Formation of Platinum–Enamine Complexes by Reaction of Zeise's Salt with Secondary Amines

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Enamine complexes of platinum [Pt($CH_2CH{=}NRR'$)Cl_2(NHRR')] are obtained in the reaction of secondary amines [HNRR' = piperidine, $HNEt_2$, or HNMe(CHMePh)] with Zeise's salt K[Pt(η^2-C_2H_4)Cl_3]. The enamine ligand results from addition of the amine to the platinum-bonded olefin and subsequent loss of two hydrogen atoms. In the case of HNMe(CHMePh) (which has two different alkyl substituents at the nitrogen atom) two isomeric enamine ligands can be formed (having configurations *E* and *Z* respectively). Isomer *E* (NMe group *cis* to the metal atom) is *ca.* ten times more favoured than the other and exhibits ${}^5J$(Pt–H) 12.5 Hz which is indicative of a through-space interaction between the methyl group and the metal.

Olefins can be either κ or η^2 bonded to a metal atom. The η^2 type of bonding is observed in complexes with non-polar or weakly polar olefins such as vinyl alcohol,[1] vinyl ethers,[2] and aromatic vinylamines.[3] On the contrary very polar olefins such as 1,1-dimethoxyethylene,[4] 1,1-bis(dimethylamino)ethylene, and 1,3-dimethyl-2-methyleneimidazoline appear to give the κ-bonded species either exclusively or in equilibrium with the η^2 complex.[5]

Aliphatic vinylamines are intermediate between the two classes of olefins outlined above, however they are rather unstable and easily hydrolysed to aldehyde and amine so that very few papers have dealt with their co-ordination chemistry. Complexes of formula *cis*-[MCl_2(amine)(enamine)] (M = Pd or Pt) have been prepared by reaction of the preformed enamine with the ethylene complex [{$MCl_2(C_2H_4)$}$_2$]; a partial hydrolysis of the enamine led to formation of the amine ligand present in the final complex.[6] Complexes of formula [{$PdCl_2$(enamine)}$_2$] were obtained by reaction of [$PdCl_2(NCPh)_2$] with a tertiary amine. In this case the enamine was formed *in situ* by dehydrogenation of one alkyl substituent of the amine.[7]

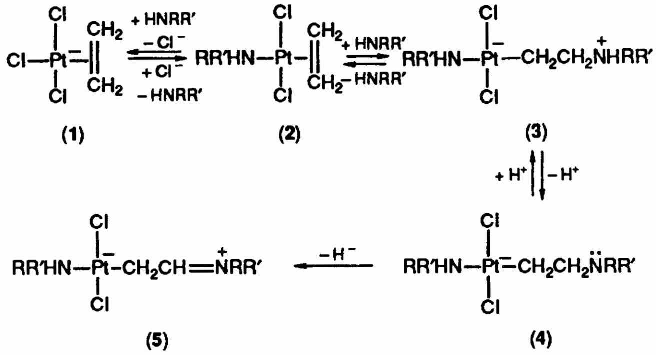
We have found a new route to enamine complexes *via* nucleophilic addition of a secondary amine to a platinum-bonded olefin and dehydrogenation of the 2-ammonioethanide ligand obtained therefrom.

Results and Discussion

Zeise's salt, K[Pt(η^2-C_2H_4)Cl_3] (**1**), reacts with nucleophiles (L) to give a chloride-ion substitution and formation of *trans*-[Pt(η^2-C_2H_4)Cl_2(L)] (**2**).[8]

Complex (**2**) can react with a second molecule of nucleophile (L′), undergoing attack on the co-ordinated ethylene and formation of *trans*-[Pt(CH_2CH_2L')Cl_2(L)] (3), in which a π to σ rearrangement of the metal–olefin bond has taken place.[9] Complex (3) is rather stable when L′ is a secondary amine of high basicity and relatively small bulk.[9,10]

On some occasions the 2-ammonioethanide ligand ($-CH_2CH_2L'$) can be deprotonated [complex (4)] and the free nitrogen base can result in nucleophilic attack either upon another molecule of olefin complex[11] or upon the same metal atom with formation of a four-membered metallacycle.[12] We have now observed another possible rearrangement of compound (3). In the case under investigation a solution of (3) in dichloromethane left to stir for a few days at room temperature undergoes extensive decomposition to platinum metal; the main product left in solution has the same elemental analysis as for (3) but i.r. and n.m.r. spectra which are in accord with the formation of a platinum–enamine complex [Pt($CH_2CH{=}NRR'$)Cl_2(NHRR′)] (**5**) (see later).



