# Ligand isotope studies of Zeise's salt derivatives (and their CO analogues) with some aza-heterocycles and their N-oxides. II : Their preparation, characterisation, and use in developing <sup>1</sup>H nmr and infrared spectra as a diagnostic tool

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Abstract - Forty-one  $\pi$ -acid complexes of the type cis-[Pt(bipyO<sub>2</sub>H)(A)X<sub>2</sub>]X and trans-[PtL(A)X<sub>2</sub>] (A = C<sub>2</sub>H<sub>4</sub>, CO; X = Cl, Br; L = pyridazine {pdz}, pyrazine N-oxide {pzO}, quinoline {quin}, quinoline N-oxide {quinO}, 2,2'bipyridine {bipy}, 1,10-phenanthroline {phen}) and their deuterated L and C<sub>2</sub>D<sub>4</sub> analogues have been characterised employing infrared and <sup>1</sup>H nmr spectroscopy. The employment of v<sub>12</sub> (CH<sub>2</sub> scissors ~1460 cm<sup>-1</sup>) of  $\eta^2$ -ethene as a diagnostic probe in distinguishing between 4- and 5-coordination is proposed, while the summed percentage decrease of v<sub>2</sub>+v<sub>3</sub> (vC=C/\deltaCH<sub>2</sub>) may be used to distinguish between N- and O-coordination. The use of chemical shifts (<sup>1</sup>H nmr spectroscopy) is confirmed as a suitable means to distinguish between 4- and 5-coordination and is also shown to be suitable for distinction between N- and O-coordination in four coordinate Pt(II)  $\eta^2$ -ethene complexes. In contradiction of previous reports, it is found that J<sub>PhH</sub> cannot be employed to determine the coordination number.

#### INTRODUCTION

Of the forty-one complexes reported, the synthesis of four have been reported previously in the literature, these being  $[Pt(quin)(C_2H_4)Cl_2]$  [1],  $[Pt(quinO)(C_2H_4)Cl_2]$  [2],  $[Pt(bipy)(C_2H_4)Cl_2]$  and  $[Pt(phen)(C_2H_4)Cl_2]$  [3]. The full infrared assignment of the Zeise's salt derivatives (and their CO analogues) are reported elsewhere [4]. Having an in depth assignment of these Zeise's salt derivatives and their CO analogues, the employment of the infrared spectra as a diagnostic tool may be made with more confidence.

# EXPERIMENTAL

The infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer using both Nujol (2000 to 200 cm<sup>-1</sup>) and hexachlorobutadiene mulls (4000 to 2000 and 1500 to 1200 cm<sup>-1</sup>) between CsI plates. Far-infrared spectra were recorded as Nujol mulls (500 to 50 cm<sup>-1</sup>) between polyethylene plates on a Digilab FTS 16B/D interferometer. <sup>1</sup>H nmr spectra in CDCl<sub>3</sub> (with TMS as reference) were recorded at 90MHz on a Bruker WH-90D/S Fourier transform spectrometer. Spectra were recorded at operating temperature (298K), except for the complexes with 2,2'-bipyridine and 1,10-phenanthroline which were recorded at 273K.

 $K[Pt(C_2H_4)X_3]$ ·H<sub>2</sub>O (X = Cl, Br) was prepared as described by CHATT and SEARLE [5]. The deuterated Zeise's salt  $K[Pt(C_2D_4)Cl_3]$ ·H<sub>2</sub>O was similarly prepared, from ethene- $d_4$  of 99% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. The N-oxide ligands and their fully deuterated analogues were prepared as previously described: quinoline N-oxide (quinO, quin- $d_7$ O) [6], pyrazine N-oxide (pzO, pz- $d_4$ O) [7] and 2,2'bipyridine N,N'-dioxide (bipyO<sub>2</sub>, bipy- $d_8O_2$ ) [8]. Quinoline- $d_7$  (quin- $d_7$ ) of 97% isotopic purity and 1,10phenanthroline- $d_8$  (phen- $d_8$ ) of 98% isotopic purity were supplied by Merck, Sharp and Dohme (Canada) Ltd. Pyridazine- $d_4$  (pdz- $d_4$ ) of 97% isotopic purity was supplied by Aldrich Chemical Co.

