Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

^{1}H NMR SPECTRA AND CHARACTERIZATION OF SOME TRIMETHYLPLATINUM(IV) COMPOUNDS

EVIDENCE FOR *cis* AND *trans* INFLUENCES

D. E. CLEGG, J. R. HALL and G. A. SWILE
Chemistry Department, University of Queensland, Brisbane, Queensland 4067 (Australia)

(Received October 12th, 1971)

SUMMARY

^{1}H NMR spectra of complexes of the types $Pt(CH_3)_3L_2X$ (L_2 = 2,2'-bipyridine, bis(pyridine), or bis(3,5-lutidine), and X = uninegative unidentate ligand); $[Pt(CH_3)_3BipyX]ClO_4$ (X = neutral unidentate ligand), and $Pt(CH_3)_3LI$ (L = substituted 2,2'-bipyridine or 1,10-phenanthroline) have been recorded. The magnitude of $J(^{195}Pt-C-H)$ for the methyl group *trans* to X has been found to be markedly dependent on X, with values ranging from 40.5 to 82.0 Hz. Much smaller variations occur in $J(^{195}Pt-C-H)$ for the methyl groups *trans* to the heterocyclic ligands as X is varied (< 6 Hz), or for the methyl *trans* to I as the heterocyclic ligand is varied (< 5 Hz). The order of *trans* influence for a series of ligands X has been found to be $CH_3 > CN > PPh_3 > NO_2 >$ amines $\sim$ Py $\sim$ SCN > NCO $\sim$ NCS $\sim$ I > Br $\sim$ Cl $\geqslant CH_3COO > NO_3 > H_2O$.

Infrared data for the vibrations of X, where X = polyatomic uninegative ligand, and for the methyl vibrations have also been recorded.

INTRODUCTION

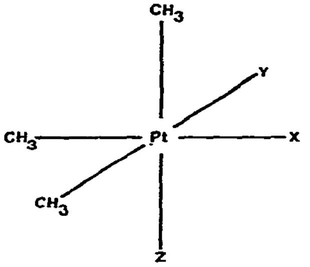
The influence of a ligand on the bond *trans* to it in complexes of platinum(II) has been studied by a variety of methods, including infrared[1,2], NMR[1,3-6] and X-ray diffraction[1], and a qualitative *trans* influence series has been determined. The present work investigates a similar influence in platinum(IV) complexes by examining the change in the coupling constants $^2J(^{195}Pt-CH)$ in series of trimethylplatinum(IV) complexes.

Although the theory of coupling between directly linked atoms is fairly well established[7], the factors influencing couplings such as $^2J(Pt-CH)$ are far less clear. However, a semi-empirical equation has been used for couplings of the type ^2J-(X–CH) with some success[8,9]. In this approach, the coupling constant is assumed to be directly proportional to $\alpha_X{}^2$, the *s*-character of the hybrid orbital of X in the X–C bond—thus the larger the value of $^2J(Pt-CH)$ in the present study, the stronger the Pt–C bond[5].

The first reported ^{1}H NMR spectra of trimethylplatinum(IV) compounds were published by Smith[10], who examined a number of compounds which exhibited a single main resonance due to the methyl groups bonded to platinum, flanked by satellites due to coupling with $^{195}Pt(I=\frac{1}{2}$, 34% abundance). Smith concluded that the coupling constants were rather insensitive to the groups in the *trans* positions and to the solvent used. Later, Kite *et al.*[11] reported a dependence of both ^2J(Pt–CH) and the chemical shift of the methyl–platinum protons in trimethylplatinum(IV) compounds on the nature of the *trans* ligands. Thus the NMR spectrum of the compound $[Pt(CH_3)_3Acac]_2en$ displayed two main methyl–platinum peaks in the intensity ratio of 2/1 each with a different coupling constant (for this compound the donor atoms in the *trans* positions constitute two equivalent oxygens and one nitrogen), while the spectrum of $Pt(CH_3)_3$OxinePy contained three main peaks in the ratio of 1/1/1, and three different coupling constants (*trans* donor atoms, one oxygen and two non-equivalent nitrogens). Kite *et al.*[11] determined the average of the coupling constants for each compound and showed that this value was relatively constant for a given combination of donor atoms in the *trans* positions.

Clegg and Hall[12], in a study of aqueous/pyridine solutions of $[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$, found only two coupling constants for all of the species observed; one value was attributable to CH_3 *trans* to water, the other to CH_3 *trans* to pyridine. These results tended to suggest that a specific *trans* influence was operating in this system, with *cis* influence being minor.

In all trimethylplatinum(IV) compounds for which the X-ray structures have been determined, the methyl groups have been found to be in a mutually *cis* arrangement, the other three groups occupying positions X, Y and Z of Fig. 1. If groups Y and Z are kept constant while X is varied, the influence of the group X on the *trans* methyl can be determined from ^2J(Pt–CH), while any *cis* influence should appear in ^2J(Pt–CH) for the other methyl groups.



In the present work several series of this type have been examined, where YZ = 2,2′-bipyridine, Y = Z = pyridine and 3,5-lutidine, and X = a uninegative ligand. Another series of bipyridine complexes was made where X = a neutral ligand. Finally, complexes of the type $Pt(CH_3)_3XL$ were prepared, where X = iodide and L = two unidentate ligands or one bidentate heteroaromatic ligand.

RESULTS

Tables 1–5 list the results of the ^1H NMR spectra of the compounds investigated. Tables 6 and 7 include infrared frequencies for methyl deformation and platinum–carbon stretching vibrations of the $Pt(CH_3)_3$ moiety and, where X is polyatomic, its characteristic frequencies.

TABLE 1

^{1}H NMR DATA FOR [Pt(CH_3)$_3$BipyX] IN NITROBENZENE

X	$J_1{}^a$ (Hz)	$J_2{}^a$ (Hz)	τ_1	τ_2
NO_3	67.2	79.5	8.52	9.33
CH_3COO	69.0	74.0	8.47	9.56
Cl	69.7	74.7	8.36	9.36
Br	69.9	74.6	8.30	9.30
I	70.8	72.4	8.19	9.22
NCS	69.8	73.0	8.65	9.63
NCO	69.5	72.3	8.56	9.78
SCN	69.3	70.5	8.61	9.35
NO_2	70.0	67.2	8.43	9.61
Acac	68.8	63.8	8.77	9.62
CN	71.0	55.5	8.50	9.94
CH_3	72.6	44.2	8.75	10.20

[a] Subscript 1 refers to CH_3 *trans* to Bipy, subscript 2 refers to CH_3 *trans* to X.

