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ORIGINAL ARTICLE

^{1}H ^{13}C NMR investigation of *E*/*Z*-isomerization around C═N bond in the trans-alkene-Pt(II)imine complexes of some ketimines and aldimines

M. Bakkar [a,*], M. Monshi [a], I. Warad [a], M. Siddiqui [b], A. Bahajaj [a]

[a] *Department of Chemistry, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*
[b] *Department of Chemistry, College of Science, Taibah University, Madinah, Saudi Arabia*

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KEYWORDS

E/*Z*-configuration;
Isomerization;
Ketimine;
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Zeise's salt

Abstract Ketimines (K1, K2) and aldimines (A1, A2, and A3) were prepared from unsubstituted acetophenone and/or benzaldehyde and primary amines (*i*-$PrNH_2$, *i*-$BuNH_2$ and *t*-$BuNH_2$). These imines were reacted with Zeise's salt (potassium ethenetrichloroplatinate(II)) to produce the respective complexes, namely, **PtK1**, **PtK2**, **PtA1**, **PtA2**, and **PtA3**. ^{1}H, ^{13}C, and ^{195}Pt-chemical shifts of the ligands and their complexes were studied to investigate the nature and mode of isomerization around C═N bond. The aldimines and their complexes were obtained as a single isomer. On the other hand, the ketimines and their complexes were obtained as a mixture of *E*/*Z*-isomers. It was found that the aldimine- and ketimine-platinum complexes undergo slow *E*/*Z*-isomerization in solution as evidenced from NMR spectra.

1. Introduction

Extensive research has been reported for the study of the metal-imine complexes of biochemical and pharmaceutical importance (Gligorijevic et al., 2009; Benito and de Jesus, 2008). The complexation (Czarkie and Shvo, 1985) of transition metals with imines has been studied for their coordination geometries, their molecular configuration and conformational forms in solution and in the solid state, their stabilization, isolation and subsequent use in chemical reactions (Fossey and Russell, 2007; Crespo et al., 2008; Bunnelle et al., 2008; Krupka and Patera, 2007). The solid-state four and five-coordinate complexes (**1**) and (**2**) (Fig. 1), were established by X-ray diffraction analysis (Van et al., 1980a,b, 1981).

The stable trans-alkene-Pt(II)-imine complexes, in which the imine molecule is mono dentate has been isolated (Al-Najjar, 1988). The importance of the *E*/*Z* isomerization supported by multinuclear NMR evidence has been reported (Al-Najjar, 1988; Al-Najjar et al., 1984). Two geometrical isomers (Patai, 1970; Tennant, 1979; Weingarten et al., 1967; Bjorgo et al., 1974) in *N*-substituted ketimines were reported to exist in more

* Corresponding author.
E-mail address: msbakkar@ksu.edu.sa (M. Bakkar).

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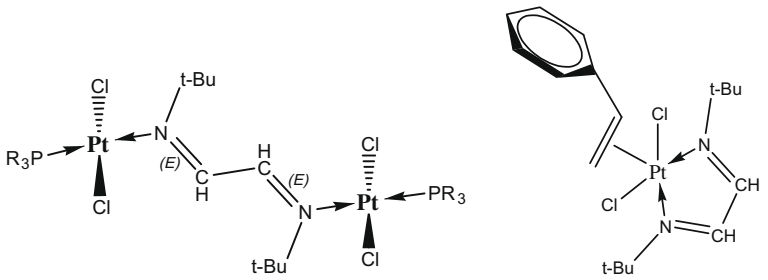


(1) **(2)**

Figure 1 Four and five-coordinate platinum (II) complexes (**1**) and (**2**).

stable-isomeric-form in the solid state, but equilibrium is established between the *E* and *Z* forms in solution.

Cuncuta et al. (2003) has studied the *E*/*Z* conformational equilibrium of *N*-substituted 2H-pyran-2-imines based on ^{1}H, ^{13}C NMR chemical shifts. The *cis–trans* isomerization around the double bond in the form aldiminium cation and vinylamine has been reported (Zilberg, 2003). Hofmann et al. (Asano et al., 1993; Hofmann et al., 1993; Cimiraglia and Hofmann, 1994) have studied the mechanism and thermal *E–Z* isomerization of a variety of substituted nitrogen containing complexes. Acetaldoxime in its *E* and *Z* forms were studied by means of *N*-matrix isolation combined with FTIR spectroscopy (Andrzejewska et al., 2002). The complexes *N*-arylsulfonylimidoyl-1,4-benzoquinoimines were found to undergo fast (on the NMR time scale) *Z*/*E* isomerization about the C/N bond in the quinonimine fragment as reported by Avdeenko et al. (2001). Buchwald (Kobayashi and Ishitani, 1999; Willoughby and Buchwald, 1994, 1996) and co-workers reported the various behavior of *E* and *Z* isomers and found that under the given reaction conditions *Z* imines reacts faster than the *E* imine and the interconversion of the imines is slow. *E*/*Z* arrangement around the C═N bond of the hybrid imine/amine ligand in palladium (II) co-ordination complexes have been recently discussed (Favier et al., 2005). The reactions at the azomethine C═N bonds in the nickel (II) and copper (II) complexes of pyridine-containing Schiff-base macrocyclic ligands and the unusual isomerization of the copper(II) complex has been studied recently by Herrera et al. (2003).

The work described in this paper concerned with the study of the properties and mode of *E*/*Z* isomerization in the new *trans*-alkene-Pt(II)-imine complexes of some ketimines and aldimines. In these complexes imines behave as unidentate bases through the nitrogen atom and form four-coordinate complexes with 1:1 metal-ligand stoichiometry. The complexes are formed by reaction of Zeise's salt with the imine according to the Eq. (1).

$$K[Pt(C_2H_4)Cl_3] + \text{imine} \rightarrow \textit{trans}\text{-}[PtCl_2(C_2H_4)(\text{imine})] + KCl \quad (1)$$

2. Experimental

Acetophenone, benzaldehyde, *i*-$PrNH_2$, *i*-$BuNH_2$ *t*-$BuNH_2$, and the solvents were purchased from Aldrich Chemicals and used without further purification. Solution state ^{1}H NMR spectra were measured in $CDCl_3$ on JEOL NMR, 400 MHz and JEOL FX-90 Q spectrometer FT-mode using TMS as internal reference. ^{13}C NMR spectra were recorded at 22.5 MHz. Mass spectral analysis data were recorded on GC/MS QP5050A, Shimadzu, Japan, using EI ionizing method. The studied imines (70–80% yield) and Zeise salt ($K[PtCl_3(C_2H_4)]\cdot H_2O$, recrystallized twice from 5 M HCl, 87% yield) were prepared according to literature procedures (Weingarten et al., 1967; Chock et al., 1973). The purity of prepared imines was tested by gas chromatography PHILPS PU 4500. The correctness of the structure assigned was inferred from their spectroscopic data.

