Nucleophilic Attack on Olefins co-ordinated to Platinum. Part 4.[1] Formation of Neutral and Cationic σ-Adducts and of Ring Compounds: Studies of Stability

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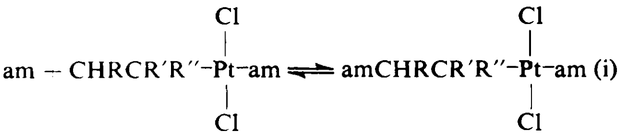
Attack by amines (am) on alkene complexes, *cis*-[$PtCl_2(\eta^2\text{-}C_2H_4)Y$], can lead to neutral acyclic, cationic acyclic, and ring compounds, *i.e.* *cis*-[$PtCl_2(CH_2CH_2am)Y$] (Y = Me_2SO or PPh_3), [PtCl(am)-($CH_2CH_2am)Y]^+Cl^-$ (Y = NH_3, pyridine, or Me_2SO), and [$PtCl(CH_2CH_2am_{-H})Y$] (Y = PPh_3, Me_2SO, or $NHMe_2$). Two isomers of the second compound exist in solution. New compounds of these types are prepared and characterised and others identified in solution. Methods of distinguishing between the species are investigated. The ring compounds can be identified from the value of δ(NC*H*CHPt). Equilibrium studies show that in most instances the neutral acyclic compounds are readily converted to the cationic acyclic species by excess amine. This has the effect of making the starting *cis*-dichloro(alkene) complexes more susceptible to nucleophilic attack than their *trans* analogues. Ring compounds are more likely to be formed if am is bulky. Values of $\Delta H^\ominus$ and $\Delta S^\ominus$ have been measured for the formation of the cationic species for Y = 4-methylpyridine and am = $NHMe_2$ for various alkenes. Some comments are made on the stability of cationic alkene complexes. A novel photochemical method is described experimentally for the preparation of some of the starting *cis*-dichloro(alkene) complexes from their *trans* isomers.

Many studies have been made of the attack of amines (am) † on olefins co-ordinated to platinum(II) and of the ensuing $\pi \longrightarrow \sigma$ rearrangement leading to the formation of σ-(2-ammonioalkanide) compounds (see refs. 1—10 of Part 3 [1]). If the platinum complex involved is a *trans*-[$PtCl_2(am)(\eta^2\text{-}CHR{=}CR'R'')$] (1) system, then the overall reaction is simple with only one type of immediate product (2), as in equation (i). However, if the starting platinum–alkene complex is a *cis*-dichloro-system (3), further types of compounds may also be formed rapidly in addition to the neutral σ species (4) (Scheme). One cationic σ-ethanide species (5) [2-4] can be produced as a result of the *trans*-labilizing effect of the σ-CH_2 group and a second (6) can be formed if the ligand Y also has this property. Moreover a ring compound (7) [4-6] may be produced. Similar behaviour is observed in analogous platinum–allene systems.[7-9]



$$\mathrm{am-CHRCR'R''-\underset{Cl}{\overset{Cl}{Pt}}-am} \rightleftharpoons \mathrm{amCHRCR'R''-\underset{Cl}{\overset{Cl}{Pt}}-am} \quad \text{(i)}$$

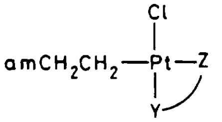
(1) (2)

Unfortunately species (4)—(7) are rather similar in some of their properties. Therefore an initial aim of this investigation was to find means of identifying and distinguishing (4)—(7). This was followed by a study of the ease of formation of each of the species and of their relative stabilities. As compounds tend to be labile in solution, ^1H n.m.r. and u.v. spectroscopy have proved to be particularly useful since data are acquired relatively rapidly using these techniques.

Variations are made of am, Y, R, R', and R'' with three points in mind. First, it has been suggested that in the alkene–PPh_3 systems studied here [5] and in the closely related allene–PPr^n_3 compounds,[8] the tendency to cyclize is increased by steric factors. Secondly, addition of am can in these systems be either Markovnikoff or anti-Markovnikoff, that is either at the more or less substituted carbon of the C=C ligand respectively.[1,10] Lastly, we were interested in extending our studies [1,11] on how equilibrium constants were affected by changes in the groups mentioned.

Results and Discussion

New Compounds.—Three neutral σ-compounds, (4), have been characterized, *cis*-[$PtCl_2(CH_2CH_2NH_2Me)(Me_2SO)$], *cis*-[$PtCl_2(CH_2CH_2NEt_3)(Me_2SO)$], and *cis*-[$PtCl_2(CH_2CH_2NEt_3)(PPh_3)$]. Although several neutral σ-ammonioethanide complexes have been isolated which contain either *trans*-dichloro-ligands, as in (2) (see refs. 1, 2, 8, and 9 of ref. 11),[1,11] or bidentate groups, Y–Z, such as acetylacetonate, pyridine-2-carboxylate, or 8-quinolinate [see compound (8)],[12] the present compounds appear to be the first to be fully characterized which are based on a *cis*-dichloro(monoalkene) system.



