Asian Journal of Chemistry Vol. 3, No. 1 (1991), 78-91

Sythesis and Characterization of Some New Platinum-Imine-Olefin Complexes

SALEM S. AL-DIAB and IBRAHIM M. AL-NAJJAR*

Department of Chemistry, College of Science
King Saud University, P.O. Box 2455, Riyadh-11451
Kingdom of Saudi Arabia

^1H and ^{13}C chemical shifts are reported for new type of Schiff bases and amine analogus and their complexes with platinum(II)-olefin compound to form complexes of the type trans-[$PtCl_2(\eta^2-C_2H_4)$(imine)], trans-[$PtCl_3(\eta^2-C_2H_4)$(amine)]. (The Schiff base ligand being derived from salicylaldehyde and appropriate primary amine, the amine ligand obtained by the reduction of the appropriate imine). The ^1H and ^{13}C spectra provide that only one single rotamer exist in Schiff base ligand solution and when the imine complexes left in solution for several hours, E–Z isomerization occurs.

INTRODUCTION

A considerable number of compounds containing salicyladiminato ligands have been examined, however, these investigations are mostly devoted to complexes of the first-row transition metals, iridium (I) and rhodium (I) complexes with 1,5-cyclooctadiene as the chelating ligand[1]. As part of our continuing interest in the coordination chemistry of platinum (II) compounds with olefin as the chelating ligand, we found that stable platinum (II)-olefin-monodentate σ-immine bonded complexes of the type [$PtCl_2(\eta^2-C_2H_4)$(imine)] can be prepared.[2] Here we report the synthesis, reactions, and characterization of new type of Schiff base (imine)-complexes. Schiff bases are prepared by condensation of salicylaldehyde and the appropriate aliphatic primary amines. In addition, secondary amines which were obtained by the reduction of the imine, were used as ligands in complex formation.

RESULTS AND DISCUSSION

The Schiff bases in the present work were obtained from the reaction of salicylaldehyde with appropriate primary amine. The products were liquids and the yields were reasonably high and mainly in the E-isomeric form (100%).

Complexes of the type trans-[$PtCl_2(\eta^2$-ethane)(sal)] (where sal = Schiff base derived from salicylaldehyde) have been isolated in almost quantitative yield form 1/1 molar reaction of K[$PtCl_3(\eta^2$-ethane)] with the respective Schiff base ligand. Furthermore secondary amines obtained from the reduction of the above mentioned Schiff bases were used as

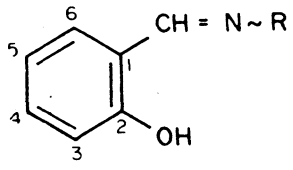
ligands and complexes with platinum (II) were prepared, trans-[$PtCl_2(\eta^2$-ethane)(NHRR')].

The Stoichiometry of the complexes was established by elemental analysis, further evidence was obtained from ^1H and ^{13}C NMR spectra.

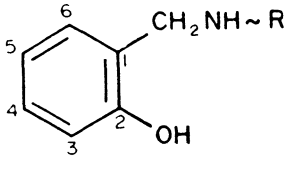
The Stereochemistry of the Free Ligands (imines)

The stereochemistry of the free imines was assigned on the basis of their ^1H and ^{13}C NMR data. Thus in chloroform-d solution, the ^1H spectrum shows that there is only one set of isomer signals (Table 1), Scheme I, i.e., 1b, R=CH_3. Thus, N–CH_3 appear as a doublet at

Scheme I



1



2

Scheme I: 1

1a, Salicylaldehyde
1b, R=$-CH_3$
1c, R=$-CH(CH_3)_2$
1d, R=$-CH_2CH(CH_3)_2$
1e, R=$-CH(CH_3)CH_2OH$
1f, R=$-C(CH_3)_3$

2

2b, R=$-CH_3$
2c, R=$-CH(CH_3)_2$
2d, R=$-CH_2CH(CH_3)_2$
2e, R=$CH(CH_3)CH_2CH_3$
2f, R=$-C(CH_3)_3$

δ 3.39 ppm; =C–H as quartet at δ 8.23 ppm and the aromatic protons were at 7.41 to 6.92 ppm as multiplets.

