Reactions of Electroneutral Alkoxy(organo)carbene Complexes of Platinum(II)

By **Gordon K. Anderson** and **Ronald J. Cross,*** Chemistry Department, University of Glasgow, Glasgow G12 8QQ

The carbene complexes *cis*-$[PtCl_2(PR_3)\{C(OR')(CH_2R'')\}]$ (1; R_3 = Me_2Ph or Et_3; R' = Me, Et, or Pr^n; R'' = Me, Et, or Ph) react rapidly with CD_3OD to yield *cis*-$[PtCl_2(PR_3)\{C(OR')(CD_2R'')\}]$, then slowly by alkoxy-group exchange to *cis*-$[PtCl_2(PR_3)\{C(OCD_3)(CD_2R'')\}]$. Dimethylamine reacts by proton abstraction to form $[PtCl(PR_3)(NMe_2H)\{C(OR')=CHR''\}]$. The carbene complexes react with chloride ions by R'Cl elimination to form the acyls $[Pt_2(\mu\text{-}Cl)_2(PR_3)_2(COCH_2R'')_2]$. Thermolyses of (1) produce the same products. These reactions are compared with those of related cationic carbene complexes. Treatment of (1) by PR_3 in the presence of $Ag[S(CF_3)O_3]$ leads to the cationic carbene complex *trans*-$[PtCl(PR_3)_2\{C(OR')(CH_2R'')\}][S(CF_3)O_3]$ which can also be made by the action of $R'SO_3CF_3$ on *trans*-$[PtCl(PR_3)_2(COCH_2R'')]$. Halogen abstraction from (1) by $Ag[S(CF_3)O_3]$, $MeSO_3CF_3$, or $EtSO_3CF_3$ produces binuclear halide-bridged cationic complexes $[Pt_2(\mu\text{-}Cl)_2(PR_3)_2\{C(OR')(CH_2R'')\}_2][S(CF_3)O_3]_2$. These are extremely powerful alkylating agents, and alkylate the $[S(CF_3)O_3]^-$ anions in solution.

IN the previous paper[1] we described the preparation and spectroscopic parameters of a series of electroneutral alkoxy(organo)carbene complexes of platinum, *cis*-$[PtX_2L\{C(OR')CH_2R\}]$ (L = PMe_2Ph or PEt_3; X = Cl, Br, or I; R = Me, Et, or Ph; and R' = Me, Et, or Pr^n). The *X*-ray crystal and molecular structure of *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$, a typical member of the series, was described and discussed.

We report here some chemical reactions of the complexes of this series, and compare them with related reactions of cationic alkoxy(organo)carbeneplatinum complexes, described by Clark and Chisholm and their co-workers.[2-4]

RESULTS AND DISCUSSION

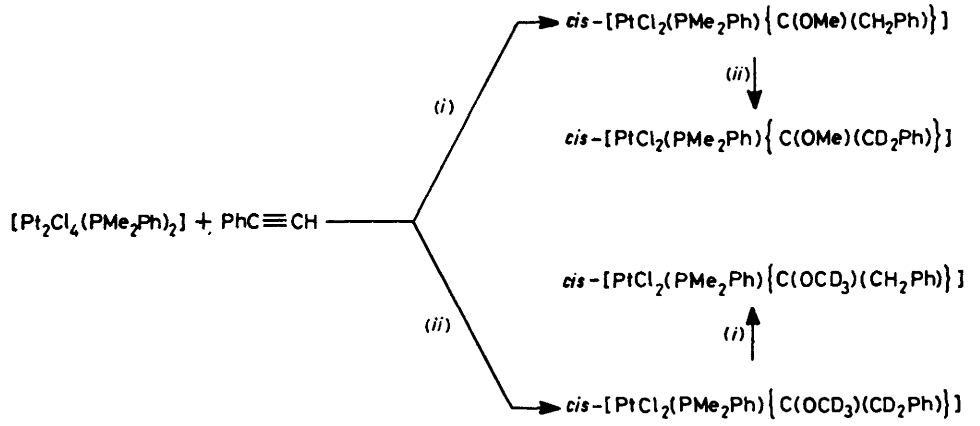
Acid-base Reactions of the Carbene Ligand.—Deuteriated alcohols react with cationic alkoxy(organo)carbene complexes by H–D exchange of the α-carbene carbon protons [equation (1)]. A slower reaction with alcohols

