Multinuclear NMR Studies on New Platinum Imine Complexes

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Received February 13, 1984

Platinum(II)–olefin complexes with Schiff bases derived from 2-acetylthiophene, and primary amines were synthesized and characterized on the basis of elemental analysis, I.R., ^1H, ^{13}C, and ^{195}Pt-NMR studies. The Schiff bases behave as unidentate bases with N as the only donor ligand and form four coordinate complexes with 1:1 metal–ligand stoichiometry at ambient temperature of composition trans-*[$PtCl_2(\eta^2$-C_2H_4)(Imine)]. Long-range coupling constants were observed between different protons of the imine and platinum-195. Addition of excess amine leads to displacement of the imine and rapidly gives the zwitterionic 2-ammonioethanide–platinum(II) complex. The platinum complex of the imine type provide the first example of stable platinum(II)–olefin-monodentate σ-imine bonded complexes. In addition, ^1H, ^{13}C and ^{195}Pt-NMR spectra show that only a single rotamer exists. Other more imine complexes were synthesized.*

Introduction

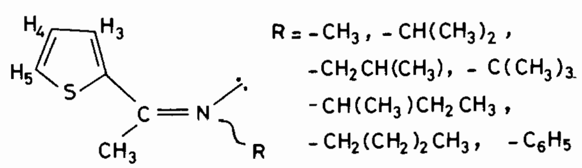
The most characteristic respect in which compounds containing the C=N bond show basic properties is in the formation of complexes with metals. These complexes provide some very characteristic series of coordination compounds, a large number of which have been prepared and their properties examined and compared [1–4]. Earlier studies suggest that the basic strength of the C=N group is insufficient by itself to permit formation of stable complexes by simple coordination of the lone pair to a metal ion. Therefore, in order that stable compounds should be formed it is necessary that there should also be present in the molecule a functional group with a replaceable hydrogen atom, preferably a hydroxyl group, near enough to the C=N group to permit the formation of a five or six membered ring by chelation to the metal atom [3, 4].

Recently a large number of metal-α-diimine complexes have been reported in which the α-diimine ligand acts as a σ,σ-chelating ligand [5–8]. To date only a limited number of complexes of α-diimine ligands with Pt, Pd, or Rh have been described [9]. The α-diimine ligand in these complexes is either σN, σN¯ bridging [10–13], σN monodentate [2, 10], or σN ⇄ σN¯ fluxional [13] bonded to the metal. The σN, σN¯ bonding seem to be consistent with the σ,σ-bonding mode found for the related bipyridine and phenanthroline ligands which like the α-diimine ligand have two N lone pairs suitably positioned for symmetric coordination. Recently, Koten [2, 10] reported the isolation and characterization of the first examples of stable metal α-diimine complexes in which the α-diimine molecule is monodentate bonded. In the present paper we report the isolation and characterization of the first examples of stable platinum(II)–imine in which the imine molecule consist of only one σN, and is monodentate bonded, *trans* to the η^2-olefin.

The imine ligand was thiophene-2-C(Me)=N~R, where R = methyl, iso-propyl, sec-butyl, iso-butyl, tert-butyl, n-butyl, and phenyl; some other imines ligand derived from 2-thienylphenylketone, 2-methylacetophenone, 2-methoxyacetophenone and 2,4,6-trimethylacetophenone and primary amines were also synthesized and characterized (Table I).

Results and Discussion

The imine ligand derived from 2-acetylthiophene and primary amines was obtained mainly in the E-isomeric form (100%) in the liquid state [14] (A).



(A)

Complexes of the type *trans*-[$PtCl_2(\eta^2$-ethene)-(imine)] have been isolated in almost quantitative yield from 1/1 molar reaction of K[$PtCl_3(\eta^2$-ethene)] with the respective imine ligand. The stoichiometry

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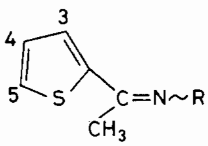
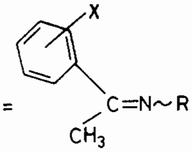
TABLE I. ^1H NMR Spectra of *trans*-[$PtCl_2(\eta^2$-Ethene)(Imine)] Complexes[a].

