Nucleophilic Attack on Olefins co-ordinated to Platinum. Part 2.[1] Stabilities of 2-Ammonioethanide σ Adducts and of Five-co-ordinate Complexes

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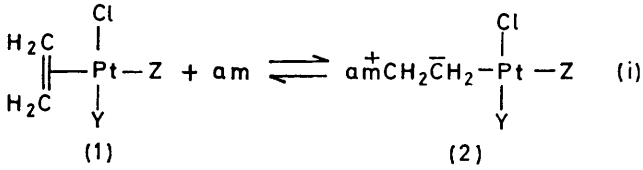
The preparation and characterization is reported of various new 2-ammonioethanideplatinum(II) complexes (*i.e.* compounds containing $am\overset{+}{C}H_2\overset{-}{C}H_2Pt$, am = amine). These have been used to assist in the identification by ^1H n.m.r. spectroscopy of other less stable relatives. The n.m.r. data give no indication of the stability of the complexes. *trans*-Labilization by the $am\overset{+}{C}H_2\overset{-}{C}H_2$ group has been studied; exchange of a *trans*-positioned amine is slow on an n.m.r. time scale. Equilibrium constants have been measured for the reaction am + $Pt^{II}(\eta\text{-}C_2H_4)$ $\rightleftharpoons$ $\sigma\text{-}am\overset{+}{C}H_2\overset{-}{C}H_2Pt$, and are discussed in terms of the nature of am, the attacking amine. Lack of bulk in am is more important than its basicity, π effects also being relevant. Data are also given on an equilibrium in which five-co-ordinate complexes are produced, *e.g.* py + $[PtCl_2(\eta\text{-}C_2H_4)(py)]$ $\rightleftharpoons$ $[PtCl_2(\eta\text{-}C_2H_4)(py)_2]$ (py = pyridine). The reaction is specific to aromatic amines, which suggests that π interactions are important in associative substitution. The susceptibility of $\eta\text{-}C_2H_4$ and Pt^{II} to nucleophilic attack is compared, the former being a harder acid.

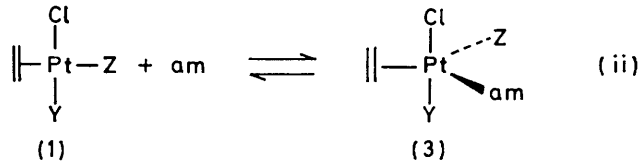
OLEFIN ligands in metal complexes are susceptible to attack by nucleophiles, and in some instances the adduct so formed can be identified. Thus attack by amines, am, on η-etheneplatinum(II) complexes, such as (1), leads to σ-bonded 2-ammonioethanide compounds, (2). In some



(1) (2) (i)

instances (2) can be isolated as a moderately stable compound, *e.g.* (2; am = Z = NEt_2H, Y = Cl),[1,2] but in other cases evidence can only be obtained for the σ adduct in solution by ^1H n.m.r. spectroscopy, *e.g.* (2; am = Z = pyridine, Y = Cl).[3]

Here an attempt is made to study the ' stability ' of the σ-(2-ammonioethanide) compounds, (2), with respect to the η-ethene complexes (1), on varying the amine, by measuring the equilibrium constant K_i. The systems used are Y = Cl with Z = am, and Y–Z = acac, the respective (2) being referred to as the amine and acac σ compounds.† The ^1H n.m.r. spectra of the $am\overset{+}{C}H_2\overset{-}{C}H_2Pt$ group of the σ adducts (2) are not related to the position of equilibrium in reaction (i).



(1) (3) (ii)

During the course of these investigations the formation of five-co-ordinate complexes (3) was observed[4] at low temperature for Y = Cl, Z = py, am = py and for Y–Z = acac, am = py. These complexes are particularly important as they may well be examples of the five-co-ordinate intermediate proposed in the associative ligand-exchange process for platinum(II) complexes.[5] In other such examples, of which there are only a few such as $[PtCl_2(bipy)(\eta\text{-}C_2H_4)]$ [6] and $[Pt(SnCl_3)_5]^{3-}$,[7] there are no corresponding four-co-ordinate starting compounds analogous to (1) that can be identified. Therefore attempts are made to measure K_{ii}.