$$trans\text{-}[PtCl(PMe_2Ph)_2\{C(OMe)(CH_2R)\}]^+ \xrightarrow[1\,h]{R'OD} [PtCl(PMe_2Ph)_2\{C(OMe)(CD_2R)\}]^+ \quad (1)$$

$$trans\text{-}[PtCl(PMe_2Ph)_2\{C(OMe)(CH_2R)\}]^+ \xrightarrow[12\,h]{R'OH} [PtCl(PMe_2Ph)_2\{C(OR')(CH_2R)\}]^+ \quad (2)$$

exchanges alkoxy-groups [equation (2)].[3] Reaction (1) proceeds *via* reversible removal of H^+ to form an α-methoxyvinylplatinum intermediate. Reaction (2) involves nucleophilic attack of the entering alcohol at the carbenoid carbon atom. Both these processes seem likely to be enhanced by the positive charges of the complex ions. Also, when the chloride ions *trans* to the carbene ligands were replaced by ligands with less electron-withdrawing ability the rates of both reactions were decreased.[3]

Surprisingly, the H–D exchange reactions of our electroneutral complexes are extremely rapid by comparison. For example, when *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$ is treated with CD_3OD, exchange of the benzyl CH_2 hydrogens for deuterium is complete within 5 min. Any accompanying exchange of alkoxy-groups, however, is so slow as to be virtually non-existent. Thus, treatment of neutral ethoxy(organo)carbene complexes with methanol, or methoxy(organo)carbene complexes with ethanol, failed to show any signs of exchange (by monitoring the ^1H n.m.r. spectra of the mixtures) after 24 h at ambient temperatures. Exchange of methoxy-groups for CD_3O during treatment of the complexes with CD_3OD proceeded only to the extent of 10% after 72 h, during which time decomposition of the complexes had progressed to a similar



SCHEME 1 (*i*) MeOH; (*ii*) CD_3OD

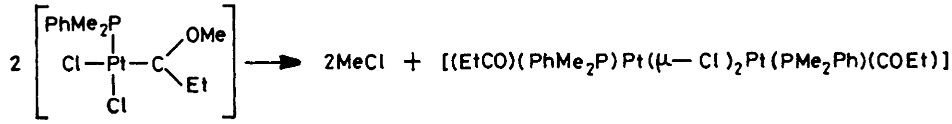
extent. The slow rate of alkoxide exchange at least is understandable in terms of the loss of the positive charge, in comparison with the rates for cationic derivatives.

The relative time scales of these two reactions has meant that a variety of partially deuteriated complexes can be isolated when deuteriated alcohols are used in the preparations (Scheme 1). This can aid spectroscopic assignments in these complexes.[1]

The rapid reaction rate for the H–D exchange steps of our electroneutral complexes suggests an enhanced acidity of the α-carbene carbon protons which is difficult to explain in view of the lack of overall positive charge. It seems unlikely that a different mechanism operates, however, since treatment of $[\mathrm{PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}}]$ with dimethylamine leads to proton abstraction and the formation of an ethoxyvinylplatinum complex [equation (3)]. Indeed this reaction serves to

$$[\mathrm{PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}}] + 2\mathrm{NMe_2H} \longrightarrow [\mathrm{PtCl(NMe_2H)(PMe_2Ph)\{C(OEt){=}CHPh\}}] + [\mathrm{NMe_2H_2}]\mathrm{Cl} \quad (3)$$

emphasise further these reaction rate differences between neutral and cationic complexes of this type. With cationic alkoxy(organo)carbeneplatinum(II) complexes, secondary amines readily liberate alcohol and produce amino(organo)carbene complexes;[4] only tertiary amines cause proton abstraction to form alkoxyvinylplatinum derivatives.[3]


(4)

$$2\,[\mathrm{PtCl_2(PMe_2Ph)\{C(OMe)Et\}}] \longrightarrow 2\mathrm{MeCl} + [\mathrm{(EtCO)(PhMe_2P)Pt(\mu\text{-}Cl)_2Pt(PMe_2Ph)(COEt)}] \quad (4)$$