TABLE 2

^{1}H NMR DATA FOR [Pt(CH_3)$_3$BipyX]ClO_4 IN NITROBENZENE

X	J_1 (Hz)	J_2 (Hz)	τ_1	τ_2	$pK_a{}^a$ *of* X
H_2O	66.5[b]	82.0[b]	8.51	9.17	
NH_3	68.9	71.7	8.71	9.57	9.28
CH_3NH_2	68.2	69.6	8.78	9.60	10.72
$C_2H_5NH_2$	68.0	69.9	8.77	9.61	10.81
Piperidine	67.3	68.8	8.85	9.66	11.12
Pyridine	67.6	70.9	8.70	9.41	5.21
PPh_3	68.0	58.5	8.60	9.45	

[a] See ref. 30. [b] Spectrum obtained at 5°. Accuracy ±1 Hz. For aqueous solution, J_1 67.0; J_2 81.5 Hz.

TABLE 3

^{1}H NMR DATA FOR [Pt(CH_3)$_3$Lut$_2$X] IN $CDCl_3$

X	J_1 (Hz)	J_2 (Hz)	τ_1	τ_2
$NO_3{}^a$	67.7	78.2	8.84	8.84
CH_3COO^a	70.2	74.2	8.81	9.10
Cl	69.5	72.7	8.81	8.96
Br	69.7	72.3	8.71	8.86
I	71.2	70.7	8.53	8.82
NCS	69.5	70.5	8.96	9.15
NCO	69.5	69.7	8.96	9.17
NO_2	69.8	64.8	8.79	9.20
CN	71.5	52.5	8.89	9.43

[a] Spectra obtained at 10°.

TABLE 4

^{1}H NMR DATA FOR $Pt(CH_3)_3Py_2X$ IN NITROBENZENE

X	J_1	J_2	τ_1	τ_1
Cl	69.2	69.7	8.54	8.83
Br	69.4	69.6	8.44	8.77
I	71.0	69.1	8.29	8.70
CH_3	73.0	40.5	8.30	9.18

TABLE 5

^{1}H NMR DATA FOR $Pt(CH_3)_3LI$ IN NITROBENZENE

L	J_1[a] (*Hz*)	J_2[a] (*Hz*)	τ_1	τ_2
Bis(pyridine)	71.0	69.1	8.29	8.70
Bis(3,5-lutidine)	70.7	70.2	8.21	8.62
Bis(4-methylpyridine)	70.2	69.6	8.31	8.70
2,2′-Bipyridine	70.8	72.4	8.19	9.22
4,4′-Dimethyl-2,2′-bipyridine	70.6	73.3	8.22	8.99
5,5′-Dimethyl-2,2′-bipyridine	70.0	73.0	8.18	9.19
4,4′,6,6′-Tetramethyl-2,2′-bipyridine	73.8	69.8	8.29	9.52
1,10-Phenanthroline	71.6	72.6	8.03	9.17
5-Methyl-1,10-phenanthroline	71.2	72.5	8.04	9.16
2-Methyl-1,10-phenanthroline	73.0	71.3	7.93	9.27
	71.9		7.97	
4,7-Dimethyl-1,10-phenanthroline	70.4	72.3	8.08	9.15
2,9-Dimethyl-1,10-phenanthroline	74.2	69.4	8.08	9.71
3,4,5,6,7,8-Hexamethyl-1,10-phenanthroline	70.0	74.0	8.07	9.13
4,7-Diphenyl-1,10-phenanthroline	71.0	73.2	8.21	9.21

[a] Subscript 1 refers to CH_3 *trans* to L, subscript 2 refers to methyl *trans* to I.

In general, the NMR spectra obtained at 34° consist as predicted of two principal methyl–platinum resonances in the intensity ratio of 2/1, each with satellites due to coupling between the methyl protons and ^{195}Pt nuclei. The notation used in Tables 1–5 is that subscript 1 refers to the more intense triplet (CH_3 *trans* to Bipy, etc.) and subscript 2 to the less intense triplet (CH_3 *trans* to X).

Some exceptions to the above simple pattern of methyl–platinum resonances were observed. The NMR spectrum of a nitrobenzene solution of the product of the reaction between $[Pt(CH_3)_3BipyH_2O]_2SO_4$ and potassium thiocyanate contained four principal resonances consistent with the presence of both *N*- and *S*-bonded thiocyanato species (see Table 1). The isomers were assigned by comparison of the coupling constants with those for the cyanato species $Pt(CH_3)_3BipyNCO$, which is almost certainly *N*-bonded. Assuming *N*-bonded thiocyanate and cyanate ligands have similar bonding ability, the coupling constants of the methyl group in the *trans* position should be similar. Thus the methyl peak with J_2 73.0 Hz was assigned to the *N*-bonded species (*cf.* 72.3 Hz for the NCO compound) while that with J_2 70.5 Hz was assigned to the *S*-bonded species. The intensity ratio of *S*- to *N*-bonded species was

TABLE 6

INFRARED DATA FOR THE COMPLEXES $[Pt(CH_3)_3BipyX]^a$

X	*δ(CH₃)*		*ν(Pt–C)*		*Anion frequencies*
			trans-Bipy	*trans-X*	
NO_3	1270 s	1239 s, 1230 m(sh)	580 m	580 m	1441 vs(b), 1282 vs(b), 1020 vs, 808 m, 708 w
CH_3COO	1267 w	1234 s, 1228 s	584 (sh)	577 m	1623 vs, 1600 vs, 1376 vs, 1020 m, 918 w, 660 m, 615 w, 499 w
Cl	1267 w	1229 s	584 w	575 w	
Br	1268 w	1228 s	582 w	570 w	
I	1269 m	1229 s	578 w	563 w	
NCS/SCN	1269 m	1233 m(sh), 1227 s	574 m	562 m	2100 vs, 2052 w, 711 m, 462 m, 441 m
NCO	1271 vw	1239 s, 1231 s	582 (sh)	577 m	2208 vs(b), 605 s
NO_2	1267 m	1232 s	583 m	569 m	1359 vs(b), 1323 vs, 809 s, 604 s
CH_3	1261 s	1229 s	573 m	480 vs	

[a] w, Weak; m, medium; s, strong; sh, shoulder; v, very; b, broad.

