fractions from preparative plates was carried out with freshly distilled acetone. Diazomethane was prepared by treating *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide with potassium hydroxide in aqueous 2-(2′-ethoxyethoxy)ethanol, and was distilled along with, and then trapped in, diethyl ether at 0 °C. Subsequent reactions with the platinum complexes were carried out in solutions cooled to 0 °C.

Dichloro(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)platinum(II),[22] (2,2′-bipyridine)dichloroplatinum(II),[22] 2,2,*N*,*N*,*N*′,*N*′-hexamethyl-1,3-propanediamine,[23] *cis*-dichlorobis(diethyl sulphide)platinum(II),[24] and *cis*-dichloro(diethyl sulphide)(quinuclidine)platinum(II)[25] were prepared according to literature methods. All phosphine complexes other than *cis*-dichloro(t-butyl isocyanide)(triethylphosphine)platinum(II) (**31**) and dichloro(*N*,*N*-dimethyl-3-diphenylphosphinopropylamine)platinum(II) (**27**) were kindly supplied by Dr. H. C. Clark; (**31**) came from the collection of the late Dr. R. G. Goel; the preparation of (**27**) is reported below.

Reactions of Platinum Complexes with Diazomethane.—Dichloro(1,5-*cyclo-octadiene*)*platinum*(II) (**1**). A solution of complex (**1**) (Aldrich, 50 mg) in dichloromethane (30 cm^3) was treated with small aliquots of diazomethane in diethyl ether until all of (**1**) had been consumed, at which stage two products were detected by analytical t.l.c. Preparative t.l.c. of the mixture gave *bis*(*chloromethyl*)(1,5-*cyclo-octadiene*)*platinum*(II), (**3**) [40.5 mg, 75%, m.p. 61—68 °C; δ_H 2.49 (br s, 8 H, allylic H), 3.84 (s, 4 H, CH_2Cl, $^2J_{Pt-H} = 60$), and 5.34 (br s, 4 H, olefinic H, $^2J_{Pt-H} = 40$ Hz); δ_C 29.4 (allylic C), 41.9 (Pt–C),* and 105.1 (olefinic C, $^1J_{Pt-C} = 68$ Hz). Found: C, 30.1; H, 4.05. $C_{10}H_{16}Cl_2Pt$ requires C, 29.85; H, 4.0%] and the more polar *chloro*(*chloromethyl*)(1,5-*cyclo-octadiene*)*platinum*(II), (**2**) [10.5 mg, 20%, m.p. 123—126 °C; δ_H 2.30—2.53 (m, 6 H, allylic H), 2.62—2.71 (m, 2 H, allylic H), 3.97 (s, 2 H, CH_2Cl, $^2J_{Pt-H} = 74$ Hz), 4.88 (m, 2 H, olefinic H, $^2J_{Pt-H} = 75$), and 5.65 (m, 2 H, olefinic H, $^2J_{Pt-H} = 32$ Hz): δ_C 28.2, 31.4 (allylic C), 37.9 (Pt–C), 91.1 (olefinic C, $^1J_{Pt-C} = 218$ Hz), and 113.5 (olefinic C). Found: C, 27.85; H, 3.65. $C_9H_{14}Cl_2Pt$ requires C, 27.85; H, 3.65%].

When complex (**1**) (70.1 mg) was treated with an excess of diazomethane essentially quantitative conversion into (**3**) (75 mg) resulted.