An alternative view of the relationship between the cationic and neutral carbene complexes is that they are related simply by a change of ligand *cis* to the carbene. Replacing one tertiary phosphine of $[\mathrm{PtCl(PMe_2Ph)_2\{C(OMe)(CH_2Ph)\}}]^+$ by $\mathrm{Cl^-}$ effects the conversion into our neutral complex. It is thus apparent that the preceding reactions of co-ordinated carbene are affected at least as much by changing a *cis* ligand as they are by a change of those *trans*.[3] Moreover, the rates of the two reactions appear to be affected in opposite directions by this change of *cis* ligand, whereas variations of the *trans* ligands affect the rates in a similar way.[3]

Thermal Decomposition and the Effect of Ionic Halides.—Chloroform solutions of the neutral carbenechloro-complexes decompose slowly (*ca.* 20% after 24 h at 60 °C) by eliminating alkyl chloride to leave an acyl complex [reaction (4)]. The same chloride-bridged acyl complex was isolated from the reaction of $\mathrm{HgEt_2}$ with *cis*-$[\mathrm{PtCl_2(PMe_2Ph)(CO)}]$.[5] In both cases, if the acyl complex is allowed to remain in solution, further slow decomposition takes place resulting in a complex mixture of products which include *cis*-$[\mathrm{PtCl_2(PMe_2Ph)(CO)}]$ and *cis*-$[\mathrm{PtCl_2(PMe_2Ph)_2}]$. This tendency towards secondary decomposition is more pronounced in the cases of the alkoxy(benzyl)carbene complexes. Under the same conditions as above, the elimination of MeCl from $[\mathrm{PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}}]$, and of EtCl from $[\mathrm{PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}}]$, could be followed by ^{1}H n.m.r. spectroscopy, but no acyl derivatives could be isolated. Instead a variety of i.r. absorptions between 2 000 and 2 200 cm^{-1} suggested the formation of complexes with terminal carbonyls, and again $[\mathrm{PtCl_2(PMe_2Ph)(CO)}]$ and $[\mathrm{PtCl_2(PMe_2Ph)_2}]$ were eventually produced amongst other, as yet unidentified, decomposition products. The same product mixture resulted from the reaction of $\mathrm{Hg(CH_2Ph)_2}$ with $[\mathrm{PtCl_2(PMe_2Ph)(CO)}]$, indicating that the complications arose from secondary processes, and not from alternative primary reactions of the carbene complexes.

Ionic halides catalyse the decomposition of the carbene complexes, *via* alkylation of the halide. Thus, treatment of chloroform solutions of $[\mathrm{PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}}]$, at room temperature, with tetraethylammonium chloride caused 100% elimination of MeCl within 24 h. The i.r. spectra revealed the presence in solution of the usual variety of decomposition products.

Ionic halides cause similar reactions with the cationic complexes, liberating alkyl halides to leave acylplatinum complexes.[4] A similar effect is obtained by adding a tertiary phosphine to the neutral complexes [reaction (5)]. The first step is presumably the formation of an

$$cis\text{-}[\mathrm{PtCl_2(PMe_2Ph)\{C(OMe)R\}}] + \mathrm{PMe_2Ph} \longrightarrow trans\text{-}[\mathrm{PtCl(PMe_2Ph)_2(COR)}] + \mathrm{MeCl} \quad (5)$$

ionic carbene complex by $\mathrm{Cl^-}$ displacement. This chloride ion can then cause MeCl elimination, as has been reported.[4] In agreement with this sequence, when the reaction is carried out in the presence of silver trifluoromethanesulphonate, to remove the chloride ion from solution, the cation can be isolated almost quantitatively as its $[\mathrm{S(CF_3)O_3}]^-$ salt [equation (6)]. These cationic

$$cis\text{-}[\mathrm{PtCl_2(PMe_2Ph)\{C(OMe)R\}}] + \mathrm{PMe_2Ph} \xrightarrow{\mathrm{Ag[S(CF_3)O_3]}} trans\text{-}[\mathrm{PtCl(PMe_2Ph)_2\{C(OMe)R\}}][\mathrm{S(CF_3)O_3}] + \mathrm{AgCl} \quad (6)$$

carbene complexes are of the type isolated by Chisholm and Clark.[2] They can also be conveniently synthesised by treating acylbis(phosphine)platinum complexes with methylating agents such as methyl trifluoromethanesulphonate [equation (7)].