Similar observations were obtained in acetone-d_6, benzene-d_6, dimethyl-d_6 sulfoxide which confirm the existence of these imines in 100% one diastereomeric form. Further evidence come from $^4J_{HCNCH}$ where imine (1b) (scheme I) shows a value of 1.47 Hz which is in good agreement of an earlier study concerning E-conformation of similar imines.[3] The Z-configuration of imines (1b) requires the $^4J_{HCNCH}$ coupling constants to be larger than E-form (*ca.* 2.2 Hz).[3] The ^{13}C NMR chemical shift of imines (1b-1f) (Table 1) leads to precise stereochemical assignments of these imines. Inspection of the spectra shows that each carbon gave one signal in the complete decoupled spectra. No satellites or any other small signal which may be due to the minor isomer have been observed. These observations confirm the existence of these imines in one diastereomeric form (E-form) only.

TABLE 1

^1H and ^{13}C NMR CHEMICAL SHIFTS (ppm FROM TMS) OF (2'-HYDROXY-N-BENZYLIDENE) ALKYL AMINE

Compound No.		$C_{(1)}$	$C_{(2)}$	$CH_{(3)}$	$CH_{(4)}$	$CH_{(5)}$	$CH_{(6)}$	CH=N	C	$PhCH_2$	CH	CH_2	CH_3	CH_3'	-OH	-NH
1a	^1H			7.4 (octet); 6.9 (sextet)				9.8(s)(CHO)							11.0(s)	
	^{13}C	120.24	160.98	116.95	136.38	119.36	133.27	196.15(C=O)								
1b	^1H			7.2 (octet); 6.8 (sextet)				8.2(q) $^4J(1.5)$					3.4(d) $^4J(1.5)$		13.4(b)	
	^{13}C	118.88	161.17	116.94	131.97	118.34	130.98	166.21					45.87			
1c	^1H			7.3 (octet); 6.8 (sextet)				8.3			3.5(m)		1.3(d)		13.5(b)	
	^{13}C	118.02	161.28	116.94	131.86	118.29	131.03	161.98			59.85		24.08			
1d	^1H			7.2 (quartet); 6.8 (quartet)				8.2(b)			1.9(m)	3.3(d)	0.9(d)		13.6(b)	
	^{13}C	118.82	161.51	117.00	132.97	118.35	131.15	164.75			29.54	67.96	20.38			
1e	^2H			7.2 (triplet); 6.9 (quartet)				8.2(b)			3.1(m)	1.5(m)	0.8(t)	1.2(d)	13.4(b)	
	^{13}C	118.82	161.40	116.88	131.85	118.29	131.15	162.69			66.25	30.72	10.63	22.08		
1f	^1H			7.2 (triplet); 6.9 (quartet)				8.3(b)					1.3		14.2(b)	
	^{13}C	118.70	161.75	116.88	131.68	117.82	130.62	159.52	56.56				29.25			

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

(a) *The Schiff base ligand*

The ^1H NMR spectrum of imine (1b) has been chosen as a model in order to simplify the NMR spectra. The N-CH_3 and =C-H groups of this imine resonate apart from each other in chloroform at 25°. The N-CH_3 signal appears as a doubled peak at δ 3.39, indicating that these protons are long-range coupled with =CH proton. $^4J_{HCNCH}$=1.47 Hz and =CH signal appears as a quartet peak at δ 8.23, $^4J_{HCNCH}$=1.47 Hz. The aromatic protons (3, 4, 5 and 6) appear as ABA'B' pattern, two multiplets centre at δ 7.22 (octet) assigned for H 3 and 6 and at 6.82 (sextet) assigned for H 4 and 5, have been observed. The OH proton appear as a broad peak at δ 13.41.

