Coupling Constants $^{n}J(^{195}Pt-^{1}H)$, $^{n}J(^{195}Pt-^{13}C)$ and Pt←H–C Interactions in New Schiff-base Complexes of *N*-Alkyl-1-(*N*-methylpyrrol-1-yl)ethanimine

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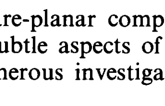
A series of complexes of the type *trans*-[PtCl$_2$(olefin)(imine)] olefin = ethene, propene, *cis*- or *trans*-but-2-ene; imine = *N*-alkyl-1-(*N*-methylpyrrol-1-yl)ethanimine; alkyl = Me, Pr^i, Bu^i, Bu^s, Bu^t) have been synthesized and studied by ^{1}H, ^{13}C, and ^{195}Pt n.m.r. spectroscopic methods. The H^3 and C^3 of the pyrrole ring couple to ^{195}Pt with $^{n}J(^{195}Pt-^{1}H)$ 8.3 Hz and $^{n}J(^{195}Pt-^{13}C)$ 16.6—20.5 Hz, which are too large for five- and four-bond coupling constants respectively, thereby suggesting a Pt←H–C interaction. Furthermore, long-range coupling constants were observed between different protons of the imine and ^{195}Pt. In addition, ^{1}H and ^{13}C n.m.r. spectra of (η^2-*trans*-but-2-ene) complexes show inequivalence of the proton and carbon atoms of the olefin. The ^{1}H, ^{13}C, and ^{195}Pt data are discussed in terms of the donor and acceptor properties of the imine ligands.

The assumption that metal olefin complexes are likely intermediates in the hydrogenation of alkenes has led to numerous studies concerned with the interaction of double bonds with metals.[1] In particular a number of ^{1}H and ^{13}C n.m.r. studies[2–8] concerned with platinum complexes of type (A) in which the olefin is frequently ethene and X an amine or imine derivative, have recently appeared. Both $\delta(^{13}C)(CH_2=)$ and $^{1}J(^{195}Pt-^{13}C)$ have been found to provide useful estimates of the *trans* influence of X and in all cases the sequence N > Cl > O was observed.[9,10]

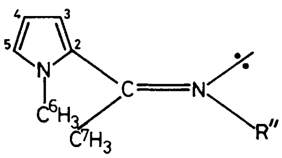


(A)

Although the Chatt–Dewar model explaining the nature of olefin bonding in square-planar complexes of Pt^{II} is widely accepted,[11] the more subtle aspects of this type of bond are still the subject of numerous investigations mainly by n.m.r spectroscopy.[5,6]

In another context, it is interesting to study the interaction of platinum with proximate carbon–hydrogen bonds. Molecular structure studies suggest M←H–C bonding interactions occur at distances of *ca.* 1.8—2.2 Å.[12,13] Pregosin and co-workers[14–16] recently showed that in compounds of the type *trans*-[PtCl$_2$(C$_9$H$_6$N-R-8)L], containing substituted quinoline (R = CHO, Me, Pr^i, or CHBr$_2$; L = PEt$_3$, PPh$_3$, or AsMePh$_2$) the aldehyde proton (R = CHO) is *ca.* 2.3 Å from the metal and couples to ^{195}Pt with a value between 12.4 and 19.7 Hz. In related complexes *trans*-[PtCl$_2${NC$_5$H$_3$(NCHR)-2-Me-3}-(AsEt$_3$)] the imine-proton–platinum separation of 2.43 Å.[17] The generality of this type of hydrogen–platinum interaction is still open to question. However we have prepared different types of platinum complexes with different ligands, that might display a similar CH←Pt interaction; compounds (**a**)—(**e**) should co-ordinate smoothly to platinum *via* the imino nitrogen, thereby bringing the methyl (C^7), or pyrrole C^3–H, bond into a position to interact with metal, *e.g.* as shown in Scheme 1.

Complexes involving ligands (**a**)—(**e**) are attractive because (*a*) the nature of olefin bonding in square-planar complexes, (*b*) the electronic and steric properties of R, and (*c*) the possibility of rotation about the C–N(imine) bond make this system somewhat less rigid than that of quinoline.



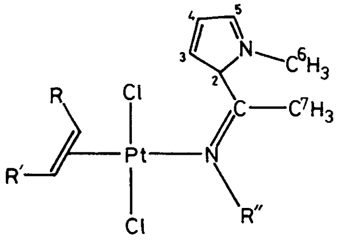
R''
(**a**) C^{8}H$_3$
(**b**) CH(C^{8}H$_3$)$_2$
(**c**) CH$_2$CH(C^{8}H$_3$)$_2$
(**d**) CH(C^{8}H$_3$)CH$_2$C^{9}H$_3$
(**e**) C^{10}(C^{8}H$_3$)$_3$

In the present study, ^{1}H, ^{13}C, and ^{195}Pt n.m.r. data have been collected for a number of platinum(II)–olefin complexes with Schiff bases and combined to study (*i*) their solution structures, (*ii*) to improve our knowledge in the field of n.m.r. spectroscopy, specifically ^{195}Pt, (*iii*) to study the structural distortions and/or differing metal–carbon bond strengths for CH= and CH$_2$=, (*iv*) to study the structural effect on $^{1}J(^{195}Pt-^{14}N)$, $^{1}J(^{195}Pt-^{13}C)$, and $^{2}J(^{195}Pt-^{13}C)$, and (*v*) to study the interaction of platinum with proximate carbon-hydrogen bonds.

Recently we reported the synthesis and characterization of some platinum(II) complexes containing imine ligands.[8,18,19] We have previously found that a stable, novel platinum(II)–olefin–unidentate σ-imine complex can be prepared and the structure and bonding studied by multinuclear n.m.r. spectroscopy.[8,18–20]

Results and Discussion

Since relatively little was known concerning either the ^{13}C or ^{195}Pt n.m.r. characteristics of a system such as (A), where X = imine, olefin = ethene, propene, *cis*-, or *trans*-but-2-ene), we have prepared and studied a series of these derivatives with different alkylimine groups.