An excess of diazomethane was added to a solution of complex (**1**) (37.4 mg) in dichloromethane (50 cm^3) and methanol (20 cm^3) and the resulting solution was allowed to stand for 1 h at room temperature. After this time the solvent was evaporated *in vacuo* and the residue was examined by ^1H n.m.r. spectroscopy which showed δ_H 2.2—2.65 (m, allylic H), 3.27 [s, OMe in (**7**)], 3.28 [s, OMe in (**6**)], 3.84 [s, CH_2Cl in (**3**)], 3.88 [s, CH_2Cl in (**6**), $^2J_{Pt-C} = 60$], 4.08 [s, CH_2O in (**6**), $^2J_{Pt-H} = 67.5$], 4.09 [s, CH_2O in (**7**), $^2J_{Pt-H} = 69$ Hz], and 5.15—5.5 (overlapping multiplets, olefinic H). From integration, (**3**) was a minor product in this mixture. The solution was evaporated *in vacuo* and the residue stored in a refrigerator. After 8 weeks it was redissolved and showed δ_H 2.15—2.7 (allylic H), 3.30 (s, OMe), 4.32 (s, CH_2O, $^2J_{Pt-H} = 85$), 4.76 (m, olefinic H, $^2J_{Pt-C} = 79$), and 5.58 (m, olefinic H, $^2J_{Pt-H} = 25$ Hz) ascribable to chloro(1,5-cyclo-octadiene)(methoxymethyl)platinum(II) (**8**), in addition to other smaller peaks due to minor constituents.

(1,5-*Cyclo-octadiene*)*di-iodoplatinum*(II) (**4**). The mixture obtained by reaction of this substrate[26] (48 mg) in dichloromethane (30 cm^3) with an excess of diazomethane was run through a short silica gel column, and the solvent was evaporated to give essentially pure (1,5-*cyclo-octadiene*)*bis*(*iodomethyl*)*platinum*(II), (**5**) [39 mg, 63%, m.p. 109—112 °C after crystallisation from diethyl ether; δ_H 2.53 (br s, 8 H, allylic H), 2.96 (s, 4 H, CH_2I, $^2J_{Pt-H} = 43$), and 5.25 (br s, 4 H, olefinic H, $^2J_{Pt-H} = 40$ Hz); δ_C −2.2 (Pt–C, $^1J_{Pt-C} = 1\,015$), 30.1 (allylic C), and 103.9 (olefinic C, $^1J_{Pt-C} = 63$ Hz). Found: C, 20.65; H, 2.7. $C_{10}H_{16}I_2Pt$ requires C, 20.5; H, 2.75%].

Dichloro(4,4-*diethyl*-2,6-*dithiaheptane*)*platinum*(II), (**10**). A suspension of platinum(II) chloride (200 mg, 0.752 mmol) in dichloromethane (50 cm^3) containing 4,4-diethyl-2,6-dithiaheptane (144 mg, 0.748 mmol; prepared as described below) was stirred at ambient temperature for 2 h, during which time virtually all of the dichloride dissolved. The resulting solution was filtered, and evaporated to small volume to give yellow crystals of *dichloro*(4,4-*diethyl*-2,6-*dithiaheptane*)*platinum*(II) (**10**), m.p. 234—235 °C [114 mg, 33%; δ_H 0.90 (t, 6 H, $J = 7.4$, CH_2CH_3), 1.59 (q, 4 H, $J = 7.4$, CH_2CH_3), 2.78 (2, 6 H, SMe, $^3J_{Pt-H} = 46.5$), 2.90 (d, 2 H, $J = 12.7$, SCH_2), and 3.04 (d, 2 H, $J = 12.7$, SCH_2, $^3J_{Pt-H} = 54$ Hz). Found: C, 23.7; H, 4.0. $C_9H_{20}Cl_2PtS_2$ requires C, 23.6; H, 4.4%].

The ligand was prepared by heating 2,2-diethyl-1,3-propanediol bis(methanesulphonate)[27] (5.0 g, 17 mmol) under nitrogen at 100 °C for 16 h with the mixture obtained by reaction of sodium (1.7 g, 74 mmol) with dimethyl disulphide (3.3 g, 35 mmol) in hexamethylphosphoramide (50 cm^3). After cooling, the reaction mixture was poured into water (200 cm^3) and then extracted with diethyl ether. The ether extract was washed with water, dried over anhydrous sodium sulphate, and evaporated to leave an oil which upon distillation (Kugelrohr, water pump)

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* Where the magnitude of a coupling to platinum is not reported, the relevant satellites were not distinguishable.

gave a fraction, b.p. 103—120 °C (1.2 g, 37% yield), of essentially pure 4,4-diethyl-2,6-dithiaheptane; δ_H 0.82 (t, 6 H, J = 7.4, $\mathrm{CH_2C}\mathit{H}_3$), 1.38 (q, 4 H, J = 7.4 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.12 (s, 6 H, SMe), and 2.56 (s, 4 H, $\mathrm{SCH_2}$); δ_C 7.80 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 17.46 (SMe), 27.61 ($\mathit{C}\mathrm{H_2CH_3}$), 41.37 ($C^4$), and 42.11 ($\mathrm{SCH_2}$).