3. Preparation of the imine-complexes

3.1. Method (A)

In 10 mL of solvent, (50:50 water/acetone, pure acetone, or pure methanol), 0.3 g of Zeise's salt was dissolved and flushed with nitrogen. The solution was cooled to 0–5 °C in a water/iced salt bath. A 1.1 equivalent of the imines (K) or (A) was dissolved in 5 mL of the solvent, cooled and added gradually (during 5 min) with stirring. The mixture was left stirring for 1–2 h and allowed to warm gradually to room temperature. The solvent was reduced to half its volume by evaporation, after which crushed ice was added to the reaction mixture to precipitate the product. A few drops of acetone were added to enhance precipitation and dissolved unreacted imine. The solid product was washed with pentane. The product was dissolved in chloroform and pentane and left in the refrigerator. The yields were ~47% and 56% for [**PtK1**] and [**PtK2**], respectively.

3.2. Method (B)

Following the same method as above, but using water as the only solvent, Zeise's salt (0.05 g) was dissolved in 2 mL of water and equivalent amount of the pure neat imine was added. The mixture was stirred at ambient temperature. The product was extracted with 3 mL chloroform. The chloroform extract was concentrated and light petroleum ether 40–60 °C was added to obtain bright yellow needles. (Yields were 81%, 86% for [**PtK1**] and [**PtK2**], respectively, and 80.7%, 87% and 88.7% for [**PtA1**], [**PtA2**] and [**PtA3**], respectively), the yield calculations were based on amount of Zeise's salt.

The mass spectral analysis of the principal ion peaks (^{195}Pt) for chosen complexes are {[**PtK1**] 455 (M^+, 2%), 391 ($M^+ - C_2H_4\cdot HCl$, 2.5%), and 353 ($M^+ - C_2H_4\cdot 2HCl$, 6.5%)};

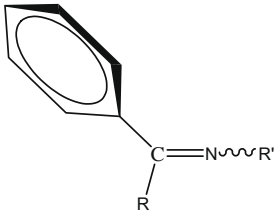
{**[PtK2]** 469 (M^+, 4.5%), 441 ($M^+-C_2H_4$, 1%), 405 ($M^+-C_2H_4$·HCl, 5%), and 367 ($M^+-C_2H_4$·2HCl, 11.4%)}; {**[PtA2]** 455 (M^+, 1%), 427 ($M^+-C_2H_4$, 1%), 391 ($M^+-C_2H_4$,HCl, 2%), and 353 ($M^+-C_2H_4$.2HCl, 2%), 295 ($M^+-C_6H_5$·C═N·C_4H_9, 0.7%}.

4. Results and discussion

4.1. The starting materials

The ^{1}H NMR of Zeise's salt dissolved in D_2O gives a singlet at δ 4.61 ppm, characteristic of alkenic protons, with platinum satellites in a 1:4:1 ratio, ^{3}JPtH = 65.9 Hz.

The structure of the imines (Fig. 2) has been confirmed by ^{1}H and ^{13}C NMR, and MS spectra. The spectral data of the prepared imines are shown in Tables 1 and 2. Previous investigations (Bjorgo et al., 1974) applying NMR techniques have concluded that aldimines exist completely in *E* configuration. The aldimines A1, A2, and A3 were obtained in one isomeric form, *E*-configuration and the ketimines (K1) and (K2) were obtained as one predominant isomer *E* as evident from their ^{1}H and ^{13}C NMR spectra. In ketimines, the ^{1}H NMR chemical shifts of *N*-alkyl groups for *Z*-isomers have been reported (Bjorgo et al., 1974) to have lower δ-values than for *E*-isomers because of the anisotropic effect of the aryl ring. The approximate ratio, estimated by integration of the ^{1}H NMR signals, was 95:5 in favor of the *E* isomer in both compounds K1 and K2. This ratio is similar to the value reported (Bjorgo et al., 1974) for the *p*-NO_2-substituted K1 analogue. A small solvent effect has been previously reported (Bjorgo et al., 1974) for the ratio of *E*–*Z* isomers of the free imines where it has been shown that a number of alkyl aryl ketimines were allowed to equilibrate in a range of solvents, and reported to be more dependent on the nature of the imine substituents rather than on the solvent used. The comparison (Al-Najjar, 1988) between the structure of different imines and the effect of the substituent groups on either the aryl or imino carbon atom on *E*–*Z* isomerization suggested that increasing the bulkiness of these substituents tends to increase the rate of isomerization. The same study showed that increasing the degree of substitution on the imino carbon atoms slows the rate of isomerization. The suggested mechanism for *E*–*Z* isomerization of the free imines is described in terms of either the rotation around the C^+–N^- bond or of inversion at the nitrogen atom. One more factor which may direct the position of equilibrium between *E* and *Z* isomers in the free imine is the repulsive interaction between the nitrogen lone pair and the aromatic π-electrons (Bjorgo et al., 1974), which may destabilize the *E*-isomer of the free ligand.



K) R = CH_3; R'= *i*-Pr(1); R'= *i* –Bu(2)
A) R = H; R'= *i*-Pr(1); R'= *i*-Bu(2), R'= *t*- Bu(3)

Figure 2 The synthesized aldimines and ketimines.

4.2. The platinum complexes

Different solvents have been used to synthesize imine complexes, of the general formula $(C_2H_4)Cl_2PtN(R')$ = C(R)ph as represented in Fig. 3. In method (B) only water was used while in method (A), mixture of water and acetone or methanol was used. When water is used as the solvent, an immediate

Table 1 ^{1}H NMR chemical shift data δ/ppm (*J*/Hz) for imines and their Pt complexes.