R = R′= H (ethene)

R″

(1a) Me

(1b) Pr^i

(1c) Bu^i

(1d) Bu^s

(1e) Bu^t

R = R′ = Me (*cis*-but-2-ene)

R″

(2a) Me

(2b) Pr^i

(2d) Bu^s

(2e) Bu^t

R = R′= Me (*trans*-but-2-ene)

R″

(3a) Me

(3b) Pr^i

(3d) Bu^s

(3e) Bu^t

R = H, R′= Me (propene)

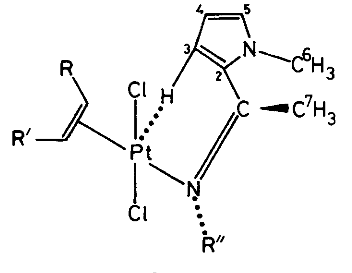
R″

(4a) Me

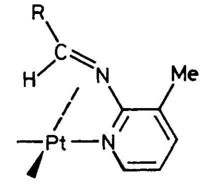
(4b) Pr^i

(4d) Bu^s

(4e) Bu^t



Scheme 1.



Scheme 2.

N.m.r. Spectroscopy.—(*a*) *Proton and* ^{13}C *chemical shifts for the co-ordinated olefins.* Upon co-ordination the olefinic H and C atoms exhibit large upfield chemical shifts with respect to the free olefin and exhibit platinum–195 satellites with sizeable coupling constants. The ^1H and ^{13}C resonance patterns of the complexes in [^2H]-chloroform solution at ambient temperature are consistent with four co-ordination, as in the solid. Support for the existence of four-co-ordinate species is provided by J(Pt–H) 59—64 Hz for the η^2-ethene protons and δ values of 4.1—4.7 shifted upfield from those expected for four-co-ordinate species. The ^1H and ^{13}C resonances of ethene in four-co-ordinated compounds *e.g. trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)$(amine)],[7] are similar to those for imine complexes, δ ($CH_2=$), at 4.5—5.0 flanked by platinum-195 satellites (33%) of 59—63 Hz, in agreement with the data in Table 1. Previous ^{13}C n.m.r. studies[8,18–20] for related molecules have shown that $\delta(^{13}C_2H_4)$ and $^1J(^{195}Pt\text{–}^{13}C)$ values for ethene complexes such as (**A**) vary from approximately 68 to 77 p.p.m. and 156 to 180 Hz respectively, with smaller δ values and larger $^1J(^{195}Pt\text{–}^{13}C)$ values corresponding to NR= ligands such as R = Bu^t and Me. The ^{13}C n.m.r. signals (main band plus ^{195}Pt satellites) of our new complexes fall between 68 and 72 p.p.m. with $^1J(^{195}Pt\text{–}^{13}C)$ values of approximately 158—185 Hz.

For platinum(II) complexes of the type *trans*-[$PtCl_2(RCH{=}CH_2)X$](X = Cl or amine)[21,22] it is known that the values $^2J(^{195}Pt\text{–}^1H)$ may vary in magnitude by 15—25 Hz.[21] The factors inducing these differences are not completely understood although explanations stemming from structural distortions and/or differing metal–carbon bond strengths for CH and CH_2 have been offered.[21] The $^{13}CH=$ and $^{13}CH_2=$ signals of our complexes exhibit small upfield chemical shifts with respect to the free olefin (X = imine), and are all flanked by ^{195}Pt satellites (Table 1). It is worth noting that the absence of inequivalence in the ^{13}C n.m.r. resonances of the propene complexes where they might be seen in principle. In contrast, inequivalences are observed in the ^{13}C n.m.r. resonances of the *trans*-but-2-ene complexes (Table 2) as expected. In addition, the values $\delta(^{13}CH_3)$ and $^2J(^{195}Pt\text{–}^{13}C)$ for *cis*- and *trans*-but-2-ene complexes differ significantly, as do the values of $^2J(^{195}Pt\text{–}^1H)$(70 and 56 Hz for *cis*- and *trans*-but-2-ene respectively). This is compatible with the supposition that the angle between the RC=C and $PtCl_2N$ planes varies considerably between complexes.

In order to appreciate the observed $J(^{195}Pt\text{–}^{13}C)$ values for imine complexes (Table 2) we consider $\delta(^{13}CH_2{=})$(or $^{13}CH{=}$) and $^1J(^{195}Pt\text{–}^{13}C)$, values for ethene (or ethene derivatives) complexes similar to imine (i.e. amine)[4,8,10] which show that $\delta(^{13}CH_2{=})$ and $^1J(^{195}Pt\text{–}^{13}C)$ values vary from approximately 60 to 80 p.p.m. and 220 to 150 Hz, respectively, and $\delta(^{13}CH{=})$ and $^1J(^{195}Pt\text{–}^{13}C)$, values vary from 89 to 92 p.p.m. and 142 to 148 Hz, respectively.[21,22] The $\delta(^{13}CH_2{=})$ values of our imine

Table 1. Proton and ^{13}C n.m.r. data for the ligands (δ/p.p.m., J/Hz)