When complex (**10**) (46 mg) was treated with an excess of diazomethane at 0 °C for 1 h, only substrate was detected by t.l.c. and ^{1}H n.m.r. spectroscopy (after evaporation of the solvent and dissolution of the residue in $\mathrm{CDCl_3}$).

[1,3-*Bis*(*diphenylphosphino*)*propane*]*dichloroplatinum*(II), (**11**). Small quantities of a diazomethane solution in diethyl ether were added every few minutes to a stirred suspension of complex (**11**) (73 mg) in dichloromethane at 0 °C until the solid dissolved (*ca.* 1 h). The resulting solution was then allowed to stir for a further 30 min at ambient temperature at which stage t.l.c. revealed the presence of two products, which were separated by preparative t.l.c. The major, less polar fraction (55 mg) gave colourless crystals of [1,3-*bis*(*diphenylphosphino*)-*propane*]*bis*(*chloromethyl*)*platinum*(II) (**13**) from dichloromethane–hexane [m.p. 189—192 °C; δ_H* 1.89 (m, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.52 (m, 4 H, $\mathrm{PCH_2}$), and 3.57 (d, 4 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 7.7, $^2J_{Pt-H}$ = 22 Hz); δ_C* 19.81 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.03 ($\mathrm{PCH_2}$, 3 lines, J_{P-C} = 17), and 41.69 [PtC, $^2J_{P-C}$ = 118 (*trans*) and 11 Hz (*cis*)]; δ_P 0.99 ($^1J_{Pt-P}$ = 1 829 Hz). Found: C, 49.2; H, 4.3. $\mathrm{C_{29}H_{30}Cl_2P_2Pt}$ requires C, 49.3; H, 4.3%]. The minor fraction (18 mg), [1,3-*bis*(*diphenylphosphino*)*propane*]*chloro*(*chloromethyl*)*platinum*(II) (**12**) also crystallised from dichloromethane–hexane [m.p. 140—143 °C; δ_H 1.94 (m, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.38 (m, 2 H, $\mathrm{PCH_2}$), 2.66 (m, 2 H, $\mathrm{PCH_2}$, $^3J_{Pt-H}$ = 10.5), and 3.35 (dd, 2 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 6.2 and 2.3, $^2J_{Pt-H}$ = 43.5 Hz); δ_C 19.45 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 26.05 ($\mathrm{PCH_2}$, $^1J_{P-C}$ = 29.5, $^3J_{P-C}$ = 2), 27.39 ($\mathrm{PCH_2}$, $^1J_{P-C}$ = 40, $^3J_{P-C}$ = 7), and 42.57 (PtC, $^2J_{P-C}$ = 120.5 and 5 Hz); δ_P −1.13 ($^2J_{P-P}$ = 23, $^1J_{Pt-P}$ = 1 638) and 1.69 ($^2J_{P-P}$ = 23, $^1J_{Pt-P}$ = 4 058 Hz). Found: C, 48.25; H, 4.05. $\mathrm{C_{28}H_{28}Cl_2P_2Pt}$ requires C, 48.55; H, 4.05%].

When a further quantity (50 mg) of complex (**11**) was treated under similar conditions with an excess of diazomethane only (**13**) was detected in the product by t.l.c. and ^{1}H n.m.r. spectroscopy.