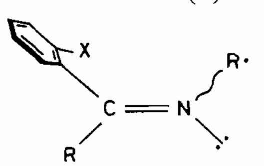
(I) = Imine =  (III) Imine = 

No	Formula	δH(3)	δH(4)	δH(5)	δ-CH_3	δ=CH_2	δ-R
I	*trans*-[$PtCl_2(\eta^2$-C_2H_4)(imine)] Imine, R = (1) -CH_3	7.9 [7.3]	7.2 [7.0]	7.7 [7.3]	2.7 (6.6) [2.2]	4.7 (60) [5.5]	-CH_3, 3.8[3.27], (23.7), ^5J(H–H), 0.73, $H_{3,4}$ and H_5; AMX pattern
	(2) -$CH(CH_3)_2$	8.0 [7.3]	7.1 [7.9]	7.7 [7.3]	2.7 (7.7) [2.2]	4.6 (61) [5.5]	-CH(c), 4.4[3.8]; -$(CH_3)_2$, 1.8(d), ^4J(Pt–H) 5.2, $H_{3,4}$ and H_5 AMX pattern.
	(3) -$CH_2CH(CH_3)_2$	7.9 [7.2]	7.1 [7.0]	7.7 [7.2]	2.6 (7.2) [2.2]	4.7 (60) [5.5]	CH_2, 3.98(33), [3.2], -CH, 3.2[1.9]; -$(CH_3)_2$, 1.1; $H_{3,4}$ and H_5 AMX pattern.
	(4) -$CH(CH_3)CH_2CH_3$	8.1 [7.3]	7.2 [7.0]	7.6 [7.2]	2.7 (7.6) [2.2]	4.6 (61) [5.5]	-CH, 4.3[3.5]; -(CH_3), 1.8[1.1], -CH_2 2.6[1.6]; -CH_3, 1.0[0.9], $H_{3,4}$ and H_5; AMX pattern.
	(5) -$C(CH_3)_3$	8.0 [7.2]	7.1 [6.9]	7.7 [7.2]	2.8 [7.8]	4.3 (63)	-$(CH_3)_3$, 1.9[1.3], ^4J(Pt–H), (4.4), $H_{3,4}$ and H_5 AMX pattern
	(6) -C_6H_5	8.0	0	7.8	3.4 [2.5]	4.7 (60)	C_6H_5-, 7.29(2H), 7.13(3H)
	(7) -$CH_2(CH_2)_2CH_3$	7.9 [7.3]	7.1 [6.9]	7.7 [7.3]	2.8 [2.2]	4.7 (60)	-CH_2, 4.0 t [3.4]; CH_2, CH_2, 1.8 1.5 C, [1.2–1.7]; -CH_3, 1.0 t [0.9].
II	When $\rangle$C=N~ becomes $\rangle$C=N~R (CH_3 → C_6H_5) (8) R = $CH(CH_3)_2$	0 [6.7]	0 [6.9]	0 [0]		4.8 (60)	-CH, 4.3 (sep) (33), [3.5]; -$(CH_3)_2$, 1.7, [1.1] (6); C_6H_5-; H_5, 7.4–7.1 (c)
	(9) R = $CH_2CH(CH_3)_2$	0	0	0		4.8 (60)	-CH_2, 3.65, (31) [3.14]; -CH, 3.3 (m) [1.9]; -$(CH_3)_2$, 1.0, [0.9], C_6H_5-, $H_{3,4}$ and H_5 (C), 7.0–7.8

No	Formula	δ
III	(10) R = -$CH(CH_3)(CH_2CH_3$ X = 2-CH_3	E,Z isomers; Ar, 7.4(C), CH_2=, 4.8(60), -CH_3(C=N), 2.6, 2.7; -CH, 4.3, 3.6 (C); -(CH_3), 3.1, 3.12 (14); -CH_2, 1.6, 1.4; -CH_3, 0.8, 0.7; Ar-CH_3, 2.33, 2.3
	(11) R = $CH_2CH(CH_3)_2$ X = 2-OCH_3	E,Z isomers; Ar, 6.9–7.9(c); CH_2=, 4.7(60); -OCH_3, 3.9, 3.8, -CH_2, 3.4, 3.3, (12), (13); -CH_3(-C=N), 2.6, 2.5(8); -$(CH_3)_2$, noneqv., d, (d-d), 1.1, (0.9, 0.83); -CH, 1.8(c).
	(12) R = $CH_2CH(CH_3)_2$ X = 2,4,6-$(CH_3)_3$	Only E isomer, Ar, 6.9; CH_2=, 4.8(60); -CH_2, 3.4; -CH_3(-C=N), 3.0(14); Ar-(o-CH_3) 2.2; Ar(p-CH_3), 2.3; -CH, 1.9(c).