† *Abbreviations:* acac = acetylacetonate (pentane-2,4-dionate); al–am = an alicyclic or aliphatic amine; am = any amine; imH = imidazole; morph = morpholine; pip = piperidine or substituted piperidine; py = pyridine or substituted pyridine; bipy = 2,2′-bipyridine.

RESULTS AND DISCUSSION

Characterization of the σ-Ammonioethanide Compounds.—The σ adducts are readily formed by addition of am to a solution of π complex, *cf.* equation (i), u.v. and n.m.r. spectroscopy showing that equilibrium is normally established in *ca.* 1 min. The following new σ adducts, *viz.* (2), were isolated as solids: Y–Z = acac, am = morph; Y = Cl, Z = am, am = morph, 4-NMe_2-py, Pr^i, or Bu^t, compositions being confirmed by microanalysis (except in the last two cases) and the proton structures by ^1H n.m.r. spectroscopy. Thus including known compounds [1,2,8,9] some nine σ adducts of this sort have been characterized. In some cases where no adduct is formed, substitution involving displacement of ethene can start after *ca.* 30 min.

However, many of the σ adducts can only be detected in solution. The structure of these compounds, as well as those that can be isolated, is substantiated by the presence in their ^1H n.m.r. spectra of resonances due to the two groups of methylene protons: $amCH_2CH_2Pt$. Both, as expected, appear as 1 : 2 : 1 triplets with ^{195}Pt satellites also showing triplet structure, δ values lying in the ranges 2.7—4.5 for $amCH_2$ and *ca.* 2 for CH_2Pt in $CDCl_3$ [Supplementary Publication No. SUP 22540 (4 pp.)].† A cross check on the formation of the σ compound is provided by the disappearance of the

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

η-C_2H_4 spectrum from the clear region at *ca.* δ 4.8—5.0. In many cases reaction (i) does not go to completion, but the coexistence of π and σ species can readily be detected by the presence of resonances due to both η-C_2H_4 and σ-CH_2CH_2 protons. It was observed that primary amines could in fact form σ adducts; the failure to detect them earlier was partly due to congestion in the methylene region of the spectrum.[1]

When the solid amine and acac σ compounds are redissolved the n.m.r. spectra of the solutions so formed indicate some reversion to π complex and free am, which is complete when am is a pyridine derivative. This demonstrates the reversibility of reaction (i) as well as the incompleteness of formation of the σ compound in solution. Presumably those σ compounds which can be isolated have low solubilities compared with their parent π complexes; indeed (2; am = 4NMe_2-py) only dissolves in $CDCl_3$ on warming.

No NH protons associated with the $\overset{+}{\text{am}}CH_2\bar{C}H_2Pt$ unit in the σ adducts can be detected by n.m.r. This poses the question of whether (2) is a correct formulation, that is whether NH protons (if any) are retained by the amine group, am, or whether they are either lost from the molecule, or undergo migration, for example, to the platinum atom. However, the σ adduct (2; Y = Cl, Z = NEt_2H) has been shown to be a non-conductor,[1] so that in it this hydrogen atom cannot be ionic. Moreover, the fact that amines, such as pyridine and quinuclidine, which contain no NH protons can form σ adducts suggests that any amino-hydrogen atoms remain bonded to the nitrogen. This has been confirmed in the solid state for (2; Y = Cl, Z = NEt_2H) by *X*-ray studies [2] which reveal a short nitrogen–chlorine distance indicating a N–H–Cl interaction. In the Raman spectrum of (2; Y = Cl, Z = am = morph) there is an absorption at **3 068** cm^{-1}, which may be due to ν(N–H) of the $\overset{+}{\text{morph}}CH_2$ group. For (2; Y = Cl, Z = am = morph) and (1; Y = Cl, Z = morph), ν(PtN–H) occurs at **3 226** cm^{-1}.

Attempts to form σ compounds containing two different amines (*viz.* Y = Cl, Z = am′ as opposed to am) were unsuccessful, except in two instances, because amine exchange is very rapid in the π complexes (1), while reactions (i) and (—i) are also fairly quick. The σ-CH_2CH_2 resonances produced from equimolar mixtures of am′ and *trans*-[$PtCl_2$(am)(η-C_2H_4)] are broadened as if they are made up of sets of overlapping spectra given by the compounds containing the four combinations of am and am′. The two exceptions are the spectra produced by the amine combinations of t-butylamine or morpholine and pyridine, which we attribute to the 'unscrambled' compounds *trans*-[$PtCl_2$-($\bar{C}H_2CH_2\overset{+}{N}Bu^tH_2$)(py)] and *trans*-[$PtCl_2$($\bar{C}H_2CH_2\overset{+}{\text{morph}}$)-(py)] respectively (see later). The problem of scrambling of am and am′ does not arise in the acac system since there is no ligand exchange.