cis-Dichlorobis(*triphenylphosphine*)*platinum*(II) (**14**). The product obtained from reaction of complex (**14**) (32 mg) with an excess of diazomethane was run through a short plug of silica gel in dichloromethane and then crystallised from dichloromethane–hexane. This gave cis-*bis*(*chloromethyl*)*bis*(*triphenylphosphine*)*platinum*(II) (**15**) (21 mg) [m.p. 125 °C (decomp.); δ_H 3.67 (d, 4 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 8.8, $^2J_{Pt-H}$ = 44.3 Hz); δ_C 42.3 (PtC, $^2J_{P-C}$ = 115 and 8.5, $^1J_{Pt-C}$ = 845 Hz); δ_P 24.06 ($^1J_{Pt-P}$ = 1 974 Hz) (Found: C, 56.0; H, 4.65. $\mathrm{C_{38}H_{34}Cl_2P_2Pt}$ requires C, 55.75; H, 4.2%]. Treatment of (**14**) (23 mg) with a limited amount of diazomethane gave, along with some unreacted (**14**), a mixture of (**15**) and its mono(chloromethyl) analogue (**16**) (ratio *ca.* 4:1, ^{1}H n.m.r. integration). The last gave δ_H 3.55 (br d, 2 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 6.0, $^2J_{Pt-H}$ = 44.0 Hz) and δ_P 19.7 ($^2J_{P-P}$ = 15, $^1J_{Pt-P}$ = 4 499) and 20.9 ($^2J_{P-P}$ = 15, $^1J_{Pt-P}$ = 1 691 Hz).

cis-*Dichlorobis*(*triethylphosphine*)*platinum*(II) (**17**). Reaction of a solution of complex (**17**) (29 mg) in methylene chloride with an excess of diazomethane at 0 °C for 30 min and then evaporation of the solvent at ambient temperature on a rotary evaporator gave a colourless gum which was substantially pure cis-*bis*(*chloromethyl*)*bis*(*triethylphosphine*)*platinum*(II) (**18**) as judged by its ^{1}H and ^{31}P n.m.r. spectra [δ_H 3.74 (d, 4 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 8.7, $^2J_{Pt-H}$ = 18.5 Hz) and δ_P 5.9 ($^1J_{Pt-P}$ = 1 914 Hz)]. The mixture obtained by reaction of (**17**) with a small amount of diazomethane gave a ^{31}P n.m.r. spectrum which contained peaks attributable to only (**17**)—(**19**). The last had δ_P 6.8 ($^2J_{P-P}$ = 17, $^1J_{Pt-P}$ = 4 204) and 10.8 ($^2J_{P-P}$ = 17, $^1J_{Pt-P}$ = 1 710 Hz). The relative peak heights gave an approximate ratio for (**18**):(**19**) of 1:1.

[1,2-*Bis*(*dicyclohexylphosphino*)*ethane*]*dichloroplatinum*(II) (**20**). Reaction of a solution of complex (**20**) (20 mg) in dichloromethane (5 cm^3) with an excess of diazomethane at 0 °C and then addition of hexane (20 cm^3) and finally evaporation on the rotary evaporator to small volume gave a colourless precipitate (21 mg). This was essentially pure [1,2-*bis*(*dicyclohexylphosphino*)*ethane*]*bis*(*chloromethyl*)*platinum*(II) (**21**) [δ_H 3.88 (4 H, $\mathrm{PtCH_2}$, $^3J_{P-H}$ = 6 and 2, $^2J_{Pt-H}$ = 47 Hz); δ_P 58.6 ($^1J_{Pt-P}$ = 1 906 Hz). Found: C, 47.45; H, 7.2. $\mathrm{C_{28}H_{52}Cl_2P_2Pt}$ requires C, 46.95; H, 7.3%]. This product was stable as a solid at ambient temperature but decomposed in solution.