[a]Chemical shift (δ) in ppm relative to TMS in $CDCl_3$; J(^{195}Pt–^{1}H) in parentheses are given in Hz; values between square bracket δ- in ppm for starting ligand (ref. 14); III, ^1H NMR of starting ligand, (10, Ar-H, 7.2 m, -CH, 3.7, 3.1(c), E,Z; Ar-CH_3, 2.3, 2.22; CH_3(-C=N), 2.21, 2.1, (E,Z); -CH_2, 1.5(c); -(CH_3), 1.37d, 1.23d; -CH_3(t), 1.1, 0.95(t), E.Z. (11), Ar-H, 7.8–7.0(c); -O-CH_3. 3.9, 3.8(s), E,Z; -CH_2, 3.2(q), 2.9(q), ^5J(H–H) 0.73(E), ^5J(H–H) 1.22 Hz(Z); -CH_3-(C=N), 2.2 t(Z); ^5J 1.22 Hz, 2.1 t(E), ^5J, 0.73 Hz; -$(CH_3)_2$, 1.0 d(E), 0.8 d(Z); -CH(m), 1.8. (Key: S (singlet); d, doublet; d-d, doublet of doublets; t, triplet, q, quartet; c, complex; o, overlaps. Thiophen protons, H_3, H_5 and H_4 exhibit AMX pattern, $^4J_{3,5}$ = 1.22 Hz; $^3J_{3,4}$ = 3.7 Hz; $^3J_{4,5}$ = 5.1 Hz).

of the complexes was established by elemental analysis, further evidence was obtained from ^1H, ^{13}C and ^{195}Pt-NMR spectra. The imines of 2-thienylphenyketone were prepared by the same method and only one major product (E-form) was isolated (100%). Imines derived from 2-methylacetophenone, 2-methoxyacetophenone, 2,4,6-trimethylacetophenone and primary amines (see Table I) were obtained as E and Z-isomeric mixtures in the liquid state [14]. This may be explained by steric interaction between the ortho-substituent and the C-substituent which may force the aromatic ring further out of the C=N bond Plane (B).



(B)

A repulsive interaction between the nitrogen lone pair and the aromatic π-electrons may destabilize the E-isomer [15, 16]. Therefore, platinum complexes of these imines were obtained as a mixture of E and Z isomers in the same ratio as that of the starting imines. (Only E-isomer was obtained from 2,4,6-trimethylacetophenone similar to the starting material).

^1H- and ^{13}C-NMR Chemical Shifts

Trans-[$PtCl_2(\eta^2$-$C_2H_4)$(imine)]

The NMR data show that the ^1H and ^{13}C resonances of the imine ligand undergo a considerable downfield shift upon coordination, particularly γ-protons and β-carbons. The ^1H and ^{13}C resonance patterns of the complexes in chloroform-d solution at ambient temperature are consistent with four-coordination, as in the solid. Support for the existence of four-coordinate species formed is provided by the δ value of 4.5–5.0 ppm and J(Pt–H) 59–63 Hz of η^2-ethene protons. ^1H and ^{13}C resonance of ethene of four-coordination compound *e.g. trans*-[$PtCl_2(\eta^2$-$C_2H_4)$(amine)] are similar to imine complexes. ^1H NMR spectra of several amines *trans* to π-C_2H_4 platinum(II) complexes [17, 18] show that the protons of ethene resonate at δ 4.5–5.0 ppm in chloroform solution and are flanked by platinum-195 satellites (33%) of 59–63 Hz, in agreement with the data in Table I.

In five-coordinate platinum olefin complexes of the type [$PtX_2(\eta^2$-olefin)(α-diimine) [9], ^{13}C-resonances showed slightly downfield shifts of the coordinated ligand, in contrast to the square-planar four-coordinate platinum complexes of the type (MX_2-(α-diimine)$_2$] [2] M = Pt or Pd, in which the ^{13}C-resonances showed a considerable downfield shift δ(-C=N), 168–169.3 ppm, similar to the value obtained in Table II.