$$trans\text{-}[\mathrm{PtCl(PMe_2Ph)_2(COR)}] + \mathrm{MeSO_3CF_3} \longrightarrow trans\text{-}[\mathrm{PtCl(PMe_2Ph)_2\{C(OMe)R\}}][\mathrm{S(CF_3)O_3}] \quad (7)$$

The use of acyl(aryl) complexes leads to alkoxy(aryl)-carbene derivatives, which have not previously been prepared, since the acetylene–alcohol route is not applicable. The methylating agents $MeSO_3CF_3$, $MeSO_3F$, and $[OMe_3][PF_6]$ all failed to react with halide-bridged binuclear acyl complexes, $[(R'CO)(R_3P)Pt(\mu\text{-}X)_2Pt(PR_3)(COR')]$, however, so cationic binuclear organocarbene complexes could not be produced by this route (see below).

Halide-abstraction Reactions.—Removal of a halide ion from *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$ by $Ag[S(CF_3)O_3]$, $MeSO_3CF_3$, or $EtSO_3CF_3$ (as AgCl, MeCl, or EtCl respectively) led to a new binuclear halide-bridged cationic carbene complex, $[Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2\{C(OMe)Et\}_2][S(CF_3)O_3]_2$. The formation of the new complex in solution was followed by ^1H n.m.r. spectroscopy, by observing the growth of a new methoxy signal (with ^{195}Pt satellites) at δ 5.1 p.p.m. The other electroneutral carbene complexes form related products on halide abstraction. In no case, however, were we able to isolate the carbene complexes so formed, since they steadily react further by alkylating the $[S(CF_3)O_3]^-$ anion to produce, finally, the same mixture of acyls and/or terminal carbonylplatinum complexes which result from the thermal decomposition of the neutral complexes. Halogen abstraction from $[PtCl_2(PR_3)_2]$ by $MeSO_3F$ produces the related halide-bridged binuclear complexes, $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][SFO_3]_2$.[6]

Further evidence for the formulation of the binuclear complexes was derived from two bridge-splitting reactions performed on solutions of the complex before decomposition progressed. Treating the complex with $[NEt_4]Cl$ regenerated the original carbene complex. The addition of tertiary phosphine to the solution, on the other hand, allowed the isolation of cationic mononuclear carbene complexes, *trans*-$[PtX(PR_3)_2\{C(OR')R\}][S(CF_3)O_3]$.

Treatment of *cis*-$[PtCl_2(PEt_3)\{C(OEt)Pr^n\}]$ with $MeSO_3CF_3$ liberated MeCl to produce the binuclear carbene complex. On standing for 4 d at room temperature, $EtSO_3CF_3$ was observed in the reaction mixture. The formation of $MeSO_3CF_3$ or $EtSO_3CF_3$ from these complexes indicates that they are extremely powerful alkylating agents, and accounts for our failure to produce carbene complexes from $[Pt_2(\mu\text{-}Cl)_2L_2(COR)_2]$ by treatment with methylating agents, since the equilibrium lies well to the side of the acyls [equation (8)].

$$[Pt_2(\mu\text{-}Cl)_2L_2(COR)_2] + 2MeSO_3CF_3 \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2L_2\{C(OMe)R\}_2][S(CF_3)O_3] \quad (8)$$

This means that binuclear alkoxy(aryl)carbene complexes cannot be obtained; hence this route (by Cl^- addition) to electroneutral aryl derivatives is also not available.

In an attempt to isolate the binuclear carbene complexes, a number of experiments were performed using $Ag[PF_6]$ or $[OMe_3][PF_6]$. These were also unsuccessful. The normally unreactive $[PF_6]^-$ anion[7] degraded to PF_5 (and PF_3O and SiF_4, presumably from trace amounts of moisture and glass), and the usual mixture of acyls and carbonyl decomposition products resulted. The reason for the powerful alkylating ability of the binuclear complexes is not understood. Both the neutral and the cationic mononuclear alkoxy(organo)carbeneplatinum(II) complexes readily alkylate halide ions, but neither shows any tendency to alkylate $[S(CF_3)O_3]^-$.

The complicated relationship between the carbene complexes and metal acyls is summarised by Scheme 2.