Scheme 1. Formation of complex (**5**) starting with Zeise's salt and amine

The sequential reaction steps are summarized in Scheme 1. This reaction mechanism implies that the ease of formation of complex (**5**) depends upon (*i*) the relative stability of (3) with respect to (**2**) and (*ii*) the extent of deprotonation of (3) to give (4). Moreover since the transformation of (4) into (5) implies the loss of an hydride ion, the possible fate of this reagent has to be accounted for.

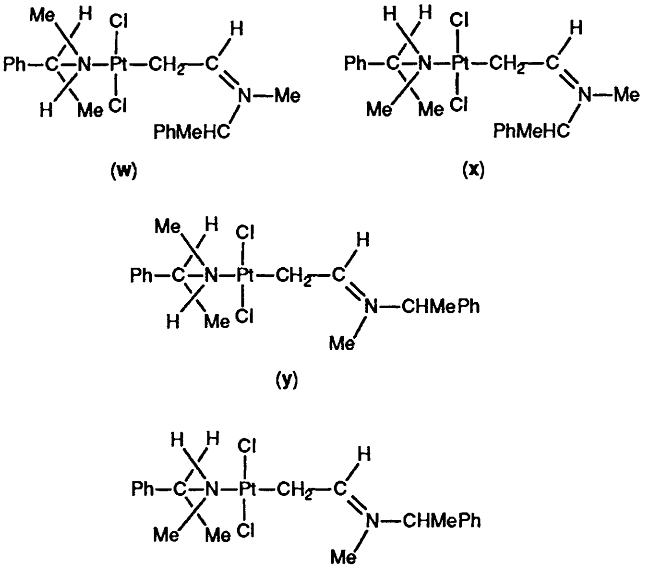
We have performed the reaction using three different amines: $HN(CH_2)_4CH_2$ (**a**), $HNEt_2$ (**b**), and HNMe(CHMePh) (**c**).[9] It was already known that in chloroform solution compound (3) is rather stable towards dissociation [into (2) and free amine] only in the case of (**a**) while dissociation occurs in the case of (**b**) and (**c**). Under the experimental conditions used, compound (3**a**) gave the better results in terms of rate and yield of formation of (**5**) which is in complete accord with the suggested mechanism.

We also demonstrated that the yield and rate of formation of complex (**5**) increase if the acidity of the reaction medium is controlled by the addition of a base (K_2CO_3) under heterogeneous conditions (it is important to avoid the addition of a base which is soluble in dichloromethane since this could cause a side reaction with rapid decomposition of the platinum complexes to platinum metal). This observation is also in accord with Scheme 1 since the presence of a base could favour the deprotonation of (3) to give (4).

Table. Proton chemical shifts (δ, downfield from $SiMe_4$) and coupling constants [J(H–H) in Hz are given in parentheses, J(Pt–H) in square brackets] of co-ordinated amine and enamine ligands in compounds (**5**). The notation used to distinguish the various protons is as follows: $[Pt(CH^k{}_2CH^l{=}\overline{NCH^m{}_2CH^n{}_2CH^o{}_2CH^n{}_2C}H^p{}_2)Cl_2(\overline{NH^qCH^r{}_2CH^s{}_2CH^t{}_2CH^s{}_2C}H^r{}_2)]$, (**5a**); $[Pt\{CH^k{}_2CH^l{=}N(CH^m{}_2CH^n{}_3)(CH^o{}_2CH^p{}_3)\}Cl_2\{NH^q(CH^r{}_2CH^s{}_3)_2\}]$, (**5b**); and $[Pt\{CH^k{}_2CH^l{=}NMe^m(CH^nMe^oPh)\}Cl_2\{NH^qMe^r(CH^sMe^tPh)\}]$, (**5c**)

	k	l	m	n	o	p	q	r	s	t
(**5a**)	3.20(9.1)	7.41(9.1)	3.41	1.70	1.41	3.45	—	3.03	1.70	1.41
(**5b**)	3.30(9.1)	7.49(9.1)	3.48(7.1)	1.19(7.1)	3.42(7.1)	1.42(7.1)	—	2.66,3.09[a](7.0)	1.49(7.0)	—
(**5c**)[b]	3.40,3.42[a](8.9)[80]	7.92(8.9)	2.86[12.5]	4.84(7.0)	1.80(7.0)	—	3.6—3.7	2.42(6.0)[24]	4.05(6.8)[4.3]	1.98(6.8)[7]
	—	—	2.78	4.60(7.0)	1.40(7.0)	—	—	2.62(6.0)[24]	—	1.62(6.8)[7]