(8)

Three σ-cationic compounds (5) have been prepared satisfactorily: [$PtCl(NH_2Bu^t)(CH_2CH_2NH_2Bu^t)Y]^+Cl^-$ (Y = NH_3, py, or Me_2SO). These join four similar chlorides (5) prepared by Natile,[2] where am and Y are 3,5Me_2-py (3,5-dimethylpyridine) and/or $CHMePhNH_2$. The new compounds will be shown later to contain the cation (5) rather than its isomer (6). They are soluble in water. The chlorides of (5; am = NH_2Bu^t, Y = NH_3 or py) have ionic conductances at infinite dilution at 25 °C in water of 101 and 98 Ω^{-1} cm^2 mol^{-1} respectively. {A value of 110 Ω^{-1} cm^2 mol^{-1} was found for K[$PtCl_3(\eta^2\text{-}C_2H_4)$].} These quantities are typical of 1 : 1 electrolytes containing one large ion.[13,14]

With regard to cyclic compounds (7), we now have a satis-

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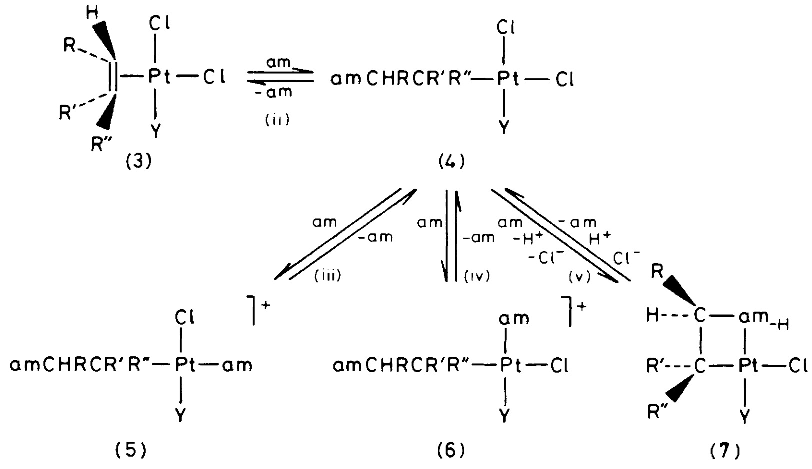
† Abbreviations: am = amine, am_{-H} = deprotonated amine, morph = morpholine, py = pyridine, pip = piperidine, pyr = pyrrolidine, i-quin = isoquinoline.



Scheme.

factory elemental analysis for [PtCl(Me$_2$SO)(CH$_2$CHEt^{15}NMe$_2$)], which previously we had identified in solution (CDCl$_3$) using ^{195}Pt n.m.r. and ^{15}NHMe$_2$,[6] a technique that had also been used to detect [PtCl(PPh$_3$)(CH$_2$CH$_2$^{15}NMe$_2$)] [5] and [PtCl(^{15}NHMe$_2$)(*Z*-CHMeCHMe^{15}NMe$_2$)].[6] Thus, as Panunzi and co-workers [4] have characterized, by elemental analysis and osmometry, [PtCl(PPh$_3$)(CH$_2$CHRNMe$_2$)] (R = H, Me, or Et) and [PtCl(Me$_2$SO)(CH$_2$CH$_2$NMe$_2$)], there are now six cyclic compounds (7) which have been clearly identified.

Two new ' double ' compounds will be described later.

Hydrogen-1 *N.M.R. Studies.*—Earlier work in this series of experiments has indicated that there were many more species present in solution, which either could not be analysed (due to deliquescence for example) or even isolated as solids. As far as identifying species in solution, the ^{15}N-labelled amines used before are expensive and ^{195}Pt n.m.r. is too lengthy a procedure for labile entities. Therefore in order to investigate in solution the existence and interconversion of (4), (5), (6), and (7), relatively rapid means of study are needed. Hydrogen-1 n.m.r. and u.v. spectroscopy proved particularly convenient, the first technique being useful in three areas: detecting ring compounds, deciding whether attack is Markovnikoff or anti-Markovnikoff, and distinguishing between the cationic isomers (5) and (6).

In Table 1 are given δ values for the NC*H*CHPt resonance for all the ring compounds and acyclic species mentioned above (apart from those in which am is a pyridine, which will be discussed later). Without exception, this resonance occurs at δ 3.7—4.5 in the cyclic species as opposed to δ 2.2—3.2 in the others. Thus we have a rule for distinguishing (7) from (4), (5), or (6).

The rule is strengthened by the following observations. If an excess of NEt$_3$, or of any of the amines (am) cited in Table 2 where Y = Me$_2$SO, is added to the alkene complex (3; R = R′ = R″ = H, Y = Me$_2$SO) in CDCl$_3$ at *ca.* 25 °C, a characteristic NC*H*$_2$CH$_2$Pt triplet with satellites [11] appears between δ 3.0 and 3.3 within manipulation time. This is still present after *ca.* 30 min if am is NEt$_3$ or any of the primary amines in Table 2. In contrast, if am is secondary, this absorption is replaced by an analogous one between δ 4.4 and 4.6, in this time interval. The spectra obtained when am is NEt$_3$ and NH$_2$Bu^t are identical (apart from peaks due to excess amine) with those of authentic *cis*-[PtCl$_2$(CH$_2$CH$_2$NEt$_3$)(Me$_2$SO)] and *cis*-[PtCl(NH$_2$Bu^t)(CH$_2$CH$_2$NH$_2$Bu^t)(Me$_2$SO)]$^+$Cl$^-$, the neutral and cationic acyclic species. That obtained with NHMe$_2$ immediately after mixing is similar in the NC*H*$_2$CH$_2$Pt region to those above, pointing to the formation of an acyclic compound; however, the new spectrum formed after 30 min is the same as that of the ring compound, [PtCl(Me$_2$SO)(CH$_2$CH$_2$NMe$_2$)]. It is difficult to find an alternative explanation for these data to the supposition that all the amines react rapidly with the starting alkene–Me$_2$SO complex to give one or more acyclic complexes, that in the case of the secondary amines a second slower reaction takes place in which a ring compound is formed, and that the rule about the position of the NC*H*CHPt resonance given above is correct.