TABLE 7

INFRARED DATA FOR THE COMPLEXES $Pt(CH_3)_3Lut_2X$

X	*δ(CH₃)*		*ν(Pt–C)*		*Anion frequencies*
			trans-Lut	*trans-X*	
NO_3	1264 s	1241 s, 1238 s	579 w(b)	579 w(b)	1461 vs(b), 1291 vs(b), 1006 vs, 826 m, 707 m
CH_3COO	1270 s	1238 s, 1230 s	580 m	580 m	1600 vs, 1375 vs, 1010 m, 613 m, 500 w(b)
Cl	1267 w	1231 s	580 w	572 w	
Br	1267 w	1232 s 1228 s	578 w	568 w	
I	1266 m	1233 s, 1227 s	576 w	552 m	
NCS	1275 m	1241 s, 1233 s	580 m	575 m	2096 vs, 2048 w, 810 m, 474 w
NCO	1273 w	1243 s, 1239 s	583 m	578 m	2196 vs(b), 1331 s(b), 608 m
NO_2	1270 m	1235 s	585 w	569 m	1359 vs(b), 1322 vs, 816 s, 500 s

~2/1. The compound $Pt(CH_3)_3Lut_2NCS$ (Table 3) was assigned as the *N*-bonded species since J_2 (70.5 Hz) is comparable with J_2 (69.7 Hz) for the cyanato complex.

The occurrence of both isomers in the bipyridine system and only the *N*-bonded isomer in the lutidine system may be due to the slightly different preparative conditions. In the lutidine system, the predominant species in solution before reaction with thiocyanate, since excess lutidine was present, was probably $[Pt(CH_3)_3Lut_3]^+$ by analogy with the pyridine system[12], while the species in the bipyridine solution before reaction with thiocyanate was $[Pt(CH_3)_3BipyH_2O]^+$ [13]. This suggests that although both *N*- and *S*-bonded thiocyanates are capable of displacing H_2O, only the *N*-bonded thiocyanate is capable of displacing a coordinated lutidine molecule.

The compound $[Pt(CH_3)_3BipyH_2O]ClO_4$ gave only a single broad resonance with two broad satellites (*J* 73 Hz). The spectrum is due to rapid exchange of the aqua group on the NMR time scale leading to site averaging of the methyl groups. On cooling the sample to just above the freezing point of nitrobenzene, a pair of triplets in the intensity ratio of 2/1 was obtained but the peaks were still rather broad. The exchange of the aqua groups in aqueous solution has been investigated in detail for $[Pt(CH_3)_3BipyH_2O]_2SO_4$[13].

In general, the NMR spectra of complexes of 3,5-lutidine showed coupling between the α-protons and ^{195}Pt with J 11–12 Hz. However, the compounds $Pt(CH_3)_3Lut_2NO_3$ and $Pt(CH_3)_3Lut_2(OOCCH_3)$ showed only a broad α-proton resonance without satellites at 34°. On cooling to 10°, satellites were evident. This confirmed that the lutidine molecules undergo exchange at room temperature and above. The methyl–platinum spectrum at 34° consisted of a single broad resonance flanked by two broad satellites. At 10°, the expected 2/1 intensity ratio of triplets was observed.

The NMR spectrum of the compound $Pt(CH_3)_3Py_2I$ removed doubt as to its behaviour in solution. Foss and Gibson[14], on the basis of molecular weight determinations at concentrations ranging from 3.85 to 29.03 g/1000 g solvent, suggested that in the more dilute benzene solutions the equilibrium existed:

$$2\ Pt(CH_3)_3Py_2I \rightleftharpoons [Pt(CH_3)_3PyI]_2 + 2\ Py\ .$$

Ivanova and Gel'man[15], however, concluded that the compound was a monomer in benzene at concentrations of 24.3 and 48.0 g/1000 g solvent. The NMR spectra in benzene, chloroform and nitrobenzene over the range 5–50 g/1000 g solvent consisted of the expected triplets in a 2/1 intensity ratio, with no evidence for formation of the dimer.

Kite *et al.*[11] were unable to obtain the NMR spectrum of $Pt(CH_3)_3BipyAcac$, where the acetylacetone group has been shown to bond through the central γ-carbon atom in the solid[16]. We found that the compound dissolved in nitrobenzene and chloroform and the NMR spectra indicated that the γ-carbon bonded structure persisted in solution. The value found for J_2 was 63.8 Hz which suggests that the Pt to γ-carbon bond is substantially weaker than the Pt–CH_3 bond *trans* to methyl in $Pt(CH_3)_4Bipy$ (J_2 44.2 Hz) (see Table 1). The γ-proton showed a coupling constant of 51.5 Hz which may be compared with the value of 42.0 Hz for $[Pt(CH_3)_3Acac]_2$[17]. This indicates that the Pt to γ-carbon bond is stronger in $Pt(CH_3)_3BipyAcac$ than in $[Pt(CH_3)_3Acac]_2$, which is confirmed by the fact that $[Pt(CH_3)_3Acac]_2$ undergoes an exchange process involving rapid breaking of the Pt to γ-carbon bond at 33° [17], while $[Pt(CH_3)_3BipyAcac]$ does not undergo exchange below 100° in nitrobenzene. The compound tends to decompose above 100°.

A value of 120 Hz has been found[18] for $^2J\,[Pt\text{–}H(\gamma)]$ in platinum(II) complexes containing C-bonded acetylacetone groups, *e.g.*, $K[PtAcac_2Cl]$ where the *trans* donor atom is oxygen. If this value is modified by allowing for (*i*) the decrease in coupling constant on passing from platinum (II) to platinum (IV) (Ruddick and Shaw[19] obtained a ratio of 0.77) and (*ii*) the change in *trans* donor groups from *O*-bonded acetylacetone to methyl groups (an approximate value may be obtained from the ratio

(0.60) of J (44.0 Hz) for CH_3 *trans* to CH_3 in $Pt(CH_3)_4$Bipy to J (73.0 Hz) for CH_3 *trans* to O(Acac) in $[Pt(CH_3)_3Acac]_2$[17]), a value of 55.4 Hz is obtained, which correlates well with the observed value of 51.5 Hz for $Pt(CH_3)_3$BipyAcac.

For the compound $[Pt(CH_3)_3BipyPPh_3]ClO_4$, each of the methyl peaks was split into a doublet owing to coupling of CH_3 protons with the P atom ($^{31}P, I=\frac{1}{2}$, 100% abundance). The coupling constants ^3J(P–Pt–CH) were substantially the same for the methyl groups in the *trans* (7.3 Hz) and *cis* (7.8 Hz) positions.