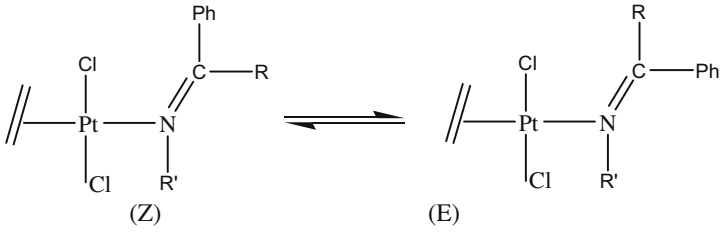
Compound	Ph	[a,b]R–C═	–CH	CH_2	$(CH_3)_2$	$(CH_3)_3$	CH_2═CH_2
K1 *E*	7.3, 7.6	2.15			3.8	–	–
Z		2.50				–	
PtK1 *E*	7.6, 7.8	3.1 (14)			4.1	–	4.8 (60.8)
Major *Z*		2.6 (8.5)			4.5	–	4.3 (61.7)
K2 *E*	7.3, 7.7	2.17 t	2.1 m	3.25 dd	1.0 d	–	–
Z				3.00 dd	0.85 d	–	–
PtK2 *E*	7.5, 7.9	3.06 (13.6)	3.05 m	3.5 dd	1.15 d	–	4.8 (59.9)
Major *Z*		2.55 (8.3)		3.9 dd	0.9 d		4.4 (60.8)
A1	7.3, 7.7	8.2	3.5 m	–	1.24 d	–	–
PtA1 *E*		10.05	3.8 m	–	1.5 d	–	4.70 (60.7)
Z	7.6, 8.6	8.85 (98.9)	4.57 m	–	1.72 d	–	4.75 (60.55)
A2		8.3	2.1 m	3.0 dd	1.1 d	–	–
PtA2 *E*	7.6, 8.6	[c]8.6 (99.7)	3.0 m	3.9 (14.7) dd	1.1 d	–	4.8 (60.29)
A3	7.4, 7.7	8.9	–	–	–	1.3 s	–
PtA3 *E*	7.6, 8.5	10 (53)	–	–	–	1.85 (3.7)	4.7 (61.5)
Major *Z*		8.9 (98)	–	–	–	1.5 s	4.6 (61.3)

^{1}H NMR chemical shift of Zeise's salt (Van et al., 1981) is 4.61 ppm with *J*PtH = 65.9 Hz.
Multiplicities; s = singlet; d = doublet; t = triplet; m = multiplet; dd = doublet of doublets.
[a] ^{4}JPtH = 14 Hz in *Z* isomers and ^{4}JPtH = 8.5 HZ in *E* isomers (for ketimine complexes).
[b] ^{3}JPtH = 98–99.9 Hz in *Z* isomers and ^{3}JPtH = 53 Hz in *E* isomers (for aldimine complexes).
[c] Double ^{4}JHH = 1.6 Hz, long range coupling.

Table 2 ^{13}C NMR chemical shift data δ/ppm (J/Hz) for imines and their Pt complexes.

Compound	R–C═	N–C[c]	CH[c]	$(CH_3)_2$[c]	$(CH_3)_3$	C═C[b]	C═N(O)
Actphnon	26	–	–	–	–	–	197.3
i-$PrNH_2$	–	41	–	24.4	–	–	–
i-$BuNH_2$	–	49	30	18.5	–	–	–
t-$BuNH_2$	–	46.9	–	–	29.7	–	–
Benzald.	–	–	–	–	–	–	192
K1 *E*	14.6	51	–	24.4	–	–	162
Z	–	52	–	–	–	–	166
PtK1 *E*	–	–	–	–	–	76.2 (160)	–
Major *Z*	24 (23)	58.5 (15)	–	23.2	–	73.3 (171)	178
K2	15.3	60	30	20.9	–	–	165
PtK2 *E*	31.6 (35.5)	65.5	28.8	–	–	76.2 (158)	179
Major *E*	24 (33)	64.6 (12)	29.7	20.6	–	76.3 (167)	180
A1	–	61.5	–	25	–	–	157.9
PtA1 *Z*	–	65.3 (13)	–	24.2 (9)	–	76 (161)	167.6
A2	–	70	30	20.8	–	–	160.8
PtA2 *Z*	–	74 (12)	28	19	–	76 (160)	169
A3	–	57	–	–	30	–	155
PtA3 *E*	–	57.5 (11)	–	–	32.1	Ovrlpd.[a]	
Z	–	67.6 (12)	–	–	31.7 (7)	74.2 (168)	168

[a] Overlapped by $CDC1_3$.
[b] ^{13}C NMR chemical shift of Zeises's salt (Van et al., 1981) is 67.3 ppm with J (Pt–C) = 194 Hz.
[c] The chemical shifts of the carbons in the free imines have been confirmed by off-resonances and quantitative ^{13}C NMR. Those carbons in the complexes were confirmed by DEPT technique.



[PtK] R = CH3; R'= *i*-Pr(1), R'= *i*–Bu (2).
[PtA] R = H; R'= *i*-Pr(1), R'= *i*-Bu(2), R'= *t*- Bu(3).

Figure 3 E/Z isomerization of imine complexes in solution.

precipitation of the formed complex took place. This might explain the absence of the E/Z isomerization in water. On the other hand, the product is soluble in acetone and methanol (method A) and this solubility might accelerate the E/Z isomerization. The platinum complexes of imines are reported to be expectedly obtained as a mixture of E and Z isomers in the same ratio of the starting imines (Al-Shalaan et al., 1986). The aldimine complexes [**PtA1**] and [**PtA2**] have been obtained as single isomers, but [**PtA3**] was obtained as a mixture of E and Z isomers, Figs. 4 and 5 show the ^1H and ^{13}C NMR of [**PtA1**]. The two isomers are distinguished by the much larger coupling of the imino proton to platinum in one isomer (ca. 100 Hz) than in the other. Assuming that the *trans*-Pt–H coupling is bigger than the *cis* (Hofmann et al., 1993), the isomer with J_{PtH} = 100 Hz is assigned as Z. Since the complexes [**PtA1**] and [**PtA2**] have couplings close to 100 Hz it follows that they exist in the Z configuration, *i.e.* the aldimine has coordinated without change in geometry (Fig. 3). The rapid isomerization noticed in complex [**PtA3**] could be attributed to the steric effect of the bulky *t*-Bu group. Similarly, ketimine complexes [$\mathbf{PtK_1}$] and [$\mathbf{PtK_2}$] were obtained as a one predominant isomer when water was used as the only solvent. Bearing in mind the evidence from the aldimine experiment, we assumed that the ketimine coordinates initially with no change in configuration. Hence, the predominant product found has been assigned the Z configuration.