Table 1. Hydrogen-1 n.m.r. data for NC*H*CHPt protons in neutral σ, cationic σ, and cyclic compounds [Pt–H and H–H coupling constants (Hz) are given in square brackets; R = R′ = R″ = H, except where stated otherwise]

Compound	δ/p.p.m.
(4; am = NH$_2$Me, Y = Me$_2$SO) [a]	
(4; am = NEt$_3$, Y = Me$_2$SO)	3.16 (t) [63, 7]
(4; am = NEt$_3$, Y = PPh$_3$)	2.3 (c)
(5; am = NH$_2$Bu^t, Y = NH$_3$) [b]	3.15 (t) [40, 9]
(5; am = NH$_2$Bu^t, Y = py) [b]	2.75 (t) [44, 7]
(5; am = NH$_2$Bu^t, Y = Me$_2$SO) [b]	3.12 (t) [65, 6]
(7; am = NHMe$_2$, Y = PPh$_3$) [c]	4.25 (t) [60, 8]
(7; am = NHMe$_2$, R = Me, Y = PPh$_3$) [d]	4.20 (c)
(7; am = NHMe$_2$, R or R′ = Et, Y = PPh$_3$) [d,e]	4.0
(7; am = NHMe$_2$, Y = Me$_2$SO)	4.46 (t) [67, 8]
(7; am = NHMe$_2$, R = Et, Y = Me$_2$SO)	4.05 (c)
(7; am = Y = NHMe$_2$, R = R′ = Me)	3.72 (c)

[a] Too insoluble in CDCl$_3$ and [^{2}H$_6$]acetone for study. [b] These are presumed to be isomer (5) rather than (6) because of the absence of *Pt*NCC*H* coupling (see text). [c] From ref. 5. [d] From ref. 4. [e] Isomeric mixture with either R or R′ = Et.

The criterion of the δ value for the NC*H*CHPt enables studies to be made on what happens when an excess of amine is added to other starting alkene complexes (3) (in CDCl$_3$ at

Table 2. Hydrogen-1 n.m.r. data: NC*H*CHPt resonances produced by adding excess amine to ethene complexes (3; R = R′ = R″ = H)

Y	am	δ/p.p.m.	*J*/Hz
CH_3CN	NH_2Bu^t, $NHMe_2$	2.9—3.1	40—44
NH_3	NH_2Pr^n, NH_2Bu^t, $NHMe_2$	3.0—3.2	40—44
$NHMe_2$	NH_2Pr^i, $NHMe_2$	2.8—3.0	40—45
$CH_2PhNHMe$	NH_2Bu^t, $NHMe_2$, $CH_2PhNHMe$	2.7—3.0	40—45
p-$O_2NC_6H_4NH_2$	NH_2Bu^t	2.95	
	$NHMe_2$, $NHEt_2$	4.5	56
py	NH_2Bu^t, $NHMe_2$	2.75—3.0	40—44
4Me-py	$NHMe_2$	2.9	44
i-quin	NH_2Pr^n, NH_2Pr^i, NH_2Bu^n, NH_2Bu^t, CH_2PhNH_2, $NHMe_2$, $NHEt_2$, $NHPr^n_2$, pip, pyr, morph	2.8—3.4	42—43
PPh_3	NH_2Pr^n, CH_2PhNH_2	2.2—2.4	
	NH_2Bu^t	4.35	60
	$NHMe_2$, $NHEt_2$, $NHPr^n_2$, $NHBu^n_2$, $CH_2PhNHMe$, pip, pyr, morph	4.1—4.4	60—75
Me_2SO	NH_2Pr^n, NH_2Pr^i, NH_2Bu^n, NH_2Bu^t, NH_2Bu^s, NH_2Bu^t, $NH_2(C_5H_9)$, $NH_2(C_7H_{13})$	3.0—3.3	60—66
	$NHMe_2$, $NHEt_2$, $NHPr^n_2$, $NHBu^n_2$, pip, pyr, morph	4.4—4.6	62—67
pip	pip	*ca.* 3.0	42

ca. 25 °C). Resonances, typical of the acyclic σ species, appear within *ca.* 5 min and usually within the manipulation time needed to run a ^1H n.m.r. spectrum. Any peaks at δ 4 characteristic of a ring compound tend to be formed more slowly (if they are produced at all), but cyclization is complete within 30 min. Table 2 lists δ values of NC*H*CHPt resonances for mixtures which have stood for this period of time. It can be seen that the resonances still fall into two clear groups with δ 3.7—4.5 and with δ 2.2—3.2, indicating the formation of cyclic and acyclic complexes respectively.

It has been suggested that bulkiness in am and Y favours the formation of ring compounds, where otherwise acyclic products would be formed.[5] However, Table 2 shows that this statement is questionable as far as Y is concerned. Certainly the CH_3CN-, NH_3-, and $NHMe_2$-containing compounds are acyclic as would be expected for a small Y, and several of the ring compounds contain the large PPh_3 group, but on the basis of the size argument the presence of $CH_2PhNHMe$, i-quin, or pip ligands also ought to lead to cyclic compounds (which are not produced). Nevertheless, if for a particular Y there is any tendency for rings to be formed, it occurs if am is secondary as opposed to primary, and sometimes if it is NH_2Bu^t. Thus the bulkiness postulate does seem applicable to am. Shaw and co-workers [8] have made a somewhat similar observation on the closely related allene complex *cis*-$[PtCl_2(\eta^2\text{-}CH_2{=}C{=}CH_2)(PPr^n_3)]$, which gives a four-membered ring if am is NH_2Bu^t but not if it is a less bulky amine. The tendency for the secondary amines to induce cyclization provides an example of the Thorpe–Ingold *gem*-dialkyl effect.