Inertness of the Pt–Z *Bond in the* σ *Compounds.*—Since unsubstituted alkyl groups exert a *trans* effect [5,10] the 2-ammonioethanide ligand, $\overset{+}{\text{am}}CH_2\bar{C}H_2$, might be labilizing in the σ compounds. No evidence was obtained from the n.m.r. spectra of the acac σ compounds in the presence of excess of amine to suggest any exchange of ligand.

Unfortunately, the study of the amine resonances in the amine σ compounds is complicated by three factors. Since reaction (i) does not go to completion it is not possible to obtain a spectrum of the σ compound uncontaminated with free amine and some η-ethene-amine complex. Secondly, owing to rapid exchange,[11] the free am and am in the π complex already produce a time-averaged spectrum,[2] which is liable to obscure the resonances of the platinum-bonded am of the σ compound if it is inert. Thirdly, in the σ compounds there are two amine groups.

At **30** °C, system (1; Y = Cl, Z = am) exhibits two sets of amine resonances, one with fixed δ values and the other whose position depends on amine concentration. We originally interpreted [1] this as indicating that the Pt–am bond of the σ compounds was labile like that of the π complex and that the $\overset{+}{\text{am}}$–CH_2 link was inert. However, at reduced temperatures (*e.g.* —40 to 0 °C) at slow scan, some of the peaks whose position is independent of concentration of free amine can be resolved into doublets (Table 1), *e.g.* the CH_3 resonance for am = NPr^iH_2 changes from a doublet to a doublet of doublets. Thus in the σ compound either there is one inert amine group, some of whose protons lose their equivalence on cooling, or there are two inert groups with almost identical spectra. Although the former is conceivable in aliphatic amine compounds, it is difficult to see how it could occur for am = pyridine or 3,5-dimethylpyridine, because of the absence of asymmetry. Therefore we follow the second interpretation making both amine groups in the σ compounds inert. Conclusive proof of this for (2; Y = Cl, Z = $^{15}NMe_2H$ or [^{15}N]py) is provided by **195**-platinum n.m.r. spectroscopy.[12]

Incidentally there is no evidence in σ adducts, such as (2; Y = Cl, Z = NMe_2H or NEt_2H), for either *Pt*–NH–

TABLE 1

δ Values at *ca.* —40 °C in $CDCl_3$ for various protons in system (1). *J* Values (Hz) are given in parentheses

am	Proton	σ Compound	π Complex	Free amine
$NEtH_2$	CH_3	1.4 (d of t, Δδ 0.0125, *J* 7.5)	1.42 (t, 7.5)	1.12 (t, 7)
NPr^iH_2	CH_3	1.44 (d, 7.0), 1.28 (d, 7.0)	1.45 (d, 7.0)	1.03 (d, 6.3)
NBu^tH_2	CH_3	1.44 (s), 1.32 (s)	1.45 (s)	1.15 (s)
NEt_2H	CH_3	1.45 (d of t, Δδ 0.015, *J* 7.5)	1.5 (t, 7.5)	1.12 (t, 7.5)
py	H_α	9.1 (d, 6.0), 8.92 (d, 6.0)	8.85 (d, 6.0)	8.74 (d, 5.5)
3,5Me_2-py	H_α	8.6 (s), 8.5 (s)	8.58 (s)	8.45 (s)
morph	NCH_2	3.4 (t, 5.0), 3.2 (t, 5.0)	3.42 (c)	2.9—3.03 (t, 5.0)
	CH_2O	4.0 (t, 5.0), 3.8 (t, 5.0)	3.84 (c)	3.7—3.8 (t, 5.0)