The mass spectrum of complex [**PtK2**] showed in Fig. 6 is a representative of the studied ketimine and aldimine platinum(II) complexes. The analysis of [**PtK2**] was confirmed by high resolution mass spectroscopy of the parent molecular ion peak M^+ (found for $C_{14}H_{21}Cl_2NPt$, 469.0699, calculated for $C_{14}H_{21}{}^{35}Cl_2N^{196}Pt$, 469.0700 and for $C_{14}H_{21}{}^{35}Cl^{37}ClN^{194}Pt$, 469.0647). Platinum metal has six natural abundant isotopes, ^{190}Pt (0.014%), ^{192}Pt (0.782%), ^{194}Pt (32.967%), ^{195}Pt (33.832%), ^{196}Pt (25.242%), and ^{198}Pt (7.163%), the contribution of the first two to the intensity of molecular ion peak

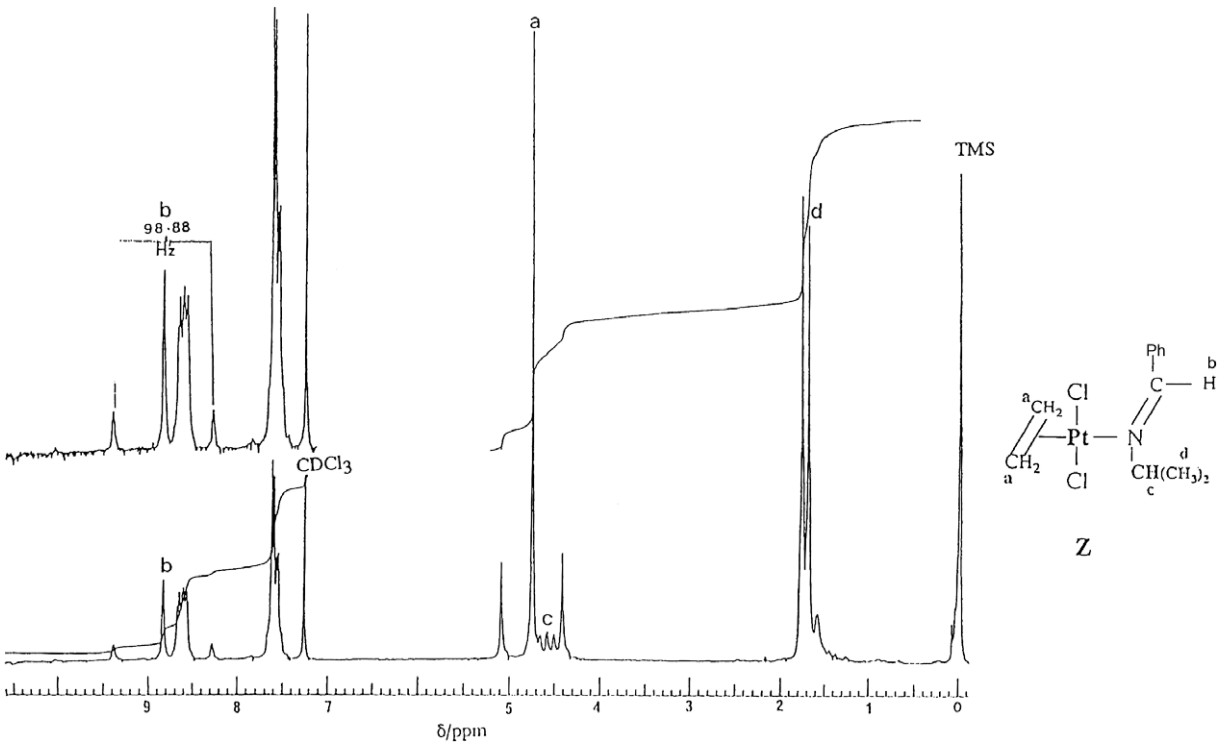


Figure 4 ^{1}H NMR spectrum of freshly prepared solution of [**PtA1**] in $CDCl_3$, 90 MHz.