EXPERIMENTAL

Infrared spectra of solid products as KBr discs were recorded on Perkin-Elmer 225 and 580 spectrophotometers, spectra of reaction mixtures in deuteriochloroform solution on a Perkin-Elmer 577 instrument (*ca*. 0.08 mol dm^{-3} solutions in 0.5 mm NaCl solution cells). Proton n.m.r. spectra were recorded in $CDCl_3$ solution using a Varian T-60 spectrometer, ^{31}P and ^{19}F n.m.r. spectra on a Varian XL-100 spectrometer. Microanalyses (C, H, and N) were performed on a Perkin-Elmer 240 analyser: for compounds containing deuterium, the sensitivity factor was corrected for the anticipated H : D ratio. The preparation and characterisation of the electroneutral complexes have been described previously.[1] Reactions were carried out under pure dry nitrogen.

Preparation of Partially Deuteriated Carbene Complexes.—To a chloroform solution (35 cm^3) of $[Pt_2Cl_4(PMe_2Ph)_2]$ (0.561 4 g) was added $PhC{\equiv}CH$ (0.20 cm^3) and CD_3OD (1 cm^3). The mixture was stirred for 18 h, when the solvent was removed. After treatment with benzene to remove soluble organic materials, the residue was recrystallised from CH_2Cl_2–Et_2O to yield *cis*-$[PtCl_2(PMe_2Ph)\{C(OCD_3)(CD_2Ph)\}]$, m.p. 127—128 °C (Found: C, 37.65; H + D, 4.65; Cl, 13.5. $C_{17}H_{16}Cl_2D_5OPPt$ requires C, 37.55; H + D, 4.85; Cl, 13.05%).

Treatment of this complex with MeOH produced *cis*-$[PtCl_2(PMe_2Ph)\{C(OCD_3)(CH_2Ph)\}]$, m.p. 121—122 °C, from CH_2Cl_2–Et_2O (Found: C, 37.55; H + D, 4.30; Cl, 13.4. $C_{17}H_{18}Cl_2D_3OPPt$ requires C, 37.71; H + D, 4.45; Cl, 13.1%). Treatment of the fully protonated complex with CD_3OD produced *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)(CD_2Ph)\}]$, m.p. 124—125 °C (Found: C, 37.95; H + D, 4.35; Cl, 13.0. $C_{17}H_{19}Cl_2D_2OPPt$ requires C, 37.8; H + D, 4.30; Cl, 13.15%).

Reaction of *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ *with* NMe_2H.—The complex (0.138 g) was dissolved in chloroform and excess of dimethylamine was added. The solution was stirred for 2 h, the solvent removed, and the oily residue pumped to remove unchanged amine. Treatment with benzene gave a small amount of a greyish solid, which was identified as $NMe_2H{\cdot}HCl$ by comparison of its i.r. spectrum with that of a genuine sample. Addition of n-pentane to the benzene solution caused precipitation of a white *solid*, $[PtCl(PMe_2Ph)(NMe_2H)\{C(OEt){=}CHPh\}]$, m.p. 175—176 °C, from diethyl ether (Found: C, 43.2; H, 5.30; N, 2.45. Calc. for $C_{20}H_{29}ClNOPPt$: C, 42.8; H, 5.20; N, 2.50%). The i.r. spectrum shows ν(NH) at 3 245 cm^{-1}, and the low value of ν(Pt–Cl) (277 cm^{-1}) suggests that Cl is *trans* to the vinyl group. The ^1H n.m.r. spectrum of the complex was complicated, indicating the presence of a mixture of isomers in solution.

