Nucleophilic Attack on Olefins co-ordinated to Platinum. Part 3.† Effect of Substituents on the Olefins on the Formation of 2-Ammonioethanide Compounds ($H_3NCHRCHR'$–Pt), of Four-membered Ring Complexes, and of Five-co-ordinate Species

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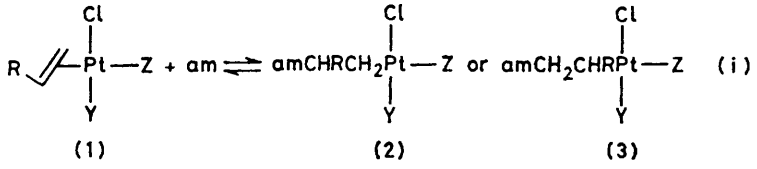
A study has been made of the attack of amines on platinum complexes containing ethene derivatives. When 2-ammonioethanide compounds ($H_3NCHRCHR'$–Pt) are formed, the direction of attack is determined by electronic rather than steric effects unless the latter are very large. Reactions are not complete, and equilibrium constants show that steric factors tend to prevent the formation of the 2-ammonioethanide compounds. The production of azaplatinacyclobutane ring complexes is enhanced by steric factors. Five-co-ordinate species are formed in some cases. Hydrogen-1 n.m.r. data are reported.

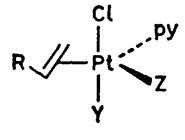
AMINES (am) can attack (η-ethene)platinum(II) complexes (1; R = H) to form σ-(2-ammonioethanide)-platinum(II) compounds [1-10] (2; R = H). In Part 2,[9] we investigated the stabilities of (2; R = H), in particular with respect to (1; R = H), measuring K_i, $\Delta H_i^\ominus$, and $\Delta S_i^\ominus$. Here we extend our studies to platinum compounds containing substituted alkenes. As amines are nucleophiles it might be anticipated that K_i [as defined by (i)] would increase in the sequence R = CH_3, H, CN on electronic grounds, but on the other hand steric factors could be important. Another question of interest is whether the point of addition to the alkene is Markovnikoff or anti-Markovnikoff, that is whether isomer (2) or isomer (3) respectively is formed: can R be sufficiently large to change the mode of attack from the former, which would be anticipated, to the latter?

RESULTS AND DISCUSSION

Formation of the 2-Ammonioethanide Complexes.—Not all 2-ammonioethanide complexes like (2) or (3) are stable enough to be isolated as solids. However, as they are formed in reaction (i) within time of mixing and manipulation, they can easily be studied *in situ* in solution from their n.m.r. spectra. [A rough indication of the extent of reaction (i) can be obtained from the appearance of NC*H*C*H*Pt peaks due to (2) or (3) at the expense of the (η^2-C*H*=C*H*)Pt resonances of (1) on addition of amine.] Tables 1 and 2 summarize the compounds that have been identified.

In the parent ethene system (1, 2; R = H) if am and Z are different amines, they usually exchange giving rise to four possible ammonioethanide complexes,[9] because of





During the work on the ethene complexes, we observed the formation of five-co-ordinate species [11,12] [4; R = H, Y = Cl, Z = py, or Y–Z = acac (acac = acetylacetonate)]. A search is made here for similar species derived from complexes of ethene derivatives.

Lastly, although *trans*-alkene(amine)dichloroplatinum(II) complexes are well known, their preparation and characterization do not seem to have been reported; data on some of them are included.

† Part 2 is ref. 9.

the lability of the Pt–Z bond in (1). Complexity in the n.m.r. spectra here suggests that the same usually occurs with the substituted alkene compounds, except however when Z is pyridine (py). This amine is such a weak nucleophile [9] towards C=C that providing am is a strong base and not in excess, species containing amCH-CHPtZ units are formed.

Hydrogen-1 N.M.R. Spectra of the 2-Ammonioethanide Compounds. Direction of Amine Attack on the Olefin Complexes.—Study of the NC*H*C*H*Pt peaks enables a

TABLE 1

Hydrogen-1 n.m.r. spectra of 2-ammonioethanide compounds, (2) or (3) *

am	Starting olefin	Y	Z	C*H*–CH–Pt	CH–C*H*–Pt	Comments
(A) $NHMe_2$	Propene	Cl	$NHMe_2$	3.41 (d of d after irradiation of R = CH_3 at δ 1.18)	1.55 (d), 1.96 (d) (both after irradiation of C*H*CHPt at δ 3.41)	Isomer (2). AMX structure: $CH^XCH^AH^M$. ^{195}Pt satellites hidden
(B) $NHMe_2$	Ethene	Cl	$NHMe_2$	2.85 (t) $J(^{195}Pt–H) = 40$ Hz	1.96 (t) $J(^{195}Pt–H) = 86$ Hz	
(C) $NHMe_2$	*cis*-But-2-ene	Cl	$NHMe_2$	3.28 (c)	2.4 (c)	Isomer (2) ≡ (3)
(D) NH_2Bu^t	CH_2=CHCN	Y–Z = acac		2.8—3.05 (c) $J(^{195}Pt–H) = 60$ Hz	3.56 (c) $J(^{195}Pt–H) = 120$ Hz	Isomer (3). AMX structure: $CH^AH^XCH^M$
(E) NH_2Bu^t	CH_2=CDCN	Y–Z = acac		2.8 (d), 3.0 (d) $J(^{195}Pt–H) = 60$ Hz		Isomer (3). AX structure: CH^AH^XCD, $J(H^A–H^X)$ = 10.5 Hz
(F) NH_2Bu^t	CH_2=CHCOOMe	Y–Z = acac		2.9—3.0 (c) $J(^{195}Pt–H) = 80$ Hz	4.12 (c) $J(^{195}Pt–H) = 132$ Hz	Isomer (3). ABX structure