Compound		C^6H_3	C^7H_3	C^8H_3	C^9H_3	CH_2	CH	C=N	C^2	C^3H	C^4H	C^5H	C^{10}
(a)	^1H	3.87(s)	2.12(dd) ^5J 0.73	3.25(dd) ^5J 0.73						6.47(dd)	6.07(dd)	6.50(dd)	
	^{13}C	38.63	15.67	37.75				160.63	133.04	112.49	106.44	127.28	
(b)	^1H	3.89(s)	2.13(s)	1.16(d)			3.79(q)			6.45(dd)	6.05(dd)	6.57(dd)	
	^{13}C	37.93	15.32	24.01			50.55	155.58	133.04	112.14	106.32	127.05	
(c)	^1H	3.91(s)	2.10(s)	1.04(d)		3.17(d)	1.94(m)			6.47	6.05	6.60	
	^{13}C	38.34	15.97	20.96		59.35	30.18	158.34	133.04	112.37	106.38	127.28	
(d)	^1H	3.90(s)	2.12(s)	1.10(d)	0.87(t)	1.55(m)	3.52(m)			6.45(dd)	6.07(dd)	6.58(dd)	
	^{13}C	38.16	15.44	21.54	11.09	31.46	56.71	155.94	133.16	112.14	106.32	127.05	
(e)	^1H	3.86(s)	2.24(s)	1.35(s)						6.47	6.10	6.60	
	^{13}C	38.10	19.43	30.82				155.76	134.03	111.49	106.03	126.93	54.95

complexes fall between 68 and 77 p.p.m. with $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ values from 156 to 180 Hz(Table 2), and the $\delta(^{13}\mathrm{CH}=)$ values vary from 84—88 p.p.m. with $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ values from 142 to 166 Hz. There seem to be only small differences between amine and imine complexes if one assumes that $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ is proportional to the *s* character in the Pt–C bond,[23] and that the *trans*-influence of a group *trans* to the olefin is reflected qualitatively by changes in the strength of the σ component of the Pt–C bond.[24]

Substituted imines, like di-imines[5] and diamines[9], are good σ-donor ligands. The σ-donation ability of imines lies in the order R = Bu^{t}(quaternary) > Pr^{i}(tertiary) > Bu^{i}(secondary) > Me > Ph.[5] Carbon-13 n.m.r. data, $\delta(^{13}\mathrm{CH}_2=)$ and $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$, demonstrate that $^{1}J(\mathrm{Pt-C})$ has a value of 167.7 Hz for imine complex (**1a**), suggesting that imine (**a**) may be more strongly bound than other imines; secondly, $\delta(^{13}\mathrm{CH}_2=)$ 72.16 p.p.m., the highest value obtained (Table 2), shows that the platinum–carbon (olefin) bond is less strong due to the *trans* effect of imine (**a**; R″ = Me). When imine (**e**; R″ = Bu^{t}) donates more electrons to the platinum [compared with imine (**a**)], this causes blooming of the b_2 orbital toward the olefin which enhances the π-back bonding, resulting in a stabilization of the platinum–olefin bond.[5,20,25] The values $\delta(^{13}\mathrm{CH}_2=)$ 68.28 p.p.m. and $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ 185.3 Hz, for complex (**1e**) support the above observation. Further evidence comes from the resonance of the olefinic proton, $\delta(\mathrm{CH}_2=)$ 4.17, the lowest value obtained (Table 2).

Interestingly, the $\delta(^{13}\mathrm{CH}_2=)$ values obtained for the other imines, where R″ = Pr^{i}, Bu^{s}, or Bu^{i}, are in between the above two values obtained for R″ = Me and Bu^{t} (Table 2), which supports the above observation. Thus as Panunzi and co-workers[26] have suggested, in order to obtain stable complexes a moderate bulk must be present at the nitrogen atoms. However, such stabilization could equally be the result of a combination of steric and electronic effects (comparing the two imine complexes with R″ = Me and Bu^{t}). Moreover, ^{1}H and ^{13}C n.m.r. spectra of imine complexes of the type *trans*-$[\mathrm{PtCl_2(olefin)(imine)}]$, where olefin = *cis*-but-2-ene, *trans*-but-2-ene, or propene, are consistent with the above observation. Comparison was also made between $\delta(^{13}\mathrm{CH}=)$ (*i.e.* for *cis*-but-2-ene), in *trans*-$[\mathrm{PtCl_2(MeCH{=}CHMe)\,(amine)}]$ where, amine = piperidine[21] or dimethylamine,[22] and $\delta(^{13}\mathrm{CH}=)$ for our new imine complexes (**2a**), (**2b**), (**2d**), and (**2e**) (Table 2). For complex (**2a**) $\delta(^{13}\mathrm{CH}=)$ 87.71 p.p.m., $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}) = 153$ Hz [for amine, $\delta(^{13}\mathrm{CH}=)$ 89.80 p.p.m., $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ 145 Hz] and for complex (**2e**) $\delta(^{13}\mathrm{CH}=)$ 84.81 p.p.m., $^{1}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}) = 166$ Hz. In addition, imine-platinum olefin complexes, where olefin = *trans*-but-2-ene or propene, give the same results (Table 2). Thus, the imines in the new complexes are good σ-donor ligands compared with amine ligands.

(*b*) $^{n}J(\mathrm{Pt-H})$, $^{n}J(\mathrm{Pt-C})$, *and* $\mathrm{Pt}\leftarrow\mathrm{H-C}$ *interactions in co-ordinated Schiff base ligands* (*i*) ^{1}H n.m.r. The most interesting aspect of the ^{1}H n.m.r. data arises from the coupling between H^{3} of the pyrrole ring and ^{195}Pt. The observed 8.3 Hz (broad peak) is similar to the reported coupling between the imine proton and ^{195}Pt in *trans*-$[\mathrm{PtCl_2\{NC_5H_3(NCHR)\text{-}2\text{-}Me\text{-}3\}(AsEt_3)}]$,[17] Scheme 2, 7.7—11.9 Hz, and slightly smaller than that found for co-ordinated quinolines[14–16], and confirms that, geometry permitting, weak covalent interactions between a proximate hydrogen and platinum are possible in systems other than that of quinoline and pyridine derivatives.[14–17] The ^{1}H n.m.r. chemical shift of H^{3} moves to low field on complexation and ^{1}H Δδ values fall in the narrow range 0.26—0.33 [Δδ = δ(complex) − δ(ligand)]. Of interest, the C^{7}H$_3$ proton resonances all shift downfield by 0.37—0.51 on complexation, and show a long-range coupling, $^{4}J(^{195}\mathrm{Pt}-^{1}\mathrm{H}) = 7.0$—8.3 Hz. For most imine complexes, (**1a**), (**2a**), (**3a**), and (**4a**), we have observed the value $^{3}J(^{195}\mathrm{Pt}-^{1}\mathrm{H}) = 33.0$ Hz for C^{8}H$_3$, which is higher than that found for similar complexes, *trans*-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(imine)}]$ (imine derived from 2-acetylthiophene and methylamine), $^{3}J(^{195}\mathrm{Pt}-^{1}\mathrm{H}) = 23.7$ Hz.[20]