[a] The two resonances originate from a diastereotopic splitting of the methylenic protons. [b] Two sets of signals were observed for this compound: the values of the more intense set is reported on the first row, those of the less intense on the second row.



Scheme 2. Four isomers of compound (**5c**) resulting from different configurations of the co-ordinated aminic nitrogen [S in (**w**) and (**y**) and R in (**x**) and (**z**)] and different geometrical isomerism of the enamine [Z in (**w**) and (**x**) and E in (**y**) and (**z**)]

Concerning the fate of the hydride ion, the release of which has been hypothesized in the transformation of (**4**) into (**5**), we suggest that it is taken up by a molecule of complex which is reduced to platinum metal. The overall stoicheiometry for the transformation of (**3**) into (**5**) would therefore be as in equation (1).

$$2[Pt(CH_2CH_2NHRR')Cl_2(NHRR')] \longrightarrow [Pt(CH_2CH{=}NRR')Cl_2(NHRR')] + Pt + 2HNRR'{\cdot}HCl + C_2H_4 \quad (1)$$

In accord with the above stoicheiometry the maximum yield of (**5**) never exceeded 50% of the total platinum substrate, no other platinum complexes were left in solution at the end of the reaction [except (**5**)], and platinum metal was deposited. Moreover, since uncomplexed amine is formed during the reaction [the ammonium salt of equation (1) can be neutralized by the potassium carbonate] and its accumulation in the dichloromethane solution can cause decomposition of the platinum substrates in a basic medium, we noticed that better yields of (**5**) can be obtained starting with complex (**2**) and $\leqslant 0.5$ equivalent of free amine, instead of (**3**). The amine which is released during the reaction reacts further with (**2**) forming (**3**).

It is finally to be noted that an intermediate species analogous to (**4**) was postulated in the reaction of tertiary amines with palladium(II) to give enamine complexes;[7] the loss of a hydride ion from the β carbon of (**4**) could be facilitated by the presence of an electron-rich aminic nitrogen adjacent to it.[13]

Of the two possible modes of binding of an enamine ligand to a metal [σ, $M{-}CH_2CH{=}NRR'$; and π, $M(CH_2{=}CH{-}NRR')$], only one (σ) is present in all the complexes investigated here (i.r. and n.m.r. data).

The most important feature in the i.r. spectra of complexes (**5**) is the appearance of a strong signal near 1 600 cm^{-1} which is indicative of a C=N double bond; ν(Pt–Cl) occurs in the region between 300 and 320 cm^{-1}.

The n.m.r. data are summarized in the Table. The resonance of the methylene protons occurs at rather high field and is characterized by strong coupling with platinum [80 Hz for (**5c**)]. The resonance of the vinyl proton, on the other hand, occurs at *ca.* δ 7.5 and is weakly coupled with platinum (9 Hz). Both data are indicative of a σ-bonded enamine complex.

The more complex spectrum of (**5c**) deserves further discussion. In this complex the two alkyl substituents at the nitrogen are different and, furthermore, one of them is asymmetric, therefore, also starting with an optically pure isomer of *N*-methyl-1-phenylethylamine (we have used that with *S* configuration at the asymmetric carbon) different isomers of compound (**5c**) can be obtained. The platinum-bonded amine has a second chiral centre at the co-ordinated nitrogen and its configuration can be either equal to or different from that of the adjacent carbon.[14] Furthermore two geometrical isomers can arise from the enamine (*E* or *Z*) depending upon the relative position of the substituents with respect to the C=N double bond. Therefore, altogether four different species can be formed as shown in Scheme 2.