* Solvent: $CDCl_3$; chemical shifts are given as δ values in p.p.m.; abbreviations: s = singlet, d = doublet, t = triplet, c = complex multiplet.

distinction to be made between isomers (2) and (3), namely those formed by Markovnikoff and anti-Markovnikoff attack respectively, on (1). [Important proton n.m.r. data are given in Table 1 and the Experimental section; additional data are deposited in Supplementary Publication No. SUP 23054 (9 pp.) * as Tables 4—7.]

TABLE 2

Direction of addition [a] in reaction (i)

am	R	Y	Z	Product
NH_2Me	Me	Cl	NH_2Me	80% M
$NHMe_2$	Me	Cl	$NHMe_2$	80% M
NMe_3	Me	Cl	NMe_3	80% M
$NHMe_2$	Me	Cl	py	80% M
$NHEt_2$	Me	Cl	py	80% M
Morpholine	Me	Cl	py	80% M
py	Me	Cl	py	90% M
$NHMe_2$	Et	Cl	$NHMe_2$	80% M
$NHMe_2$	Et	Cl	py	80% M
$NHEt_2$	Et	Cl	py	80% M
py	Et	Cl	py	90% M
$NHMe_2$	Ph	Cl	$NHMe_2$	80% M
$NHMe_2$	Pr^i	Cl	$NHMe_2$	*ca.* 60% [b] M+ *ca.* 40% a-M

am	R	Y–Z	Product
NH_2Et	Me	acac	80% M
NH_2Bu^t	Me	acac	80% M
$NHMe_2$	Me	acac	80% M
py	Me	acac	90% M
NH_2Pr^i	CN	acac	95% a–M
NH_2Bu^t	CN	acac	95% a–M
$NHMe_2$	CN	acac	95% a–M
py	CN	acac	95% a–M
NH_2Bu^t	COOMe	acac	95% a–M

[a] M = Markovnikoff and a–M = anti-Markovnikoff.
[b] In this case the percentages are lower limits.

This, we will illustrate using the adduct formed when $NHMe_2$ reacts with *trans*-[$PtCl_2$(η^2-propene)($NHMe_2$)]. Investigation of the closely related adducts, *trans*-[$PtCl_2$($CH_2CH_2NHMe_2$)($NHMe_2$)] and *trans*-[$PtCl_2$-(CHMeCHMeNHMe_2)($NHMe_2$)], enables the following four types of protons MeC*H*CPt, CH_2CPt, CC*H*MePt, and CCH_2Pt to be assigned δ values at approximately 3.3, 2.8, 2.4, and 1.95 respectively [see (B) and (C) in Table 1]. The analogue formed on adding $NHMe_2$ to *trans*-[$PtCl_2$(η^2-propene)($NHMe_2$)] absorbs at *ca.* δ 3.4 and δ 1.8 (Table 1), which illustrates that isomer (2) is formed, addition being Markovnikoff. (The NC*H*Me–CH_2Pt bands are complicated, being an AMX system, but simplify on double irradiation, see Table 1.) Isomer (3) would absorb at *ca.* δ 2.8 and 2.4; however, these resonances being AMX would be broad and perhaps spread under the three CH_3N peaks at δ 2.85, 2.75, and 2.45 due to $(CH_3)_2NCH_2$, $PtNH(CH_3)_2$, and free $(CH_3)_2$-NH respectively. On this basis formation of up to 20% of the (anti-Markovnikoff) isomer (3) could pass unnoticed. However, integration of the δ 1.8 region compared with that around δ 3.4 and that around δ 1.18 due to CHCH_3 indicate 2.0 ± 0.1 protons. Moreover the δ 1.18 signal is a simple doublet as expected if just one type of CHCH_3 group is present as opposed to two, one from isomer (2) and one from (3). Thus the figure of 80% Markovnikoff attack quoted in Table 2 is a cautious lower limit for the position of addition for the propene system.