(*ii*) ^{13}C N.m.r. Data for the complexes (Table 2) provide strong evidence for $\mathrm{Pt}\leftarrow\mathrm{H-C}$ interactions in our platinum complexes. The resonance of C^{3} (pyrrole ring) for most complexes experiences a 3.1—5.2 p.p.m. downfield shift on complexation and is accompanied by a $^{n}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{3})$ value of 17.64 Hz. For complexes (**1e**) and (**4d**), $^{n}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{3})$ 20.5 Hz. The presence of a relatively large $J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{3})$ value is suggestive of a coupling mechanism other than through the N-imino bonding framework. We have also obtained a $^{1}J(^{13}\mathrm{C}^{3}-^{1}\mathrm{H}^{3})$ value for imine (**a**) and its platinum complex (**1a**) and find these to be identical, within experimental error (170 and 168 Hz respectively). Moreover, $^{1}J(^{13}\mathrm{C}^{5}-^{1}\mathrm{H}^{5})$ is larger than $^{1}J(^{13}\mathrm{C}^{3}-^{1}\mathrm{H}^{3})$, 184 Hz, and we take this as further support for a platinum–hydrogen(3) interaction. The value of $^{n}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{3})$ for our complex is comparable to that of corresponding quinoline complexes $^{n}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{11})$ 12—39 Hz.[15,16] *X*-ray crystallography for *trans*- $[\mathrm{PtCl_2\{C_9H_6N\text{-}(CHO)\text{-}8\}(PEt_3)}]$ clearly shows the C–H vector of the aldehyde group to be situated favourably for an interaction with the platinum.[16] The ^{13}C n.m.r. spectrum of imine (**a**; R″ = Me) and its platinum(II) complexes (**3a**) and (**4a**) are shown in Figures 1 and 2. Further support for the structure (Scheme 1) comes from the long range coupling of the imine proton, $^{5}J(\mathrm{HCCNCH})$ 0.75 Hz. This value shows that the two methyl groups C^{7}H$_3$ and C^{8}H$_3$ are in *trans* position [complex (**3a**), *E* isomer].

A cross-check on the ^{13}C n.m.r. spectrum of the previously reported[20] *trans*-$[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(imine)}]$ complexes (imine derived from 2-acetylthiophene and primary amines) show that the resonance of C^{3} of the thienyl ring is flanked by platinum-195 satellites (33%) of 17.0 Hz (value not reported before), and in agreement with the $^{n}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{3})$ value reported here.

It is worth noting that the carbon-13 resonances of the methyl group C^{7}H$_3$ experience a 7.6—10.4 p.p.m. downfield shift on complexation, and show a long-range coupling $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{7}) = 29.4$—32.36 Hz. Of interest is that both ^{13}C resonances of ^{13}C=N and ^{13}C of N-R″ [*e.g.* C^{8}H$_3$ in complexes (**1a**)—(**4a**)], β to platinum, exhibit large downfield shifts ranging from 11 to 15 and 6 to 10 p.p.m. respectively upon co-ordination with respect to the free imine (Tables 1 and 2); $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$ (C$_{\beta}$ = Me, CH$_2$, CH, or C)(not imino-carbon) = 14.6—23.5 Hz. Of particular interest in this connection are the values of $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{7})$ and $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$ for the imine complexes; the $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{7})$ values clearly demonstrate that C^{7}H$_3$ is *trans* to platinum and therefore shows a large vicinal coupling (Scheme 1), 29.4—33.36 Hz, compared with $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}^{7})$ values when C^{7}H$_3$ is *cis* to platinum, $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{gauche}) = <5$ Hz.[2] There are relatively few values of $^{3}J(\mathrm{PtNCC})$ in the literature[2] and $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ for pyridine complexes is ≈34—37 Hz. Values of the order of 20—50 Hz have also been found[27,28] for some ethylene diamine couplexes. Thus it would seem that the observed values of $^{3}J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ are within the expected boundaries for this coupling. From the data in Table 2 it may be seen that the two-bond coupling to C$_{\beta}$, $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$, are within the expected values, $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$, for *N*-methylpyridine derivatives, 14.7—19.1 Hz,[2] and for analogous imine complexes, $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$ 12.2—14.7 Hz.[20] We note the significant difference in $^{2}J(^{195}\mathrm{Pt}-^{13}\mathrm{C}_{\beta})$ for the reported compounds, *i.e.* when olefin = ethene or *cis*-but-2-ene, we find that two-bond coupling to C$_{\beta}$ is higher than that recorded for ^{2}J when olefin is *trans*-but-2-ene or propene; this may be due to the complex geometry.

Comments. The ^{1}H and ^{13}C n.m.r. resonance patterns of the complexes in [^{2}H]chloroform solution at ambient temperature are consistent with four-co-ordination, as in the solid. Support

Table 2. Proton, ^{13}C and ^{195}Pt n.m.r. data for the complexes (δ p.p.m., *J*Hz)