Preparation of trans-[PtL( $C_2H_4$ ) $X_2$ ] and their  $C_2D_4$  analogues (X = Cl, Br; L = quin, quinO, p2O and their fully deuterated analogues).

These complexes were prepared by the dropwise addition of an aqueous solution of ligand (L) (0.26mmole in 5-10 ml) to an aqueous solution of K[Pt( $C_2H_4$ )X<sub>3</sub>]·H<sub>2</sub>O or K[Pt( $C_2D_4$ )Cl<sub>3</sub>]·H<sub>2</sub>O (0.26mmole in 20 ml) with stirring. After 20 minutes the product was filtered, washed thoroughly with water and dried over silica gel, under reduced pressure. Yields of between 73 and 91% were obtained. Microanalytical data are given in Table 1.

Attempts to prepare these complexes with  $L = pzO_2$  and  $bipyO_2$  were not successful. These were repeated in D<sub>2</sub>O and monitored by <sup>1</sup>H nmr. The absence of a change in chemical shift of the ligand protons (at 8.42ppm) with  $pzO_2$  and the absence of a change in chemical shift of the ethene protons (at 4.57ppm) with both  $pzO_2$  and  $bipyO_2$ shows no complexation occurs with Zeise's salt for these two ligands in an aqueous medium.

# Preparation of trans-[Pt(pdz)( $C_2H_4$ ) $X_2$ ] (X = Cl, Br) and their $C_2D_4$ and pdz-d<sub>4</sub> analogues.

These complexes were prepared as above except that the precipitate was *immediately* filtered (if allowed to stir for 10 minutes before filtering, the product loses  $C_2H_4$ ), and washed with cold (~0°C) water and dried over silica gel, under reduced pressure. Yields of between 68 and 94% were obtained. Microanalytical data are given in Table 1.