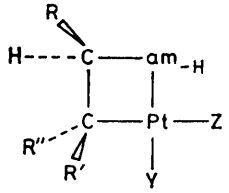
Use of pyridine as am eliminates the problem of the CH_3N peaks around δ 2.8 enabling the lower limit to be raised. In *trans*-[$PtCl_2$(CH_2CH_2py)(py)] the CH_2py and CH_2Pt protons absorb at δ 4.54 and δ 2.45 respectively.[9] It seems fair to assume that, as in the $NHMe_2$ system, a change from a methylene to a methine proton would add *ca.* 0.45 to δ, thus moving the respective values to *ca.* δ 5.0 and *ca.* δ 2.9. In the pyridine adducts formed from *trans*-[$PtCl_2$(propene)(py)], signals are seen at δ 5.26, but not between these peaks and the δ 2.7 region where CH_2Pt absorbs. Thus it is possible from the absence of small peaks to increase the lower limit on the formation of isomer (2) compared with (3) to 90%, a conclusion supported by integrations.

The proton resonances of the ethanide group produced by attack of amines on complexes of prop-2-ene-1-nitrile (acrylonitrile) are also complicated. They can be simplified however by the use of CH_2=CDCN as a ligand, see (D) and (E) in Table 1.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

In the case of the prop-2-ene-1-nitrile adducts, there is unfortunately no reference compound containing the Pt–C*H*CN–am group which would enable the δ values of the protons indicated to be fixed. However, in all the adducts made there is a complex signal at *ca.* δ 2.9 which is reasonable for an NC*H*$_2$CPt assignment by analogy with the earlier alkene compounds. A second signal, also complex, centred at *ca.* δ 3.6 could reasonably be due to CH$_2$C*H*CNPt. However, a more convincing argument for assigning these second signals is their large J(¹⁹⁵Pt–H) coupling constants (*ca.* 120 Hz) compared with those of the first (*ca.* 60 Hz). Working backwards from the anti-Markovnikoff assignments of *ca.* δ 3.6 and *ca.* δ 2.9, one would expect corresponding Markovnikoff values of *ca.* δ 3.05 and *ca.* δ 3.35. As the spectra of the adducts formed from pyridine and from NH$_2$Bu^t with [Pt(acac)Cl(η²-CH$_2$=CHCN)] contain only the signals specified above and nothing else between δ 5.0 and δ 2.0, at least 95% of the addition must be anti-Markovnikoff.

Other systems have been investigated in the same way. Their n.m.r. data are summarized in the Experimental section. On the basis of the freedom of the NC*H*C*H*Pt regions from overlapping spectra, the estimates of the amount of isomer (2) as opposed to (3), or *vice versa*, given in Table 2 were made. No conclusions have been included on *cis* complexes (1; Z = Cl, Y = PPh$_3$ or SOMe$_2$) for while these compounds can form σ adducts, they can within a few minutes owing to the *trans* labilising nature of Y, also produce cyclic systems [13-15] (5; Z = Cl, Y = PPh$_3$ or SOMe$_2$), which increase the complexity of the ¹H n.m.r. spectra (am$_{-H}$ = am less one amino-proton).



(5)

The σ adducts studied here show no tendency to cyclize within a short period of time, perhaps owing to lack of *trans* labilisation when Y is Cl, except in two instances (see later).

Markovnikoff versus *anti-Markovnikoff Attack.*—Models of (2) and (3) suggest considerable crowding of atoms, so that the introduction of bulky groups into am or R could favour the formation of one isomer rather than the other. However, Table 2 illustrates that with one exception, when R = Pr^i, there is no significant evidence that steric effects are important in any of the systems studied here in determining direction of attack. (Later it will be shown that they do affect extent of attack, however.) Apart from the one instance, only electronic effects are important, as is illustrated in cases where R is an acceptor such as CN and COOMe. Change in temperature made no difference to the direction of attack: ¹H n.m.r. spectra were run at −40 °C and, if stability with relation to (1) permitted, up to 30 °C. In order to test whether (2) could isomerize to (3) over a period of time (2; am = Z = py, Y = Cl) was left to stand for 1 h at −40 °C, but no change was detected in the ¹H n.m.r. spectrum.

Previous investigations [2,4,5] of the direction of attack involved degradation of the ammonioethanide compound, (2) or (3), with fission of the C–Pt bond, followed by identification of the amine so formed, *viz.* (6), (am$_{-H}$)-CHRCH$_3$, or (7) (am$_{-H}$)CH$_2$CH$_2$R, respectively.

Apart from various *cis* complexes [1; Z = Cl, Y = PPh$_3$, SOMe$_2$, or P(OMe)$_3$ (see above)] where steric factors are important in influencing direction of attack,[5] these degradation studies are limited to systems in which Z is an amine and do not extend to acac complexes. Just as we find here, attack by NHEt$_2$ as am on propene-containing compounds (1; R = Me, Y = Cl, Z = PhCHMeNH$_2$ or CH$_3$C$_6$H$_4$NH$_2$) is Markovnikoff. However, degradation after attack of NHEt$_2$ on the but-1-ene complex (1; R = Et, Y = Cl, Z = *p*-CH$_3$C$_6$H$_4$NH$_2$) yields equal amounts of (6) and (7) (R = Et, am$_{-H}$ = NEt$_2$), but each only representing 15% of the products with respect to (1), 70% being unaccounted for. In our but-1-ene systems formation of just 15% of anti-Markovnikoff product would probably not be noticed, but of 50% would be. The possible contrast with our results suggests that some rearrangement may occur in the degradation process. While it is difficult to compare (2) and (3), (7) is clearly preferable to (6) from the point of view of reducing strain. However, treatment with neither HCl nor Na[BH$_4$] (which were used in the degradations) causes a hindered amine such as (6) to rearrange to (7). Therefore perhaps the C–Pt bond in (3; R = Et) is somewhat weaker than in (2; R = Et), enabling (7) to be formed on degradation from trace amounts of the former in equilibrium with the latter.