Further support was obtained from the spectrum of (1c). The spectrum of this compound is also simple. Assignments are given in Table 1. The =CH signal appears as a single peak at 8.30 in chloroform-d, no long-range coupling appears, this may be due to its low value. The N-CH signal appears as a multiplet at δ 3.79 ($^3J_{H\text{-}CH}$=6.35 Hz). The aromatic protons appear as ABA'B' pattern as described before. The -OH proton appears as a broad peak at δ 13.49.

The ^{13}C chemical shifts of the imines are given in Table 1. Signal assignment was straightforward in most cases as the alkyl, aromatic and imine carbons all resonate at characteristic positions.

The quaternary carbon C-1, C-2 and the imino group C=N are readily identified since they are less intense compared with other signals as a result of long relaxation times of the quaternary carbons[4]. The ^{13}C spectrum (1b) shows (in chloroform-d) signals at δ 166.21 assigned to the C=N group and at δ 118.88, 161.17 assigned to the C-1 and C-2 quaternary carbons respectively and confirmed by using the NOE technique and inspection of substitutent chemical shift (SCS) effect of both OH and imino C=N groups on the α-position. N—CH_3 resonates at δ 45.87. Aromatic carbons, C-3, 4, 5, and C-6 appear at 116.94, 131.97, 118.34 and 130.98 respectively. These values were confirmed by using the substituent chemical shift (SCS) effect of the OH and the imino C=N groups on the aromatic ring carbons, and comparison with the parent salicylalde hyde ^{13}C chemical shifts (1a), Table 1.

The ^{13}C chemical shifts of other imines are listed in Table 1. It is worth noting that the C=N carbon is sensitive to the (R) group attached to the C=N group (Table 1). Of interest that when the attached group is *t*-butyl (1f), a considerable shift to high field occurred for the ^{13}C=N, which appears at δ 159.52. Compare with (1b), R=CH_3, δ ^{13}C=N, 166.21. It is possible that the differing extents of long range transmission relate to difference in hyperconjugative-type interactions between the N-tert-butyl and N-methyl group orbitals and the imino π-system. Comparison

TABLE 2

^1H AND ^{13}C NMR CHEMICAL SHIFTS (ppm FROM TMS) OF 2'-HYDROXY-SUBSTITUTED N-BENZYL AMINE

Compound No.		$C_{(1)}$	$C_{(2)}$	$CH_{(3)}$	$CH_{(4)}$	$CH_{(5)}$	$CH_{(6)}$	CH=N	C	$PhCH_2$	CH	CH_2	CH_3	CH'_3	-OH	-NH
2b	^1H			7.3			6.6(b)					3.9(s)	2.4(s)			6.7(b)
	^{13}C	122.17	158.29	116.23	128.63	118.82	128.51					54.33	34.95			
2c	^1H			7.2			6.6(c)			3.9(s)	2.8(m)		1.1(d)		6.5(b)	6.5(b)
	^{13}C	123.05	158.46	116.35	128.51	118.88	128.10			50.04	48.10		22.44			
2d	^1H			7.1			6.7(c)			3.9(s)	1.8(m)	2.5(d)	0.9(d)		6.7(b)	6.7(b)
	^{13}C	122.64	158.35	116.29	128.63	118 88	128.21			56.74	28.07	52.86	20.50			
2e	^1H			7.1			6.7(c)			3.9(s)	2.6(m)	1.4(m)	0.9(t)	1.1(d)	6.7(b)	6.7(b)
	^{13}C	123.11	158.46	116.35	128.51	118.89	128.04			53.74	49.98	29.13	10.04	19.21		
2f	^1H			7.2			6.6(c)			3.8(s)			1.1(s)			
	^{13}C	123.52	158.40	116.35	128.28	118.70	127.81		50.86	45.93			28.37			