C*H* or Pt–N*H*–C*H* coupling, both of which occur in the corresponding π complexes (1; Y = Cl, Z = NMe_2H or NEt_2H). Thus in (2; Y = Cl, Z = NEt_2H) both sets of NCH_2 protons appear at 30 °C at δ 3.3 as one quartet (not as stated earlier [1]), with J(H–H) 7.5 Hz, which splits into a very narrow doublet on cooling to −40 °C. In neither set are the CH_2 protons inequivalent which they should be, since the Pt–N*H*–CH_2 and C–N*H*–CH_2 groupings correspond to ABX, not A_2X, systems. We have discussed the phenomenon more fully elsewhere, attributing the absence of coupling and of inequivalence to the lability of each of the NH protons.[12]

amCH_2CH_2Pt *N.M.R. Data and* K_i.—δ(CH_2Pt) is affected to a small extent by Z and by am. δ(NCH_2) varies to a much greater extent, chiefly due to changes in am, *viz. ca.* 2.7—3.0 for am = al-am, and *ca.* 4.0—4.5 for am = py or imH. There is no correlation between K_i and δ(NCH_2). The relevant n.m.r. data are to be found in SUP 22540.

Equilibrium Studies between the π Complex and σ Adduct.—In principle it ought to be possible to obtain K_i by adding aliquots of am to the π complex and following the changes in absorbance in the visible–u.v. spectrum or the decreases in the area of the η-C_2H_4 n.m.r. peak at δ *ca.* 4.9. Suitable changes in the region 300—350 nm enable the first method to be used for Y = Cl and Z = am between 0 and 30 °C. (The change in spectrum is complete within the time of mixing and manipulation. However, in some instances further changes become apparent after *ca.* 10 min.) K_i was obtained graphically using the Benesi–Hildebrand Equation [13,14] (see Experimental section). These values together with corresponding $\Delta H^{\ominus}_i$ and $\Delta S^{\ominus}_i$ are given in Table 2.

TABLE 2

Thermodynamic data [a] for reaction (i)

		Y = Cl, Z = am					Y–Z = acac	
		K [c]/dm³ mol⁻¹		$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$298\Delta S^{\ominus}/\Delta H^{\ominus}$	K [c]/dm³ mol⁻¹	
am	pK_a (am) [b]	298 K	229 K	kJ mol⁻¹	J K⁻¹ mol⁻¹	dm³ mol⁻¹	298 K	229 K
NPr^nH_2	10.7	20, *ca. 20*		−60 ± 4	−176 ± 14	0.87 ± 0.13	*ca. 73*	
NPr^iH_2	*ca.* 11	10		−44 ± 6	−127 ± 20	0.86 ± 0.25		
NBu^nH_2	10.7	25		−56 ± 8	−162 ± 27	0.86 ± 0.27	*ca. 70*	
NBu^iH_2	10.6	27		−46 ± 5	−128 ± 17	0.83 ± 0.20		
NBu^sH_2	10.6	7.5		−40 ± 8	−120 ± 28	0.89 ± 0.38		
NBu^tH_2	10.7	7, *ca. 14*		−36 ± 4	−106 ± 14	0.88 ± 0.24	*ca. 10*	
$N(C_6H_4)H_2$	10.6	27		−64 ± 8	−189 ± 10	0.87 ± 0.15		
Cyclopentylamine	10.7	19		−48 ± 10	−140 ± 40	0.87 ± 0.43		
Cyclohexylamine	10.7	6.5		−44 ± 11	−130 ± 37	0.88 ± 0.47		
Cycloheptylamine	10.6	8		−59 ± 10	−181 ± 10	0.91 ± 0.21		
$EtO_2CCH_2NH_2$	7.6	*<0.1*	*<0.1*				*<0.1*	*<0.1*
NEt_2H	11.0	12, *ca. 8*	*490* [d]	−31 ± 7	−84 ± 25	0.81 ± 0.42	*ca. 23*	*ca. 142*
$NPr^n{}_2H$	10.9	7		−29 ± 3	−82 ± 3	0.84 ± 0.12		
$NPr^i{}_2H$	11.0	*ca. 0.2*					*ca. 0.2*	
$NBu^n{}_2H$	11.3	8		−15 ± 3	−32 ± 11	0.64 ± 0.34		
$NBu^i{}_2H$	11.0	*ca. 0.2*					*ca. 0.2*	
$NBu^s{}_2H$	11.0	*ca. 0.2*					*ca. 0.2*	
$NBu^t{}_2H$		*ca. 0.2*					*ca. 0.2*	
Cyclohexyl(methyl)-amine	11.0	18		−45 ± 6	−126 ± 20	0.83 ± 0.24		
NEt_3	10.7	*<0.2*	*ca. 1*				*0.1*	
$N(CH_2Ph)H_2$	9.4	*ca. 1*					*ca. 11*	
N[CH(Me)Ph]H_2	9.4	*ca. 1*						
pip	11.1	*>500*					*>1 000*	
2Me-pip	11.0	30						
3Me-pip	11.1	>500						
4Me-pip		>500						
2,6Me_2-pip		*0.1*	*<0.1*					
Pyrrolidine	11.1	>500					*>1 000*	
morph	8.4	53		−36 ± 3	−89 ± 3	0.74 ± 0.34	*ca. 12*	
Quinuclidine		*ca.* 25						
imH	7.1	*<0.1*	*ca. 20*				*<0.1*	*ca. 0.1* [e]
py	5.2	*<0.1*	*ca.* 1 [e]				*<0.1*	*<0.1* [e]
2Me-py	5.9	*<0.1*	*0.2*				*<0.1*	*<0.1* [e]
3Me-py	5.6	*<0.1*	*ca. 6.5*	*ca. −47*	*ca. −189*		*<0.1*	*<0.1* [e]
4Me-py	6.0	*<0.1*	*ca. 9.6*	*ca. −57*	*ca. −231*		*<0.1*	*<0.1* [e]
3,5Me_2-py	6.2	*<0.1*	*ca. 11.7* [e]	*ca. −43*	*ca. −167*		*<0.1*	*<0.1* [e]
4CN-py	1.9	*<0.1*	*<0.1*				*<0.1*	*<0.1*
Aniline	4.6	*<0.1*	*<0.1*				*<0.1*	*<0.1*
N-Methylaniline	4.8	*<0.1*	*<0.1*				*<0.1*	*<0.1*
Pyrrole	*ca. 4*	*<0.1*	*<0.1*				*<0.1*	*<0.1*
Quinoline	4.9	*<0.1*	*<0.1*				*<0.1*	*<0.1*