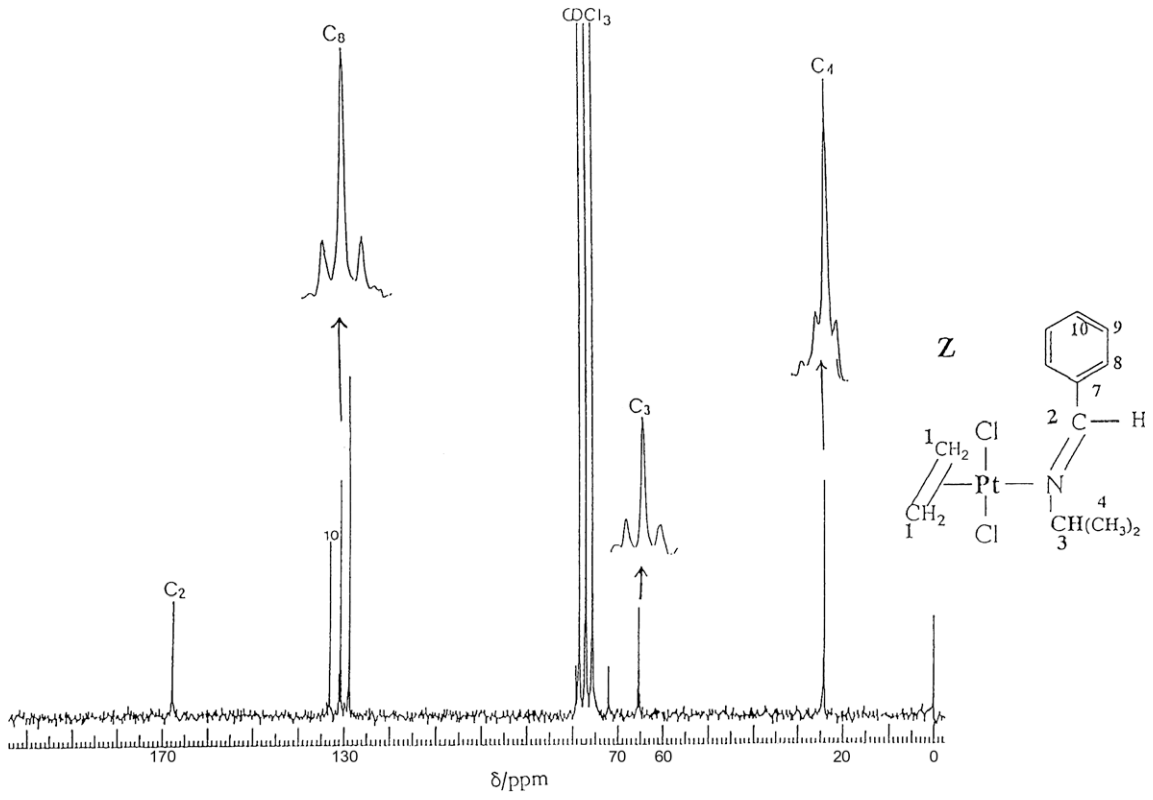


Figure 5 ^{13}C NMR spectrum of the two isomers of [**PtA1**] in $CDCl_3$, recorded at 22.5 MHz.

is negligible due to their very low natural abundance. Chlorine also has two natural isotopes, ^{35}Cl (75.47%) and ^{37}Cl (24.52%). Characteristic (Haake and Mastin, 1971) patterns of peak intensities have been obtained, caused by the isotopic

distributions of naturally abundant platinum and chlorine atoms. The parent molecular ion (M^+ 469, 4.5%) has been assigned to the various isotopes of Pt and Cl (Table 3). The combination of ^{35}Cl, ^{37}Cl isotopes and ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt isotopes gives the complex peak which consists of eight lines (Fig. 7). Table 3 presents the assignment of the lines contained in the parent molecular ion peak. This was supported by a simple model compound $PtCl_2$. The mass spectrum of which was simulated using OPUS software to assess the molecular ion peak of different Pt and Cl isotopes Fig. 8 and Table 4. The intensities of these lines reflect the combinations of different possible isotopomers, *i.e.* the highest intensity line (3) came from the combination of $^{37}Cl_2$ ^{196}Pt and ^{35}Cl ^{37}Cl ^{194}Pt. The line intensity (line 8) aroused from $^{37}Cl_2$ ^{198}Pt is ignored in the model Fig. 8 because it is a combination from three low natural abundant isotopes. The combination of the fragmentation pattern showed loss of C_2H_4, loss of C_2H_4 + HCl, and loss of $C_6H_5C{=}NC_4H_9$. This clearly demonstrates that although the cleavage of the bond to the nitrogen is favored, many covalent bonds cleave competitively during fragmentation, in this type of Pt(II) complexes Haake and Mastin, 1971.

The products of the reaction of Zeise's salt and imines were found to be *trans*-[$Pt(C_2H_4)Cl_2$(imine)] in accordance with literature (Al-Najjar et al., 1984). Four-coordinate geometry of ethene-Pt(II)-imine compounds was supported by the resulting ^1H and ^{13}C resonances (Tables 1 and 2). Three- and five-coordinated Pt-complexes have been reported to exhibit larger upfield chemical shifts of the ethene resonance than four-coordinate ones (Van et al., 1981). A comparison (Van et al., 1981) has been made between ^1H and ^{13}C NMR data of coordinated alkene in some three-, four-, and five-coordinated platinum complexes and that of free alkene. The ^1H and ^{13}C NMR resonances of the alkene exhibit large upfield chemical shifts upon coordination and are all flanked with ^{195}Pt satellites.

Table 3 The assignment of the lines contained in the parent molecular ion M^+ (469) in Fig. 5.

Peak no. (mass)	Intensity (%)	Assignment
(1) 467	63	$^{35}Cl_2{}^{194}Pt$
(2) 468	67	$^{35}Cl_2{}^{195}Pt$
(3) 469	100	$^{35}Cl_2{}^{196}Pt$ and $^{35}Cl^{37}Cl^{194}Pt$
(4) 470	55	$^{35}Cl^{37}Cl^{195}Pt$
(5) 471	60	$^{37}Cl_2{}^{194}Pt$, $^{37}Cl_2{}^{198}Pt$, $^{35}Cl^{37}Cl^{196}Pt$
(6) 472	15	$^{37}Cl_2{}^{195}Pt$
(7) 473	15.5	$^{37}Cl_2{}^{196}Pt$ and $^{35}Cl^{37}Cl^{198}Pt$
(8) 475	5	$^{37}Cl_2{}^{198}Pt$

The magnitude of the couplings $^nJ_{195Pt-1H}$, $^nJ_{195Pt-13C}$ and the upfield chemical shift of the ^1H and ^{13}C resonances are characteristic for this type of coordination geometry around the central platinum atom; *i.e.* four coordinate. The largest coupling constant $J_{195Pt-13C}$ of this type was reported (Van et al., 1980b) to be 297 Hz in a five-coordinate complex; *i.e.* [$PtCl_2(C_2H_4)$(*t*-Bu-dim)]. The assignment of ^1H and ^{13}C NMR spectra, including $^nJ_{195Pt-1H}$ and $^nJ_{195Pt-13C}$ coupling constants for *N*-alkyl group in the complexes prepared are reported in Tables 1 and 2; *e.g.* complex [**PtK1**] shows the two equivalent methyl as doublet at δ 1.5 (^4JPtH 3.9 Hz) for *E* isomer, and at δ 1.74 (^4JPtH 4.8 Hz) for *Z* isomer. The integration for the two methyls of these two isomers is consistent with the corresponding values of the coordinated ethene. The methine group is overlapped by the ethene resonance in its ^1H NMR for both [**PtK1**] and [**PtA1**].