No data are included in Table 2 for the acyclic species in which am is py. Table 3 shows that δ for pyC*H*CHPt lies within the range for cyclic compounds and so appears to violate the rule given above. However, py is known to move the NC*H* resonance upfield in the *trans*-dichloro-species (3) [11] (which are acyclic) so that it would be very awkward if the same did not happen in the present *cis*-dichloro-systems also.

Hydrogen-1 n.m.r. data also enable a distinction to be made between Markovnikoff and anti-Markovnikoff addition. In the *trans*-dichloro-compounds (2) the positions of the NC*H*CHPt and the NCHC*H*Pt peaks depend on whether they are due to C*H*$_2$ or C*H*(alkyl) protons.[1] In Table 3, δ values are given for these resonances for the cationic σ-isomer mixtures (5 and 6; am = py, Y = Me_2SO; various R, R′, and R″) produced when excess py is added to the corresponding alkene complex (3) in $CDCl_3$ at *ca.* −20 °C. It can be seen that py adds at the more substituted position despite steric hindrance, as in a Markovnikoff addition. Although some anti-Markovnikoff product could pass unnoticed, integrations of the supposed NC*H* and C*H*$_2$Pt peaks when R is Me or Et confirm that at least 80% of the addition is Markovnikoff. The same is true of related compounds containing this range of R groups.[1,10]

Table 3. Hydrogen-1 n.m.r. data for the NC*H*CHPt and NCHC*H*Pt resonances of (5; am = py, Y = Me_2SO) and (6; am = py, Y = Me_2SO), with various R, R′, and R″, in $CDCl_3$ at *ca.* −20 °C

R	R′	R″	Ethanide group	δ (NC*H*)	δ (C*H*Pt)
H	H	H	NCH_2CH_2Pt	4.76	1.9
Me	H	H	$NCH(Me)CH_2Pt$	5.05	2.18
Et	H	H	$NCH(Et)CH_2Pt$	5.08	2.28
Me	H	Me	$NCH(Me)CH(Me)Pt$	5.22	3.00
Me	Me	H	$NCH(Me)CH(Me)Pt$	5.28	2.6

Distinguishing between neutral and cationic σ species using ^1H n.m.r. depends on resolving and identifying C*H* resonances of as many as five possible am groups. While we [3] have done this in the case of (4) and (5) for am = Y = 4Me-py (4-methylpyridine), u.v. spectroscopy provides a much quicker method of following the formation of (4) and of (5) or (6), see later. However, there is a criterion which can be used to distinguish cationic σ isomers (5) and (6) in solution, namely *Pt*NC*H* coupling in the Pt–am group. Normally for this interaction, *J* = *ca.* 40 Hz, *e.g.* in *trans*-$[PtCl_2(\eta^2\text{-}CHR{=}CR'R'')(am)]$ compounds (see SUP 23054 of ref. 1), but earlier we observed [15] that it is absent in the σ compounds (2), and suggested that it was in some way suppressed when the Pt–am group is *trans* to a σ-CH ligand. This suggests that coupling might be observed when am is *trans* to Y as in (6), but not in isomer (5) when it is *trans* to CH. Compound (6) would not be expected to be formed rapidly on adding excess amine to (3) unless Y is *trans*-labilising, *e.g.* Me_2SO or PPh_3. When an excess of pyridine is added to (3; Y = Me_2SO) in $CDCl_3$ at *ca.* −20 °C, H^α proton resonances of py are seen, some of which have platinum satellites, while others do not (see Table 4), pointing to the formation of both (5) and (6). Compounds of this system appear to be stable at −20 °C, but they decompose on standing at *ca.* 25 °C. Both isomers can also be detected in the homologous systems listed in Table 3 (am = py, Y = Me_2SO; R = Me or Et, R′ = R″ = H; R = R′ = Me, R″ = H; and R = R″ = Me, R′ = H) formed in the same way at −40 °C, while in the complicated spectrum pro-

Table 4. Hydrogen-1 n.m.r. data [δ values, and $J(Pt\text{NC}H)$/Hz in square brackets] [a] of H^{α} (py) for isomers (5) and (6) ($R = R' = R'' = H$)

Compound	T/°C	δ (*py*CHCHPt)	δ (*trans*-CHPt*py*)	δ (*cis*-CHPt*py*)
(4; am = py, Y = Me_2SO)	−20	8.88		
(5; am = py, Y = Me_2SO)	−20	8.55	9.58	
(6; am = py, Y = Me_2SO)	−20	8.55	8.95	8.95 [36]
(4; am = Y = 4Me-py) [b]	25	8.45		
(5; am = Y = 4Me-py) [b]	25	8.36	9.27	8.7 [40]
(5; am = py, Y = PPh_3)	−20		9.12	
(6; am = py, Y = PPh_3)	−20			8.96 [40]

[a] Platinum satellites are only observed on peaks in the last column. [b] From ref. 4.

duced from excess py and (3; Y = PPh_3) at −20 °C, two H^{α} (py) peaks can be discerned, one with and the other without platinum satellites.

From the range of compounds indicated in Table 2 we found no evidence of *Pt*–N–C*H* coupling to suggest the formation of (6) when am is a primary or secondary aliphatic or acyclic amine. Therefore although this criterion cannot be used on the NH_2Bu^t compounds characterized earlier, we consider by analogy that they contain isomer (5) rather than (6). In any case two of them contain Y (*viz.* NH_3 or py) which are not *trans*-labilizing, so that it is doubtful whether (6) could form in the time available.