Only two sets of signals are observed either for the co-ordinated amine or for the enamine, and the intensity ratio is, in both cases, 10:1. This could be interpreted by presence of only two out of the four possible stereoisomers of (**5c**), however a more simple and likely explanation is that the ^1H resonances for each ligand are not affected by the configuration of the ligand in *trans* position so that for the amine ligand only one set of resonances arises from isomers (**w**) and (**y**) and another set from isomers (**x**) and (**z**). Similarly for the enamine ligand one set of resonances arises from (**w**) and (**x**) and another set from (**y**) and (**z**).

The more stable configuration of the amine occurs in isomers (**w**) and (**y**) in which the C and N atoms have equal absolute configuration and the steric interaction between the substituents at the two adjacent chiral centres is at a minimum. Therefore the most-intense set of signals will come from these two isomers, the less-intense set from the other two isomers (**x**) and (**z**). The degree of diastereoselectivity is similar to that already observed in compound (**2**) and results in an isomer ratio [(**w**) + (**y**)]/[(**x**) + (**z**)] of 10:1.[14]

On the other hand the more stable configuration for the enamine occurs in isomers (**y**) and (**z**), in which the configuration is *E* and the steric interaction between *cis* substituents with respect to the C=N double bond is at a minimum. Therefore the most-intense set of signals of the enamine arises from isomers (**y**) and (**z**), the less-intense from (**w**) and (**x**). As shown by the n.m.r. data also in this case the degree of selectivity results in an isomer ratio [(**y**) + (**z**)]/[(**w**) + (**x**)] of *ca.* 10:1.

As a consequence of the above interpretation of the n.m.r. data the most stable isomer of (**5c**) is (**y**) in which both the amine and the enamine adopt the more-stable configuration. This is followed by isomers (**w**) and (**z**) in which only one of the two organic ligands adopts the more-stable configuration [the amine in (**w**) and the enamine in (**z**)], the abundance of each of these isomers is expected to be *ca.* 1:10 that of the most abundant isomer (**y**). Finally isomer (**x**) is the least abundant since both the amine and the enamine adopt the less-stable configuration [the relative abundance of this isomer is expected to be *ca.* 1:10 that of (**w**) and (**z**) and 1:100 that of (**y**)]. The interpretation of the n.m.r. data given above is supported by the observation that the more intense set of signals of the co-ordinated amine [arising from isomers (**w**) and (**y**)] has two resonances for the NMe group which are 0.03 p.p.m. apart and have an intensity ratio of *ca.* 10:1. The most likely interpretation is that the two resonances arise, respectively, from isomers (**w**) and (**y**) the relative abundance of which is exactly 10:1.

Therefore, as expected, the amine co-ordinates to the metal with a high degree of enantioselectivity, the form with equal configuration at the C and N atoms being *ca.* ten times more abundant than the other; a comparable degree of enantioselectivity was observed in compound (**2**).[14]

Also the enamine is formed with a high degree of regioselectivity the *E* configuration being *ca.* ten times more abundant than the *Z* one. The NMe protons of the enamine in the *E* form exhibit a ^{195}Pt coupling constant of *ca.* 12.5 Hz, despite of a five-bond separation from the metal. This can be explained on the basis of a through-space interaction between these protons and the metal atom which are *cis* to one another.

Experimental

Starting Materials.—Commercial reagent-grade chemicals were used without further purification. The amine HNMe[CHMePh(*S*)] was prepared by methylation of the corresponding optically pure primary amine, following the method of Johnstone *et al.*[15] Zeise's salt, K[Pt(C_2H_4)Cl_3], was prepared from potassium tetrachloroplatinate(II) and ethylene gas.[16]