In *trans*-[$PtCl_2(\eta^2$-$C_2H_4)$(imine)] complexes it was found that $^3J(^{195}Pt–H)$ and $^4J(^{195}Pt–H)$ coupling on the imine protons (imine, *i.e.* 4) ~40 Hz and ~7 Hz, respectively, is very characteristic for the coordination number four of the central platinum atom *e.g. trans*-[$PtCl_2(\eta^2$-$C_2H_4)(NH_2Me)$], ^3J(Pt–N–C–H), 40 Hz [19]. Unexpected $^3J(^{195}Pt–H)$ coupling of low value was obtained for imine(1) complex, R = CH_3, 23 Hz.

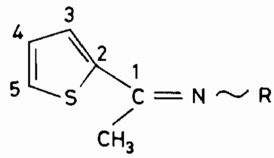
Upon coordination the olefinic H and C atoms exhibit large upfield chemical shifts with respect to the free olefin and are all flanked by ^{195}Pt satellites with sizeable coupling constants. A comparison of the olefinic ^1H and ^{13}C NMR data of η^2-olefins in some three-, four-, and five-coordinate platinum complexes with those of the free olefins is given in Table III. This comparison shows that, particularly in the case of the ethene platinum complexes, the magnitude of ($^{195}Pt–^{13}C$) and the upfield chemical shift of the ^1H and ^{13}C resonances are characteristic of the coordination geometry around the central platinum atom.

In order to appreciate the observed $J(^{195}Pt–^{13}C)$ values in imine complexes (Table II) we consider $\delta^{13}CH_2$=, and $^1J(^{195}Pt–^{13}C)$, values for ethene complexes similar to imine (*i.e.* amine) [20, 21] which show that $\delta^{13}CH_2$=, and ^1J(Pt, C) values vary from approximately 60–80 ppm and 220 to 150 Hz, respectively, with smaller δ values and larger ^1J(Pt, C) values corresponding to ligands. Typical values for 4-substituted pyridine derivatives are in the range 75–77 ppm and 160–166 Hz, respectively [20, 21]. The $^{13}CH_2$= in our imine complexes fall between 70–75 ppm with ^1J(Pt, C) values (Table III). There seem to be only small differences between amine and imine complexes if one assumes that ^1J(Pt, C) is proportional to the s-character in the Pt, C bond [22], and that the *trans*-influence of a group *trans* to the ethene is reflected qualitatively by changes in the strength of the σ-component of the Pt–C-bond [23].

R-imine, like R-diimine [9] and R-diamine [9] is a good σ-donor ligand. Hence, σ-donation ability of imines, R, *i.e.*, $(CH_3)_3C$(C-quaternary) > $(CH_3)_2$-HC(C-tertiary) > $CH_3(CH_2)_2CH_2$(C-secondary) > CH_3 > Ph [9]. ^{13}C-data of $^{13}CH_2$=, and ^1J(Pt, C) demonstrate that ^1J(Pt, C) has a value of 160 Hz for imine (1) complex, R = CH_3, suggesting that this imine may be more strongly bound than other imines; secondly, $^{13}CH_2$= with a value of 74.7 ppm, the highest value obtained (Table II), shows that the Pt–olefin-carbon bond is less bound to the platinum due to the *trans* effect of imine (1), R = CH_3. When imine (5), R = $(CH_3)_3C$, R, donates more electrons to the platinum (compared with R = CH_3, imine (1)), 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 [9, 24]. $\delta^{13}CH_2$=, 70.5 ppm and ^1J(Pt, C), 176.5 Hz, imine,

TABLE II. ^{13}C-NMR Spectra of *trans*-[$PtCl_2(\eta^2$-Ethene)(Imine)] Complexes[a]