The ^{13}C NMR of N–CH in K1 shows a downfield shift from 51 ppm to 58.5 ppm in the complex [**PtK1**]; $\Delta\delta$ = 7.5 ppm (Table 3). The values of ^2JPtC = 11–15 Hz for N–C of the gem-alkyl groups. In **PtK1**, the C-methyl group

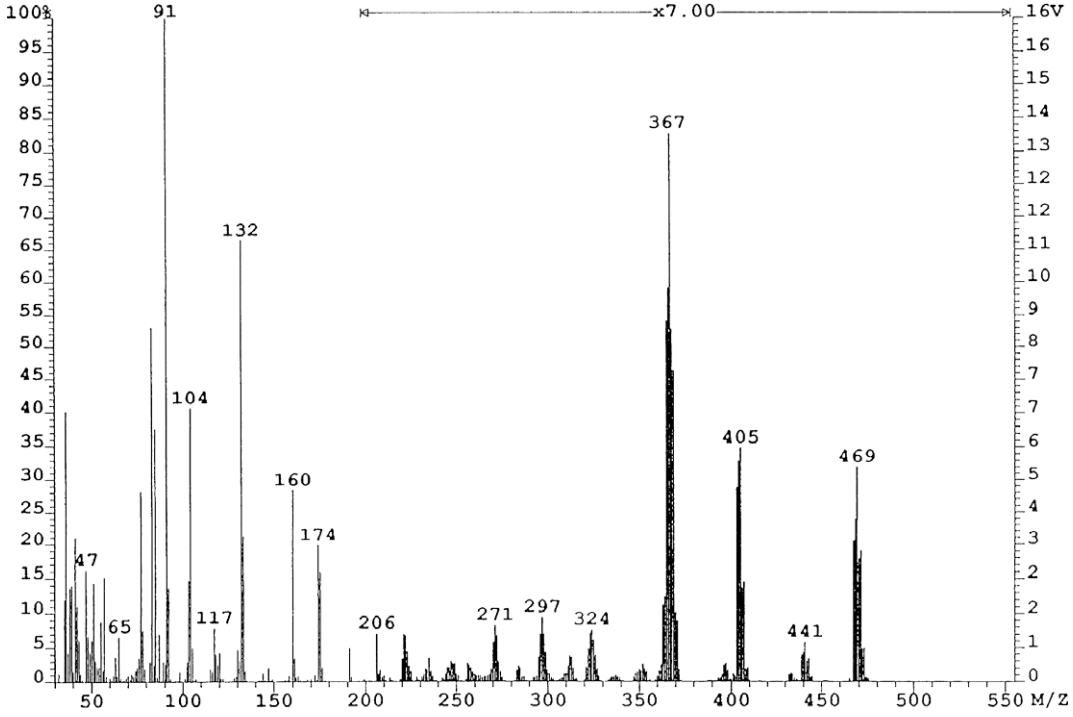


Figure 6 The mass spectrum of [**PtK2**].

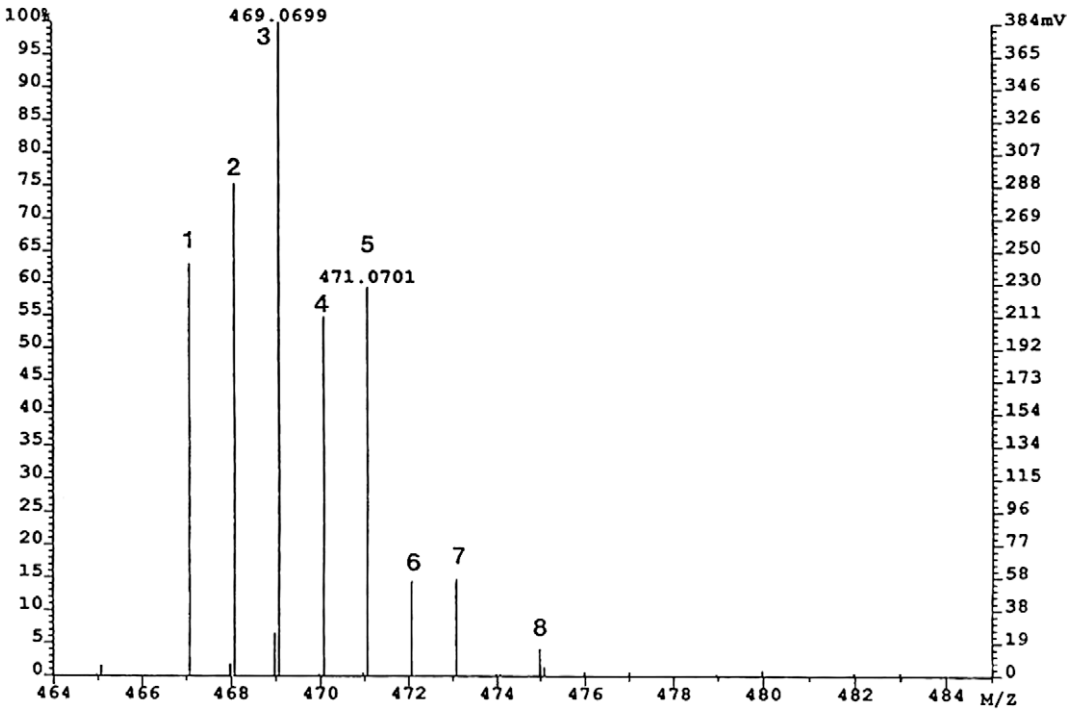


Figure 7 The experimental mass spectrum of the parent molecular ion for [**PtK2**].