Two Possible Double Compounds.—In the Experimental section the preparation is described of a compound which analyses as a σ-cationic complex, $[PtCl(NHMe_2)(CH_2CHEtNHMe_2)(Me_2SO)]^+Cl^-$. However, an alternative isomer is the double compound $[\overline{\text{PtCl(Me}_2\text{SO)(CH}_2\text{CHEtN}}\text{Me}_2)][\text{Me}_2\text{NH}_2]^+\text{Cl}^-$. The second formulation is probably correct since the substance produces a ^1H n.m.r. signal at *ca.* δ 4.2 and since recrystallization gives authentic $[\overline{\text{PtCl(Me}_2\text{SO)(CH}_2\text{CHEtN}}\text{Me}_2)]$. A similar possible double compound can be produced from the cyclic system (7; $R = R' = R'' = H$, am = $NHMe_2$, Y = PPh_3).[5] In neither case is there any difference in the ^1H and ^{195}Pt n.m.r. spectra between the double compound and the corresponding ring complex (apart from the ^1H resonances due to $Me_2NH_2^+$).

Ultraviolet Studies.—The equilibrium constant for a system such as the equilibrium (vi) can be obtained by adding B to A,

$$A + nB \rightleftharpoons AB_n \qquad \text{(vi)}$$

noting the resulting absorbance, and plotting graphs, which should be linear, of either (*a*) $(A_0 - A_x)/(A_x - A_\infty)$ against $[B]^n$ or (*b*) $1/|A_0 - A_x|$ against $1/[B]^n$ where A_0, A_x, and A_∞ are absorbances after addition to a solution of A of zero, an aliquot, and a large excess of amine respectively.[11]

Such studies were made on the following systems with $R = R' = R'' = H$: (3; Y = Me_2SO) + primary amines, (3; Y = i-quin) + primary amines, and (3; Y = 4Me-py) + 4Me-py. In the last case R was also varied between H, Me, and Et. Changes in the u.v. spectra show that equilibrium is established within *ca.* 5 min. The ^1H n.m.r. data presented earlier suggest that in these systems both (4) and (5) may be produced, but not (6). Good linear graphs were obtained in all cases on plotting $(A_0 - A_x)/(A_x - A_\infty)$ *versus* $[\text{am}]^2$ when [am] > [Pt]. This appears to indicate a stoicheiometry

$$(3) + 2\,\text{am} \rightleftharpoons (5) + Cl^- \qquad \text{(vii)}$$

Pt : am of 1 : 2 as in reaction (vii). However methods (*a*) and (*b*) both break down if species other than just AB_n are produced on the right-hand side of the equilibrium (vi), which is what occurs in reaction (vii) as written. Nevertheless, better linear graphs were obtained by using method (*a*) in its simplest form as above, than by introducing modifications to it to allow for the production of Cl^-. The fact that the simple plots are linear suggests that Cl^- is not formed as an entity discrete from compound (5) in $CDCl_3$, the aprotic solvent which was used in these experiments.

Table 5. Data [a] for equilibria (ii) and (vii) in $CHCl_3$ at 25.0 °C ($R = R' = R'' = H$)

	Y = Me_2SO			Y = i-quin
am	K_{ii}/$\text{dm}^3\ \text{mol}^{-1}$	K_{vii}(rel.) [b]	K_{iii}(rel.) [c]	K_{vii}(rel.)
NH_2Pr^n	50	1	1	11
NH_2Pr^i	28	0.7	1.3	
NH_2Bu^n	38	0.9	1.3	0.9
NH_2Bu^i	19	0.2	0.7	0.1
NH_2Bu^s	19	0.2	0.7	
NH_2Bu^t	14	0.4	1.6	
$NH_2(C_5H_9)$	28	0.7	1.3	
$NH_2(C_7H_{13})$	8	0.6	3.9	
$NHMe_2$				6
$NHEt_2$				0.7
$NHPr^n_2$				0.2
pip				20
pyr				12

[a] All approximate. [b] K_{vii}(rel.) = $K_{\text{vii}}/(K_{\text{vii}}$ for am = NH_2Pr^n, Y = Me_2SO). [c] K_{iii}(rel.) = $(K_{\text{vii}}/K_{\text{i}})/[K_{\text{vii}}/(K_{\text{i}}$ for am = NH_2Pr^n, Y = Me_2SO)].

In the two systems with Y = Me_2SO or i-quin, the gradients obtained using method (*a*) all lie between 10^5 and 10^7 $\text{dm}^6\ \text{mol}^{-2}$. Unfortunately these figures are far too large to be interpreted as reliable absolute values of K_{vi}; however, since K_{vii} is simply the gradient of a graph, reasonably reliable relative values, K_{vii} (rel.), can be obtained, which are given in Table 5. The data suggest that there is a steric effect, small for the Me_2SO system and somewhat greater if Y = i-quin, bulky groups displacing equilibrium (vii) to the left. A similar effect has been observed in equilbrium (i), with alicyclic amines behaving as non-bulky groups (as pip and pyr do here).[11]

In the system with Y = 4Me-py, the gradients are small enough to be interpreted as K_{vii} and values are given in Table 6. Introduction of substituents, R, displaces the equilibrium to the left, the effect being determined by $\Delta S^{\ominus}_{\text{vii}}$ becoming more negative. If the variation in $\Delta H^{\ominus}_{\text{vii}}$ is significant, the changes in this term as R becomes more bulky operate in the opposite direction. As R is probably too remote from the centre of substitution to affect equilibrium (iii), similar trends are probably present in K_{ii}, $\Delta H^{\ominus}_{\text{ii}}$, and $\Delta S^{\ominus}_{\text{ii}}$. If this is true, then there is a parallel with related system (i); K_{i}, $\Delta H^{\ominus}_{\text{i}}$, and $\Delta S^{\ominus}_{\text{i}}$ all decrease in the sequence R = H, Me, and Et.[1]