(I) = Imine =



No	Formula	δC(1)	δC(2)	δC(3)	δC(4)	δC(5)	δ-CH_3	δ=CH_2	δ-R
I	*trans*-[$PtCl_2(\eta^2$-C_2H_4)(imine)] Imine, R = (1) -CH_3	170.0 [161.6]	[147.6]	133.8 [128.3]	127.2 [126.4]	132.4 [127.1]	22.3 [14.9]	74.7 (160) [122.8]	-CH_3, 44.3[38.9]
	(2) -$CH(CH_3)_2$	169.5 [156.6]	142.6 [148.3]	133.0 [127.9]	127.0 [126.1]	131.1 [127.0]	24.5 [14.9]	73.4 (166)	-CH, 59.2[50.8]; -$(CH_3)_2$, 23.7, 33.9[23.5]
	(3) -$CH_2CH(CH_3)_2$	169.6 [158.9]	142.4 [148.2]	133.1 [128.1]	127.2 [125.9]	131.4 [126.9]	23.7 [15.1]	73.7	-CH_2, 64.9[59.4]; -CH, 30.29-[29.9]; $(CH_3)_2$, 20.6, 19.4-[20.8]
	(4) -$CH(CH_3)CH_2CH_3$	169.9 [156.9]	143.0 [148.5]	132.9 [127.9]	127.0 [125.9]	130.9 [127.0]	21.1 [15.1]	73.2 (168)	-CH, 65.5[57.0]; -(CH_3), 24.4-[21.1]; -CH_2, 30.7[31.1], CH_3, 11.6[11.1]
	(5) -$C(CH_3)_3$	172.4 [156.4]	143.3 [147.7]	131.7 [127.4]	126.3 [125.3]	128.9 [126.9]	[18.6]	70.5 (176.5)	-C, 65.8[55.0], (14.7); -$(CH_3)_3$, noneqv. 30.3, 29.4, 29.1; [30.6]
	(6) -C_6H_5	179.7 [160]		130.3	126.6	128.2	29.0	74.8	C_6H_5-not resolved.
	(7) -$CH_2(CH_2)_2CH_3$	171.0 [159.1]	139.2 [148.0]	130.9 [128.0]	127.2 [126.0]	[126.9]	20.5 [15.0]	74.2 (*ca.* 160)	-CH_2, 57.5[51.4]; -CH_2, 31.8-[32.9], -CH_2, 20.1[20.7], -CH_3, 13.8[13.8].

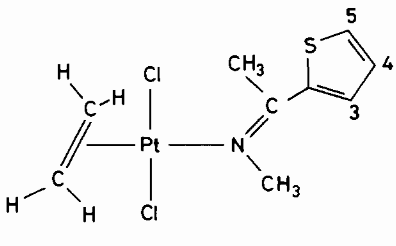
[a]Complex (10) R = $CH(CH_3)CH_2CH_3$, X = CH_3; (11) R = $CH_2CH(CH_3)_2$, X = OCH_3, δ = CH_2, 76.2, 76.0 ppm, J(Pt–H) *ca.* 156 Hz; δ-C=N, *ca.* 180.0 ppm.

TABLE III. Olefinic ^1H and ^{13}C NMR Data[a] of some Three-, Four- and Five-Coordinated Platinum–Olefin Complexes.

Formula	$(^1H)H_2C=$	Ref.	$(^{13}C)C=C$	Ref.	Coord. no.
C_2H_4 (free)	5.5	17	122.8	17	
K[$PtCl_3(\eta^2$-C_2H_4)]	4.42(67)[b]	17	67.3(194)	17	4
trans-[$PtCl_2(\eta^2$-C_2H_4)(amine)]	4.5–5.0(60)	17	70–75(166)	20	4
$PtCH_3(\eta^2$-$C_2H_4)(HBPz_3)$	2.14(69), 2.27(80)	31	24.7(384)	33	5
trans-[$PtCl_2(\eta^2$-C_2H_4)(t-Bu-diimine)]	3.53(71)	9	38.1(297)	9	5
$Pt(\eta^2$-$C_2H_4)_2(PPh_3)$	2.5(57)	32	42.3(146)	34	3
PtCl(acac)(η^2-C_2H_4)	4.55(66)	33	67.4(214.8)	35	4
PtCl(acac)(η^2-CH_2=CHCN)	4.75(65)[1], 4.75(65)[2]	33	47.7(255)[1], 65.7(217)[2]	35	4
trans-[$PtCl_2(\eta^2$-C_2H_4)(imine)]	4.3–4.8(60–63)	p.	70–75(160–177)	c	4

[a]^1H and ^{13}C NMR spectra in $CDCl_3$ relative to TMS. [b]In acetone-d_6. [c]Present work; coord. no. (coordination number).