Compound		C^6H_3	C^7H_3	C^8H_3	C^9H_3	CH_2	CH	C=N	C^2	C^3H	C^4H	C^5H	C^{10}	=CH(ol)	CH_3(ol)	δ(^{195}Pt)^b
(1a)	$^1H^a$	3.62(s)	2.43(s)	3.62(s) [33.0]						6.78(b) [*ca.* 8.3]	6.26(b)	7.22(b)		4.42[60.0]		(*Z*) −2 712(br)
	^{13}C	35.64	23.01 [32.36]	43.50 [23.0]				171.13	134.45	116.72 [17.64]	108.08	127.99		72.16[167.7]		(*E*) −2 862[210]
(1b)	^{1}H	3.62(s)	2.50(s)	1.74(d)			4.40(m)			6.78(b)	6.26(b)	7.22(b)		4.34[61.5] 4.77[59.1]		(*Z*) −2 669[251]
	^{13}C	35.70	23.25	23.25			57.36	169.25	133.75	116.48	107.73	127.11		70.86[175.0] 76.32[158.0]	(*Z*) (*E*)	(*E*) −2 815(br)
(1c)	^{1}H	3.61(s)	2.42(s)	1.13(d)		3.76(d)	3.10(m)			6.78(b)	6.26(b)	7.26(b)		4.38[60.5]		(*Z*) −2 750[278]
	^{13}C	35.57	23.54	20.55		67.75	30.29	169.90	134.91	116.36	107.84	127.58		71.16[170.6]		(*E*) −2 884(br)
(1d)	^{1}H	3.62(s)	2.48	1.72(d)	1.04(t)		2.24(m)			6.77(b)	6.26(b)	7.17(b)		4.32[62.0] 4.76[59.0]		(*Z*) −2 662[254]
	^{13}C	35.87	23.77	20.95	11.68	30.59	63.82 [17.6]	170.08	134.09	116.66	107.85	127.34		70.75[175.0]		(*E*) −2 816(br)
(1e)	^{1}H	3.62(s)	2.61(s) [7.80]	1.88(s)						6.71(b)	6.27(dd)	7.26(dd)		4.17[64.0]		(*Z*) −2 599[250]
	^{13}C	35.69	27.47	31.18 30.35(n) [8.82]				171.78	132.92	115.54 [20.5]	106.97	125.52	64.23	68.28[185.3]		
(2a)	^{1}H	3.61(s)	2.39 [8.00]	3.58(s) [33.0]						6.77(dd)	6.26(dd)	7.23(dd)		5.17(qq) [68.0]	1.55(d) [32.0]	(*Z*) −2 678[250]
	^{13}C	35.58	22.96 [32.36]	43.68 [23.52]				170.06	134.0	116.06 [17.64]	107.79	127.28		87.71[153.0]	14.91 [23.5]	
(2b)	^{1}H	3.61(s)	2.46(s)	1.43(d) 1.26(b)(n)						6.76(b)	6.26(b)	7.26(b)		5.05(qq)	1.75(d) [33.0]	(*Z*) −2 570(br)
	^{13}C	35.87	29.82	23.60 23.42			57.01	169.90		115.89	107.73	126.58		86.48[148.0]	14.91 [23.5]	
(2d)	^{1}H	3.62(s)	2.45(s) [7.0]	1.73(d)	1.03(t)	2.23(m)	3.70(m)			6.76(dd)	6.26(dd)	7.24(dd)		5.07(qq)[70.0]	1.42(d) [33.5]	(*Z*) −2 565(br)
	^{13}C	35.81	23.78	20.72	11.57	30.47	63.23 [14.6]	169.84	134.25	115.83 [17.64]	107.61	126.52		86.19[162.0]	14.79 [23.5]	
(2e)	^{1}H	3.61(s)	2.59(s) [8.2]	1.88(s)						6.71(dd)	6.24(dd)	7.27(dd)		4.95(qq)	1.37(d) [23.0]	(*Z*) −2 514(br)
	^{13}C	35.27	27.59	29.83, 27.59(n) 31.23				171.67		114.60 [17.64]	107.14	124.81	63.64	84.81[166.0]	14.50(d) [23.5]	

Table 2 (*continued*)

Compound		C^6H_3	C^7H_3	C^8H_3	C^9H_3	CH_2	CH	C=N	C^2	C^3H	C^4H	C^5H	C^{10}	=CH(ol)	CH_3(ol)	$\delta(^{195}Pt)^b$
(3a)	^{1}H	3.61(s)	2.39(q) ^5J(H–H) (0.75)	3.61(s) [33.0]						6.76(b)	6.24(dd)	7.29(dd)		5.06, 5.04(b) [*ca.* 58]	1.71, 1.54(b) [38.0]	(*Z*) −2 688(br)
	^{13}C	35.64	22.96 [29.4]	43.92 [17.4]				170.73	134.68	116.13 [17.64]	108.03	127.34		91.35, 90.12 [*ca.*160.0, *ca.*142.0]	19.90 [32.2]	
(3b)	^{1}H	3.60(s)	2.46(s)	1.25(d)			4.03			6.74(b)	6.20(b)	7.26(b)		4.96, 4.93(b)	1.76, 1.71(b) [38.0]	(*Z*) −2 586(br)
	^{13}C	35.70	23.66	22.72			56.48 [17.64]	170.03		115.83	107.85	126.51		90.12, 89.06 [166.0, 158.0]	19.72 [33.0]	
(3d)	^{1}H	3.62(s)	2.44(s) [8.30]	1.76(d)	1.05(t)	2.41(m)	4.09(m)			6.75(dd)	6.24(dd)	7.12(dd)		5.04, 4.99 [60, 62]	1.76,1.60 [38.0, 38.0]	(*Z*) −2 578(br)
	^{13}C	35.87	32.95	23.31	11.68	30.82	63.06	170.20		115.95	107.97	126.10		90.18, 88.94 [166.0, 160.0]	19.90,19.32 [32.0, 33.0]	
(3e)^c																(*Z*) −2 537(br)
(4a)	^{1}H	3.61(s)	2.41(q) ^5J(0.73)	3.61(s)						6.78(b)	6.25(dd)	7.27(dd)		=CH, =CH_2 5.52(m) 4.38(m) [*ca.* 65.0 *ca.* 63.0]	1.64(d) (32.7]	(*Z*) −2 716(br)
	^{13}C	35.04	23.07 [32.36]	43.62 [17.40]				171.02	134.56	116.36 [17.64]	108.32	127.58		95.52, 69.81 [156.00, 160.00]	20.49 [26.5]	
(4b)	^{1}H	3.61(s)	2.48 [7.80]	1.74(pt)	(n)		4.20(m)			6.76(dd)	6.25(dd)	7.20(dd)		5.48(m), 4.16(m) [*ca.*65, *ca.*63]	1.53(d) [35.6]	(*Z*) −2 611[238]
	^{13}C	35.70	23.43	23.13			57.30 [17.64]	169.90	133.86	116.01 [17.64]	107.73	126.70		94.05, 68.40 [164.0, 168.0]	20.08 [26.5]	
(4d)	^{1}H	3.62(s)	2.47(s)	1.03(n)	(n)	2.23(m)	4.26(m)			6.77(b)	6.25(dd)	7.20(dd)		5.40(m), 4.10(m)	1.60(d) [35.0]	(*Z*) −2 605(br)
	^{13}C	35.75	23.78	20.96	11.57	30.58	63.41	170.08	134.15	116.13 [20.6]	107.79	126.81		93.99, 68.22 [166.0, 168.0]	20.00 [26.5]	