[a] Determined from u.v. spectroscopy, except for italicized values which were obtained by n.m.r. spectroscopy. [b] At 25.0 °C error ±0.01; D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, Oxford, 1965. [c] Measured, not extrapolated, values. [d] Calculated from $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. [e] Five-co-ordinate species (3) formed.

The n.m.r. method enabled equilibrium (i) to be studied over a much wider temperature range (−60 to 40 °C), but the values of K_i so obtained were less reproducible and less accurate than those obtained from u.v. spectra, although the former do agree with the latter to within a factor of two. The N*H* resonances of the π complexes lie close to the C_2H_4 peaks and are broadened not only by ^{14}N-quadrupole relaxation but by breaking of the Pt–N and N–H bonds. Since these are labilized by traces of Lewis bases such as acetone, water, and free amine, the lack of reproducibility may be due to the N*H* resonances broadening through the C_2H_4 absorptions.

Unfortunately in the acac σ compounds strong absorption bands obscure the *d–d* transitions, so that u.v. spectroscopy cannot be used.

Uncertainty in K_i is also introduced in cases in which the five-co-ordinate complexes (3) are formed [see reaction (ii)], but this only occurs with a few heterolytic amines at low temperature.

Where π complex and σ adduct can coexist in the presence of excess of amine, lowering of the temperature always moves equilibrium (i) to the right. However, in some cases, *e.g.* am = pyridine, Y–Z = acac, no σ adduct could be detected at our lowest temperature (*ca.* −65 °C, the freezing point of a chloroform–am mixture), while in others, *e.g.* am = piperidine with either Y = Cl, Z = am or Y–Z = acac, conversion into the σ adduct appears to be nearly quantitative, even at the upper temperature limit (*ca.* 40 °C). The values of K_i for the acac compounds in which am is a strong amine are equal to or slightly greater than those for the amine systems at 298 K. However, at lower temperature the semiquantitative n.m.r. data indicate that the acac σ compounds are more stable than the amine ones if am is diethylamine, but less so if it is heterocyclic, a point which will be taken up later.