R = $(CH_3)_3C$, support the above observation. Thus as Panunzi *et al.* [25] 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 R = CH_3 and R = $(CH_3)_3C$). Of interest is that both ^{13}C resonances of ^{13}C=N, and ^{13}C of R-carbon data, (β-to the platinum atom), exhibit large downfield shifts ranging from 13 to 16 ppm and 6 to 10 ppm respectively upon coordination of imine ligand with respect to free imine. Long-range coupling between ^{195}Pt and ^{13}C, obtained in complexes R = $CH(CH_3)_2$, $^2J(Pt, C)$ 12.2 Hz; R = $C(CH_3)_3$, $^2J(Pt, C)$ 14.7 Hz, Table II, showed results similar to those obtained from analogous amine complexes [26].



(C)

The ^1H NMR spectrum of complex (C), *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(imine)]$ (1) Fig. 1, showed two doublets with platinum satellites for N–CH_3 at δ 3.7 $^3J(Pt–H)$, 23.7 Hz; long-range coupling of imines proton, $^5J(H–H)$ 0.75 Hz and for =C–CH_3 at δ 2.7 [$^4J(Pt–H)$ 6.6 Hz, $^5J(H–H)$ 0.75 Hz]. Comparisons were made between the imine complex and free imine: in free imine the two methyl groups show two quartets due to long-range coupling, the difference may be due to the small value of $^5J(H–H)$. CH_2= olefinic protons peaks appear as a single peak with platinum satellites of 60 Hz at δ 4.7. The thienyl protons (3, 4 and 5) appear as a AMX pattern. H_3 appear at δ 7.9 as doublet of doublets of $^3J_{3,4}$ = 3.8 Hz, $^4J_{3,5}$ = 1.2 Hz and H_5 at δ 7.7 as doublet of doublets of $^4J_{5,3}$ = 1.2 Hz and $^3J_{5,4}$ = 5.0 Hz. H_4 signal appears in between, at δ 7.0, as a doublet of doublets of $^3J_{4,3}$ and $^3J_{4,5}$ as above. The simple first order pattern of AMX does not exist in the spectra of the free imine ligand [B_2A pattern] [14]

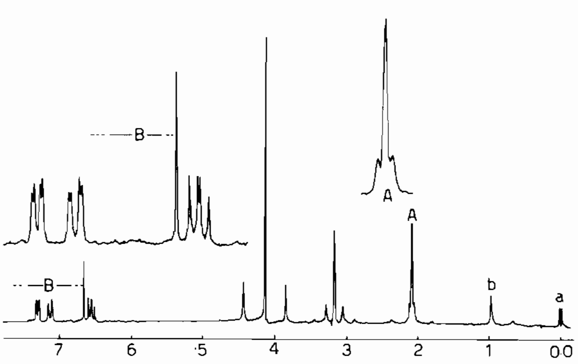


Fig. 1. 100-MHz Proton NMR spectrum of *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(imine\text{-}1)]$. 0.1 *M*, in chloroform d at room temperature. (a) TMS suppresed; (b) trace of water in chloroform-d.

(in $CDCl_3$ at ambient temperature. The same behavior was observed in all imine complexes having thienyl groups (complexes 1–9, Table I). Long-range coupling between ^{195}Pt and different imine protons were observed in most imine complexes. Values given in Table I, $^nJ(^{195}Pt–^1H)$ in parentheses are given in Hz.

^{195}Pt Chemical Shifts and $^{195}Pt–^{14}N$ Coupling Constants

In recent years interest in ^{195}Pt–NMR has grown rapidly [27], there being still no definitive theory governing the interpretation of platinum chemical shifts. All authors agree that σp, the paramagnetic screening contribution to the total screening, σ_t, is dominant for the platinum nucleus [26, 27]. The ^{195}Pt chemical shifts shown in Table IV range between 2638 to 3012 ppm upfield (lower frequency) for Na_2PtCl_6. The results suggest that more substituted carbons of imines (=N–R) result in low field (high frequency) shift of δ ^{195}Pt, relative to unsubstituted carbons (*i.e.* R = $C(CH_3)_3$, R = CH_3; δ ^{195}Pt, 2638, 2834 ppm respectively, also, R = $CH(CH_3)C_2H_5$, $CH_2CH(CH_3)_2$, $(CH_2)_3CH_3$; δ ^{195}Pt, 2680, 2762 and 2786 ppm respectively). But in the case of R = phenyl a lower frequency was obtained, δ ^{195}Pt, 3012 ppm.

TABLE IV. ^{195}Pt-NMR Spectra of *trans*-$[PtCl_2(\eta^2\text{-}Ethene)(Imine)]$ Complexes.