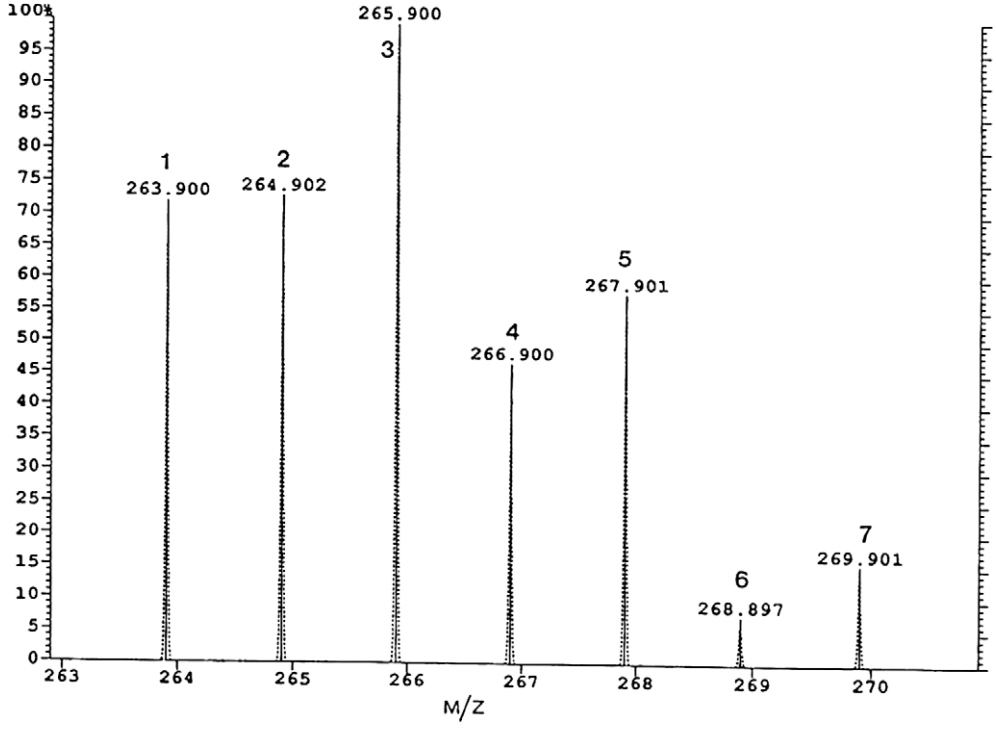


Figure 8 The calculated mass spectrum for model compound $PtCl_2$.

has ^{1}H resonances at δ 2.6 (JPtH = 8.5 Hz) and δ 3.1 (JPtH = 13.8 Hz) for *Z* and *E* isomers, respectively. Comparable δ and JPtH values have been obtained for complexes [**PtK2**] and [**PtK1**] (Table 1). Long range coupling, ^{5}JHH = 0.7 Hz, obtained for **PtK2**; *i.e.* CH_3–C═N–CH_2 (Table 2) was not found on complexation. For [**PtA2**] ^{4}JHH = 1.3 Hz was found both for the ligand and its complex [**PtA2**]. The ^{13}C resonances of the methyl group in *Z* isomer of [**PtK2**] came at δ 24, ^{3}JPtH = 33 Hz, and at δ 31.6, ^{3}JPtH = 35.5 Hz in *E* isomer, (Table 2).

Table 4 The possible mass spectrum lines for the model molecule $PtCl_2$: the value in square is the sum of the masses of $PtCl_2$ and $C_{14}H_{21}N$.

Isotope	^{194}Pt	^{195}Pt	^{196}Pt	^{198}Pt
$^{35}Cl_2$	264[476]	265[468]	266[469]	268[471]
$^{37}Cl_2$	268[471]	269[472]	270[473]	272[475]
$^{35}Cl^{37}Cl$	266[469]	267[470]	268[471]	270[473]

In *Z* isomer of the compounds [**PtA1**], [**PtA2**], and [**PtA3**], the chemical shifts of the imino hydrogen (H–C═N) has its δ values at 8.85, 8.6 and 8.9 ppm, respectively, and are flanked with platinum satellites showing a large ^3JPtH = 98–99.7 Hz (Table 1). A smaller coupling has been recorded for the *E* isomer of the compounds [**PtA3**] (53 Hz) and [**PtA1**] (75.8 Hz). However, the intensities of the platinum satellites of *E* isomer of imino proton (H–C═N) appear broad (Mann et al., 1971) and much smaller than those of *Z* isomer. A coupling constant ^3JPtH = 100 Hz, has been reported (Van et al., 1981) for the four-coordinate Pt complexes.

A large downfield shifts for the ^{13}C═N of the complexes was exhibited with respect to their starting free imines; *i.e.* for aldimine complexes $\Delta\delta$ = 10–13 ppm, and for ketimine complexes $\Delta\delta$ = 12–15 ppm. A large ^2JPtC might be expected of C═N, but no satellites could be detected. In previous reports, ^2JPtC values fell in the range 5–15 Hz (Van et al., 1981; Motschi et al., 1980), for diimine complexes. The authors (Van et al., 1981; Motschi et al., 1980) commented that these values were lower than expected.

All the aldimine complexes are quite stable compounds; *i.e.* when the solid has been left in the air at room temperature for few weeks no changes have been noticed. However, chloroform solution of aldimine complexes isomerizes if they are left for few hours. New peaks assigned to the most stable *E* isomer appeared when the complexes were left in $CDCl_3$ overnight, and 78% conversion to the *E* isomer was noticed after few weeks Fig. 9. Similar results were observed for ketimine complexes [**PtK1**] and [**PtK2**] in accordance with literature (Al-Najjar, 1988). It was suggested that the mechanism for *E*–*Z* isomerization in the imine complexes depends on the importance of the zwitterionic resonance form which then rotates about the C^+–N^- bond similar to that in the free imines (Fig. 10).

The results of our study show that the coupling of Pt–H of, the imino-hydrogen, is very weak in *E* isomers of aldimine complexes, probably due to the rotation of the imine ligand around the Pt–N bond. This rotation is hindered by the phenyl ring in *E* isomer. This can be explained if we imagine the product undergoes internal rotation about the platinum-ligand of ligand–ligand bond (Kegley, 1987). Each individual conformation will have slightly different values of *J*PtH, and the average of the platinum-ligand coupling will be observed. In the alternative orientation; *i.e.* of the other isomer, rotation is presumably inhibited (locked conformation) and a discrete value of *J*PtH observed in *Z* isomer. The same behavior was noticed previously (Hofmann et al., 1993) on the alkenyl Pt(II) complexes and attributed partly to the relaxation phenomenon of the Pt nucleus.