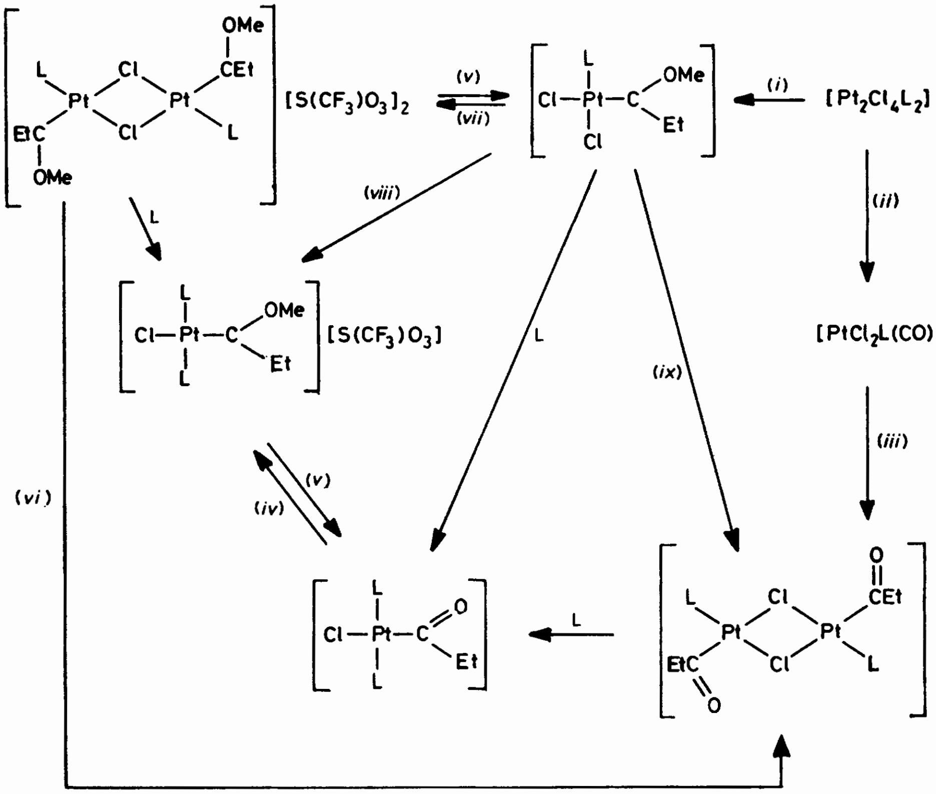
Di-μ-chloro-bis[(dimethylphenylphosphine)propionylplatinum(II)].—The complex *cis*-$[PtCl_2(PMe_2Ph)(CO)]$ (1.29 g, 298 mmol) was suspended in benzene (50 cm^3). Diethylmercury (0.32 cm^3, 0.78 g; 3.01 mmol) was added, and the solution was stirred for 1 h. The black solution was filtered, the solvent removed, and the residue pumped to remove trace amounts of unchanged $HgEt_2$. Ethylmercury(II) chloride was removed by sublimation at 55 °C (0.001 Torr) for 48 h.* The remaining brown solid was crystallised from benzene–pentane, then from methylene chloride–diethyl ether to yield colourless *crystals* of $[Pt_2Cl_2(PMe_2Ph)_2(COEt)_2]$, m.p. 136—138 °C, $\nu(C{=}O)$ at 1 654 cm^{-1} (Found: C, 31.2; H, 3.75; Cl, 8.80. $C_{22}H_{32}Cl_2O_2P_2Pt_2$ requires C, 31.0; H, 3.80; Cl, 8.35%).

Decomposition of cis-*Dichloro(dimethylphenylphosphine)[ethyl(methoxy)carbene]platinum*(II).—The complex (33.4 mg) was dissolved in $CDCl_3$ (2.5 cm^3) and the solution was heated in air at 60 °C for 5 d. The solution i.r. spectrum then showed the growth of an intense band at 1 654 cm^{-1}, due to $[Pt_2Cl_2(PMe_2Ph)_2(COEt)_2]$, and several weaker bands in the 2 000—2 200 cm^{-1} region. The ^1H n.m.r. spectrum showed a complex pattern in the phosphine methyl region, and the absence of a methoxy signal at δ 4.92 p.p.m. from the starting material.

After further standing at room temperature for 55 d, the ^{31}P n.m.r. spectrum showed the presence of *cis*-$[PtCl_2(PMe_2Ph)(CO)]$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ [$^1J(Pt-P)$ 2 850 and 3 550 Hz, respectively, identical to values from authentic samples] among other products. The solution i.r. spectrum no longer showed the presence of the binuclear acyl complex, but exhibited several bands in the 2 000—2 200 cm^{-1} region.

Reactions of *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$.—*With* $[NEt_4]Cl$. The complex (32.4 mg) was dissolved in methylene chloride (3 cm^3). Tetraethylammonium chloride (11.3 mg) was added and the solution stirred for 18 h. The ^1H n.m.r. spectrum showed the presence of methyl chloride (sharp singlet at *ca.* δ 3.0). The solvent was removed and the residue dissolved in $CDCl_3$. The total loss of the OMe signal at 4.92 p.p.m. showed the reaction to have gone to completion. The solution i.r. spectrum showed several bands in the 2 000—2 200 cm^{-1} region, identical to those present after thermolysis of *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$.