No.	Formula	δ^a	$^1J(^{195}Pt–^{14}N)$ Hz
1	Imine I, R = $\text{-}CH_3$	–2834	271
2	R = $\text{-}CH(CH_3)_2$	–2988	280
3	R = $\text{-}CH_2CH(CH_3)_2$	–2762	283
4	R = $\text{-}CH(CH_3)C_2H_5$	–2680	278
5	R = $\text{-}C(CH_3)_3$	–2638	288
6	R = C_6H_5	–3012	br^b
7	R = $\text{-}(CH_2)_3CH_3$	–2786	280
10	R = $\text{-}CH(CH_3)C_2H_5$	–2890	br^b
		–2804	br^b
		E and Z	
11	R = $\text{-}CH_2CH(CH_3)_2$	–2882	br^b
		–2806	br^b
		E and Z	

^{a}In ppm from the platinum resonance of Na_2PtCl_6(aq).
^{b}br = broad peak observed.

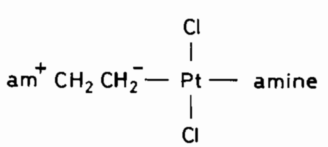
In most imine complexes, Table IV, we have observed the value $^1J(^{195}Pt–^{14}N)$ directly from well-resolved triplet structure ($\Delta 1/2\nu < 120$ Hz). Coupling constant values are shown in Table IV, $^1J(^{195}Pt–^{14}N)$, range 271–288 Hz. These values are comparable to the values of $^1J(^{195}Pt–^{14}N)$ obtained from analogous square-planar platinum complexes, *i.e.* *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)$ (substituted pyridine)] [28], $^1J(^{195}Pt–^{14}N)$, 292–304 Hz, N-*trans* to C_2H_4

or can be compared with ^{15}N complexes of *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{pyridine-}^{15}N)]$, $^1J(^{195}Pt-^{15}N)$, 409 Hz (N-*trans* to C_2H_4) and for isonitrile Schiff's base complex $[Pt(OC_6H_4CH{=}^{15}NCH_2CH_2O)(C{\equiv}NC_6H_{11})$ [28, 30], $^1J(^{195}Pt-^{15}N)$, 387 Hz [N-*trans* to $C{\equiv}NC_6H_{11}$]. Assuming no isotope effect, ^{15}N-coupling should be larger than ^{14}N-coupling by the ratio of their gyromagnetic constants (a factor of 1.4). The observed value for $^1J(^{195}Pt-^{14}N)$ of 283 Hz is in agreement with the observed and calculated value of $^1J(^{195}Pt-^{15}N)$ of analogous compounds when this value is multiplied by a factor of 1.4, or 396 Hz [28–30]. When R = phenyl, broad resonance due to the ^{14}N splitting is not fully resolved, due to ^{14}N relaxation.

Ligand–Ligand Exchange

In *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{amine})]$ the Pt–N bond is always labile [29] (on an NMR time scale) if free amine is present, unless the amine is very hindered sterically [31]. From the point of view of NMR studies compounds containing *trans*-labilizing ligands, such as $\eta^2\text{-}C_2H_4$, $\sigma\text{-}CH_2$, CO, PPh_3, are particularly instructive as reaction and relaxation rates are of the same general order. *Trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{imine})]$ shows a platinum-195 coupling to the imine protons (Table 1), which persists on addition of excess imine. In contrast, rapid addition of one mol equivalent of amine to the imine complex results in an amine-imine exchange and the coupling between the platinum-195 and imine protons disappears (free imine observed) resulting in the formation of *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{amine})]$, amine; CH_3NH_2, $(CH_3)_2NH$, (primary and secondary aliphatic amines).

When excess amine was added it resulted in the formation of σ-zwitterionic 2-ammonioethanideplatinum complex (D) [17, 18]. Thus $\eta^2\text{-}C_2H_4$ is strong



(D)

trans-labilizing, but there is no evidence for imine–imine exchange. This can be explained by the large sterically-hindered effect of the added imines. It is generally believed that ligand substitution reaction in square-planar four-coordinated *trans*-$[PtX_2(\eta^2\text{-ethene})(\text{amine})]$ complexes occur *via* five-coordinate intermediate [31, 32].