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	E	perimen	tal	(	Calculated	
	%C	%H	%N	%С	%H	%N
trans-[Pt(quin)(C2H4)Cl2]	31,30	2,60	3,30	31,22	2,62	3,31
trans-[Pt(quin)(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> ]	25,75	2,20	2,70	25,80	2,17	2,74
trans-[Pt(quin)(C2D4)Cl2]	30,80	2,60	3,30	30,92	2,60	3,28
trans-[Pt(quin- $d_7$ )(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	30,80	2,60	3,25	30,71	2,58	3,26
trans-[Pt(quin)(CO)Cl <sub>2</sub> ]	28,25	1,65	3,30	28,38	1,67	3,31
trans-[Pt(quin)(CO)Br <sub>2</sub> ]	23,50	1,45	2,75	23,46	1,38	2,74
trans-[Pt(quin-d7)(CO)Cl2]	27,35	1,75	3,20	27,35	1,84	3,19
trans-[Pt(quinO)(C2H4)Cl2]	30,30	2,60	3,15	30,08	2,52	3,19
trans-[Pt(quinO)(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> ]	25,15	2,20	2,65	25,02	2,10	2,65
trans-[Pt(quinO)(C2D4)Cl2]	29,95	2,55	3,15	29,81	2,50	3,16
trans-[Pt(quin-d7O)(C2H4)Cl2]	29,85	2,50	3,15	29,61	2,48	3,14
trans-[Pt(quinO)(CO)Cl <sub>2</sub> ]	27,45	1,70	3,10	27,34	1,61	3,19
trans-[Pt(quinO)(CO)Br <sub>2</sub> ]	22,95	1,40	2,65	22,75	1,34	2,65
trans-[Pt(quin-d7O)(CO)Cl2]	27,20	1,65	3,20	26,92	1,58	3,14
trans-[Pt(PzO)(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	18,60	2,10	7,10	18,46	2,07	7,18
trans-[Pt(PzO)(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> ]	15,10	1,70	5,90	15,10	1,69	5,87
trans-[Pt(PzO)(C2DH4)Cl2]	18,70	2,10	7,10	18,28	2,05	7,11
trans-[Pt(Pz- $d_4$ O)C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	18,40	2,05	7,10	18,28	2,05	7,11
trans-[Pt(PzO)(CO)Cl <sub>2</sub> ]	15,45	1,05	7,15	15,39	1,03	7,18
trans-[Pt(PzO)(CO)Br2]	12,45	0,85	5,75	12,54	0,84	5,85
trans-[Pt(Pz-d4O)(CO)Cl]	15,20	1,05	7,00	15,24	1,02	7,11
trans-[Pt(pdz)(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	19,25	2,15	7,40	19,25	2,16	7,49
trans-[Pt(pdz)( $C_2H_4$ )Br <sub>2</sub> ]	15,55	1,75	6,00	15,62	1,75	6,07
trans-[Pt(pdz)( $C_2D_4$ )Cl <sub>2</sub> ]	19,15	2,10	7,40	19,06	2,13	7,41
trans-[Pt(pdz- $d_4$ )(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	18.95	2,15	7,35	19,06	2,13	7,41
trans-[Pt(pdz)(CO)Cl <sub>2</sub> ]	15,95	1,15	7,40	16,05	1,08	7,49
trans-[Pt(pdz)(CO)Br <sub>2</sub> ]	13,00	0,95	6,05	12,97	0,87	6,05
trans-[Pt(pdz- $d_4$ )(CO)Cl <sub>2</sub> ]	16,05	1,10	7,35	15,88	1,07	7,41
cis-[Pt(bipyO <sub>2</sub> H)(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]Cl	27,70	2,50	5,40	27,79	2,52	5,39
cis-[Pt(bipyO2H)(C2H4)Br2]Br	22,00	2,00	4,25	22,16	2,01	4,31
cis-[Pt(bipyO2H)(C2D4)Cl2]Cl	27,60	2,50	5,35	27,57	2,51	5,36
cis-[Pt(bipy-d8O2H)(C2H4)Cl2]Cl	27,30	2,50	5,25	27,36	2,49	5,32
cis-[Pt(bipyO2H)(CO)Cl2]Cl	25,65	1,90	5,35	25,47	1,75	5,40
cis-[Pt(bipyO <sub>2</sub> H)(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> ]Br	20,30	1,45	4,30	20,26	1,39	4,30
cis-[Pt(bipy-d8O2H)Cl2]Cl	24,80	1,80	5,25	25,08	1,72	5,32
trans-[Pt(bipy)(C2H4)Cl2]	31,80	2,50	6,25	32,01	2,69	6,22
trans-[Pt(bipy)(C2H4)Cl2]	31,90	2,70	6,20	31,73	2,66	6,17
trans-[Pt(bipy-d8)(C2H4)Cl2]	31,55	2,60	6,15	31,45	2,64	6,11
trans-[Pt(phen)(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	35,35	2,60	5,95	35,46	2,55	5,91
$trans-[Pt(phen)(C_2H_4)Cl_2]$	35,00	2,65	5,75	35,16	2,52	5,86
trans-[Pt(phen- $d_8$ )(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> ]	34,40	2,40	5,90	34,86	2,51	5,81

Table 1. Microanalyses of Zeise's salt derivatives

Preparation of cis-[Pt(bipyO<sub>2</sub>H)(C<sub>2</sub>H<sub>4</sub>)X<sub>2</sub>]X (X = Cl, Br) and their  $C_2D_4$  and bipy- $d_8O_2$  analogues.

The complexes were prepared as above except that 2ml HX (5M) was added to the solution of K[Pt(C<sub>2</sub>H<sub>4</sub>)X<sub>3</sub>]·H<sub>2</sub>O. The addition of the ligand results in immediate precipitation of the cationic species. Yields of between 63 and 98% were obtained. Microanalytical data are given in Table 1. The complexes are insoluble in water and ethanol and only very sparingly soluble in acetone and chloroform.

Attempts to prepare these complexes with  $L = pzO_2$  yielded only the starting materials.

Preparation of  $[PtL(C_2H_4)Cl_2]$  and their  $C_2D_4$  analogues (L = bipy), phen and their fully deuterated analogues). The complexes were prepared by the addition of a cold (-0°C) aqueous solution of ligand (L) (0.26mmole in 10 ml) to a cold (-0°C) aqueous solution of K[Pt( $C_2H_4$ )Cl\_3]'H<sub>2</sub>O or K[Pt( $C_2D_4$ )Cl\_3]'H<sub>2</sub>O (0.26mmole in 10 ml) with stirring. The precipitate was immediately filtered and washed well with cold water (-0°C) and dried and stored over silica gel, under reduced pressure at -5°C. These complexes rapidly lose ethene in solution at room temperature. Yields of between 86 and 96% were obtained. Microanalytical data are given in Table 1.