With $[NEt_4][S(CF_3)O_3]$. The complex (20.0 mg) was dissolved in $CDCl_3$ and $[NEt_4][S(CF_3)O_3]$ (2.7 mg, 0.25 equivalent) was added. After 5 d the ^1H n.m.r. spectrum was identical to that run immediately after $[NEt_4][S(CF_3)O_3]$ addition, corresponding entirely to a mixture of starting materials.



SCHEME 2 L = PEt_3 or PMe_2Ph. The geometry of the binuclear complexes has not been determined. (*i*) $MeC{\equiv}CMe$, MeOH; (*ii*) CO; (*iii*) $HgEt_2$; (*iv*) $MeSO_3CF_3$; (*v*) $[NEt_4]Cl$; (*vi*) $-MeSO_3CF_3$; (*vii*) $Ag[S(CF_3)O_3]$ or $MeSO_3CF_3$; (*viii*) $Ag[S(CF_3)O_3]$ + L; (*ix*) heat or $[NEt_4]Cl$

Reaction between *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$ *and* PMe_2Ph.—The complex (60.3 mg) in $CDCl_3$ (1 cm^3) was introduced into a n.m.r. tube. Dimethylphenylphosphine (18.1 µl) was added and the solution set aside for 24 h, by which time the OMe signal previously at δ 4.92 p.p.m. had vanished. The solvent was removed and the oily residue crystallised from methylene chloride–hexane solution by cooling to −78 °C, giving white crystals of *trans*-$[PtCl(PMe_2Ph)_2(COEt)]$, m.p. 128—129 °C, $\nu(C{=}O)$ at 1 635 cm^{-1}, $^1J(Pt-P)$ 3 175 Hz (Found: C, 40.55; H, 4.80; Cl, 6.80. $C_{19}H_{26}ClOP_2Pt$ requires C, 40.45; H, 4.85; Cl, 6.30%).

In the presence of $Ag[S(CF_3)O_3]$. The complex (49.5 mg) and $Ag[S(CF_3)O_3]$ (26.3 mg) were stirred together in pure chloroform (2 cm^3). After 2 min dimethylphenylphosphine (14.5 µl) was introduced, and the solution was stirred for

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* Throughout this paper: 1 Torr ≈ (101 325/760) Pa.

1 h, then filtered. The solvent was evaporated from the pale yellow filtrate. The oily residue was crystallised from CH_2Cl_2–Et_2O by cooling to −78 °C, to obtain white crystals of *trans*-$[PtCl(PMe_2Ph)_2\{C(OMe)Et\}][S(CF_3)O_3]$, m.p. 120—122 °C (Found: C, 34.8; H, 4.20; Cl, 4.75. Calc. for $C_{21}H_{30}ClF_3O_4P_2PtS$: C, 34.65; H, 4.15; Cl, 4.85%). The methoxy-group at δ 4.92 p.p.m. showed J(Pt–H) of 8.5 Hz.

trans-*Chloro[methoxy(phenyl)carbene]bis(triethylphosphine)platinum*(II) *Trifluoromethanesulphonate*.—To a solution of *trans*-$[PtCl(PEt_3)_2(COPh)]$ [8] (1.147 g) in chloroform (50 cm^3) was added methyl trifluoromethanesulphonate (0.230 cm^3) and the solution stirred for 48 h. The solvent was removed to leave an oily orange-brown material which solidified on standing. This was dissolved in methanol and filtered. Addition of diethyl ether caused precipitation of colourless *crystals* of *trans*-$[PtCl(PEt_3)_2\{C(OMe)Ph\}][S(CF_3)O_3]$ (0.688 g, 47%), m.p. 126—127 °C (Found: C, 34.15; H, 5.15; Cl, 4.90. Calc. for $C_{21}H_{38}ClF_3O_4P_2PtS$: C, 34.25; H, 5.20; Cl, 4.80%). The ^1H n.m.r. spectrum showed the methoxy-group at δ 5.2 p.p.m., J(Pt–H) 9.5 Hz.

Similar reactions were carried out using $MeSO_3F$ or $[OMe_3][PF_6]$ instead of $MeSO_3CF_3$ as methylating agent. Related ionic carbene complexes were produced in each case, but the yields were poorer than above. Similarly, *trans*-$[PtCl(PMe_2Ph)_2\{C(OMe)Et\}][S(CF_3)O_3]$ was prepared by treating a chloroform solution of *trans*-$[PtCl(PMe_2Ph)_2(COEt)]$ with $MeSO_3CF_3$.

