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Isomerization of Imines in Platinum–Imine Complexes

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Abstract

Multinuclear ^{1}H, ^{13}C and ^{195}Pt spectroscopy provides strong evidence for *E–Z* isomerization of imine ligands coordinated to platinum(II) of the type *trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)$(imine)].

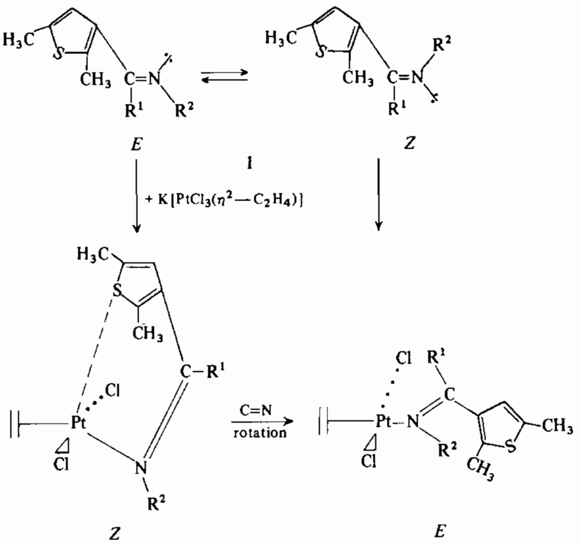
Introduction

In the course of our investigations on the coordination behaviour of σ-imines towards platinum(II), we found that stable platinum(II)–olefin–monodentate σ-imine bonded complexes of the type *trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)$(imine)] can be prepared [1]. Recently [2] NMR spectroscopy enabled us to look at the *E–Z* isomerization of imine ligands of the type aryl–(R^1)C=N–R^2 (where aryl = furan, thiophene, R^1 = H, CH_3, Ph; R^2 = primary amines) coordinated to the platinum(II). The free imines were each obtained in one isomeric form (*E* = 100%). Therefore, platinum complexes of these imines were obtained as a single rotamer similar to the starting material.

In this paper we report the synthesis, reactions, and characterization of new type of imine-complexes. Imines derived from 2,5-dimethyl-3-acetylthiophene and primary amines (Table I) were obtained as *E* and *Z*-isomeric mixtures in the liquid state.

Results and Discussion

This type of imine has been chosen particularly to show *E–Z* isomerization. This may be explained by steric interaction between the ortho-substituent (here 2-methyl-group) and the C-substituent which may force the aromatic ring further out of the C=N bond plane. A repulsive interaction between the nitrogen lone pair and the aromatic π-electrons may destabilize the *E*-isomer [3, 4]. Previous studies of *E–Z* equilibria in analogous aryl alkyl ketones [3, 5] have shown that the N-alkyl group can prefer to reside *cis* to the aryl group which possesses ortho-substituents (1–*E*). Therefore, platinum complexes of these imines were expected to be obtained as a mixture of *E* and *Z* isomers in the same ratio as that of the starting imines. Unfortunately, the NMR spectra of a freshly prepared solution of complex 2 in chloroform-d showed the presence of only one rotamer 2-*Z* (Table I).



2

2	R^1	R^2
a	CH_3	CH_3
b	CH_3	i-Pr
c	CH_3	i-Bu

When freshly prepared solution of 2 in chloroform-d was left for few minutes, and the ^{1}H NMR spectrum was remeasured new peaks were observed downfield from the original ones (*i.e.* $\eta^2\text{-}C_2H_4$ protons of **2a**, *Z*: δ = 4.46 ppm, *J*(Pt–H) 59 Hz; and *E*: δ = 4.78 ppm, *J*(Pt–H) 60 Hz) (Table I). The solution was left for additional periods 10, 20, 30, 60, 120 and 180 min and the NMR spectra were recorded in each case. They showed a gradual increase in the intensity of the new peaks at the expense of the original peaks until the isomerization was nearly completed. These results indicate that the original complex tends to isomerise to a new, more stable, complex 2-*E* (Table I).

E–Z isomerization of imines derived from 2-acetylfuran and 2-furaldehyde coordinated to platinum was observed after 1 h in chloroform-d solution, but isomerization of analogous 2-acetylthiophene imines was complete only after *ca.* 3 days [2] (Table I).

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TABLE I. ^{1}H, ^{13}C and ^{195}Pt NMR Spectra of *trans*-[PtCl$_2$(η^2-ethene)(imine)] Complexes