The one clear case in which steric factors are important is the attack of NHMe$_2$ on the 3-methylbut-1-ene complex (1; R = Pr^i, Y = Cl, Z = am = NHMe$_2$), the two possible products being formed in approximately equal amounts (Table 2). Addition is entirely anti-Markovnikoff on the corresponding P(OMe)$_3$ complex [5] [1, 2; R = Pr^i, Y = P(OMe)$_3$, Z = Cl, am = NHEt$_2$].

Completeness of Formation of the Ammonioethanide Compounds (*judged by Hydrogen-1 N.M.R.*).—As in the case of the ethene system [9] (1, 2; R = H, Y = Cl, Z = am, or Y–Z = acac), ¹H n.m.r. gives a semi-quantitative indication in equilibrium (i) of the completeness of formation of the 2-ammonioethanide (2), lowering of temperature favouring its production. Of the attacking amines, am, in Table 2, pyridine is the most feeble.

When Z is py and R is Me or Et, or when Y–Z is acac and R is Me, attack on the co-ordinated olefin can only be detected at reduced temperatures (< *ca.* −10 °C). In the corresponding ethene systems (1, 2; R = H), similar behaviour is observed when Z is py, but no pyridinioethanide complex can be detected even at −40 °C when Y–Z is acac. The contrast between the

ethene and propene complexes in the acac case is surprising since the methyl group, being a donor, might be expected to discourage attack by a nucleophile.

However, the prop-2-ene-1-nitrile acac complex behaves just as expected on the basis of an electron-accepting CN group; attack occurs much more readily and formation of the pyridinioethanide complex is complete even at *ca.* 25 °C. The same completeness is true of the other systems in Table 2 in which R is CN, and also for the one example where R is COOMe, another acceptor group. [Where reaction (i) is 'complete' according to ^{1}H n.m.r., $K \geqslant 150$ dm^3 mol^{-1}.]

On the basis of n.m.r. spectra there is little difference in reaction (i) in the nucleophilicity of the aliphatic and alicyclic amines in Table 2, apart from the case where am = Z = NMe_3, where the ethanide complex cannot be detected until the temperature is reduced below *ca.* −10 °C. Similarly in the ethene systems (R = H) when am = Z = strong amine, steric effects were observed to be more important than the basicity of am.[9]

Values of K_i.—The relationship between the alkene in the starting π complex and the extent of formation of the ammonioethanide compound was investigated quantitatively by measuring equilibrium constants K_i in $CHCl_3$ for some of the dimethylamine systems (1,2; am = Z = $NHMe_2$, Y = Cl). [All the additions are Markovnikoff so that K_i refers to (1) ⇌ (2) and not (1) ⇌ (3) in equation (i)].

The Benesi–Hildebrand method was used as in earlier similar studies[9] on *trans*-[$PtCl_2(\eta$-$C_2H_4)$(am)] in which am, the amine, was varied. Thus the change in absorbance at 288 nm, ΔA, of a solution made up from *trans*-[$PtCl_2(\eta$-alkene)$(NHMe_2)$] was observed as $NHMe_2$ was added; then, provided the stoicheiometry of the reaction is 1 : 1 (and $K < 500$ dm^3 mol^{-1}), a plot of $1/\Delta A$ against 1/[am] is linear and K_i is equal to the ratio of intercept to slope. Temperatures were varied between 25 °C and 5 °C.

In the case of the ethene, addition of the amine caused an alteration in spectrum in mixing time, which was not followed by any subsequent change for at least 30 min. Good linear Benesi–Hildebrand plots were obtained, giving the values of K_i, $\Delta H_i^\ominus$, and $\Delta S_i^\ominus$ recorded in Table 3. In the propene, but-1-ene, and phenylethene systems, a further change in spectrum started after about 3 min, so that experiments had to be completed within this time. Again good linear Benesi–Hildebrand plots were obtained; data are given in Table 3.