Pure bromo- analogues could not be prepared, repeated attempts yielding a mixture of  $[PtL(C_2H_4)Br_2]$  and  $[PtLBr_2]$  (L = bipy, phen).

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#### Preparation of the CO analogues of the Zeise's salt derivatives.

The complexes *trans*-[Pt(CO)X<sub>2</sub>] (L = quin, quinO, pzO, pdz and their fully deuterated analogues, X = Cl, Br) and cis-[Pt(LH)(CO)X<sub>2</sub>]X (L = bipyO<sub>2</sub> and bipy- $d_8O_2$ ; X = Cl, Br) were prepared by bubbling CO through a solution of the ethene analogue in dry chloroform (or a suspension in the case of the cation with L = bipyO<sub>2</sub>), until the colour changed from bright yellow to pale yellow or ivory. Precipitation of the complexes was induced by the addition of dry *n*-hexane. The precipitates were filtered, washed well with dry hexane and dried over silica gel, under reduced pressure. Yields were practically quantitative. Microanalyses are given in Table 1.

The CO analogues decompose in the presence of water. The CO analogues of the Zeise's salt derivatives with bipy and with phen could not be prepared because of rapid loss of ethene in solution.

#### RESULTS

The full infrared assignment of the Zeise's salt derivatives (and their CO analogues) are reported elsewhere [4]. In Tables 2 and 3 the five- and four-coordinate complexes have been arranged in order of increasing vPt-CO, and  $v_a$ Pt-C<sub>2</sub> and  $v_s$ Pt-C<sub>2</sub>.

The results of the <sup>1</sup>H nmr investigation of the  $\eta^2$ -ethene complexes are given in Table 4.

#### DISCUSSION

It is to be noted that, as a result of a large degree of vibrational coupling within the  $\eta^2$ -ethene, there is some disagreement between authors [9-14] regarding the vibrational spectra of K[Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>]·H<sub>2</sub>O (particularly with respect to the -d<sub>4</sub> isotopomer).

The extent of the coupling is demonstrated by the assignments of modes  $v_2$  and  $v_3$ , the C-C stretch (vC=C) and CH<sub>2</sub> scissor ( $\delta$ CH<sub>2</sub>) modes. For ethene- $d_0$  the lower frequency band contains more vC=C and may be considered the C-C stretch [11-15]. However, in the mono-substituted olefins the coupling is more extensive, involving a third fundamental  $v_{12}$ ( $\delta$ CH<sub>2</sub>) [16, 17] and differs in that the higher frequency band contains more vC=C and is therefore the predominant C-C stretch. The coupling between  $v_2$ ,  $v_3$  and  $v_{12}$  is therefore important, since it makes questionable the use of only one of these frequencies as a quantitative measure of the coordinate bond. None the less, the summed percentage of vC=C, and  $\delta$ CH<sub>2</sub> (modes  $v_2$ ,  $v_3$  and  $v_{12}$ ) has been employed as a measure of the decrease of the double bond character of the olefin upon coordination [15-18], but, this relationship must be restricted to complexes of the same olefin [15].

Furthermore, an inverse relationship between the symmetric  $Pt-C_2$  stretch and the C-C stretch ( $v_2$ ) has also been noted [13]. This is to be expected since an increase in the strength of the coordinate bond should occur at the expense of the C-C double bond character.

The assignments for K[Pt(CO)Cl<sub>3</sub>] and its bromo- analogue are more certain [19-22]. From Table 3 there is a direct relationship between the Pt-CO stretch (vPt-CO) and the strength of the  $\sigma$  donor (L) However, the Pt-C=O bend ( $\delta$ Pt-C=O) is found at a frequency close to the Pt-CO stretch which makes their assignment difficult [4, 7, 20], and consequently less useful diagnostically. Furthermore there may be coupling between vPt-CO and vPt-L [4].