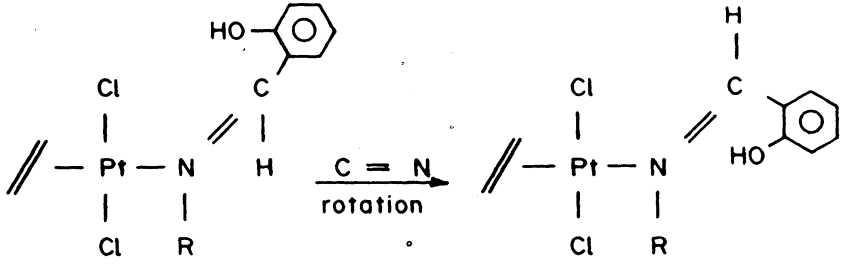
was also made between $^{13}C{=}N$ values obtained here and of similar system[5] i.e., $PhCH{=}N{-}CH_3$, (δ 162.44) $PhCH{=}N{-}^tBu$ (δ 155.08) the only difference is the exist of the hydroxyl group in the ortho position to the imino group. Thus, substitution with electron releasing group -(OH) shifts the $^{13}C{=}N$ resonance to lower field ($\Delta\delta$ 3.77 and 4.44 ppm respectively). The mechanisms by which the inductive/field effect influences distant carbon chemical shifts is not well understood but, following the suggestion of Jones and Wilkins[6], field effects from electron withdrawing substituents might decrease the polarization ($C^+{-}N^-$) in the imino bond and shift the carbon resonance to higher field.

(b) *The Amine Ligand*

Secondary amines in the present work, obtained from the reduction of the above mentioned imines, were used as ligands and complexes with platinum (II) were prepared. The ^1H and ^{13}C NMR spectra of the secondary amines are also simple. Assignments are given in Table 2. The imino ($C{=}N{\sim}$) group change to $CHNH{\sim}$ group. The ^1H NMR spectrum of CH_2 group resonate at δ 3.88 (2b) and the ^{13}C chemical shift resonate at δ 54.33 (2b). The ^1H and ^{13}C chemical shifts of alkyl and aromatic ring protons and carbons resonates at characteristic positions.

Interestingly, the carbon chemical shift of the amine derivatives, ^{13}C-1 (ipso) resonate downfield compared with ^{13}C-1 of the corrosponding imine, and ^{13}C-3, 5 and ^{13}C-4 (*ortho* and *para* position) resonates upfield compared with analagous carbons in the imines. This shift arised from substituent chemical shift effect (SCS) by the new CH_2 group (compared with $CH{=}N$ group). The ^1H NMR of NH and OH groups appears as a broad peak.

Scheme II



R = b) Me, c) ^{i}Pr, d) ^{t}Bu, e) ^{s}Bu, f) ^{t}Bu

(c) *Trans*-$[PtCl_2(\eta^2{-}C_2H_4)(imine)]$.

The ^1H and ^{13}C NMR resonances of the complexes in chloroform-d

TABLE 3

^1H AND ^{13}C NMR SPECTRA OF *TRANS*-[$PtCl_2(\pi^2$-ETHENE) (IMINE)] COMPLEXES[a]

Compound No.		$C_{(1)}$	$C_{(2)}$	$CH_{(3)}$	$CH_{(4)}$	$CH_{(5)}$	$CH_{(6)}$	CH=N	C	$PhCH_2$	CH	CH_2	CH_3	CH'$_3$	OH	NH	CH_2=	^1J(Pt-^{1}Hol) ^1J(Pt-^{13}Col)
3b	^1H			7.5(t)			7.0(m)						3.9				4.7	60.2
	^{13}C	117.58	161.68	119.82	136.97	117.58	133.74	166.50					44.40				75.06	160.00
3c	^1H			7.5(t);			7.0(m)	8.5			3.7(m)		1.42(dd)				4.7	60.2
	^{13}C	117.52	163.45	119.82	134.56	118.58	132.80	163.45			57.97		24.44;				75.18	161.78
											48.40		23.55					
3d	^1H			7.6			6.8					3.48(d)	1.0(dd)				4.7	60.5
	^{13}C	118.35	162.30	117.60	132.68	117.41	131.60	165.04			29.54	66.70	20.40;				74.8;	162.80
													19.73					
3e	^1H			7.6			6.8										4.7	60.0
	^{13}C	117.32	161.80	119.82	133.80	117.50	133.70	163.40			64.02	30.34	10.91	21.37			74.00	168.0
											53.85							
3f	^1H			7.5			7.0						1.5				4.5	60.0
	^{13}C	117.50	163.00	119.53	134.50	118.31	132.4	165.30	64.80				29.19				63.49	176.0

[a] ^1H and ^{13}C NMR spectra in $CDCl_3$ relative to TMS. J Values are given in Hz.