The nucleophilicity of an amine can depend on both electronic and steric effects.[15] For strong aliphatic amines both factors are important in determining N–B bond dissociation energies in $(alkyl)_3N$–$B(alkyl)_3$ systems, for example. In the amine systems here the steric factor is much the more significant as is illustrated by the fall in K_i on going from a primary to a tertiary amine or from a linear to a branched isomer: the small differences in basicity of the strong aliphatic amines do not correlate with K_i, and it is only with the less basic glycine ethyl ester that there is a clear electronic effect. Another system in which nucleophilic attack is governed by steric rather than electronic factors is the somewhat related reaction (iii) in which alcohols attack activated CO.[16] k_{iii} is governed by the lack of bulk in R rather than in its donor capacity.

$$ROH + [PtCl(CO)(PPh_3)_2]^+ \rightleftharpoons [PtCl(CO_2R)(PPh_3)_2] + H^+ \quad \text{(iii)}$$

In both the amine and acac systems, the values of K_i when am is piperidine, pyrrolidine, or quinuclidine are much larger than for comparable secondary and tertiary aliphatic compounds. Again this also can be ascribed to steric effects, the alicyclic amines being more compact. (Substitution at the 2 position in piperidine reduces K_i drastically.) Piperidine, pyrrolidine, and quinuclidine also form strong N←B links in amine–BMe_3 adducts.[15] The σ adducts of morpholine show enhanced stabilities in different ways. K_1 (Y = Cl, Z = morph) is large compared with values for secondary aliphatic amines, while the adduct (Y–Z = acac) is the only member of the acac family which has been isolated as a solid (see earlier).

Very weak bases (pK_a <5) do not form σ adducts at all. Providing there is no steric hindrance, as there is in 2-methylpyridine, stronger bases ($5 < pK_a < 8$) will form adducts at 229 K if they are aromatic provided Z is an amine. Glycine ethyl ester, which is comparable in basicity to imidazole, will not form an adduct, and none of these moderate bases will react to give a σ-acac compound. These observations, together with that noted earlier that the acac adducts with strong bases are more stable at lower temperatures than the comparable amine ones, indicate that π as well as σ effects must be important in determining the values of K_i. This is logical since there is considerable π bonding between the olefin and platinum in the π complexes (1), and presumably very little involving the ethanide group in the σ adducts (2).

It is interesting that, although steric factors appear to be much more important in determining K_i than basicities, the ratios of entropy to enthalpy of activation are roughly constant, *viz.* $298\Delta S^{\ominus}_i/\Delta H^{\ominus}_i$ lies fairly close to 0.8 for all the strong amines. The strain that is introduced by formation of the σ adducts is manifest in both thermodynamic parameters. Incidentally, the $\Delta S^{\ominus}_i$ values are all negative as would be expected for equilibria in which adducts are formed.

Five-co-ordinate Complexes.—Another type of nucleophilic attack by amines has already been reported,[4] namely direct attack at the platinum as in reaction (ii) to give five-co-ordinate species (3) at below *ca.* −30 °C. Reaction (ii) is fast, so that the existence of (3) is inferred by movement of the time-averaged ^{1}H n.m.r. spectra of the η-C_2H_4 ligand from δ *ca.* 4.9 to *ca.* 3.9.[4] However, the reaction is very selective from the point of view of am; no aliphatic or alicyclic amines appear to form five-co-ordinate species, nor do very weak bases. It is only for a few heterocyclic amines that (3) can be detected (see footnote *e* in Table 2).

In the acac systems a five-co-ordinate system is formed provided the pK_a of the base is greater than 5. The need for the base to be heterocyclic is illustrated by imidazole (pK 7.1) and glycine ethyl ester (pK 7.6), the latter forming no five-co-ordinate compound. K_{ii} can be estimated approximately, being 1.4 dm^3 mol^{-1} at 229 K for am = py, Z–Y = acac.