For the *trans*-[PtL(CO)Cl<sub>2</sub>] complexes, as for [Pt(CO)Cl<sub>3</sub>]<sup>-</sup>, the planar Pt-C $\equiv$ O bend is characteristically found at a higher frequency than its out-of-plane counterpart,  $\pi$ Pt-C $\equiv$ O [4]. This is opposite to the finding for *cis*-[Pt(CO)<sub>2</sub>X<sub>2</sub>] [20].

At present, <sup>1</sup>H nmr spectroscopy is regarded as the best technique for distinguishing between four- and five-coordination of Pt(II). Four-coordinate Pt(II) complexes yield chemical shifts of 4.40 to 5.00 ppm for the olefin protons, with Pt-H coupling constants of approximately 60 Hz. A substantial upfield shift (> 1 ppm) of the olefin proton resonance, with larger Pt-H coupling constants (> 70 Hz) is generally regarded as evidence of a fivecoordinate platinum complex [3, 23-28].

While the authors agree with the former criterion, the Pt-H coupling constants of about 70 Hz found for  $[Pt(quinO)(C_2H_4)X_2]$  (which are in agreement with those found for substituted pyO [29, 30]) indicate that Pt-H coupling *cannot* be used to distinguish between four- and five-coordination. It is also noted here that the chemical shift of the olefin protons provides a suitable means of distinguishing between nitrogen and oxygen coordination in four-coordinate Pt(II) complexes since the aromatic N-oxides yield shifts of 4.4 ppm while

				gil	gand (L)				
	X-	phen	bipy	pdz	quin	Dzq	bipyO <sub>2</sub> ·HX	quinO	
~ <sup>1</sup> ~	3013 (2224)	3018 (2203)	3017 (2201)	3010 (2219)	3015 (2226)	3013 (2264)	m (2266)	3006 (2213)	
۲,	1515 (960)	1486 (951)	1492 (957)	1519 (957)	1515 (m)	1516 (983)	(H)	1512 (951)	
× 3	1240 (1380)	1263 (1368)	(-) E	1253 (1366)	1254 (1369)	1250 (1358)	( <b>B</b> )	1221 (1333)	
V.4	1020 (726)	1021 (770)	(8) 8	1031 (m)	1019 (m)	1016 (757)	1017 (m)	1028 (m)	
۲ <sub>5</sub>	3100 (2349)	3084 (2309)†	3102 (2340)	3097 (2323)	3097 (2333) <sup>†</sup>	3097 (2332)	3089 (2324) <sup>†</sup>	3081 (2320)	•
, <sup>9</sup>	1180 (963?)	1182 (930)	1182 (922)	(E) E	( <b>1</b> )	(1226) -	(B) B	1187 (m)	
۷٫	1010 (790)	1010 (814)	1005 (811)	1009 (814)	1000 (812)	1004 (808)	1005 (m)	1014 (m)	
82	975 (812)	(09L) 866	965? (m)	994 (763)	977 (752)	937 (767)	(U) H	982 (m)	
° ^	3080 (2331)	3066 (2309)†	3060 (2308)	3070 (2310)	3074 (2333)	3079 (2298)	3076 (2324) <sup>†</sup>	3057 (2320)	•
V10	845 (610)	795 (603)	818 (605)	819 (595)	811 (m)	818 (625)	m (626)	(E) E	
v11	2988 (2184)	2988 (2174)	2981 (2173)	2973 (2188)	2977 (2194)	2983 (2223)	2960 (2185)	2996 (2183)	
<b>v</b> 12	1425 (1060)	1460 (1050)	1459 (1052)	1426 (1064)	1418 (1058)	1421 (1059)	1426 (1052)	1416 (1058)	
V13	720 (514)	770? (484)	п (489)	702 (513)	701 (513)	720 (518)	m (484)	m (492)	
v Pt-C	493 (430)	486 (462)	498 (456)	472 (430)	486 (447)	484 (446)	499 (m)	507 (505)	
v,Pt-C2	405 (370)	(-) -		378 (362)	388 (373)	401 (394)	407 (392)	431 (413)	
v,PLCI	338 (336)	336 (335)	336 (334)	348 (347)	345 (344)	342 (342)	340 (341)	346 (346)	
[v, Pt-37Cl]	E	[322] [m]	E	[336] [337]	[340] [-]	E E	E E	[-]	
v,Pt-Cl	327 (326)	(-) -	• •	(-) -	-	•	331 (331)	⊙	
[vsPt-37CI]	EI EI	E E	E E	E E	E E	E E	[-]	Ξ	
v <sub>a</sub> Pt-Br	Э	• •	(-) -	255 <sup>‡</sup> (-)	259t (-)	250t (-)	242 (-)	250 (-)	
v"PtBr	⊙	•	• •	•	•	•	200 (-)	•	
SPI-C2	219 (200)	228 (215)	(161) 661	200# (191)	213# (205)	1984 (196)	(B) E	167? (m)	
SCI-PI-CI	152 (151)	153 (152)	157 (156)	165 (169)	160 (159)	152 (151) <sup>1</sup>	(II) II	158 (159)	
#CI-Pt-CI	123 (114)	(H) H	(-) -	139 (139)	135 (135)	137 (135)	(E) E	138 (136)	
<b>ðBr-Pt-Br</b>	•	•	• •	120 (-)	109 (-)	-) ,	110 (-)	126 (-)	
яBr-Pt-Br	:	⊙ ,	•	(-) 8	91 (-)	85 (-)	(-) E	111 (-)	
% Decrease of v <sub>2</sub>	+ v <sub>3</sub> 15,32	•	•	14,00	14,22	14,46	ı	17,05	
<pre>† = band assigned twice</pre>									