n = Non-equivalent, br = broad, and pt = pseudo-triplet. [a] Proton and ^{13}C chemical shifts (δ) in p.p.m. in $CDCl_3$ relative to $SiMe_4$, $J(^{195}Pt–^1H)$ and $J(^{195}Pt–^{13}C)$ values (in Hz) are given in square brackets. [b] In p.p.m. from the platinum resonance of $Na_2[PtCl_6]$(aq). [c] δ(Pt) only obtained.

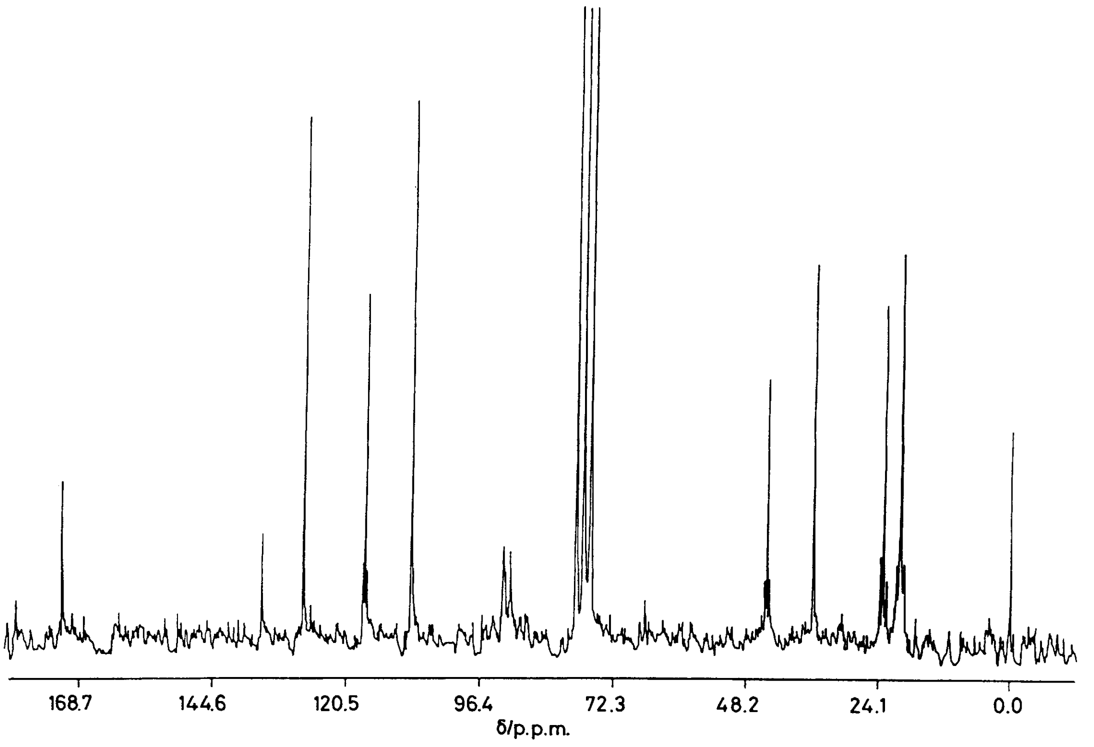


Figure 1. Fully coupled pulsed Fourier-transform ^{13}C n.m.r. spectrum of complex (**3a**) (0.1 mol dm^3) in $CDCl_3$ at 25 °C

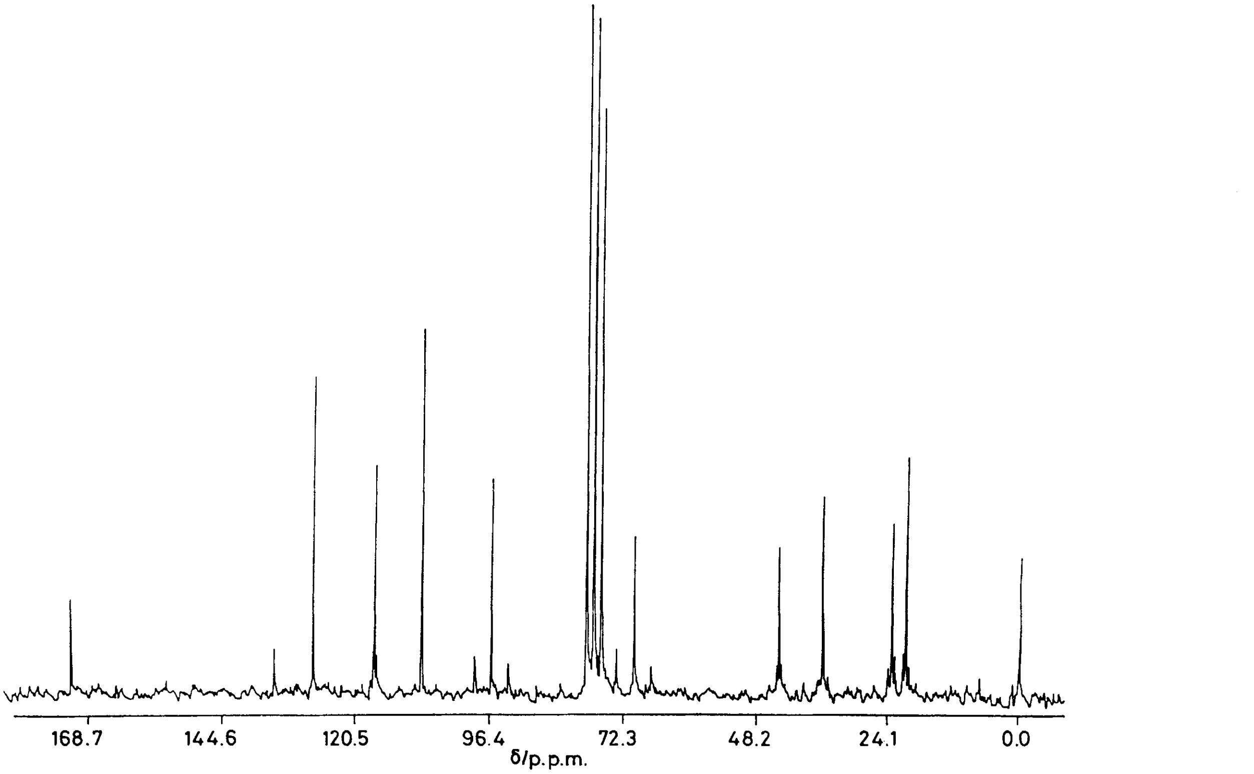
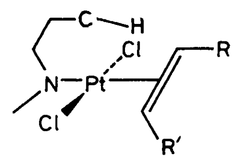