In the amine systems, it is only in the case of am = py that the large shift in the ^{1}H n.m.r. spectrum associated with the formation of the five-co-ordinate species can be seen, although there is some change in the 3,5-dimethylpyridine case. At 229 K, K_{ii} is lower than in the acac

system being *ca.* 0.3 dm^3 mol^{-1} (*i.e.* for Y = Cl, Z = am = py). K_i is larger, namely *ca.* 1 dm^3 mol^{-1}. Since the σ adduct and five-co-ordinate species are formed competitively, we probably would not be able to detect the latter using ^1H n.m.r. if $K_{ii}/K_i > 10$. Hence the absence of such compounds for Y = Cl and am = Z = most methylpyridines or imidazole could be due to an increase in the basicity of am having a greater stabilizing effect on the am–CH_2 link in (2) than on the second Pt–am bond in (3). For all the systems, Y = Cl, am = Z = al-am in which am is strong and unhindered, K_i is large enough to prevent the formation of five-co-ordinate species in detectable quantities. However, in the case of Y = Cl and am = Z = glycine ethyl ester where no σ adduct is formed at 229 K, no five-co-ordinate species is produced either.

Taken with the results for the acac systems, this last result seems to indicate that aromaticity, and hence π character, in am may be an essential requirement for the stabilization of the five-co-ordinate compounds. An interesting implication is that an associative substitution process may be facilitated by π bonding by the exchanging ligands.

Contrast in the Nucleophilicity of Amines towards Pt *and* η-C_2H_4.—In the amine systems (1; Y = Cl, Z = am) soft nucleophiles such as phosphines, dimethyl sulphoxide, dimethyl sulphide, and pyridine *N*-oxide readily attack the platinum atom causing the replacement of Z in the first instance. However, we have been able to find no evidence from ^1H n.m.r. studies between 30 and −65 °C of addition of those soft bases to the CH_2CH_2 group. (Such reactions as there are involving the ethene are ones of ligand exchange.) This illustrates the contrast between the platinum(II) centre as a soft acid and the CH_2CH_2 unit as a hard one.

The same effect can be seen to some extent in the behaviour of strong amines compared with pyridines. If equimolar amounts of a pyridine and (1; Y = Cl, Z = al-am) are mixed at room temperature, considerable exchange occurs resulting in a mixture of products, one of the chief ones being (2; am = al-am, Y = Cl, Z = py). In fact this is the sole product if Z is morpholine. However, if an excess of al-am is then added (2; am = Z = al-am, Y = Cl) is formed, showing that nucleophilicity of pyridine even to the platinum is less than that of a strong amine.

In addition to electronic effects, steric factors influence the relative nucleophilicity of the am towards the C_2H_4 and Pt position. Thus, while treatment of 1 mol of (1; Y = Cl, Z = py) with 2 mol of NEt_2H yields (2; Y = Cl, am = Z = NEt_2H) almost quantitatively, 2 mol of NBu^tH_2 produce a large amount of (2; Y = Cl, am = NBu^tH_2, Z = py).

Further Reactions.—The processes discussed so far are rapid. However, in some cases further reactions can be detected in the chloroform solutions of π complex and free amine after *ca.* 10 min at 25 °C. Ligand exchange occurs, ethene being displaced by am, the reaction being particularly apparent in instances where the σ compound is not stable, *e.g.* when am is a pyridine. With pyridine itself, yellow and white deposits of $[PtCl_2(py)_2]$ and $[Pt(py)_4]Cl_2$ eventually are precipitated.

EXPERIMENTAL

Preparations.—$[PtCl_2(am)(\eta\text{-}C_2H_4)]$. To $K[PtCl_3(C_2H_4)]$ (1 mmol) in water (20 cm^3) cooled to 0.5 °C was added slowly with stirring am (1 mmol) in water (10 cm^3). The yellow crystals which separated were washed with cold water followed by a little pentane, and recrystallized from chloroform–pentane. (When am was not soluble in water, methanol or acetone was used as solvent, crystallization being induced by freeze-drying.)

$[PtCl_2(am)(\bar{C}H_2\overset{+}{C}H_2am)]$. (*a*) *am* = NBu^tH_2 *or* NPr^iH_2. The compound $[PtCl_2(am)(\eta\text{-}C_2H_4)]$ (0.5 mmol) was dissolved in acetone (10 cm^3) at −10 to 0 °C in an atmosphere of dry nitrogen and to this was added with stirring amine (0.5 mmol) in acetone (2.6 cm^3). After 40 min the solvent was removed at reduced pressure, the reaction mixture being kept at a temperature lower than 0 °C. The yellow crystals were washed with n-pentane, and dried *in vacuo* at 0 °C.