TABLE 4

^1H AND ^{13}C NMR SPECTRA OF *TRANS*-[$PtCl_2$ (π^2-ETHENE) (AMINE)] COMPLEXES*

Compound No.		$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$CH_{(4)}$	$CH_{(5)}$	$CH_{(6)}$	C	$PhCH_2$	CH	CH_2	CH_3	CH'_3	—OH	—NH	OH_2=	$^1J(Pt-^1Hol)$ $^1J(Pt-^{13}Col)$
4b	^1H			7.4		6.7				2.7		2.7				4.5	60.0
	^{13}C	121.05	154.59	115.80	132.44	120.82	130.40			54.85		39.18				74.95	156.0
4c	^1H			7.6		6.6	6.6		4.0					5.4(b)		4.4	60.10
	^{13}C	120.63	153.53	114.94	132.82	119.87	129.21		53.39	50.05		22.43;				73.95	164.72
4d	^1H			7.6			6.6									4.5	60.0
	^{13}C	121.40	154.59	115.82	132.44	120.99	133.33		60.55	27.10	54.152	20.73; 19.79				74.00	166.0
4f	^1H			6.8			7.6					1.6		60.0(b)		4.5	60.0
	^{13}C	121.64	154.60	115.18	133.74	120.99	130.27	60.50	47.52			29.07				63.24	170.96

* ^1H and ^{13}C NMR spectra in $CDCl_3$ relatives to TMS. J values are given in Hz.

TABLE 5

OLEFINIC ^1H AND ^{13}C NMR DATA* OF SOME THREE-, FOUR- AND FIVE-COORDINATED PLATINIUM-OLEFIN COMPLEXES

Formula	(^{1}H)H$_2$C=	Ref.	(^{13})CC= C	Ref.	Coord. no.
C_2H_4 (free)	5.5	7	122.8	7	
K[PtCl$_3$(η^2-C$_2$H$_4$)]	4.4(67)[b]	7	67.3(194)	7	4
trans-[PtCl$_2$(η^2-C$_2$H$_4$)(amine)]	4.5-5.0(60)	7	70-75(166)	11	4
PtCH$_3$(η^2-C$_2$H$_4$)(HBPz$_3$)	2.1(69), 2.3(80)	19	24.7(384)	23	5
trans-[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-diimine)]	3.5(71)	9,10	38.1(297)	9,10	5
Pt(η^2-C$_2$H$_4$)$_2$(PPh$_3$)	2.5(57)	20	42.3(146)	24	3
PtCl(acac)(η^2-C$_2$H$_4$)	4.6(66)	23	67.4(214.8)	25	4
PtCl(acac(η^2-CH$_2$=CHCN)	4.75(65)[1], 4.75(65)[2]	23	47.7(255)[1], 65.7(217)[2]	25	4
trans-[PtCl$_2$(η^2-C$_2$H$_4$)(imine)]	4.3-4.8(60-63)	C	70.75(160-177)	c	4

[a] ^{1}H and ^{13}C NMR Spectra in CDCl$_3$ relative to TMS. [b]In acetone-d$_6$. [c]Present work; coord. no. (coordination number). J values in parentheses are given in Hz.

solution at room 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 4.4–5.0 ppm and J(Pt—H) 60.0 Hz of η^2-ethene protons. ^{1}H NMR spectra of several amines trans to π-C_2H_4 platinum(II) complexes[7,8] 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 3.