TABLE 3

Values of K, $\Delta H^\ominus$, and $\Delta S^\ominus$ for reaction (i; am = Z = $NHMe_2$, Y = Cl)

Alkene	K(298)/ dm^3 mol^{-1}	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}
Ethene	100	−18.2 ± 1.5	−21.5 ± 4.1
Propene	35	−27.6 ± 0.3	−63.1 ± 0.1
But-1-ene	21	−29.0 ± 1.3	−72.3 ± 4.6
trans-But-2-ene	1.7	−12.8 ± 0.1	−39.3 ± 0.0
Phenylethene	4.5	−71.0 ± 9.8	−225.0 ± 33.0

The value of K_i falls as the olefin becomes more bulky showing a dependence on steric rather than electronic factors. The trend in $\Delta H^\ominus$ shows that as steric hindrance increases, reaction (i) becomes more exothermic. This implies that from the point of view of enthalpy a bulky substituent causes more destabilization on an ethene ligand than on an ethanide group in its 2-position. This is reasonable as in the latter there is a greater distance between the Cl–Pt–Cl system and any such substituent. The fall in K_i with increase in bulkiness is caused by the decrease in $\Delta S_i^\ominus$. Molecular models of the $NCHRCH_2Pt$ unit indicate crowding and there could well be considerable loss of rotational freedom as R increases in size. Unfortunately the n.m.r. spectra were too complicated to provide information on this point.

In the case of the *trans*-but-2-ene complex, changes in the u.v. spectra show that another reaction in addition to (i) starts immediately after mixing, and absorbances were extrapolated to zero time for the Benesi–Hildebrand plot. Nevertheless, values of K_i, $\Delta H_i^\ominus$, and $\Delta S_i^\ominus$ look reasonable (Table 3): the bulky methyl group α to the platinum in the ethanide complex would be expected to lower the equilibrium constant and exothermicity for reaction (i). Moreover, extrapolation leads to a value for K_i of *ca.* 8 dm^3 mol^{-1} at 223 K, which corresponds to the extent of reaction indicated by ^{1}H n.m.r. at that temperature.

In the case of all the alkenes mentioned so far in this section, ^{1}H n.m.r. spectra confirm that the initial compound formed within manipulation time (*ca.* 2 min) is the expected alkanide complex (2). However the *cis*-but-2-ene complex is different: *trans*-[$PtCl_2$(CHMeCHMeNHMe$_2$)$(NHMe_2)$] is only stable at −40 °C.* When it is warmed to 25 °C or when *trans*-[$PtCl_2(\eta$-*cis*-but-2-ene$)(NHMe_2)$] and $NHMe_2$ are mixed at this temperature, change is rapid, ^{1}H n.m.r. indicating quantitative production of the cyclic compound (5; R = R′ = Me, R″ = H, am = Y = $NHMe_2$, Z = Cl) within about 30 min. It is strange that the Y and Z ligands change position, since the isomerization of *trans*-[$PtCl_2$(alkene)(amine)] complexes in the absence of free amine usually takes 1 or 2 days at room temperature, as indicated by precipitation in cases where the *cis* complex is insoluble. This change in geometry is discussed in the next section. Attempts to obtain thermodynamic parameters for the *cis*-butene system using Benesi–Hildebrand plots based on absorbances extrapolated to zero time lead to values for K_i(298), $\Delta H_i^\ominus$, and $\Delta S_i^\ominus$ of 4.5 dm^3 mol^{-1}, 64.5 kJ mol^{-1}, and 228 J K^{-1} mol^{-1} respectively. While the first figure is plausible, the second and third imply negligible values for K_i at reduced temperatures, *e.g.* 223 K, where ^{1}H n.m.r. studies show that a significant amount of the alkanide complex is formed (rather more, in fact, than is produced in the *trans*-but-2-ene system).

Because of the formation of isomer (3) as well as (2),

* Hydrogen-1 n.m.r. indicates that the reaction of $NHMe_2$ with the *trans*-Cl_2 (*cis*-butene) and the *trans*-Cl_2 (*trans*-butene) compounds gives two distinct ammonioethanide compounds (see Table 5) as expected since the reaction is stereospecific (see text later).

discussed earlier, no equilibrium studies were made on the reaction of *trans*-[$PtCl_2(\eta^2$-$Pr^iCH{=}CH_2)(NHMe_2)$] and dimethylamine.

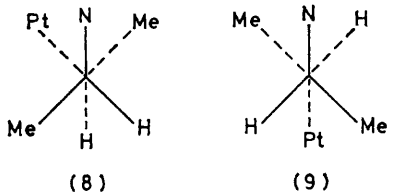
Values of K_i at 298 K were also obtained in a similar manner for some of the acac complexes (1, 2; am = $NHMe_2$, Y–Z = acac). The initial change was complete within mixing time, but in the cases of the propene and but-1-ene systems a further change occurred after a few minutes. However, good linear Benesi–Hildebrand plots were obtained in these two cases and for the ethene system. Values at 298 K of K_i (1, 2; am = $NHMe_2$, Y–Z = acac) are R = H, 188; Me, 110; Et, 63 $dm^3\ mol^{-1}$, illustrating a steric rather than an electronic effect as in the case of the amine complexes (Table 3). However, u.v. studies supported the ^1H n.m.r. conclusion that the propene-1-nitrile complex reacts ' completely '; K_i (1, 3; am = $NHMe_2$, Y–Z = acac) at 298 K (R = CN) can be raised to $\geqslant 500\ dm^3\ mol^{-1}$ which provides one example where electronic effects are paramount. (In this single case addition is anti-Markovnikoff so perhaps comparison with R = Me is not strictly fair, but it is valid with R = H.)