Table 2. Characteristic  $\eta^2$ -ethene frequencies of ligand complexes with K[Pt( $C_2H_4$ )X<sub>3</sub>] (X = Cl, Br) and their  $C_2D_2$  analogues

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† = band assigned twice ‡ = coupled vibration ¶ = mean of split band

m = masked

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				ligand (L)	)	
	X·†	pdz	quin	pzO	bipyO <sub>2</sub> ·HX	quinO
vC=O	2097	2115	2122	2123	2094‡	2118
[v <sup>13</sup> C≡O]	[2050]	[2073]	[2070]	[2065]	[2047]	[2060]
δPt-C≡O	540	548	549	551	536	585
πPt-CmO	508	498	536	500	499	522
vPt-CO	497	473¶	486 <sup>¶</sup>	490¶	499	506¶
v Pt-Cl	344	351	352	359	347	354
[v,Pt- <sup>37</sup> Cl]	[-]	[339]	[335]	[338]‡	[333]	[335]
v <sub>s</sub> Pt-Cl	345	-	-	-	322	-
[v <sub>s</sub> Pt- <sup>37</sup> Cl]	[-]	[-]	[-]	[-]	[-]	[-]
v_PtBr	246	257 <b>1</b>	261¶	253¶	244	255
v₅Pt-Br	227	-	-	•	205	-
ðPt-CO	166	186?¶	170?	168¶	158¶	162¶
8Cl-Pt-Cl	152	154	149	143	masked	147
πCl-Pt-Cl	129	125	123	118	masked	125
ðBr-Pt-Br	112	113	-	•	masked	126
πBr-Pt-Br	<del>9</del> 8	97	87	88	masked	100

† From GOGGIN and NORTON [22] and BROWNING et al. [20].

‡ mean of split band.

¶ coupled band.

Table 3. Characteristic frequencies for complexes of the type  $[PtL(CO)X_2]$  (X = Cl, Br)

the heterocycles yield shifts of 4.9 ppm. Hence, the pzO derivatives show Pt-N rather than Pt-O bonding (Table 4).

The downfield shift of the olefin protons upon replacement of Cl by Br is a result of a sterically induced polarisation of the C-H bond in ethene by the Br atom [18].