Moreover, the ^{13}C-resonances of five-coordinate platinum olefin complexes of the type [$PtX_2(\eta^2$-olefin) (α-diimine)[9,10], showed slightly downfield shifts of the coordinated ligand, in contrast to the square-planar four-coordinate platinum complexes[10].

Upon coordination the olefinic H and C atoms exhibit large upfield chemical shifts with respect to the free olefin and accompanied with ^{195}Pt satellites with sizeable coupling constants. A comparison of the olefinic ^{1}H 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 5. [data from ref. 22]. 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 ^{1}H and ^{13}C resonances are characteristic of the coordination geometry around the central platinum atom.

In order to obtain further insight into the ^{1}J(^{195}Pt–^{13}C) values in imine complexes (Table 3, 4) we consider δ $^{13}CH_2$=, and ^{1}J(^{195}Pt–^{13}C), values for ethene complexes similar to imine (i.e. amine)[11,12] which show that δ $^{13}CH_2$=, and ^{1}J(Pt, C) values vary from approximately 60–80 ppm and 220 to 150 Hz, respectively, with smaller δ values and larger ^{1}J(Pt, C) values corresponding to ligands. Typical values for 4-substituted pyridine derivatives are in the range 75–77 ppm 160–166 Hz, respectively[11,12]. The $^{13}CH_2$= in our new imine complexes fall between 63–75 ppm with ^{1}J(Pt, C) values (Table 3 & 4). Thus there is only small difference between amine and imine complexes if we consider that ^{1}J(Pt, C) is proportional to the s-character in the Pt, C bond[13], and that the trans-influence of a group trans to the ethene reflected qualitatively by changes in the strength of the σ-component of the Pt-C-bond[14].

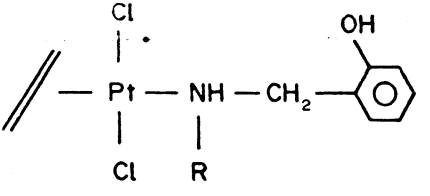
It was assumed that R-imine, like R-diimine and R-diamine[15] is a good σ-donor ligand. Hence, σ-donation ability of imines, R, i.e., $(CH_3)_3C$ (C-quaternary) ≥ $(CH_3)_2HC$(C-tertiary) ≥ $CH_3(CH_2)_2CH_2$(C-secondary) ≥ CH_3 ≥ Ph[15]. ^{13}C-data of $^{13}CH_2$=, and ^{1}J(Pt, C) demonstrate that ^{1}J(Pt, C) has a value of 160 Hz for imine (3b) complex, R=CH_3, suggesting that this imine may be more strongly bound than other imines; secondly, $^{13}CH_2$= with a value of 75.06 ppm, the highest value obtained (Table 3), shows that the Pt-olefin-carbon bond is less bound to the platinum due to the *trans* effect of imine (3b), R=CH_3. When imine (3f), R=$(CH_3)_3C$, R, donates more electrons to platinum (compared with R=CH_3, imine (3b)), 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[15,16]. δ $^{13}CH_2=$, 63.5 ppm and ^1J(Pt, C), 176.0 Hz, imine, R=$(CH_3)_3C$, support the above observation. Thus as Panunzi *et al*[17], 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=$(CH_3)_3C$). 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, showed results similar to those obtained from analogous amine complexes[18]. Returning briefly to the CH=, ^{13}C data of available common amine for complexes, *trans*-[$PtCl_2$(amine)(η^2-C_2H_4)], Pregosin *et al*[18] found that ^1J(Pt, C) has a value of 157–162 Hz for secondary amines. However, this result compared with our amine, ^1J(Pt, C) and δ ^{13}C $CH_2=$ data, we find that our amine shows higher ^1J(Pt, C) values and a lower δ ^{13}C $CH_2=$ value, which indicate that this type of amine may donate more electrons to the platinum[18] and enhances the π-back bonding, resulting in a stabilization of the platinum-olefin bond.