Preparation of Complexes.—*trans*-[Pt(C_2H_4)Cl_2(L)] [L = $H\overline{N(CH_2)_4CH}_2$, (**2a**); HNEt$_2$, (**2b**); *or* HNMe(CHMePh), (**2c**)]. To a solution of Zeise's salt (1.00 g, 2.37 mmol) in cold water (15 cm^3), was added dropwise an equimolar amount of the amine hydrochloride (in 5 cm^3 of water) with stirring. The reaction flask was cooled to 0 °C (ice-bath) and brought to neutrality by addition of a solution of KOH (0.1 mol dm^{-3}). The yellow precipitate which formed was collected by filtration of the mother-liquor, washed with a small amount of water, and dried in a desiccator over KOH. Yield 80% [Found: C, 22.4; H, 4.2; Cl, 18.3; N, 3.8. Calc. for $C_7H_{15}Cl_2NPt$, (**2a**): C, 22.2; H, 4.0; Cl, 18.7; N, 3.7. Found: C, 19.8; H, 4.2; Cl, 19.0; N, 3.8. Calc. for $C_6H_{15}Cl_2NPt$, (**2b**): C, 19.6; H, 4.1; Cl, 19.3; N, 3.8. Found: C, 30.8; H, 4.0; Cl, 16.6; N, 3.2. Calc. for $C_{11}H_{17}Cl_2NPt$, (**2c**): C, 30.8; H, 4.0; Cl, 16.9; N, 3.3%].

trans-[Pt(CH_2CH_2L)Cl_2(L)] [L = $H\overline{N(CH_2)_4CH}_2$, (**3a**); HNEt$_2$, (**3b**); or HNMe(CHMePh), (**3c**)]. These complexes were prepared according to the method of Benedetti *et al.*[9] To a solution of [Pt(C_2H_4)Cl_2(L)] in cold acetone (0 °C) was added dropwise, with stirring, an equimolar solution of the amine in the same solvent. After reaction for 0.5 h the solution was filtered, the solvent evaporated under reduced pressure, and the solid residue pumped *in vacuo.* No attempt to crystallize the products was made [Found: C, 31.3; H, 5.8; Cl, 15.0; N, 6.1. Calc. for $C_{12}H_{26}Cl_2N_2Pt$, (**3a**): C, 31.0; H, 5.6; Cl, 15.3; N, 6.0. Found: C, 27.6; H, 5.9; Cl, 15.6; N, 6.6. Calc. for $C_{10}H_{26}Cl_2N_2Pt$, (**3b**): C, 27.3; H, 5.9; Cl, 16.1; N, 6.4. Found: C, 43.0; H, 5.7; Cl, 12.2; N, 5.1. Calc. for $C_{20}H_{30}Cl_2N_2Pt$, (**3c**): C, 42.6; H, 5.4; Cl, 12.6; N, 5.0%].

trans-[Pt{CH_2CH=(L − H)}Cl_2(L)] [L − H = *deprotonated* L; L = $H\overline{N(CH_2)_4CH}_2$, (**5a**); HNEt$_2$, (**5b**); or HNMe(CHMePh), (**5c**)]. These compounds could be prepared starting with compound (**3**) or with a mixture of (**2**) and free amine. In a typical experiment a solution of (**2**) in CH_2Cl_2 (1 mmol in 30 cm^3) was treated with K_2CO_3 (1.5 mmol) and free amine [0.2 mmol in the case of piperidine (**a**) and *N*-methyl-1-phenylethylamine (**c**), 1 mmol in the case of diethylamine (**b**)]. The resulting mixture was allowed to react at room temperature for 1 week (4 d were sufficient in the case of piperidine) with stirring; in that time a certain amount of platinum metal was formed. The final solution was concentrated and chromatographed on an open column of silica gel using CH_2Cl_2 as eluant. The first fraction of eluate was collected, the solvent was evaporated under reduced pressure, and the solid residue dried *in vacuo.* Yields (referred to the starting material): 43, (**5a**); 36, (**5b**); and 32%, (**5c**) [Found: C, 31.1; H, 5.4; Cl, 15.5; N, 5.7. Calc. for $C_{12}H_{24}Cl_2N_2Pt$, (**5a**): C, 31.2; H, 5.2; Cl, 15.3; N, 6.1. Found: C, 26.8; H, 5.4; Cl, 15.5; N, 6.1. Calc. for $C_{10}H_{24}Cl_2N_2Pt$, (**5b**): C, 27.4; H, 5.5; Cl, 15.8; N, 6.4. Found: C, 42.3; H, 5.0; Cl, 12.2; N, 4.7. Calc. for $C_{20}H_{28}Cl_2N_2Pt$, (**5c**): C, 42.7; H, 5.0; Cl, 12.5; N, 5.0%].

Physical Measurements.—I.r. spectra were recorded as KBr pellets on a Perkin-Elmer 283 spectrophotometer, proton n.m.r. spectra with a Varian XL 200 spectrometer ($CDCl_3$ as solvent).

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