Figure 2. Fully coupled pulsed Fourier-transform ^{13}C n.m.r. spectrum of complex (**4a**) (0.1 mol dm^3) in $CDCl_3$ at 25 °C

for the existence of four-co-ordinate species is provided by the δ and *J* values for the η^2-olefin protons and carbons.[2,7,8,20–22] The observation of an ^nJ(PtH) and ^nJ(PtC) for C^3H^3, suggests that the H^3 spends more time, on average, directed towards the metal (Scheme 3). This results in a weak Pt$\leftarrow$H–C interaction. Taken together, the physical data[14–17] suggest a weak C–H···M interaction although they do not support hydridic character for the hydrogen.

(*iii*) *Platinum-*195 *chemical shifts and* ^{195}Pt–^{14}N *coupling constants.* In recent years interest in ^{195}Pt n.m.r-spectroscopy



Scheme 3.

has grown rapidly,[2] but there is still no definitive theory governing the interpretation of platinum chemical shifts. All authors agree that σ_p, the paramagnetic screening contribution to the total screening σ_t, is dominant for the platinum nucleus.[2,29] The ^{195}Pt chemical shifts shown in Table 2 range between 2514 and 2884 p.p.m. upfield (lower-frequency) of $Na_2[PtCl_6]$. The results suggest that more substituted imine carbons (=NR″) result in low-field (high-frequency) shifts of $\delta(^{195}Pt)$ relative to unsubstituted carbons [*i.e.* for R″ = $\mathrm{Bu^t}$ and Me, $\delta(^{195}Pt)$ 2 599 and 2 862 p.p.m. respectively for complexes (**1e**) and (**1a**); in Table 2]. This result is in agreement with those previously reported for a similar system, *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{imine})]$.[8,20] For some imine complexes, Table 2, we have observed $^1J(^{195}Pt\text{-}^{14}N)$ directly from well-resolved triplet structure ($\Delta\nu_{\frac{1}{2}} \leqslant 120$ Hz): range 230—278 Hz. These values are comparable to those obtained for analogous square-planar platinum complexes, *i.e.* trans-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{substituted pyridine})]$,[30] 292—304 Hz for N-*trans* to C_2H_4.

E-Z *Imine Isomerization in Platinum Imine complexes.*—Previously we reported the synthesis and characterization of some platinum imine complexes of the type *trans*-$[PtCl_2(\text{imine})(L)]$, (L = $\eta^2\text{-}C_2H_4$ or PR_3).[8,18,19] The multinuclear n.m.r. data for both these complexes and those now reported have enabled us to look at the *E*—*Z* isomerization of the co-ordinated imines. The free imines (Table 1) were each obtained in one isomeric form (100%) in the liquid state. The ^{1}H, ^{13}C, and ^{195}Pt n.m.r. spectra of freshly prepared solutions showed that in each case only a signle rotamer existed (only one single peak for each ^{1}H or ^{13}C atom). When the solution was left for a few hours and the n.m.r. spectrum remeasured, new peaks were observed downfield from the original ones. When the solution was left for additional periods a gradual increase in intensity of the new peaks at the expense of the original peaks occurred until the isomerization was nearly complete. This was fully discussed in previous papers.[8,18,19] The ^{195}Pt n.m.r. chemical shifts of both the original and the new complex (*Z* and *E*) in [^{2}H]chloroform solution at ambient temperature are consistent with four-co-ordination.[8,18,19] The shifts of the *Z*-complexes appear at lower field (higher frequency) than those of the *E* complexes [*e.g.* $\delta(^{195}Pt)$ $-2\,712$ and $-2\,862$ p.p.m. for *Z*- and *E*-(**1a**), respectively]. This is in agreement with previous results for a similar system, *trans*-$[PtCl_2(\eta^2C_2H_4)(\text{amine})]$ (amine = primary or secondary amine).[2] It was suggested that the more bulky amine may result in a downfield shift of the platinum-195 resonance of > 40 p.p.m. [$NHMe_2$, $-3\,074$; $\mathrm{NHMePr^i}$, $-3\,030$ p.p.m.[2] However, in this study the *Z* configuration is more sterically crowded than that of the *E* configuration which may result in the downfield shift observed of > 146 p.p.m. [$\delta(^{195}Pt)$ $-2\,669$ and $-2\,815$ p.p.m. for *Z*- and *E*-(**1b**)]. This observation may support the existence of a platinum–hydrogen interaction ($Pt\leftarrow H^3\text{–}C$).