		X =	CI	X =	Br	
	Solvent	Chem. shift	J <sub>(Pt-H)</sub>	Chem. shift	J <sub>(Pt-H)</sub>	Conformation
$K[Pt(C_2H_4)X_3]$	CDCl <sub>3</sub>	4.57 ppm.	72.0 Hz	4.70 ppm.	70.0 Hz	sq.pl.
trans-[Pt(phen)(C <sub>2</sub> H <sub>4</sub> )X <sub>2</sub> ]	CDCl <sub>3</sub>	3.76 ppm.	70.0 Hz	-	-	trig. bipyram.
trans-[Pt(bipy)(C2H4)X2]	CDCl <sub>3</sub>	3.61 ррт.	69.0 Hz	-	-	trig. bipyram.
trans-[Pt(pdz)(C <sub>2</sub> H <sub>4</sub> )X <sub>2</sub> ]	CDCl <sub>3</sub>	4.97 ppm.	58.0 Hz	5.10 ppm.	63.0 Hz	sq. pl.
trans-[Ptquin)(C2H4)X2]	CDCl <sub>3</sub>	5.02 ppm.	66.0 Hz	5.16 ppm.	63.0 Hz	sq. pl.
trans-[Pt(pzO)(C <sub>2</sub> H <sub>4</sub> )X <sub>2</sub> ]	CDCl <sub>3</sub>	4.91 ppm.	63.0 Hz	5.06 ppm.	64.0 Hz	sq. pl.
trans-[Pt(quinO)(C2H4)X2]	CDCl3	4.39 ppm.	70.0 Hz	4.47 ррт.	77.0 Hz	sq. pl.
cis-[Pt(bipyO2H)(C2H4)X2]	X †	-	-	-	-	sq. pl.

 $\dagger = \text{complex insoluble in CDCl}_3, (CD_3)CO \text{ or } D_2O.$ 

sq. pl. = square planar, trig. bipyram. = trigonal bipyramidal.

Table 4 <sup>1</sup>H nmr spectra of various ligand complexes with Zeise's salt.

It is clear from Table 4 that only the Zeise's salt derivatives with the ligands bipy and phen are five-coordinated. As bipy is a relatively poor  $\pi$ -acceptor compared to aliphatic diimines [34], and as the pyridine nitrogen is a weaker  $\sigma$ -donor, the stabilization of the fivecoordinate Pt(II) complexes with bipy and phen must depend predominantly upon that stability inherent in a 5-membered chelate ring [25, 32]. The rapid loss of ethene by these two Zeise's salt derivatives is indicative of the relative instability of these complexes, although the great insolubility of the products undoubtedly helps to drive the reaction to completion. (The rapid loss of ethene from the five-coordinate complexes with bipy and phen prevents the preparation of their carbonyl analogues.) Our inability to produce the pure five-coordinate complexes of bipy and phen from the bromine analogue of Zeise's salt may be understood in terms of the greater *trans*-effect of  $Br^-$  than Cl<sup>-</sup>. This would increase the relative labilizing of the ethene in the unstable five-coordinate intermediate with its axial/equatorial halogens [33]. The result would then be a rate increase of this, the slow step, of the two step dissociation/association mechanism [33].

That the stabilization of the five-coordinate bipy and phen derivatives is induced by the resultant 5-membered chelate ring is further demonstrated by the tetra-coordination experienced by the Zeise's salt derivative with pdz. The sterically favoured bidentate coordination by pdz results in the formation of a three-membered chelate ring only with the loss in solution of ethene, as opposed to the production of a more stable five-membered chelate ring, five-coordinate species with bipy or phen.

The Zeise's salt derivative (and its CO analogue) with  $bipyO_2$  exists as the *cis*coordinated cationic species [Pt( $bipyO_2H$ )( $C_2H_4$ )X<sub>2</sub>]X (X = Cl, Br); two vPt-Cl are observed in the far infrared spectrum (Table 3), with protonation of the second donor site [4]. Clear identification of vPt-O is not yet possible as a major assignment problem has been shown to exist concerning vPt-O for *N*-oxide complexes [4], even employing various deuteration studies. This is the first report of such a cationic species for Zeise's salt derivatives with an oxygen donor, and is the only cation of this type to be reported for platinum-carbonyl complexes.

The inability to form a neutral complex from  $bipyO_2$  and Zeise's salt must be attributed to the weaker bonding of oxygen donors to platinum compared with nitrogen donors, and the relative instability of the 7-membered chelate ring which would occur on coordination. The decomposition of this Zeise's salt derivative to platinum metal in the absence of HCl is typical of the behaviour of the open-handed cationic species in which the coordination site is not taken up by the halogen or by the second donor site [32], and is evidence of the weakness of the oxygen donor.