The two tetramethylplatinum(IV) species showed two principal resonances in the intensity ratio of 1/1, each with satellites, consistent with two CH_3 groups *trans* to Bipy (or two pyridine molecules), and two CH_3 groups *trans* to each other. The coupling constants for the mutually *trans* CH_3 groups were 44.2 Hz (Bipy compound) and 40.5 Hz (bispyridine compound), which are in agreement with the value of 44 Hz obtained by Ruddick and Shaw[19] for other tetramethylplatinum(IV) compounds.

DISCUSSION

Coupling constants

Trans influence. Reference to Tables 1–4 shows that there is a dependency of the coupling constant J_2 on the nature of the *trans* group X, with values ranging from 82.0 Hz in $[Pt(CH_3)_3BipyH_2O]ClO_4$ to 44.2 Hz in $Pt(CH_3)_4$Bipy for the bipyridine series, and from 78.2 Hz for $Pt(CH_3)_3Lut_2NO_3$ to 52.5 Hz in $Pt(CH_3)_3Lut_2CN$ for the lutidine series. Since the value of the coupling constant may be assumed proportional to the Pt–C bond strength[8,9], an order of decreasing *trans* influence (increasing Pt–C bond strength may be drawn up for each series. Comparison between the series shows that this order is similar in each case. The order (in decreasing *trans* influence) is roughly, $CH_3 > CN > Acac > NO_2 > SCN > NCO \sim NCS \sim I > Br \sim Cl \geqslant CH_3CO\text{-}O > NO_3$.

Values of ^2J(X–CH) have been used to determine orders of *trans* influence for both platinum(II)[5] and mercury(II)[20] complexes. For the Pt^{II} series the order of decreasing *trans* influence is, $CN > NO_2 > NCS > NCO >$ halides $> NO_3$ and for Hg^{II} the order is, $CH_3 > CN > SCN \sim$ halides $> CH_3COO > NO_3$.

There is good agreement between the orders obtained, and this suggests that the same factors must be operating irrespective of the nature of the metal or the stereochemistry of the complex. The *trans* influence has also been studied using the variation in couplings such as ^1J(Pt–H)[4] and ^1J(Pt–P)[6,21]. These also produce a similar order of anionic species. When the results for the neutral ligands from the present work are included, the *trans* influence series for trimethylplatinum(IV) compounds becomes, $CH_3 > CN > PPh_3 > NO_2 >$ amines $\sim$ Py $\sim$ SCN $>$ NCO $\sim$ NCS $\sim$ I $>$ Br $\sim$ Cl $\geqslant CH_3COO > NO_3 > H_2O$. Again there is quite good correlation with the series of ^1J(Pt–P) values obtained when both anionic and neutral ligands are included[6].

As with the platinum(II) series studied[5], the value of ^2J(Pt–CH) depends on the donor atom, and there seems to be a decrease in J_2 with donor atom in the order, $O > Cl \sim Br > I > N \sim S > P > C$. As noted by Allen *et al.*[6] the order $O > N > C$ is consistent with the first row of donor atoms exerting an inductive effect on the covalency of the *trans* bond. From the above studies, a similar order for the second row donor atoms also seems to apply, *viz.*, $Cl > S > P$. As with the platinum (II) compounds studied[5], there is very little variation in the effects produced by the halogen atoms, so that once again the electronegativity of the donor atom does not appear to play any great role in the inductive effect.

Cis influences. Reference to the values of J_1 in Tables 1–4 reveals a relatively small variation throughout each series. The extreme values in the bipyridine series are 66.5 Hz for $[Pt(CH_3)_3BipyH_2O]^+$ and 72.6 Hz for $Pt(CH_3)_4Bipy$, a range of 6.1 Hz compared with a range of 37.8 Hz for J_2 in the reverse direction. It thus appears that the *cis* influence in these systems is small compared with the *trans* influence. Once again, a similar situation appears to exist in platinum(II) complexes. Although extended Hückel MO calculations predicted that the magnitudes of *cis* and *trans* influences in platinum(II) compounds should be similar[1], several studies have shown that the coupling changes induced by a ligand X are much smaller when the ligands are *cis* to X than when *trans*[4,6]. This has been interpreted in terms of the *trans* influence being mainly due to a rehybridization of the metal orbitals which does not affect the *cis* bonds[4].

Comparison of the values of J_2 for the three series where X is an anion (Tables 1, 3 and 4) shows that although the effects of different *trans* ligands on $^2J(Pt\text{–}CH)$ follow the same order, the magnitudes of J_2 for a given anion differ by a fairly constant amount from series to series, the values decreasing in the order Bipy $>$ Lut_2 $>$ Py_2. Such differences represent the *cis* influence of these ligands on the Pt–C bond *trans* to the X group. By keeping the X group constant while extending the range of ligands in the Y, Z positions (Fig. 1), such *cis* influences may be investigated in more detail. Table 5 lists the NMR data for a series of iodo compounds $Pt(CH_3)_3LI$ where L represents two unidentate heteroaromatic ligands or one bidentate ligand.

Table 5 shows that substitution of methyl groups on pyridine or 2,2′-bipyridine at either the *m*- or *p*-positions produces only small variations in coupling constants (ΔJ_1, $\Delta J_2 < 1.5$ Hz). The use of 1,10-phenanthroline results in values not significantly different from those for 2,2′-bipyridine, and substitution of the *m*- and *p*-positions by either methyl or phenyl groups again produces changes no greater than 1.5 Hz in J_1 or J_2, even up to six methyl groups (Table 5).

However, if one or both of the *o*-positions in either of the 2,2′-bipyridine or 1,10-phenanthroline complexes is substituted by methyl groups, larger variations are noted. Thus in the 4,4′,6,6′-tetramethylbipyridine compound, J_1 increases from 70.8 to 73.8 Hz compared with the 2,2′-bipyridine compound, while J_2 decreases from 72.4 to 69.8 Hz. Similar effects are observed in the 2,9-dimethylphenanthroline complex where J_1 increases from 71.6 to 74.2 compared with the phenanthroline complex and J_2 decreases from 72.6 to 69.4 Hz.

Obviously the reason for these marked changes in the values of J is that the methyl groups in the 6,6′-positions of 2,2′-bipyridine or the 2,9-positions of 1,10-phenanthroline introduce steric hindrance at the coordination sites. Although it is not sufficient to prevent the formation of a stable compound it must leave the Pt–N bonds sufficiently weakened to produce these changes. As a consequence the *trans* Pt–C bonds are strengthened and J_1 is observed to increase. At the same time the *cis* Pt–C bond must be weakened, since J_2 decreases.