(*d*) *Trans*-[$PtCl_2$(η^2-C_2H_4)(*amine*)]

The ^{1}H and ^{13}C NMR spectra of complex 4 of the type *trans*-[$PtCl_2$(η^2-C_2H_4)(amine)] (Scheme III, Table 4) (amine was obtained by the reduction of the appropriate imine, see experimental), are in good agreement with those complexes prepared from imine or from available commercial amines, i.e., Me_2NH, Et_2NH[7-9].

Scheme III



R = b) Me, c) ^{i}Pr, d) ^{t}Bu, e) ^{s}Bu, f) ^{t}Bu

Ligand-Ligand Exchange

In trans-[$PtCl_2$(η^2-C_2H_4)(amine)] the Pt-N bond is always labile[9,19] (on an NMR time scale) if free amine is present, unless the amine is very hindered sterically.[20] From the point of view of NMR studies compounds

containing *trans*-labilizing ligands, such as η^2-C_2H_4, σ-CH_2, CO, PPh_3, are particularly instructive as reaction and relaxation rates are of the same general order. *Trans*-[$PtCl_2(\eta^2$-$C_2H_4)$-(imine)] shows a platinum-195 coupling to the imine protons (Table 3), 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*-[$PtCl_2(\eta^2$-$C_2H_4)$(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.[7,8] Thus η^2-C_2H_4 is strong *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-(η^2-C_2H_4)(amine)] complexes occur *via* five-coordinate intermediate.[20,21]

Stability of the Complexes

Elemental analysis supports the stoichiometry of the complexes. The complexes showed sufficient solubility and stability in chloroform-d solution to allow an extensive study of their structure in solution by ^1H, and ^{13}C NMR spectroscopy. When the solution was left for several days at room temperature, E/Z isomerism occurred. When the solid complexes (yellow colour) were left at room temperature for a week, these decomposed slowly and colour changed to dark-yellow; leaving the solid complex at 0°C for 6 months no change was observed.

Infrared Spectroscopy

Assignment of ν(C=N) was made for the imine compound. The strong ν(C=N) band at 1597 cm^{-1} with respect to the free ligand (1625 cm^{-1}, s) was observed in KBr disc. However, the observation of a strong ν_{asym} (Pt-Cl) at 325 cm^{-1} established the presence of *trans* positioned Cl atoms (Cl-Pt-Cl).[22]

EXPERIMENTAL

Salicylaldehyde, primary amines and K[$PtCl_3(\eta^2$-$C_2H_4)$] were obtained from Lancaster Synthesis Ltd., Aldrich Chemicals and Winlab Comp., and were used without any further purification.

Preparation of Ethene-Imine Complexes

To K[$PtCl_3(\eta^2$-$C_2H_4)$] (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. Ethylene-amine complexes[4] were prepared by a method similar to the reported method in ref. [8, 9] and were recrystallized from chloroform-pentane.

Secondary amines used in complex[4] were obtained by reduction of the imine ligand used in complex[3], by $NaBH_4$ in absolute methonal similar to the reported procedure.[23]

All NMR spectra were measured on a JEOL JNM FX-100 spectrometer operating in the Fourier transform mode. All the spectra were recorded at ambient temperature, 25°C. ^{13}C NMR spectra; observation frequency 25 MHz; pulse width 10 μs (45°); pulse delay 5s, acquision time auto set; data points 8k; spectral width 5000 Hz, effective resolution 0.015 ppm, sample tube 10 mm; probe $^1H/^{13}C$ dual probe, ^1H noise decoupling and internal lock of the deuterium signal of the solvent. ^1H NMR spectra; observation frequency 100 MHz; pulse width 20 μs (45°); pulse delay auto set, acquisition time auto set, data points 8k; spectral width 1000 Hz; effective resolution 0.1 Hz, probe temperature 25°, sample tubes 10 mm, probe $^5H/^{13}C$ dual probe and deuterium internal lock.

ACKNOWLEDGEMENTS

This research (Chem/1409/21) was supported by the Research Center, College of Science, King Saud University, Riyadh, Saudi Arabia.