Complex	Configuration (%)	^{1}H NMR^a					^{3}C NMR^a			^{195}Pt NMR^b	
		δ(R^1)	δ(R^2)	δ(CH$_2$=)	δ(H^4)	^5J (Hz)	δ(R^1)	δ(R^2)	δ(CH$_2$=)	δ	^1J(^{195}Pt–^{14}N)
2a	*Z* (100)	2.49	3.6(27)	4.46(59)	7.35	0.73	23.37	43.44	73.92(162)	*ca.* 2851	*ca.* 253
	E (100)	2.45	3.38	4.78(60.4)	6.46	1.22	d		74.03(164)	*ca.* 2936	*ca.* 283
	Free imine *E* (68)	2.12	3.27		6.73	0.75	28.53	39.04			
	Z (32)	2.17	3.04		6.36	1.34	29.77	40.80			
2b	*Z* (100)	2.49	CH, ^{g}; (CH$_3$)$_2$, 1.67	4.36(61)	7.19		23.19	57.71; 14.79	73.71(162)	–2729	258
	E (100)	g	CH, ^{g}; (CH$_3$)$_2$, 1.52	4.67(62)	6.40		d		76.00(160)	–2810	*ca.* 280
	Free imine *E* (62)	2.11	CH, 3.77; (CH$_3$)$_2$, 1.19		6.69		28.65	50.90; 23.72			
	Z (38)	2.15	–CH, 3.38; (CH$_3$)$_2$, 1.06		6.3		23.8	52.60; 23.72			
2c	*Z* (100)	g	–CH$_2$, 3.8; –CH, ^{g}; (CH$_3$)$_2$, 1.10	4.42(59)	7.35		20.43	64.99; 29.71; 20.43	74.32(62)	–2710	c
	E (100)	3.00(15)	3.5; ^{g}, 0.85	4.75(60)	6.40						
	Free imine *E* (67)	2.10	–CH$_2$, 3.18; –CH, 2.00; (CH$_3$), 1.00		6.72		29.65	59.49; 29.94; 20.96	76.40	–2795	c
	Z (33)	2.18	CH$_2$, 2.96; –CH–, 2.00; (CH$_3$)$_2$, 0.85		6.31		29.94	61.35; 29.65; 20.78			
For *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(C$_4$H$_3$O(CH$_3$)C=N^{i}Bu)]^e								*Z*	73.00	–2815	255
								E	68.51	–2876	297
For *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(C$_4$H$_3$S(CH$_3$)C=N^{s}Bu)]^e								*Z*	73.2(168)	–2680	278
								E	d	–2808	*ca.* 240
For *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(C$_6$H$_4$-2-CH$_3$(CH$_3$)C=N^{s}Bu)]^f								*Z*	76.2(156	–2804	c
								E	76.0	–2890	c

[a] Chemical shift (δ) in ppm relative to SiMe$_4$ in CDCl$_3$; J(^{195}Pt–^{1}H) in parentheses are given in Hz. [b] δ in ppm from the platinum resonance of Na$_2$PtCl$_6$ (aq). [c] Broad peak observed. [d] No spectra were taken. [e] Data from ref. 2. [f] Data from ref. 1. [g] Overlaps.

The ^1H and ^{13}C resonance patterns and ^{195}Pt chemical shifts of both the original and the new complex (2-*Z* and 2-*E*) in chloroform-d solution at ambient temperature are consistent with four-coordination. Support for the existence of four-coordinate species formed is provided by the δ CH_2 = 4.5–5.0 ppm and $^2J(^{195}Pt-^1H)$ 59–63 Hz; δ $^{13}CH_2$ = 75–77 ppm and $^1J(^{195}Pt-^{13}C)$ 160–166 Hz; δ ^{195}Pt range between 2638–3012 ppm upfield (lower frequency) for Na_2PtCl_6 and in most amine and imine of analogous complexes $^1J(^{195}Pt-^{14}N)$ range 250–300 Hz [1, 2, 6–8].

E–Z isomerization was also obtained when traces of amine (or pyridine) (0.005 mol equivalent) were added to freshly prepared solution in chloroform-d. ^1H NMR spectrum recorded immediately and showed rapid and complete isomerization of 2-*Z* to the new complex 2-*E*. (Addition of amine to the free imine (*E–Z* mixture) has no change in the isomeric ratio.) These results indicate that amines catalyse the isomerization of imines coordinated to the platinum. When 1 mol equivalent of amine (*i.e.* Et_2NH) added to the above solution results in an amine–imine exchange and the coupling between the platinum-195 and imine protons disappears and free imine observed of the same ratio as that of the starting imine and *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(NHEt_2)]$ was formed (Table I). The above observation may support the existence of platinum–sulphur interaction in 2-*Z*. Hence, addition of a traces of amine will disrupt this interaction. It is well known, in *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{amine})]$, the Pt–N bond is always labile [9, 10] (on an NMR timescale) if free amine is present. Bond dissociation between platinum and sulphur will favour amine–imine exchange which occur via five-coordinate intermediate [1, 10, 11].

Imine complexes (2-*Z*) have been isolated in almost quantitative yield from 1/1.1 molar reaction of $K[PtCl_3(\eta^2\text{-ethane})]$ with the respective imine ligand in water or methanol [1, 2]. Platinum–imine complexes precipitated in water (D_2O used). The water is subject to examination using ^1H and ^{13}C NMR, the results indicate no sign of any of the imine isomers in the solution. These results indicate that the *Z* isomer isomerized to the more favour *E*-form, which then coordinate to the platinum (1-*Z* to 1-*E*).

The mechanism of *E–Z* isomerization in free imines is a subject of considerable debate, being generally considered in terms of either rotation around the C=N bond or planar inversion at the nitrogen atom [12]. Here we suggest that the mechanism for *E–Z* isomerization in the imine ligands coordinated to the platinum complex involves formation of Zwitterion intermediate which then rotates about the $\overset{+}{C}-\overset{-}{N}$ bond. However, *cis–trans* isomerization of dialkylsulphurdiimine ligand coordinated to platinum has been observed in solution at lower temperature [13], *viz.* for *trans*-$[PtCl_2(RN{=}S{=}NR)L]$; L = C_2H_4, Ph_3P; R = Me, Et, ^{i}Pr; N *trans* to L).

The NMR spectra were recorded on a JEOL JNM FX-100 spectrometer operating in The Fourier-transform mode at ambient temperature.

Conclusions

It has been shown that imine-ligands coordinated to platinum(II) isomerized rapidly in solution and catalyzed by amine. Also, isomerization takes place in liquid state to give one isomer during the coordination with platinum.

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