The presence of a methyl group in only one of these positions (*e.g.*, 2-methyl-1,10-phenanthroline) imposes a lack of symmetry on the environments of the methyl groups *trans* to the ligand, sufficient to resolve the normally single resonance τ_1 into two of equal intensity. Thus the situation has been produced where there is non-equivalence of all three positions X, Y and Z (Fig. 1). As anticipated, the coupling constant for the methyl group *trans* to the nitrogen adjacent to the *o*-substituted methyl group (73.0 Hz) is larger than that for the other methyl group (71.9 Hz).

It is apparent from Table 5 that changing ligands from bispyridine to, for example, Bipy causes a measurable effect, and that the steric factor is also an important issue in determining *cis* influences.

The coupling constants for the methyl group *trans* to iodide in the complexes $Pt(CH_3)_3L_2I$ ($L=PMe_2Ph$[19] and $AsMe_2Ph$[22]) are 69 and 70 Hz respectively, which lie within the range found for the methyl group *trans* to iodide in the complexes with nitrogen donors studied (69.1 to 74.0 Hz). Similar results apply also to the corresponding bromo and chloro derivatives $Pt(CH_3)_3L_2X$ ($X=Cl$, Br; $L=PMe_2Ph$[19] and $AsMe_2Ph$[22]). This suggests that the *cis* influence of the P and As donors is not significantly different from that of N donors. However, larger differences in J are observed when neutral ligands are replaced by uninegative ligands. Comparison of J_2 for $Pt(CH_3)_3BipyCN$ (55.5 Hz) and $Pt(CH_3)_3Lut_2CN$ (52.5 Hz) with $^2J(Pt\text{–}CH)$ for $[Pt(CH_3)_3(CN)_3]^{2-}$ (60.8 Hz)[12] shows that variations in *cis* influence of the order of 5–8 Hz can be obtained. Such effects are however still small compared with *trans* influence differences.

Reference to Table 2 shows that for $X=NH_3$ and aliphatic nitrogen bases there is a reasonable correlation of J_2 with pK_a, J_2 decreasing as the pK_a value increases.

Chemical shifts

Theories of chemical shifts are not particularly well developed, but some comments may be made on the trends observed. There is no definite correlation between the values of J_2 and τ_2 (a reasonable correlation has been found in Hg^{II} complexes)[20], although the compounds with $X=CN$ and $X=CH_3$ do have the greatest upfield shifts. There is, however, a correlation between the chemical shifts τ_2 and the chemical shifts observed for Hg^{II} complexes and to a lesser extent for the Pt^{II} complexes[5].

One point of interest is the separation between τ_1 and τ_2 for the various series. For the bipyridine complexes, $\tau_2-\tau_1$ is generally about 1.0 ppm and this increases to ~1.45 ppm for the compounds $Pt(CH_3)_4Bipy$ and $Pt(CH_3)_3BipyCN$. In the bis(pyridine) compounds, the separation is 0.3–0.4 ppm for the halogeno complexes, and increases to 0.88 ppm for the compound $Pt(CH_3)_4Py_2$. The orientation of the aromatic pyridine rings would undoubtedly contribute to the anisotropy of the environment of the methyl groups. The degree to which it does would be greater for the bipyridine complexes than for the pyridine complexes since in the latter the opportunity for rotation about the Pt–N bond would average out to a considerable extent the effect of the aromatic ring currents.

Calculations made using the formulae of Johnson and Bovey[23] (which were devised for benzene-like molecules) were applied to the pyridine rings of these complexes in order to estimate the contribution to the chemical shift difference made by the presence of the ring currents. Bond lengths were based on values given in an X-ray crystallographic study by Swallow and Truter[16] of $Pt(CH_3)_3BipyAcac$, and bond angles around the Pt atom were taken as 90° for ease of calculation. The results indicate that the aromatic rings alone in the fixed orientation of the bipyridine ligand could contribute no more than 0.06–0.10 ppm to the difference in the positions of the methyl resonances. Since the observed differences vary from 0.74 ppm in $Pt(CH_3)_3$-BipySCN to 1.45 ppm in $Pt(CH_3)_4$Bipy, it is concluded that other factors are responsible for these changes.

Infrared spectra

The infrared spectra of the compounds support the proposed formulae. Bands assignable to the coordinated ligands and to coordinated anions appear for the compounds $Pt(CH_3)_3$BipyX and $Pt(CH_3)_3Lut_2X$, while the spectra of the compounds $[Pt(CH_3)_3BipyX]ClO_4$ show the presence of coordinated bipyridine, neutral ligand, and ionic perchlorate. Peaks assignable to vibrations of the methyl groups are, in general, quite readily observed. Frequencies attributed to methyl deformation, Pt–C stretching and anion vibrations are listed in Tables 6 and 7.

Methyl–platinum vibrations

Trimethylplatinum compounds. In the C–H stretching region of all the present complexes the same pattern was found as has been noted for other trimethylplatinum-(IV) compounds[24], with three bands at approx. 2960, 2900 and 2820 cm^{-1}, the first two assignable to C–H stretching vibrations, the third to the overtone of the asymmetric stretching vibration at 1420 cm^{-1} (see Fig. 2).

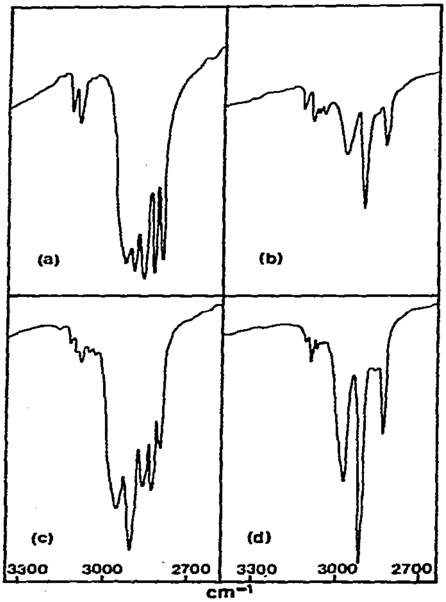


Fig. 2. Infrared spectra over the range 2700–3300 cm^{-1}, for (a) $Pt(CH_3)_4$Bipy, (b) $Pt(CH_3)_3$BipyI, (c) $Pt(CH_3)_4Py_2$ and (d) $Pt(CH_3)_3$PyI in hexachlorobutadiene mulls.