Dichloro(N,N-*dimethyl*-3-*diphenylphosphinopropylamine*)-*platinum*(II) (**27**). *N*,*N*-Dimethyl-3-diphenylphosphinopropylamine has been prepared[13] previously but, for the present study, it was formed in quantitative yield by u.v. irradiation of a stoicheiometric mixture of diphenylphosphine and allyldimethylamine. The ligand (89 mg, 0.2 mmol) in deuteriochloroform (1 cm^3) was added to a solution of *cis*-dichlorobis(diethyl sulphide)platinum(II) (54 mg, 0.2 mmol) in the same solvent (3 cm^3). A proton n.m.r. spectrum of the resulting solution contained resonances attributable to free and complexed diethyl sulphide (ratio, 1:1) and uncomplexed $\mathrm{NMe_2}$. Upon heating at 50 °C, the proportion of free diethyl sulphide increased and a pale yellow solid started to crystallise out. After 2 weeks the crystals (56 mg) were filtered off and the residue from the mother-liquors was subjected to preparative t.l.c. (methanol–dichloromethane, 1:49) which gave two major fractions. The less polar of these (18 mg) consisted of the crystalline product obtained previously while the ^{1}H n.m.r. spectrum of the more polar one [a yellow gum (32 mg)] showed resonances for complexed diethyl sulphide and free $\mathrm{NMe_2}$. A solution of this gum in deuteriochloroform (1 cm^3) was heated at 50 °C for an additional 2 weeks, whereupon a further crop (17 mg) of crystals was obtained. After recrystallisation from dichloromethane–chloroform, the combined fractions (91 mg) of *dichloro*(N,N-*dimethyl*-3-*diphenylphosphinopropylamine*)*platinum*(II) (**27**) had m.p. 248—252 °C [δ_H 2.06 (m, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.43 (m, 2 H, $\mathrm{PCH_2}$), 2.85 (m, 2 H, $\mathrm{NCH_2}$, $^3J_{Pt-H}$ = 52), and 3.16 (s, 6 H, NMe, $^3J_{Pt-H}$ = 31 Hz); $\delta_P(\mathrm{CH_2Cl_2})$ −5.5 ($^1J_{Pt-P}$ = 2 948 Hz). Found: C, 37.6; H, 4.15. $\mathrm{C_{17}H_{22}Cl_2NPPt}$ requires C, 37.95; H, 4.15%]. When a suspension of platinum(II) chloride (53 mg, 0.2 mmol) was stirred at ambient temperature with a solution of the aminophosphine ligand (54 mg, 0.2 mmol) in dichloromethane (30 cm^3) for 16 h the solid gradually dissolved. The small amount of solid remaining was filtered off and the solvent evaporated *in vacuo* to leave a solid which upon crystallisation from acetone gave pale buff crystals, m.p. 233—235 °C, of the bridged species (**30**) [δ_H 1.61 (s, 2 H, $\mathrm{H_2O}$, see analysis below), 2.81 (br s, 6 H, $\mathrm{Me_2NPtP}$), and 3.01 (s, 6 H, $\mathrm{Me_2NPtCl_3}$, $^3J_{Pt-H}$ = 98 Hz) (remaining aliphatic resonances form complex series of broad multiplets 1.4—3.9); δ_P 7.3 ($^2J_{P-P}$ = 15.5, $^1J_{Pt-P}$ = 3 691) and 13.2 ($^2J_{P-P}$ = 15.5, $^1J_{Pt-P}$ = 3 548 Hz). Found: C, 37.0; H, 4.05. $\mathrm{C_{34}H_{44}Cl_4N_2P_2Pt_2{\cdot}H_2O}$ requires C, 37.35; H, 4.25%].

Treatment of complex (**27**) (32 mg) in dichloromethane with an excess of diazomethane at 0 °C for 10 min and evaporation of the solvent rapidly *in vacuo* gave a gum which was immediately dissolved in cold deuteriochloroform. A ^{1}H n.m.r. spectrum of this material was run immediately and then the entire procedure was repeated before a ^{31}P n.m.r. spectrum was obtained. These spectra indicated that the material consisted mainly of the monoinsertion product (**28**) [δ_H 3.01 (s, 6 H, NMe, $^3J_{Pt-H}$ =

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* For brevity, ^{1}H and ^{13}C resonances for the phenyl rings are not reported in this and other cases.

38) and 3.94 (d, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 3$, ${}^{2}J_{Pt-H}$ 51 Hz); δ_P 2.15 (${}^{1}J_{Pt-P} = 2\,016$ Hz)]. During several hours in deuteriochloroform the signals due to (**28**) were replaced by those for its isomer (**29**) [δ_H 2.80 (br s, 6 H, NMe) and 3.50 (d, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 5.9$, ${}^{2}J_{Pt-H} = 54$ Hz); δ_P 6.9 (${}^{1}J_{Pt-P} = 4\,713$ Hz)]. The resonances for complex (**29**) were gradually replaced during several days with those for (**27**).