Alkyl-imines, like alkyl-diimines and allyl-diamines, are good σ-donor ligands (Al-Najjar, 1988), having the sequence of their σ-donation ability as follows; *t*-Bu(C-quaternary) > *i*-Pr(C-tertiary) > (C-secondary) > CH_3 > ph. ^{13}C-data for ethene of both types of complexes demonstrate that

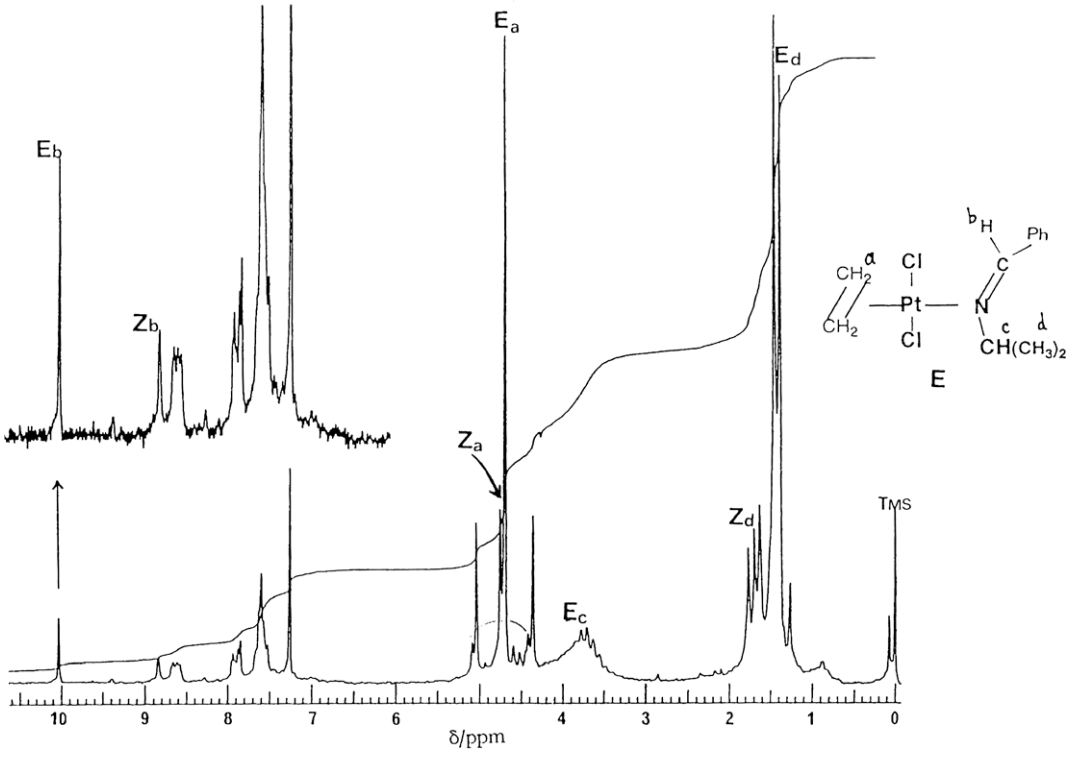


Figure 9 ^{1}H NMR spectrum of the two isomers of [**PtA1**] in $CDCl_3$, 90 MHz. (*E* isomer is 78% after few weeks).

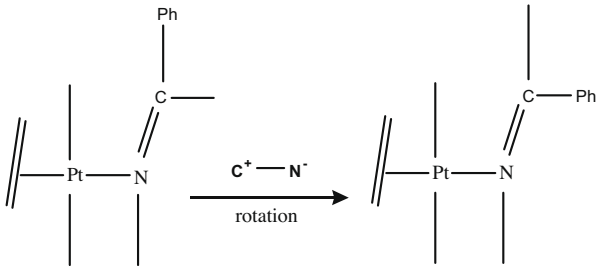


Figure 10 Possible mechanism for E/Z isomerization.

[**PtA3**] has the highest $^{1}J_{PtC}$ = 168 HZ. Since the *N*-alkyl group in the compound [**PtA3**]; *i.e.* *t*-Bu, is more electron donating towards the platinum atom (compared with the other alkyls), the π-back bonding to the alkene is enhanced, resulting in stabilization of the platinum alkene bond. Such stabilization could be the result of both steric and electronic effects. The alkene ^{13}C-signal in Zeise's salt resonates at 67.3 ppm; upon complexation a significant upfield shift was observed indicating less π-electron donation to the metal (Table 2). This was attributed to the competition with the imino carbon (C═N) bond[35] Garrett, 2007. Similarly, an upfield shift was observed for the imino carbon when complexed with Pt metal as shown in Table 2. Such observation reveals the effect of Pt on both ligands (C═C and C═N).

5. Conclusion

The comparative study of aldimine and ketimine complexes concludes the following points:

(a) The formation of imine-metal complexes shows that the basicity of the C═N group, in both aldimine and ketimine ligands, is sufficient by itself to permit simple coordination between the lone pair and the metal ion (Van et al., 1981).
(b) Due to the anisotropic effect (Bjorgo et al., 1974) of the aryl ring, the *N*-alkyl groups have higher δ values in *E*-configuration than in *Z*-configuration for the free imines. However, this is not always the case in the complexes.
(c) *E* isomers of the starting free ketimines and aldimines produce *Z* isomers of their platinum complexes. However, slow conversion takes place in $CDCl_3$ from the *Z* to *E*-configuration substantiated by ^{1}H NMR.
(d) The ^{1}H resonances of the four-coordinated ethene-Pt(II)-imine complexes are similar to those of amine (Pergosin et al., 1977) complexes *e.g.* *trans*-$[PtCl_2(C_2H_4)(amine)]$ which resonate at δ 4.5–5.0 with ^{195}Pt–H couplings of 59–63 Hz.
(e) The ^{13}C shifts of these amine complexes were reported (Al-Najjar et al., 1984) to be similar to those in the imine complexes, but the ^{1}J(PtC) values were generally larger for a given ligand. The similarity between the imine and the amine complexes may be due to the relationship between the (PtC) coupling and the s-character in the Pt–C bond (Kobayashi and Ishitani, 1999). The changes in the strength of the σ-component of the Pt–C bond reflects qualitatively the *trans*-influence of a group *trans* to the ethene in the complex (Al-Najjar et al., 1984).

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