In trimethylplatinum(IV) compounds of C_{3v} symmetry, bands in the region of 1420 and 1230 cm^{-1} were assigned to asymmetric methyl deformations, and a band near 1270 cm^{-1} to the totally symmetric methyl deformation[25]. The band at 1420 cm^{-1} in the present complexes is obscured by ligand vibrations. However, as seen in Tables 6 and 7 the asymmetric deformation at 1230 cm^{-1} is split into components for a number of the compounds studied. This splitting does not appear to have any correlation with the nature of the anion, nor is it consistent in the two series of compounds studied.

Platinum–carbon stretching modes are found in the 500–600 cm^{-1} region in trimethylplatinum(IV) compounds. Due to the low symmetry of the compounds and the non-equivalent CH_3 groups, more than one Pt–C stretch may be expected in this region. For the compounds in both series two bands attributable to Pt–C stretches are usually observed. There is good correlation between the values for the two series. Since one band remains relatively constant throughout the series while the other varies somewhat, it is possible that one peak is predominantly due to the methyl groups *trans* to the nitrogen donor atoms while the other is predominantly due to the methyl group *trans* to the anionic species.

The order of Pt–C stretching frequencies for the methyl group *trans* to X (Tables 6 and 7) is $NO_3 \sim CH_3COO \sim NCO > Cl > Br \sim NO_2 > I \gg CH_3$ which compares well with that obtained by Adams *et al.*[26] in a series of methylplatinum(II) complexes. Such a correlation does lend some support to the above assumption. In the case of the bipyridine and bis(lutidine) thiocyanato complexes, the relevant Pt–C stretching frequencies are 562 and 575 cm^{-1} respectively. The latter value suggests that the thiocyanate ligand is *N*-bonded since it fits in well with the series found by Adams. The low value of 562 cm^{-1} for the Bipy complex may indicate the effect of an *S*-bonded thiocyanate group. Both conclusions are in agreement with the interpretation of the infrared spectrum of the coordinated thiocyanate discussed later.

Tetramethylplatinum compounds. The compounds $Pt(CH_3)_4$Bipy and $Pt(CH_3)_4Py_2$ show several interesting features in their infrared spectra. The C–H stretching region for $Pt(CH_3)_4$Bipy shows a more complex pattern than that found in trimethylplatinum(IV) bipyridine complexes. A similar complex pattern occurs in the spectrum of the compound $Pt(CH_3)_4Py_2$. Figure 2 shows the C–H stretching region for $Pt(CH_3)_4$Bipy, $Pt(CH_3)_4Py_2$ and the corresponding iodotrimethylplatinum(IV) complexes for comparison.

The most noticeable difference in the spectrum of $Pt(CH_3)_4$Bipy from those of trimethylplatinum compounds is the appearance of a very intense band at 480 cm^{-1}. This can only be attributed to an effect of the methyl groups *trans* to each other on Pt–C stretching. Not only is there a shift to lower frequency as expected, but also a dramatic change in the intensity of the band, since all other Pt–C stretching modes in the compounds $Pt(CH_3)_3$BipyX appear only weakly. A strong band at about 450 cm^{-1} appears in the spectrum of the compound $Pt(CH_3)_4Py_2$ also. Ruddick and Shaw[19] have found strong peaks in this region for a number of phosphine derivatives of tetramethylplatinum(IV) and have also suggested they are largely associated with the Pt–C stretching of two mutually *trans* methyl groups.

Anion vibrations

Nitrato. The spectra of the nitrato species $Pt(CH_3)_3BipyNO_3$ and $Pt(CH_3)_3Lut_2NO_3$ are both consistent with the presence of unidentate nitrate[27]. Bands at 1020 and 1006 cm^{-1} respectively are due to the symmetrical N–O stretching frequency while bands at 1441 and 1282 cm^{-1} in $Pt(CH_3)_3BipyNO_3$ and 1461 and 1291 cm^{-1} in $Pt(CH_3)_3Lut_2NO_3$ may be assigned to asymmetric stretching modes. The out-of-plane bend appears at 808 and 826 cm^{-1} respectively in the two compounds. The in-plane bend is ascribed to a peak at 708 cm^{-1} in $Pt(CH_3)_3BipyNO_3$ and to a peak at 707 cm^{-1} in $Pt(CH_3)_3Lut_2NO_3$.

Acetato. The spectra of the compounds $Pt(CH_3)_3Bipy(OOCCH_3)$ and $Pt(CH_3)_3Lut_2(OOCCH_3)$ are also consistent with the presence of unidentate acetato ligands[27]. The asymmetric and symmetric C–O stretches appear at about 1600 and 1375 cm^{-1} in both complexes, and such a large splitting compared with that found in the free acetate ion is usually associated with unidentate acetate. The other acetate peaks correspond fairly closely with those found in sodium acetate[27].

Thiocyanato. The spectrum of $Pt(CH_3)_3Lut_2NCS$ was quite consistent with the presence of *N*-bonded thiocyanate. This is in agreement with the NMR spectrum described previously. Bands at 2096 (C–N stretch), 810 (C–S stretch) and 474 cm^{-1} (NCS bend) all lie within the regions found for other *N*-bonded thiocyanato species[28]. The spectrum of the bipyridine thiocyanato species, which showed evidence for *N*- and *S*-bonded isomers in solution, was less readily interpretable. The C–N stretching region was similar in shape and frequency to that of $Pt(CH_3)_3Lut_2NCS$, where only *N*-bonded thiocyanate is present. However, in the C–S stretching region, a peak at 711 cm^{-1} was observed, which is in the range of C–S stretching for *S*-bonded thiocyanate[28], while no band was observed in the region (760–880 cm^{-1}) where the C–S stretch of *N*-bonded thiocyanate is found[28]. The band, however, may lie beneath bipyridine peaks at $\sim$765 cm^{-1}. In the NCS bending region, peaks were observed at 462 and 441 cm^{-1}, which are more consistent with *S*-bonded than with *N*-bonded thiocyanate, although the former value may be attributable to *N*-bonded thiocyanate. Overall, the spectrum confirms the presence of *S*-bonded thiocyanate in the solid, but the presence of the *N*-bonded isomer is less certain.

Cyanato. The cyanato species $Pt(CH_3)_3BipyNCO$ and $Pt(CH_3)_3Lut_2NCO$ show bands respectively at 2208 and 2196 cm^{-1} assignable to the C–N stretching frequency, and bands at 605 and 608 cm^{-1} due to the N–C–O bending mode. $Pt(CH_3)_3Lut_2NCO$ has a band at 1331 cm^{-1} corresponding to the C–O stretch, while the corresponding band in the bipyridine complex is obscured by a bipyridine vibration.