REFERENCES

1. R. Bonnaire, J. M. Manoli, C. Povtvin, N. Platzer and N. Goasdone, *Inorg. Chem.*, **20**, 2691 (1981).
2. I. M. Al-Najjar, *Spectrochim. Acta*, **44**, 57 (1981).
3. J. Bjorgo, D. R. Boyd, W. B. Jennings and Jerina, *J. Chem. Soc. Perkin*, **II**, 1081 (1974).
4. S. S. Al-Showiman, I. M. Al-Najjar and H. B. Amin, *Org. Magn. Reson.*, **20**, 105 (1982).
5. W. B. Jennings, V. E. Wilson, D. R. Body and P. B. Coulter, *Org. Magn. Reson.*, **21**, 279 (1983).
6. R. G. Jones and J. M. Wilkins, *Org. Magn. Reson.*, **11**, 20 (1978); J. Bromilo, R. T. C. Brownlee, D. J. Craik, P. R. Fiske, J. E. Rowe and M. Sedek, *J. Chem. Soc. Perkin Trans.*, 2, 753 (1981).
7. I. M. Al-Najjar and M. Green, *J. Chem. Soc. Dalton Trans*, 1651 (1979).
8. M. Green, J. K. K. Sarhan and I. M. Al-Najjar, *J. Chem. Soc. Dalton Trans.*, 1565 (1981).

9. M. Green, I. M. Al-Najjar and D. Holdings, *Transition Met. Chem.*, **4**, 308 (1979).

10. H. Van der Poel, G. Van Koten and K. Vrieze, *Inorg. Chem.*, **19**, 180, 1145 (1980).

11. M. A. M. Meester, D. J. Stufkens and K. Vrieze, *Inorg. Chem. Acta*, **14**, 25 (1975); **16**, 191 (1976); **21**, 251 (1977).

12. (a) T. Iwayanagi and Y. Satio, *Inorg. Nucl. Chim. Lett.*, **11**, 459 (1975); (b) D. G. Cooper and J. Powell, *Inorg. Chem.*, **15**, (1976); M. A. Meester, D. J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, **15**, 137 (1975).

13. B. E. Mann, *Advances in Organometallic Chemistry*, **12**, 134 (1974).

14. H. C. Clerk and J. C. H. Ward, *J. Am. Chem. Soc.*, **96**, 1741 (1974): M. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stother and J. E. H. Word, *J. Am. Chem.*, **93**, 8574 (1973).

15. H. Van Der Poel, G. Van Koten and M. Kokkes, *an Stam. C. H. Chem.*, **20**, 2941 (1981).

16. T. Ziegler and A. Rank, *Inorg. Chem.*, **18**, 1558, 1565 (1979).

17. A. De Renzi, A. Pannuzi, A. Saporito and A. Vitaglino, *Gazz. Chem. Ital.*, **107**, 549 (1977).

18. P. S. Pregosin, S. N. Sze, P. Salvadori and R. Lazaroni, *Helv. Chem. Acta*, **60**, 2514 (1977).

19. I. M. Al-Najjar, M. Green, S. J. Kerrison and P. J. Sadler, *J. Chem. Res. (s)*, 206 (1979).

20. G. Natile, L. Maresca and L. Cattlini, *J. Chem. Soc. Dalton Trans.*, 212 (1977).

21. I. M. Al-Najjar and M. Green, *Chem. Soc. Chem. Comm.*, 212 (1977).

22. I. M. Al-Najjar, S. S. Al-Showiman and H. M. Al-Hizimi, *Inorg. Chim. Acta*, **57**, 89 (1984).

23. H. Brunner, B. Reiter and G. Riepl, *Chim. Bir.*, **117**, 1330 (1984).

24. L. E. Manzer, *Inorg. Chem.*, **15**, 2354 (1976).

25. N. C. Harrison, M. Murray, J. L. Spencer and F.G. A. Stone, *J. Chem. Soc. Dalton Trans.*, 1337 (1978).

26. I. M. Al-Najjar and M. Green, *Transition Met. Chem.*, 3, 142 (1978).

(Received: 9 January 1990; Accepted: 12 March 1990) AJC-150