Table 6. Thermodynamic data for equilibrium (vii) for (3; am = Y = 4Me-py, R′ = R″ = H), at 25 °C in $CHCl_3$

R	K_{vii}/ dm^6 mol^{-2}	$\Delta H^{\ominus}_{vii}$/kJ mol^{-1}	$\Delta S^{\ominus}_{vii}$/J K^{-1} mol^{-1}
H	1 131	-25 ± 4	-28 ± 4
Me	576	-27 ± 6	-40 ± 2
Et	371	-29 ± 5	-49 ± 5

Attempts were also made using the same three systems to obtain direct evidence for equilibrium (ii) by studying change in absorbance when [am] < [Pt]. In the cases where Y = i-quin or 4Me-py, linear graphs are obtained using method (*b*) on plotting $1/(A_0 - A_x)$, not against 1/[am], but against $1/[\mathrm{am}]^2$. This implies that the neutral σ-species has a strong tendency to disproportionate into the starting alkene compound and the cationic σ-complex. However, the ^{1}H n.m.r. experiments described earlier (where [Pt] is much greater) have provided evidence for the neutral species (4; Y = 4Me-py). When Y = Me_2SO, 1/[am] does lead to a linear plot. Unfortunately, however, the intercepts are very small so that the resulting values of K_{ii} (which is equal to intercept/gradient) must be regarded only as semi-quantitative, see Table 5. However, the data do once again follow the trend shown by reaction (i),[11] that increase in the bulkiness of am displaces the equilibrium slightly to the left.

The data above indicate that for the Me_2SO systems K_{viii} (see below) lie in the range 10^3—10^6. These large values illustrate the readiness of the neutral compound to ' disproportionate ' into an alkene complex and the cationic species.

$$(4) + (4) \rightleftharpoons (3) + (5) \text{ or } (6) \qquad \text{(viii)}$$

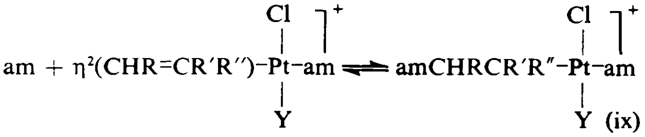
Tertiary amines tend to produce insoluble materials when added to the starting alkene complexes (3). However, changes in absorption can be studied satisfactorily when triethylamine is added to (3; Y = Me_2SO). Linear graphs were obtained using method (*a*) and plotting am (to the first power) even when [am] ≫ [Pt]. Thus this particular tertiary amine has little tendency to form a cationic σ-complex (5) or (6), preferring to produce (4; am = NEt_3, Y = Me_2SO) which is one of the three neutral σ-species listed in Table 1. Another is (4; am = NEt_3, Y = PPh_3) which also contains a bulky Y ligand. Perhaps steric factors prevent the formation of charged σ species in these two instances.

K_{ii} for (3; am = NEt_3, Y = Me_2SO) is 8 dm^3 mol^{-1}. This value once again indicates that bulkiness in am lowers K_{ii} since the analogous quantities for am = NH_2Pr^n or NH_2Pr^i are *ca.* 50 and *ca.* 28 dm^3 mol^{-1} respectively (Table 5).

These K_{ii} values (for a *cis*-dichloro-system) are slightly larger than the corresponding values of K_i (for the *trans*-dichloro-species) which for the three am = NEt_3, NH_2Pr^n, or NH_2Pr^i, are <0.2, 20, and 10 dm^3 mol^{-1} respectively.[1] Thus it is possible that Cl in the Y position is not as good as ligands with some π-character at stabilizing the σ-CHPt system. Support for this idea is also provided by the fact that (4; Y = am = 4Me-py), as formed in reaction (ii), is detectable at 25 °C, but (2; am = 4Me-py) is only produced in (i) at lower temperatures.[1]

Susceptibility to Nucleophilic Attack.—There is, however, a more significant difference between the *cis*-dichloro(alkene) complexes investigated here and the *trans* ones studied earlier:[1] that is the much greater ease with which the former can be attacked by a nucleophile. This arises from the ability of the *cis* systems to form the σ-cationic ions (5), or sometimes (6). The high stabilities of these cations compared with the neutral compounds, (4) or (2), with respect to the alkene complexes, (3) or (1), and amine can be illustrated by considering what concentration of amine is needed to sustain a 1 : 1 mixture of reactant and product. Thus if am is a typical aliphatic amine, [(2)]/[(1)] and [(4; Y = Me_2SO)]/[(3; Y = Me_2SO)] = 1, when [am] = 10^{-2}—10^{-1} mol dm^{-3}. In contrast, in the *cis*-dichloro(Me_2SO) system, [(5), or perhaps (6)]/[(3)] = 1, when [am] is of the order of 10^{-3} mol dm^{-3}. Thus relative to the alkene complexes, the σ-cationic complexes are 10—100 times more stable than the neutral σ-species. The stability of the cationic species (5) is logical since a nucleophile would be expected to be held more strongly in a positively charged unit.