cis-*Dichloro*(*t-butyl isocyanide*)(*triethylphosphine*)*platinum*(II) (**31**). Reaction of complex (**31**) (40 mg) with an excess of diazomethane gave the bis insertion product (**32**) as an oil after evaporation of the solvent. This oil had δ_H 3.48 (d, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 8.6$, ${}^{2}J_{Pt-H} = 47$ Hz) and 4.04 (d, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 3.9$, ${}^{2}J_{Pt-H} = 49$ Hz); δ_C 33.2 (PtC, ${}^{1}J_{Pt-C} = 800$) and 40.5 (PtC, ${}^{2}J_{P-C} = 119$, ${}^{1}J_{Pt-C} = 746$ Hz); δ_P 9.28 (${}^{1}J_{Pt-P}$ 1 825 Hz). This oil could not be induced to crystallise. When (**31**) (10 mg) was treated with small aliquots of diazomethane until all the substrate had reacted, two products were detected by analytical t.l.c. This mixture gave ${}^{1}H$ n.m.r. and ${}^{31}P$n.m.r. resonances attributable to a 5:1 mixture of (**33**) and (**32**). The former had δ_H 3.93 (d, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 3.7$, ${}^{2}J_{Pt-H} = 57$ Hz); δ_P 14.08 (${}^{1}J_{Pt-P} = 1\,591$ Hz).

trans-*Dichlorobis*(*triphenylphosphine*)*platinum*(II) (**34**). Two products, the *trans*-mono(chloromethyl) (**35**)[17] and *cis*-bis-(chloromethyl) (**15**) derivatives, were formed in a *ca.* 2:1 ratio when (**34**) was treated at 0 °C with a slight excess of diazomethane. The compounds were identified in the mixture by ${}^{1}H$ and ${}^{31}P$ n.m.r. spectroscopy. Compound (**35**) had δ_H 3.03 (t, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 8$, ${}^{2}J_{Pt-H} = 52$ Hz); δ_P 27.40 (${}^{1}J_{Pt-P} = 3\,155$ Hz). Treatment of a sample of (**35**), prepared from (**2**) by reaction with the stoicheiometric quantity of triphenylphosphine, with a large excess of diazomethane converted it into (**15**) (${}^{1}H$ and ${}^{31}P$ n.m.r. evidence).

trans-*Chloro*(*methyl*)*bis*(*triphenylphosphine*)*platinum*(II) (**38**). Reaction of complex (**38**) (75 mg) with an excess of diazomethane at ambient temperature for 6 h achieved only partial conversion of this compound into a new product (t.l.c. evidence). Attempts at isolating a sample of this product (**39**) by preparative t.l.c. led to its decomposition. The ${}^{1}H$ and ${}^{31}P$ n.m.r. spectra of the reaction mixture showed resonances attributable to (**38**) and (**39**) (4:3 ratio). The latter had δ_H −0.49 (t, 3 H, $PtCH_3$, ${}^{3}J_{P-H} = 6.2$, ${}^{2}J_{Pt-H} = 47.3$), 2.98 (t, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 7.6$, ${}^{2}J_{Pt-H} = 41.2$ Hz); $\delta_P(CH_2Cl_2)$ 32.38 (${}^{1}J_{Pt-P} = 3\,224$ Hz).

trans-*Iodo*(*trifluoromethyl*)*bis*(*triphenylphosphine*)*platinum*(II) (**41**). A solution of complex (**41**) (56 mg) in methylene chloride (40 cm^3) was treated with aliquots of diazomethane until all the substrate had reacted (t.l.c.). The solvent was evaporated *in vacuo* and ${}^{1}H$ and ${}^{31}P$ n.m.r. spectra obtained for the residue. These contained resonances for a single, major, product (**42**), which was recovered by preparative t.l.c. (dichloromethane–methanol, 49:1; least polar major band) and then precipitation from a dichloromethane solution with hexane as a very pale brown solid. This had δ_H 1.83 (t, 2 H, $PtCH_2I$, ${}^{3}J_{P-H} = 9.6$ Hz); δ_P 24.98 (${}^{3}J_{F-P} = 11.5$, ${}^{1}J_{Pt-P} = 3\,222$ Hz) (Found: C, 49.0; H, 3.25. $C_{38}H_{32}F_3IP_2Pt$ requires C, 49.1; H, 3.45%). This compound (**42**) was stable when stored for 6 weeks at ambient temperature, however, it gradually decomposed when dissolved in deuteriochloroform.