Formation of Cyclic Complexes.—The compound *cis*-[$PtCl_2(\eta^2$-*cis*-but-2-ene)($^{15}NHMe_2$)] forms a cyclic complex (5; R = R′ = Me, R″ = H, am = Y = $^{15}NHMe_2$, Z = Cl), which has been characterised by ^1H, ^{13}C, and ^{195}Pt n.m.r.[15] The new compound was originally observed serendipitously after the mixture had been standing for about 2 days, but it is formed in manipulation time. Like many *cis*-[$PtCl_2$(alkene)(amine)] compounds, the starting complex here is of low solubility in chloroform only entering solution to an appreciable extent when at least two equivalents of $NHMe_2$ are added. The ^1H n.m.r. of the resulting decanted solution indicates the formation of the cyclic compound, rather than of an acyclic 2-ammonioalkanide complex as observed in the case of the simple *trans*-[$PtCl_2$(alkene)-(amine)] systems. The rapidity of the cyclisation is remarkable as $NHMe_2$ is not *trans* labilizing. Moreover, it is a poor entering ligand as such and its cation would be worse. There must be a strong steric effect.

The same cyclic complex is also formed readily at *ca.* 15 °C on mixing *trans*-[$PtCl_2(\eta^2$-*cis*-but-2-ene)($NHMe_2$)] and dimethylamine (as mentioned earlier), the am and Cl in the Y and Z positions having changed places. Somewhat similar behaviour is exhibited by *trans*-[$PtCl_2(\eta^2$-$Pr^iCH{=}CH_2)(NHMe_2)$]. A solution of this compound in $CHCl_3$ containing excess of dimethylamine on standing for 2 days at *ca.* 0 °C yields a solution, which on the basis of ^1H n.m.r. appears to be (5; R or R′ = Pr^i, am = Y = $NHMe_2$, Z = Cl). On evaporating under vacuum, a white solid is produced which gives an identical spectrum on redissolving in $CDCl_3$. Significant features in the ^1H n.m.r. spectrum are the presence of two sets of NCH_3 peaks, the coupling of both to platinum, and the size of these interactions, which together indicate two $PtNCH_3$ systems. Both systems show $NHCH_3$ coupling (see later), δ 2.73(d), J(Pt–H) 49 Hz; δ 2.94(d), J(Pt–H) 47 Hz. All the NCH_3 protons exhibit Pt–H coupling, for which reason the non-deprotonated amine is assigned to the Y rather than the Z position: NC*H* protons in an amine *trans* to an alkanide group show neither *Pt–H* nor C*H*–N*H* coupling, *e.g.* (2; R = H, Y = Cl, Z = am or py) studied earlier [16,17] and (2; R ≠ H, Y = Cl, Z = am) investigated here (see Tables 5 and 6); hence the assignment of the *cis*-*C*-Pt–*N*CH_3 geometries, as in (5; am = Y = $NHMe_2$, Z = Cl). The spectrum shows a complex peak at δ 3.8 which is assigned to NC*H*CPt on the basis of an analogous resonance at δ 3.72 in (5; R = R′ = Me, am = Y = $NHMe_2$, Z = Cl). There is also a peak of about equal area at δ 3.3, which can be assigned to NCH_2CPt on the basis that δ for both C*H*Pt and CH_2CPt resonances are increased by *ca.* δ 0.5 from their values of *ca.* δ 3.3 and δ 2.8 in the acyclic compounds when the ring system is formed. (Unfortunately in both cyclic complexes resonances due to C*H*Pt are obscured.) The peaks at δ 3.8 and δ 3.3 suggest that the Markovnikoff and anti-Markovnikoff isomers, *viz.* (5; R = Pr^i, R′ = R″ = H) and (5; R′ = Pr^i, R = R″ = H), are both formed in approximately equal amounts [just as (2) and (3) are in the acyclic system (Table 2)].

A difference between the *trans*-[$PtCl_2(Me_2$NH-alkanide)($NHMe_2$)] compounds of 3-methylbut-1-ene and *cis*-but-2-ene is that the former changes into a cyclic complex less quickly. The corresponding compounds from ethene, propene, phenylethene, and *trans*-but-2-ene do not appear to cyclize, which suggests (but for the last system) that bulky groups, particularly on the carbon α to the platinum, encourage cyclization from the thermodynamic point of view. The speed of cyclization of the *cis*-but-2-ene compound suggests that steric factors are also important kinetically, since there are no electronic labilizing factors which could apply to this *trans*-dichloro-complex any more than they did in the *cis*-dichloro-case mentioned earlier. Bulkiness in am seems to favour cyclization when Y is PPh_3.[14]