Reaction of cis-$[PtCl_2(PEt_3)\{C(OEt)Pr^n\}]$ *with* $MeSO_3CF_3$.—Two drops of $MeSO_3CF_3$ were added to a $CDCl_3$ solution of the complex in a n.m.r. tube. After *ca.* 24 h the presence of methyl chloride was observed in the ^1H n.m.r. spectrum. After 96 h the volatile fraction was transferred *in vacuo* to another vessel. The n.m.r. spectrum showed the presence of $EtSO_3CF_3$ [δ 4.7 (q), J 7; 1.6 (t) p.p.m., J 7 Hz], by comparison with an authentic sample.

In a similar experiment, *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$ (18.7 mg) was dissolved in $CDCl_3$ and 1 equivalent of $EtSO_3CF_3$ (5.1 μl) was added. On standing for 6 d the ^1H n.m.r. spectrum showed the presence of EtCl, as well as several other peaks in the δ 3.0—4.5 p.p.m. region. One of these corresponded to the singlet produced by $MeSO_3CF_3$. The OMe peak had diminished considerably. The i.r. spectrum of the solution at this stage showed a strong band at 1 654 cm^{-1} due to the formation of $[Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2(COEt)_2]$.

Reactions of cis-$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$.—*With* $MeSO_3CF_3$, *followed by* $[NEt_4]Cl$. The complex (*ca.* 20 mg) was dissolved in $CDCl_3$ and two drops of $MeSO_3CF_3$ were added. The ^1H n.m.r. OMe signal, originally at δ 4.92 p.p.m., was replaced by a new signal at *ca.* 5.1 p.p.m. (slightly broadened), and a strong singlet at 3.0 p.p.m., due to methyl chloride, was observed after 24 h. The solvent was removed and excess of $MeSO_3CF_3$ pumped away. The residue was dissolved in fresh $CDCl_3$ and excess of $[NEt_4]Cl$ was added. A 1 : 4 : 1 triplet was observed at 4.9 p.p.m. due presumably to re-conversion to *cis*-$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$.

With $Ag[S(CF_3)O_3]$ *followed by* PMe_2Ph. The complex (17.6 mg) was dissolved in $CDCl_3$ and $Ag[S(CF_3)O_3]$ (9.5 mg) was added. The solution was stirred for 1.5 h and the precipitated silver chloride was filtered off. The ^1H n.m.r. spectrum showed a broadened OMe signal at δ 5.1 p.p.m. One mol equivalent of PMe_2Ph (5.3 μl) was introduced. After 21 h the n.m.r. spectrum showed a broadened triplet at 4.8 p.p.m., and a 1 : 2 : 1 triplet in the phosphine methyl region, indicating the formation of *trans*-$[PtCl(PMe_2Ph)_2\{C(OMe)Et\}][S(CF_3)O_3]$ (by comparison with an authentic sample).

With $[OMe_3][PF_6]$: *isolation of* $[Pt_2Cl_2(PMe_2Ph)_2(COEt)_2]$. The complex (39.7 mg) was dissolved in deuteriochloroform and added to a n.m.r. tube containing $[OMe_3][PF_6]$ (17.0 mg). The tube was then sealed. After 3 h, Me_2O and MeCl were evident from the ^1H n.m.r. spectrum. After 5 d, quantitative reaction had occurred, and the OMe signal of the starting complex had been replaced by a broadened signal at δ 5.1 p.p.m. After 12 d the ^{19}F n.m.r. spectrum showed the presence of $[PF_6]^-$, PF_5, PF_3O, and SiF_4 (the last two being formed from PF_5 by reaction with trace amounts of moisture and with glass [7]). Removal of the solvent and recrystallisation of the residue from MeOH–Et_2O (1 : 1) produced crystals of $[Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2(COEt)_2]$, m.p. 137—138 °C, i.r. spectrum identical to that of an authentic sample.

We thank Dr. D. S. Rycroft of this Department for ^{19}F and ^{31}P n.m.r. spectra, Johnson, Matthey and Co. Ltd. for a loan of platinum halides, and the S.R.C. for a maintenance award (to G. K. A.).

[8/812 *Received*, *2nd May*, 1978]

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