Stability of Cationic Alkene Complexes.—An alternative interpretation to that in the previous paragraph is to regard (5) as resulting from nucleophilic attack on the alkene cationic complex (9) as in equation (ix). Since an alkene is *trans*-labilising, (9) can be assumed to be in equilibrium with (5) and hence also with (4) and (3). A nucleophile would be expected to attack a cationic species more readily than a neutral one (a supposition which has been used for some interesting syntheses [16,17]) so that it seems reasonable to assume that K_{ix}/K_{iii} (see below) is at least 10, if not considerably greater. Because of the equilibria, K_{ix}/K_{iii} also equals [neutral σ-species]/[cationic π-species], which shows that the latter compounds are not favoured thermodynamically. During the present work no evidence, for example from η^2-CH=C*H* resonances, was found indicative of cationic alkene complexes (9). Perhaps failure to observe such species, except in special circumstances,[17] arises from preferential formation of neutral σ-compounds (4).



$$\mathrm{am} + \eta^2(\mathrm{CHR{=}CR'R''}){-}\left[\overset{\mathrm{Cl}}{\underset{\mathrm{Y}}{\mathrm{Pt}}}{-}\mathrm{am}\right]^{+} \rightleftharpoons \mathrm{amCHRCR'R''}{-}\left[\overset{\mathrm{Cl}}{\underset{\mathrm{Y}}{\mathrm{Pt}}}{-}\mathrm{am}\right]^{+} \qquad \text{(ix)}$$

(9) (5)

Experimental

cis-$[PtCl_2(CH_2CH_2am)Y]$.—The compound *cis*-$[PtCl_2(\eta^2\text{-}C_2H_4)Y]$ (*ca.* 0.06 g) was dissolved or suspended in $CHCl_3$ (1 cm^3). The amine, am (1 mol equiv., dissolved in $CHCl_3$ in the case of NH_2Me), was added and the mixture shaken for *ca.* 1 min. The solid so formed was washed with a little $CHCl_3$ and dried [Found (am = NEt_3, Y = Me_2SO): C, 25.3; H, 5.35; N, 2.8. $C_{10}H_{25}Cl_2NOPtS$ requires C, 25.35; H, 5.3; N, 2.95%. Found (am = NEt_3, Y = PPh_3): C, 47.35; H, 5.3; N, 1.95. $C_{26}H_{34}Cl_2NPPt$ requires C, 47.5; H, 5.2; N, 2.1%. Found (am = NH_2Me, Y = Me_2SO): C, 14.65; H, 4.0; N, 3.55. $C_5H_{15}Cl_2NOPtS$ require C, 14.8; H, 3.75; N, 3.4%].

$[PtCl(NH_2Bu^t)(CH_2CH_2NH_2Bu^t)Y]^+Cl^-$.—The compound *cis*-$[PtCl_2(\eta^2\text{-}C_2H_4)Y]$ (*ca.* 0.08 g) was suspended in $CHCl_3$ (1 cm^3), and NH_2Bu^t (2 mol equiv.) was added with shaking. After some removal of solvent, *in vacuo* if necessary, fine white crystals separated which were washed with a little $CHCl_3$ and dried [Found (Y = Me_2SO): C, 27.85; H, 6.3; N, 5.5. $C_{12}H_{32}Cl_2N_2OPtS$ requires C, 27.8; H, 6.2; N, 5.4%. Found (Y = py): C, 34.6; H, 5.8; N, 7.9. $C_{15}H_{31}Cl_2N_3Pt$ requires C, 34.65; H, 5.95; N, 8.1%. Found (Y = NH_3): C, 26.15; N, 6.5; H, 9.1. $C_{10}H_{29}Cl_2N_3Pt$ requires C, 26.25; H, 6.35; N, 9.1%].

$[\mathrm{PtCl(Me_2SO)(CH_2CHEtNMe_2)}][\mathrm{Me_2NH_2}]^+\mathrm{Cl}^-$.—The compound *cis*-$[\mathrm{PtCl_2(\eta^2\text{-}CH_2{=}CHEt)(Me_2SO)}]$ (0.4 g) in $\mathrm{CHCl_3}$ (10 cm^3) and dimethylamine (0.07 cm^3) were mixed at -20 °C. Solvent was removed under vacuum at 0 °C. The resulting solid was recrystallized from distilled water under vacuum (Found: C, 24.6; H, 5.9; Cl, 14.3; N, 6.0. $\mathrm{C_{10}H_{28}Cl_2N_2OPtS}$ requires C, 24.5; H, 5.7; Cl, 14.4; N, 5.7%), δ (NC*H*C-Pt): in $\mathrm{CDCl_3}$, 4.25 (complex); in $\mathrm{D_2O}$, 4.3 (complex); therefore the formulation as a double compound is preferred.

$[\mathrm{PtCl(Me_2SO)(CH_2CHEtNMe_2)}]$.—By recrystallization of the compound above from toluene–$\mathrm{CH_2Cl_2}$ (Found: C, 23.7; H, 5.1; Cl, 8.8; N, 3.55. $\mathrm{C_8H_{20}ClNOPtS}$ requires C, 23.5; H, 4.95; Cl, 8.7; N, 3.4%).