The Zeise's salt derivative with pzO is coordinated through the nitrogen atom rather than the oxygen. This is evident in the shift of the N-O stretch to higher frequencies on complexation [4] and in the observation of the Pt-N stretch at 241 cm<sup>-1</sup> [4]. The infrared evidence of N-coordination by pzO supports the suggestion that the chemical shift of the olefin protons may be used to determine the site of coordination in molecules with both N-O and aza-nitrogen donors.

The inability to form a bridged dinuclear Pt(II) complex with pzO as well as the absence of a reaction of  $pzO_2$  with Zeise's salt to form either the Pt-O bonded mono- or dinuclear species must be attributed to the weaker oxygen donor capacity of the diazine *N*-oxides compared with that of pyO. This is explained by the greater contribution of the back-donation of the N-O moiety into the ring in diazine *N*-oxides than in pyO [34, 35] as indicated by the higher vN-O frequency of pzO (1307 cm<sup>-1</sup> [4]) compared with pyO (1252 cm<sup>-1</sup>).

As expected for mixed ligand systems, the assignments of several of the ethene and carbonyl fundamentals are complicated by masking from the fundamentals associated with other ligands [4]. Furthermore, the assignment of the far-infrared spectra of these complexes is made difficult by the extent of coupling, with slight coupling between vPt-L and vPt-C<sub>2</sub> or vPt-CO, with halide sensitivity of these vibrations, and also with coupling of the planar and non-planar bends [4]. An important strong coupling between vPt-N of aza-nitrogens and vPt-Br has also been demonstrated [4], which further complicates the use of the far-infrared spectrum as a diagnostic tool.

However, there are some useful diagnostic data available from the infrared spectrum. From Table 3 it is noted that the absence of the symmetric vPt-C<sub>2</sub> is apparently typical of the five-coordinate Pt(II) species, as is the frequency of the Pt-Cl stretch. The latter is found some 6 to 10 cm<sup>-1</sup> lower than that found for the four-coordinate Pt(II) complexes as a result of the increased coordination number. By contrast, the  $\delta$ Pt-C<sub>2</sub> bands of the trigonal bipyramidal complexes are 20-30 cm<sup>-1</sup> higher than those of the square planar complexes.

A more useful diagnostic tool is the observation that the CH<sub>2</sub> scissors mode  $v_{12}$  (a strong band in the infrared) occurs some 35 to 40 cm<sup>-1</sup> higher in frequency for the five-coordinate species than it does for the four-coordinate species. This can therefore be used to

distinguish between the two. Since  $v_{12}$  has been shown to couple with  $v_2$  and  $v_3$  in substituted olefins, it is probable that the higher frequency of  $v_{12}$  reflects a difference in coupling within the olefin and that the use of this variation as a diagnostic tool is likely to prove limited to complexes with the same olefin.

A final comment is made on the use of the summed percentage decrease of the  $vC=C/\delta CH_2$  frequencies ( $v_2$  and  $v_3$ ) as a rough estimate of the double bond character of the  $\eta^2$ -ethene. The summed percentage decrease of  $v_2$  and  $v_3$  is a measure of the shift in frequencies of modes  $v_2$  and  $v_3$  of the complex with respect to those for free ethene (1623 and 1343 cm<sup>-1</sup>, respectively [18]). From Table 3 the percentage decrease of 17% for quinO is the largest and is significantly different from those of the nitrogen donors. The decrease for 4-CH<sub>3</sub>-pyO [36] (which is calculated to be 16.5%) indicates this to be a typical value for an *N*-oxide donor, while that for substituted pyridines (incorrectly reported as 12.5% by MEESTER *et al.* [18]) is about 13.5% [18, 36] which is similar for the aza-nitrogen donors observed in this work. The percentage decrease of the vC=C/\delta CH<sub>2</sub> frequencies may therefore be employed to distinguish between nitrogen and oxygen coordination in Pt(II) complexes which contain *N*-oxide and aza-nitrogen donors. However, as is observed for the cationic complex with bipyO<sub>2</sub>, internal fundamentals may mask either  $v_2$  or  $v_3$  to make such a measurement impossible.

In conclusion it is noted that the double bond character of the C=C bond decreases inversely with the increase in the frequency of the two  $Pt-C_2$  stretches. Clearly the weaker the platinum-ligand bond, the stronger the platinum-ethene bond and the lower the C=C bond order of the ethene.

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