Nitro. The ligand spectrum in both cases is consistent with an *N*-bonded nitro group[28]. The nitro species $Pt(CH_3)_3Bipy\ NO_2$ has peaks at 1359, 1323 and 809 cm^{-1}, and $Pt(CH_3)_3Lut_2NO_2$ peaks at 1359, 1322 and 816 cm^{-1}, which are assignable to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ and $\delta(ONO)$ respectively. Bands at 504 and 500 cm^{-1} are apparently due to the wagging mode $\rho_\omega(NO_2)$, although these are lower than that normally found in nitro complexes (651–585 cm^{-1})[28].

EXPERIMENTAL

Analytical results are contained in Table 8.

A. Preparation of $Pt(CH_3)_3BipyX$

(*a*). *X* = *Cl, Br and I.* These compounds were prepared using a modification of the procedure of Lile and Menzies[29] for $Pt(CH_3)_3BipyI$. A benzene solution of $[Pt(CH_3)_3X]_4$ was mixed with a benzene solution containing a stoichiometric (1/1) quantity of 2,2'-bipyridine, the solution filtered immediately, and the filtrate allowed to stand. Crystallization of the product was complete in about one hour. The product was filtered, washed with n-hexane and air-dried. Yield 80–90%.

(*b*). *$X=NO_3$ and CH_3COO.* Lile and Menzies[29] reported that from aqueous acetone solutions of $Pt(CH_3)_3$BipyI titrated with $AgNO_3$ solution, a yellow solid could be isolated which they believed to be $Pt(CH_3)_3BipyNO_3$, although analytical figures were not good. By using a modification of this procedure, both $Pt(CH_3)_3BipyNO_3$ and $Pt(CH_3)_3Bipy(OOCCH_3)$ have now been obtained.

A chloroform solution of $Pt(CH_3)_3$BipyI was treated with a large excess of finely ground AgX ($X=NO_3$, CH_3COO). The mixture was refluxed for 10 min with constant stirring, the solid becoming coated with yellow AgI. The solid was then filtered off, and the filtrate concentrated to a small volume by heating. Addition of n-hexane to the solution precipitated very pale yellow crystals of the product. Yield 80–85%.

(*c*). *$X=NO_2$, SCN, NCO and CN.* $[Pt(CH_3)_3]_2SO_4 \cdot 4\ H_2O$ was dissolved in water and a stoichiometric (1/1) amount of 2,2'-bipyridine added. The mixture was heated and stirred until the bipyridine had dissolved. An aqueous solution containing excess NaX or KX was added causing immediate formation of a pale yellow precipitate which was extracted into chloroform. The chloroform layer was washed with water, dried with Na_2SO_4 and filtered. On concentration of the filtrate to a small volume and addition of n-hexane, pale yellow crystals of the product resulted. Yields from 70–95% were obtained.

The product from the reaction of $[Pt(CH_3)_3BipyH_2O]_2SO_4$ and KCN gave an infrared spectrum with two peaks in the C–N stretching region. Recrystallization of the compound from MeOH or chloroform/hexane solutions gave a product containing only a single C–N stretch, but a broad peak was observed in the O–H stretching region. Analytical figures for this compound were not satisfactory.

(*d*). *X=acetylacetonate.* This was prepared from $[Pt(CH_3)_3Acac]_2$ by a modification of the method of Lile and Menzies[29]. $[Pt(CH_3)_3Acac]_2$ was dissolved in hot n-hexane and a stoichiometric quantity of 2,2'-bipyridine in n-hexane added. $Pt(CH_3)_3$BipyAcac precipitated immediately as yellow plates in almost quantitative yield. The precipitate was washed with n-hexane and air-dried.

(*e*). *$X=CH_3$.* This is one of the few examples of tetramethylplatinum(IV) derivatives as yet reported, the only other examples being the phosphine and arsine derivatives prepared by Ruddick and Shaw[19,22]. A benzene suspension of $Pt(CH_3)_3$ BipyI [4.84 g (0.093 mole) in 100 ml of benzene] was treated with an excess of CH_3Li in ether (10 ml of a 2 *M* solution) at ice temperature, the CH_3Li being added slowly to the stirred benzene slurry while both reactants were kept under dry nitrogen. The mixture was stirred for one hour and then hydrolysed with 10% ammonium chloride solution. The organic layer was decanted off and the aqueous layer extracted twice with small portions of benzene. The combined organic extracts were dried over sodium sulphate, filtered, and the filtrate evaporated to dryness in a stream of air. Yield of crude material was 2.9 g (77%). Pure product was obtained by dissolving 1 g of the crude material in 50 ml of acetone and passing the solution through a short cellulose column. To the eluate, 35 ml of water were slowly added. The resultant precipitate was washed with an ice-cold mixture of acetone and water, and dried over $CaCl_2$ in a vacuum desiccator.