cis-$[\mathrm{PtCl_2(am)(\eta^2\text{-}C_2H_4)}]$.—Three methods were used. (*i*) For am = $\mathrm{CH_2PhNHMe}$, *p*-$\mathrm{O_2NC_6H_4NH_2}$, and $\mathrm{NH_3}$, the traditional approach [18,19] of treating $[\mathrm{PtCl_3(C_2H_4)}]^-$ with am was adopted. (*ii*) A photochemical method of irradiating the corresponding *trans* isomer, which has been used for am = i-quin,[20] was modified for am = py or 4Me-py. *trans*-$[\mathrm{PtCl_2(am)(\eta^2\text{-}C_2H_4)}]$ (0.08 g) was dissolved in $\mathrm{CHCl_3}$ (0.5 cm^3) in a stoppered vessel which was irradiated with u.v. light ($\lambda_{\mathrm{max.}} =$ 366 nm) for 6 h. For am = py, crystals began to appear after 2 h, but some evaporation of solvent *in vacuo* was required for am = 4Me-py [Found (am = py): C, 22.7; H, 2.4; N, 3.9. $\mathrm{C_7H_9Cl_2NPt}$ requires C, 22.5; H, 2.4; N, 3.7%]. (*iii*) In method (*ii*) above the μ-dichloro-platinum species, $[\mathrm{Pt_2Cl_4(am)_2}]$, can also be formed for some am ligands.[21] For (*iii*), it was convenient to isolate this intermediate (see below) and then to treat it with ethene. For am = $\mathrm{NHMe_2}$, pip, py, 4Me-py, or i-quin, $[\mathrm{Pt_2Cl_4(am)_2}]$ (0.3 g) was suspended in $\mathrm{CHCl_3}$ (20 cm^3) and the orange mixture treated with a stream of ethene in the dark. After 2—4 h, the colour disappeared and a white solid appeared which was washed with $\mathrm{CHCl_3}$ and dried. (For am = 4Me-py, precipitation was effected by addition of n-pentane.) Crystallisation was from n-pentane–chloroform. Satisfactory analyses were obtained [*e.g.* Found (am = $\mathrm{NHMe_2}$): C, 14.2; H, 3.35; N, 4.2. $\mathrm{C_4H_{11}Cl_2NPt}$ requires C, 14.2; H, 3.3; N, 4.15].

cis-$[\mathrm{PtCl_2(\eta^2\text{-}}$*cis*$\mathrm{\text{-}MeCH{=}CHMe)(NHMe_2)}]$.—This was prepared by treating $[\mathrm{Pt_2Cl_4(am)_2}]$ with the appropriate alkene as in method (*iii*) above.

cis-$[\mathrm{PtCl_2(\eta^2\text{-}CHR{=}CR'R'')(4Me\text{-}py)}]$ ($R' = R'' = H$; $R =$ Me *or* Et).—Propene or 1-butene was bubbled through *cis*-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(4Me\text{-}py)}]$ (0.3 g) in $\mathrm{CHCl_3}$ (20 cm^3) for 40 min. The solution was left for 60 min, then solvent removed under vacuum. Crystallisation was from pentane–chloroform [Found (R = Me): C, 26.85; H, 3.2; N, 3.5. $\mathrm{C_9H_{13}Cl_2NPt}$ requires C, 26.9; H, 3.25; N. 3.5%. Found (R = Et): C, 28.8; H, 3.7; N, 3.4. $\mathrm{C_{10}H_{15}Cl_2NPt}$ requires C, 28.9; H, 3.65; N, 3.35%].

$[\mathrm{Pt_2Cl_4(am)_2}]$.—For am = $\mathrm{NHMe_2}$, pip, py, 4Me-py, or i-quin, *trans*-$[\mathrm{PtCl_2(am)(\eta^2\text{-}C_2H_4)}]$ (0.3 g) was dissolved in the minimum of chloroform, and four times as much (by volume) light petroleum (b.p. 40—60 °C) added. The solution was irradiated with u.v. light ($\lambda_{\mathrm{max.}} =$ 366 nm); after 2 h an orange-yellow precipitate began to form. After 12 h, in most cases, the precipitation of orange-yellow solid was complete. It was filtered off, washed with hexane, and dried. Satisfactory analyses were obtained [*e.g.*, Found (am = $\mathrm{NHMe_2}$): C, 7.8; H, 2.3; N, 4.55. $\mathrm{C_4H_{14}Cl_4N_2Pt_2}$ requires C, 7.7; H, 2.25; N, 4.5%].

cis-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(NCCH_3)}]$ *and* *cis*-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(PPh)_3}]$.—These were prepared by the published methods (refs. 22 and 19 respectively).

cis-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(Me_2SO)}]$.—This compound can be prepared from $\mathrm{K[PtCl_3(Me_2SO)]}$.[19,23] However, we found that a better yield was obtained starting from $\mathrm{K[PtCl_3(\eta^2\text{-}C_2H_4)]}$: 2 g of this complex in water (30 cm^3) were treated with a solution of $\mathrm{Me_2SO}$ (0.4 cm^3) in water (2 cm^3) under an atmosphere of ethene. After 45 min the greyish product was separated from the solution and washed with 1% hydrochloric acid, alcohol, and diethyl ether. The complex was taken up in a small volume of boiling acetone and then filtered under gravity to remove small amounts of platinum metal. Shining white crystals were produced by the slow addition of hexane to the warm solution (Found: C, 13.0; H, 2.7. $\mathrm{C_4H_{10}Cl_2OPtS}$ requires C, 12.9; H, 2.7%).

cis-$[\mathrm{PtCl_2(alkene)(Me_2SO)}]$.—Compounds containing higher alkenes were prepared by displacing ethene from *cis*-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(Me_2SO)}]$.[24]

$[\mathrm{PtCl(Me_2SO)(CH_2CH_2NMe_2)}]$ was prepared according to ref. 4.

Equilibrium Studies.—Equilibrium constants were evaluated by observing changes in absorbance of solutions of *cis*-$[\mathrm{PtCl_2(\eta^2\text{-}CHR{=}CR'R'')Y}]$ in the u.v. spectra on addition of aliquots of amine using the procedures described previously.[11]

Instruments.—Spectrometers used were a PE 554 (u.v.–visible) and a JEOL JNM-MH-100 (^{1}H n.m.r., 100 MHz).

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