When complex (**41**) was treated with a large excess of diazomethane for 2 h, ${}^{1}H$ and ${}^{31}P$ n.m.r. spectra of the resulting mixture contained resonances attributable to (**42**) and its *cis* isomer (in a ratio of *ca.* 1:1), in addition to those corresponding to several minor products. The *cis* isomer had δ_H 2.77 (d, 2 H, $PtCH_2I$, ${}^{3}J_{Pt-H} = 9.7$, ${}^{2}J_{Pt-H} = 31$ Hz); δ_P 20.88 (${}^{3}J_{F-P} = 11.0$, ${}^{1}J_{Pt-P} = 2\,185$) and 21.07 (${}^{1}J_{Pt-P} = 1\,961$ Hz). This compound decomposed during attempts to purify it by preparative t.l.c.

trans-*Chlorohydridobis*(*triphenylphosphine*)*platinum*(II) (**43**). Reaction of complex (**43**) (24 mg) with an excess of diazomethane in dichloromethane (5 cm^3) gave (as judged by ${}^{1}H$ and ${}^{31}P$ n.m.r.) (**44**) mainly, along with small amounts of (**38**) and (**39**). The first of these gave δ_H −5.86 (t, 1 H, PtH, ${}^{2}J_{P-H} = 18.3$, ${}^{1}J_{Pt-H} = 625$) and 3.04 (t, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 7.1$, ${}^{2}J_{Pt-H} = 33.5$ Hz); δ_P 33.7 (${}^{1}J_{Pt-P} = 3\,132$ Hz). Attempts to isolate this compound by chromatography were not successful and, upon standing in $CDCl_3$ at room temperature, complex (**44**) in a mixture of the type described above was largely converted into (**38**) (${}^{1}H$ and ${}^{31}P$ n.m.r.). After several days at ambient temperature this solution contained mainly (**38**) along with some (**39**) and traces of (**14**).

trans-*Chlorohydridobis*(*triethylphosphine*)*platinum*(II) (**45**). When complex (**45**) (24 mg) was dissolved in dichloromethane and treated with an excess of diazomethane at 0 °C for 30 min, several compounds were detected in the resulting mixture by ${}^{31}P$ n.m.r. spectroscopy. In order of decreasing concentrations these were the (chloromethyl)hydrido species (**54**), substrate (**45**), the (chloromethyl)methyl species (**55**), the (chloro)methyl species (**56**),[28] the *cis*-(**17**), and the *trans*-dichloride (**57**). When this mixture was allowed to stand in deuteriochloroform at ambient temperature for several days the signals arising from (**55**) were lost, those from (**54**) were substantially reduced, those from (**45**) essentially unchanged, and those from (**56**), (**17**), and (**57**) were enhanced in intensity. Compound (**54**) had δ_H −7.62 (t, 1 H, PtH, ${}^{2}J_{P-H} = 18.7$, ${}^{1}J_{Pt-H} = 393$) and 3.79 (t, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 7.2$, ${}^{2}J_{Pt-H} = 33.6$ Hz); δ_P 16.0 (${}^{1}J_{Pt-P} = 2\,794$ Hz). Compound (**55**) had δ_H −0.17 (t, 3 H, $PtCH_3$, ${}^{3}J_{P-H} = 5.6$, ${}^{2}J_{Pt-H} = 97.6$) and 3.72 (t, 2 H, $PtCH_2Cl$, ${}^{3}J_{P-H} = 8.3$ Hz); δ_P 19.2 (${}^{1}J_{Pt-P} = 2\,789$ Hz). Compound (**56**) had δ_H 0.34 (t, 3 H, $PtCH_3$, ${}^{3}J_{P-H} = 5.9$, ${}^{2}J_{Pt-H} = 84.2$ Hz); δ_P 16.5 (${}^{1}J_{Pt-P} = 2\,818$ Hz).

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