(*b*) *am* = *morph or* 4NMe_2-py. The compound $[PtCl_2(amine)(\eta\text{-}C_2H_4)]$ in chloroform solution (1 cm^3) was cooled to −40 °C, then am (0.25 mmol) added. The yellow crystals which precipitated were filtered off and dried under vacuum (Found: C, 25.85; H, 4.70; N, 5.70. Calc. for am = morph: C, 25.6; H, 4.70; N, 5.90%).

$[Pt(acac)Cl(\bar{C}H_2\overset{+}{C}H_2morph)]$. Morpholine (0.055 mmol) was added to $[Pt(acac)Cl(\eta\text{-}C_2H_4)]$ (0.5 mmol) in chloroform (0.5 cm^3) at −40 °C. The pale yellow crystals which precipitated immediately were filtered off and dried in vacuum (Found: C, 29.65; H, 4.20; N, 3.05. Calc.: C, 29.7; H, 4.40; N, 3.15%).

U.v. Spectroscopy.—Values of K_i were found using the Benesi–Hildebrand [13,14] equation (iv), in which $[Pt]_T$

$$\frac{1}{\Delta A} = \frac{1}{K_i(\Delta\varepsilon)l[Pt]_T} \cdot \frac{1}{[am]} + \frac{1}{(\Delta\varepsilon)l[Pt]_T} \qquad \text{(iv)}$$

represents the total concentration of platinum. Aliquots of am were added to a solution of (1) and the alteration (usually a decrease) in absorbance, ΔA, noted at the wavelength at which the maximum change occurs (between 300 and 350 nm). A graph of $1/\Delta A$ against 1/[am] will be linear providing that the stoicheiometry is as shown in reaction (i), *i.e.* [(1)] : [am] = 1 : 1, and providing that the amount of added am converted into (2) is small, *i.e.* that K_i is small; in fact here $K_i < 500$ dm^3 mol^{-1}. K_i then follows from the ratio of intercept to slope, the other parameters not being needed: Δε = difference in absorption coefficient of (1) and (2); l = path length. Since Δε, l, and $[Pt]_T$ should all be independent of temperature so should the intercept be, which provides a useful check. Of all the amines studied, those for which $\Delta H^\ominus$ and $\Delta S^\ominus$ are quoted gave, within experimental error, linear Benesi–Hildebrand plots with constant intercepts between 5 and 35 °C.

An alternative plot was also tested based on equation

$$\log[(A_0 - A_x)/(A_x - A_\infty)] = \log K_i + n\log[am] \qquad \text{(v)}$$

(v).[17] Here A_0, A_x, and A_∞ are absorbances after addition addition of zero, an aliquot, and a large excess of amine

respectively, and the equation assumes a $1 : n = [Pt] : [am]$ stoicheiometry and that (1) is converted into (2) completely at the A_∞ measurement. Plots of log $[(A_0 - A_\infty)/(A_x - A_\infty)]$ against log [am] for those amines which had behaved conventionally in the Benesi–Hildebrand treatment gave straight lines of gradient 1.0 ± 0.1, with values for K_i which agreed reasonably with those obtained by n.m.r. spectroscopy.

However, when am was pyrrolidine or an unhindered piperidine, Benesi–Hildebrand plots which were linear and log–log plots with gradients near to 1.0 were only obtained at temperatures above *ca.* 25 °C. Below that temperature the latter gave larger gradients and the former curved plots even after iterative corrections based on approximate K_i had been made to [am] to allow for the amine which has been converted into (2). Therefore while we feel reasonably confident of the values quoted in Table 2 for these amines at 25 °C, they do neglect the fact that more complicated reactions seem to occur at lower temperatures.

N.M.R. Spectroscopy.—A 100-MHz JEOL machine was used, the solvent for all quantitative studies being $CDCl_3$. Where K_{ii} was negligible, K_i was estimated from changes in the area of the η-C_2H_4 peak of (1) at *ca.* δ 4.9. Where K_i was negligible, K_{ii} was estimated from the position of the average η-C_2H_4 due to (1) and (3), that for the latter being at *ca.* δ 3.9. When both were finite, approximate values of K_i and K_{ii} were obtained using the same measurements and including the area of the CH_2 peak of (2) at *ca.* δ 2.45.

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