Stability of the Complexes

Elemental analysis supports the stoichiometry of the complexes (see Experimental). The complexes showed sufficient solubility and stability in chloroform-d solution to allow an extensive study of their structure in solution by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy. When the solution was left for several days at room temperature, *cis–trans* isomerism occured. When the solid complexes (yellow color) were left at room temperature for a week, these decomposed slowly and color changed to dark-yellow; leaving the solid complex at 0 °C for 6 months no change was observed. Imine complexes derived from acetophenone and its derivatives are not stable and decompose at room temperature.

Infrared Spectroscopy

Assignment of $\nu(C{=}N)$ was made for the compound 1, 3, 6 and 7. The strong $\nu(C{=}N)$ band at 1597 cm^{-1} with respect to the free ligand (1625 cm^{-1} s) was observed in KBr disk, Table V, showed little changes upon coordination to the platinum. However, the observation of a strong $\nu_{asym}(Pt-Cl)$ at 325 cm^{-1} established the presence of *trans* positioned Cl atoms (Cl–Pt–Cl) [9–13].

TABLE V. Infrared Spectra of *trans*-$[(PtCl_2(\eta^2\text{-}C_2H_4)(\text{Imine})]$ Complexes.

Compound	$\nu(C{=}N)$ cm^{-1}		$\nu(Pt-Cl)$ cm^{-1}
Free ligand	a	b	
Imine (I), R = $-CH_3$	1625s	1620s	
Imine (I), R = $-CH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	1625s	1625m	
Imine (I), R = C_6H_5-	1620s	1617s	
Imine (I), R = $-(CH_2)_3CH_3$	1625s	1623s	
Complexes			a
Imine (1), R = $-CH_3$	1597s	1590s	325s
Imine (3), R = $CH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	1597s	1590s	325s
Imine (6), R = C_6H_5-	1598m	1577s	335s
Imine (7), R = $-(CH_2)_3CH_3$	1595s	1587s	320s

[a]All free ligand spectra run as pure liquids (a) and as nujol mulls. [b]Complexes spectra run as KBr pellets (a) and as in nujol mulls (b).

Experimental

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 H_2O (2 cm^3). The mixture was cooled in ice and stirred for 10 min. Yellow precipitates were rapidly formed. To enhance the yield, a few drops of acetone were added. Acetone enhances the solubility of the starting imine in water and force the imine complex to precipitate. The yellow precipitate which separated was washed with cold water (*ca.* 2 cm^3) followed by pentane, and dried *in vacuo*. The complexes were recrystallized from $CHCl_3$: pentane mixture. In the case of imine complexes derived from acetophenone and its derivatives, methanol was used instead of water. *Anal.* Imine 1, $R = CH_3(C_9H_{13}PtCl_2NS)$: Found: C, 24.94; H, 3.04; N, 3.54. Calcd.: C, 25.02; H, 3.00; N, 3.23. Imine 2, $R = CH(CH_3)_2(C_{11}H_{17}$-$PtNSCl_2)$: Found: C, 27.77; H, 3.58; N, 3.16. Calcd.: C, 28.63; H, 3.69; N, 3.04. Imine 3, $R = CH_2CH$-$(CH_3)_2(C_{12}H_{19}PtNSCl_2)$: Found: C, 29.38; H, 3.87; N, 3.38. Calcd.: C, 30.32; H, 4.00; N, 2.94. Imine 5, $R = C(CH_3)_3(C_{12}H_{19}PtNSCl_2)$: Found: C, 30.20; H, 4.00; N, 3.26. Calcd.: C, 30.32; H, 4.00; N, 2.94. The melting points of the imine complex were: imine: (1) 124–126; (2) 95–98; (3) 96–98; (4) 87–90; (5) 103–105; (6) 130–132; (7) 81–83.

All NMR spectra were measured on JEOL JNM FX-100 spectrometer operating in the Fourier transform mode. All the spectra were recorded at ambient temperature, 25 °C. Natural abundance ^{13}CNMR spectra were recorded at 25 MHz, and ^{1}HNMR spectra were run at 100 MHz. The compounds were studied for 0.1 *M* solutions in $CDCl_3$. Chemical shift data of ^{1}H and ^{13}C NMR spectra were determined relative to the internal standard TMS, and platinum-195 relative to Na_2PtCl_6. Infrared spectra were measured on a Beckman 4240 spectrophotometer as nujol mulls between NaCl plates, as pure liquids or as KBr pellets.

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