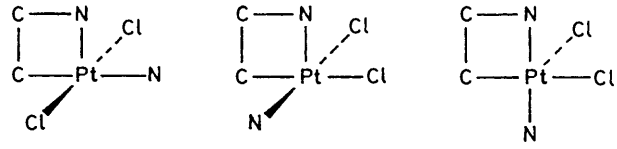
The strong tendency of the *cis*-but-2-ene complexes to cyclize compared with the *trans*-but-2-ene one can be rationalized on the basis that the attack of the amine on the alkene in (1) is intermolecular [3,18] (*i.e. trans* to the platinum) if it is assumed that the bulky substituents on the C–C bond in the ethanide complex tend to keep apart. Then (8) depicts the favoured rotamer for the *cis*-but-2-ene σ adducts; the Pt and N are relatively close, particularly compared with (9) which represents



(8) (9)

the favoured rotamer of the *trans*-but-2-ene compound. If the ammonio-N loses a proton and forms a link to Pt, cyclic five-co-ordinate structures (10) or (11) are formed, depending whether the starting compound was the *trans*- or the *cis*-dichloro-complex respectively. As five-

co-ordinate complexes isomerize more easily than four, (12) ought to be formed fairly readily, which will yield the observed cyclic compound by loss of chloride.



(10) (11) (12)

Five-co-ordinate Species.—At the same time as the ammonioethanide compound is formed at *ca.* −40 °C, the ^{1}H n.m.r. resonances of the =C*H* protons in [Pt(acac)-Cl(η^2-CH_2=CDCN)] move progressively from δ 4.75 to δ 3.3 and δ 3.6 on addition of aliquots of pyridine. Similar behaviour [11] in the corresponding η-C_2H_4 complex has been attributed to the formation of the isomer corresponding to (4; R = CN, Y–Z = acac), rather than that in which py is axial with acac lying in the symmetrical equatorial position.

However there is a contrast in the reactions of the propenenitrile and ethene complexes, *viz.* R = CN and H in (4; Y–Z = acac), with pyridine in that the latter does not form an ammonioethanide derivative. The propene complex (4; R = CH_3, Y–Z = acac) is different again; change in the =C*H* resonance indicated formation of an ammonioethanide compound but not of anything else. Thus the acceptor and donor groups, CN and CH_3, on the ethene ligand stabilize and destabilize the five-co-ordinate species respectively. As pyridine is a nucleophile this is reasonable and accords with the earlier observation that Y–Z = acac enhances the formation of these species compared with Y = Cl, Z = py, if it is assumed that the portion of acac in the Y position is a better acceptor (presumably π) than Cl is. However, the same sort of simple donor/acceptor argument does not rationalize satisfactorily the tendency of pyridine to add to the C=C bond, since both CH_3 and CN in the R position enhance attack compared with H.

No shift in the =C*H* resonance was observed in any other of the systems mentioned in Tables or text.

EXPERIMENTAL

The compounds *trans*-[$PtCl_2$(amine)(olefin)] were prepared from corresponding *trans*-[$PtCl_2$(amine)(η-ethene)] complexes.[1] The latter (0.4 g) in 30 cm^3 acetone was treated with a stream of propene, but-1-ene, or *cis*-but-2-ene for 30 min as appropriate, or 0.1 g in 20 cm^3 chloroform was stirred with excess of phenylethene for the same length of time. The solution was left for another 30 min, the solvent removed under vacuum, and the yellow solid recrystallized from chloroform containing a little pentane [(*i*) olefin = $MeCHCH_2$, am = $NHMe_2$. Found: C, 17.15; H, 3.8; N, 3.8. Required C, 17.0; H, 3.7; N, 4.0%. (*ii*) olefin = $EtCHCH_2$, am = $NHMe_2$. Found: C, 19.8; H, 4.25; N, 3.8. Required C, 19.6; H, 4.1; N, 3.8%. (*iii*) olefin = *trans*-MeCHCHMe, am = $NHMe_2$. Found: C, 19.9; H, 4.2; N, 3.85. Required C, 19.6; H, 4.1; N, 3.8%. (*iv*) olefin = *cis*-MeCHCHMe, am = $NHMe_2$. Found: C, 19.85; H, 4.05; N, 3.7. Required C, 19.6; H, 4.1; N, 3.8%].

The *cis*-[$PtCl_2$(amine)(olefin)] complexes are sometimes obtained as pure precipitates on irradiation of a solution in $CHCl_3$ of the corresponding *trans* isomer for *ca.* 6 h with u.v. light (*ca.* 366 nm), *e.g.* amine = pyridine.[19] In other instances the precipitate contains [Pt_2Cl_4(amine)$_2$], which can be converted to the desired material by shaking with the appropriate olefin.[20] The complex *cis*-[$PtCl_2$(*trans*-but-2-ene)($NHMe_2$)] was obtained as a white solid by irradiating a saturated solution in $CHCl_3$ of *trans*-[$PtCl_2$(*trans*-but-2-ene)($NHMe_2$)] as above, then shaking the resulting precipitate with half an equivalent of *trans*-but-2-ene for 12 h (all at *ca.* 15 °C). The precipitate was washed with a little chloroform and dried under vacuum (Found: C, 19.8; H, 4.15; N, 3.7. Required C, 19.6; H, 4.1; N, 3.8%).