Stability of the Complexes.—Elemental analysis supports the stoicheiometry of the complexes (see Experimental Section). The complexes showed sufficient solubility and stability in [^{2}H]chloroform solution to allow an extensive study of their structure in solution by ^{1}H, ^{13}C, and ^{195}Pt n.m.r. spectroscopy. When the solution was left for several hours at room temperature, *E*—*Z* isomerism occurs. When the solid complexes (yellow) were left at room temperature for 1 week they decomposed slowly and changed in colour to dark yellow; on leaving the solid complex at 0 °C for 6 months no change was observed.

Experimental

Preparation of Imine Ligands.—The imine ligands derived from *N*-methyl-2-acetylpyrrole and primary amines were obtained mainly in the *E* form (100%) in the liquid state by a standard method.[31]

Preparation of Ethene–Imine Complexes.—To $K[PtCl_3(\eta^2\text{-}C_2H_4)]$ (400 mg, *ca.* 1 mmol) in water (10 cm^3) cooled to 1 °C was added slowly with stirring imine (*ca.* 1.1 mmol) dissolved in ice-cold water (2 cm^3). The mixture was cooled in ice and stirred for 10 min, whereupon a yellow precipitate was rapidly formed. To enhance the yield, a few drops of acetone (or methanol) were added which enhances the solubility of the starting imine in water and forces the imine complex to precipitate. The yellow precipitate was washed with cold water (*ca.* 2 cm^3) followed by pentane, and dried in *vacuo*. The complexes were recrystallized from chloroform–pentane mixtures [Found for (**1a**; R″ = Me): C, 27.30; H, 3.80; N, 6.55. $C_{10}H_{16}Cl_2N_2Pt$ requires C, 27.90; H, 3.70; N, 6.50. Found for (**1b**; R″ = $\mathrm{Pr^i}$): C, 30.80; H, 4.05; N, 6.30. $C_{12}H_{20}Cl_2N_2Pt$ requires C, 31.45; H, 4.35; N, 6.10%. Found for (**1c**; R″ = $\mathrm{Bu^i}$): C, 33.65; H, 4.40; N, 5.55. $C_{13}H_{22}Cl_2N_2Pt$ requires C, 33.10; H, 4.65; N, 5.95. Found for (**1d**; R″ = $\mathrm{Bu^s}$): C, 32.70; H, 4.60; N, 6.00. Found for (**1e**; R″ = $\mathrm{Bu^t}$); C, 33.30; H, 4.50; N, 6.05%].

Preparation of Olefin–Imine Complexes (*Olefin* = cis-*or* trans-*But-2-ene or Propene*).—The compound *trans*-$[PtCl_2(\eta^2\text{-olefin})(\text{imine})]$ was prepared from the corresponding *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{imine})]$. The latter (400 mg) in acetone (30 cm^3) was treated with a stream of *cis*- or *trans*-but-2-ene or propene for 30 min as appropriate. The solution was left for another 1 h, the solvent removed under vacuum, and the yellow solid recrystallized from a chloroform–pentane mixture. [Found for (**2a**; R″ = Me): C, 30.80; H, 4.05; N, 6.30. $C_{12}H_{20}Cl_2N_2Pt$ requires C, 31.45; H, 4.35; N, 6.10. Found for (**2b**; R″ = $\mathrm{Pr^i}$): C, 33.90; H, 4.55; N, 5.70. $C_{14}H_{24}Cl_2N_2Pt$; requires C, 34.55; H, 4.95; N, 5.75. Found for (**2d**; R″ = $\mathrm{Bu^s}$): C, 36.40; H, 5.00 N, 5.65. $C_{15}H_{26}Cl_2N_2Pt$ requires C, 36.00; H, 5.20; N, 5.60. Found for (**2e**; R″ = $\mathrm{Bu^t}$): C, 35.55; H, 5.00; N, 5.45. Found for (**3a**; R″ = Me): C, 31.40; H, 4.25; N, 5.90. $C_{12}H_{20}Cl_2N_2Pt$ requires C, 31.45; H, 4.35; N, 6.10. Found for (**3b**; R″ = $\mathrm{Pr^i}$): C, 33.90; H, 4.60; N, 5.80. $C_{14}H_{24}Cl_2N_2Pt$ requires C, 34.55; H, 4.94; N, 5.75. Found for (**3d**; R″ = $\mathrm{Bu^s}$): C, 35.60; H, 5.35; N, 5.40: $C_{15}H_{26}Cl_2N_2Pt$ requires C, 36.00; H, 5.20; N, 5.60. Found for (**3e**; R″ = $\mathrm{Bu^t}$): C, 35.50; H, 5.00; N, 6.00. Found for (**4a**; R″ = Me): C, 29.65; H, 4.15; N, 6.55. $C_{11}H_{18}Cl_2N_2Pt$ requires C, 29.75; H, 4.05; N, 6.30. Found for (**4b**; R″ = $\mathrm{Pr^i}$): C, 33.50; H, 4.45; N, 6.30. $C_{13}H_{22}Cl_2N_2Pt$ requires C, 33.10; H, 4.65; N, 5.95. Found for (**4d**; R″ = $\mathrm{Bu^s}$): C, 33.75; H, 5.30; N, 5.80. $C_{14}H_{24}Cl_2N_2Pt$ requires C, 34.55; H, 4.95; N, 5.75. Found for (**4e**; R″ = $\mathrm{Bu^t}$): C, 34.80; H, 4.90; N, 5.70%].

All n.m.r. spectra were measured on a JEOL JNM FX-100 spectrometer operating in the Fourier-transform mode at ambient temperature, 25 °C. Natural-abundance ^{13}C n.m.r. spectra were recorded at 25 MHz, ^{1}H at 100 MHz. The compounds were studied as 0.1 mol dm^{-3} solutions in $CDCl_3$. Chemical shift data for ^{1}H and ^{13}C were determined relative to the internal standard $SiMe_4$, and ^{195}Pt relative to $Na_2[PtCl_6]$.

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