The preparation of [Pt(acac)Cl(η^2-CH_2=CHCN)] and of [Pt(acac)Cl(η^2-CH_2=CDCN)] is described elsewhere.[21] The former shows a curious accidental degeneracy in its ^{1}H n.m.r. spectrum.[21] The compound [Pt(acac)Cl(η^2-CH_2-CHCOOMe)] was made in a similar way using an excess of $CH_2CHCOOMe$. The compounds [Pt(acac)Cl(olefin)] were prepared following published methods.[22]

The 2-ammonioethanide compounds were made *in situ* [9] in $CDCl_3$ and identified from their ^{1}H n.m.r. spectra.

The mixture of new cyclic complexes (5; am = Y = $NHMe_2$, Z = Cl, and R = Pr^i, R′ = R″ = H; or R′ = Pr^i, R = R″ = H) was prepared by allowing a solution in $CHCl_3$ of *trans*-[$PtCl_2$(η^2-3-methylbut-1-ene)($NHMe_2$)] and excess of $NHMe_2$ to stand for 2 days at *ca.* 15 °C; on cooling *in vacuo* a white solid separates. Shaking of this with chloroform leaves a residue of [NH_2Me_2]Cl, giving a solution which on cooling *in vacuo* gives the new compound.

Hydrogen-1 n.m.r. were recorded on a 100-MHz JEOL machine. Ultraviolet studies were made on a Perkin-Elmer 554 spectrophotometer. The use of this more precise instrument enabled Benesi–Hildebrand studies to be made on the acac systems as well as the amine ones.[9] Changes in absorbances were measured at 370 and 288 nm respectively. Solvents throughout were $CHCl_3$ or $CDCl_3$.

Details of ^{1}H n.m.r. spectra are given in Tables 4—7 (SUP 23054). Important features are given in Table 1 and below (δ values in p.p.m. and *J* values in Hz).

trans-[$PtCl_2$(η^2-alkene)($NHMe_2$)]. π-CH_2=, 4.4—4.8, *J*(Pt–H) 60—65; π-CH=, 5.3—5.5, *J*(Pt–H) 60—70; CH_3CH=, *ca.* 1.8, *J*(Pt–H) 33—38; $NHCH_3$, 2.7—2.9, *J*(Pt–H) 33; a notable feature to be discussed elsewhere [23] is the apparent inequivalence of the NCH_3 protons in *trans*-[$PtCl_2$(*trans*-MeCH=CHMe)($NHMe_2$)].

trans-[$PtCl_2$(CHRCHRam)Z]. NCH_2CPt, NCHCPt, $NCCH_2Pt$, and NCCHPt, Table 1; $amCH_3CPt$ (am is aliphatic) 1.0—1.2, *J*(H–H) 7; (am = py) *ca.* 1.4, *J*(H–H) 7; $amCCCH_3Pt$ (am is aliphatic) 0.8—1.1, no well resolved satellites, *J*(H–H) 7; NCH_3 in $NHMe_2$ (as am) 2.85, (as Z), 2.75; CH_2 in alkyl, 1.2—2.5 (rather a nuisance when investigating other CH_2); H in py (as Z) 9.0, 8.8, 7.6, (as am) 9.4, 9.1, 8.6.

[Pt(acac)Cl(CH_2CHMeam)]. Much as in dichloro-complexes, δ values tend to be slightly larger or equal to those above.

[Pt(acac)Cl(CHRCH_2am)] (am = NH_2Bu^t; R = CN, COOMe). Table 1; CH_3N, 1.45; CH_3(acac), 1.75, 1.85; CH(acac), 5.2.

Cyclic compounds (5). $\overline{\text{NCHCPt}}$ 3.6—3.8, NCH_2CPt 3.3,

NCH_3CCPt 0.90, $NCCCH_3Pt$ 0.74, J(Pt–H) 85; NCH_3 (ref. 15) 2.65—2.95, J(Pt–H) 40—50. Distinctive features of the cyclic complexes (5; am = Y = $NHMe_2$) compared with the acyclic systems (2, 3; am = Z = $NHMe_2$) include: $PtNCH_3$ coupling (see text); $PtNHCH_3$ coupling (see text); satellites from $PtCCH_3$ coupling broad but detectable (in the acyclic systems they are too broad to be seen conclusively); $\overline{NCH}CPt$ and $\overline{NCH_2}CPt$ *ca.* δ 0.5 higher (see text).*

* *Note added at proof:* Recently, Eisenstein and Hoffmann [24] have shown using overlap criteria that nucleophilic attack on a co-ordinated alkene should become easier as the character of the bonding changes from η^2 to σ. Table 3 shows that, from the point of view of enthalpy, introduction of two methyl groups symmetrically on to ethene makes the reaction harder, presumably because of their donor effects. However, a single methyl or ethyl substituent makes addition easier (*vis-a-vis* $\Delta H^{\ominus}$); perhaps in these less symmetrical cases the bonding has a larger σ contribution.

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