TABLE 8

ANALYTICAL DATA FOR TRIMETHYLPLATINUM(IV) COMPOUNDS

Compound[a]	*Analysis found (calcd.) (%)*				
	C	*H*	*N*	*Pt*	*X*
$PtCH_3)_3BipyNO_3$	34.0	3.7	9.2	42.3	
	(34.1)	(3.7)	(9.2)	(42.6)	
$Pt(CH_3)_3BipyOOCCH_3$	39.3	4.4	6.3	42.6	
	(39.5)	(4.4)	(6.1)	(42.8)	
$Pt(CH_3)_3BipyCl$	36.2	4.0	6.4	45.5	8.2
	(36.2)	(4.0)	(6.5)	(45.2)	(8.2)
$Pt(CH_3)_3BipyBr$	32.9	3.8	6.0	40.8	16.8
	(32.8)	(3.6)	(5.9)	(41.0)	(16.8)
$Pt(CH_3)_3BipyI$	30.1	3.5	5.4	37.5	24.3
	(29.8)	(3.3)	(5.3)	(37.3)	(24.2)
$Pt(CH_3)_3BipyNCS$	36.8	3.8	9.4	42.8	
	(37.0)	(3.8)	(9.2)	(42.9)	
$Pt(CH_3)_3BipyNCO$	38.5	4.1	9.0	44.7	
	(38.4)	(3.9)	(9.6)	(44.5)	
$Pt(CH_3)_3BipyNO_2$	35.2	4.0	9.6	44.0	
	(35.3)	(3.9)	(9.5)	(44.1)	
$Pt(CH_3)_3BipyAcac$	43.7	5.0	5.6	39.0	
	(43.6)	(4.9)	(5.6)	(39.4)	
$Pt(CH_3)_4Bipy$	41.1	4.9	6.9	47.2	
	(40.9)	(4.9)	(6.8)	(47.5)	
$Pt(CH_3)_3Lut_2NO_3$	39.4	5.3	8.2	37.6	
	(39.5)	(5.3)	(8.1)	(37.8)	
$Pt(CH_3)_3Lut_2Cl$	41.6	5.7	5.8	40.0	7.3
	(41.7)	(5.5)	(5.7)	(39.8)	(7.2)
$Pt(CH_3)_3Lut_2Br$	37.8	5.1	5.5	36.3	14.8
	(38.2)	(5.1)	(5.2)	(36.5)	(14.9)
$Pt(CH_3)_3Lut_2I$	34.8	4.7	4.7	33.3	22.0
	(35.1)	(4.7)	(4.8)	(33.5)	(21.8)
$Pt(CH_3)_3Lut_2NCS$	42.5	5.4	7.9	37.9	
	(42.2)	(5.3)	(8.2)	(38.1)	
$Pt(CH_3)_3Lut_2NCO$	44.0	5.6	8.2	39.0	
	(43.5)	(5.5)	(8.5)	(39.3)	
$Pt(CH_3)_3Lut_2NO_2$	41.1	5.6	8.4	39.0	
	(40.8)	(5.4)	(8.4)	(39.0)	
$Pt(CH_3)_3Py_2Cl$	36.7	4.6	6.4	44.6	8.2
	(36.9)	(4.4)	(6.5)	(45.0)	(8.2)
$Pt(CH_3)_3Py_2Br$	32.9	4.4	6.1	40.5	16.9
	(32.6)	(4.0)	(5.9)	(40.8)	(16.7)
$Pt(CH_3)_3Py_2I$	29.8	3.6	5.4	23.9	37.4
	(29.7)	(3.7)	(5.3)	(24.2)	(37.2)
$[Pt(CH_3)_3BipyH_2O]ClO_4$	30.4	3.4	5.5	38.0	
	(30.5)	(3.5)	(5.5)	(38.3)	
$[Pt(CH_3)_3BipyNH_3]ClO_4$	31.1	4.0	8.6	38.3	
	(30.4)	(3.9)	(8.2)	(38.1)	
$[Pt(CH_3)_3BipyCH_3NH_2]ClO_4$	32.2	4.4	7.8	37.2	
	(31.9)	(4.2)	(8.0)	(37.0)	
$[Pt(CH_3)_3BipyEtNH_2]ClO_4$	33.3	4.5	7.5	36.4	
	(33.3)	(4.5)	(7.8)	(36.1)	

(Table continued)

TABLE 8 (*continued*)

Compound[a]	*Analysis found (calcd.) (%)*				
	C	*H*	*N*	*Pt*	*X*
$[Pt(CH_3)_3BipyPip]ClO_4$	37.3 (37.2)	4.9 (4.9)	7.2 (7.2)	33.6 (33.6)	
$[Pt(CH_3)_3BipyPy]ClO_4$	37.7 (37.6)	3.9 (3.9)	7.2 (7.3)	33.9 (33.6)	
$[Pt(CH_3)_3BipyPPh_3]ClO_4$	48.8 (49.1)	4.2 (4.2)	3.6 (3.7)		
$Pt(CH_3)_3Pic_2I$	36.6 (32.6)	4.3 (4.2)	4.9 (5.1)	35.0 (35.3)	22.7 (22.9)
$Pt(CH_3)_3(4,4'\text{-}Dmb)I$	32.5 (32.7)	4.0 (3.8)	5.0 (5.1)	35.6 (35.4)	22.9 (23.0)
$Pt(CH_3)_3(5,5'\text{-}Dmb)I$	32.5 (32.7)	3.9 (3.8)	5.3 (5.1)	35.5 (35.4)	23.8 (23.0)
$Pt(CH_3)_3(Tmb)I$	35.6 (35.2)	4.5 (4.3)	4.7 (4.8)	33.6 (33.7)	22.2 (21.9)
$Pt(CH_3)_3PhenI$	33.1 (32.9)	3.3 (3.1)	5.0 (5.1)	35.6 (35.7)	23.1 (23.2)
$Pt(CH_3)_3(5\text{-}Mp)I$	34.5 (34.3)	3.7 (3.4)	4.9 (5.0)	34.5 (34.8)	22.6 (22.6)
$Pt(CH_3)_3(2\text{-}Mp)I$	34.6 (34.3)	3.6 (3.4)	4.8 (5.0)	34.5 (34.8)	22.5 (22.6)
$Pt(CH_3)_3(5,6\text{-}Dmp)I$	35.7 (35.4)	3.9 (3.7)	4.7 (4.9)	33.1 (33.9)	21.9 (22.1)
$Pt(CH_3)_3(4,7\text{-}Dmp)I$	35.6 (35.4)	3.8 (3.7)	5.0 (4.9)	33.8 (33.9)	22.1 (22.1)
$Pt(CH_3)_3(2,9\text{-}Dmp)I$	35.4 (35.4)	3.7 (3.7)	4.9 (4.9)	33.9 (33.9)	22.0 (22.1)
$Pt(CH_3)_3(Hmp)I$	39.7 (40.0)	4.7 (4.6)	4.2 (4.4)	31.1 (30.9)	20.2 (20.1)
$Pt(CH_3)_3(4,7\text{-}Dpp)I$	46.3 (46.2)	3.6 (3.6)	4.0 (4.0)	27.9 (28.2)	18.2 (18.2)

[a] Pip = piperidine, Pic = 4-methylpyridine, Dmb = dimethylbipy, Tmb = 4,4′,6,6′-tetramethylbipy, Mp = methylphen, Dmp = dimethylphen, Hmp = 3,4,5,6,7,8-hexamethylphen, Dpp = diphenylphen.

Properties. The compounds $Pt(CH_3)_3BipyX$ are all white to pale yellow solids except for $Pt(CH_3)_4Bipy$ which is a bright orange, microcrystalline solid. Apart from $Pt(CH_3)_4Bipy$, the compounds are only sparingly soluble in most organic solvents. $Pt(CH_3)_4Bipy$ is soluble in benzene, chloroform, acetone, dioxane and nitrobenzene. The compound, however, appears to be photo-sensitive, and a chloroform solution decomposed to $Pt(CH_3)_3BipyCl$ on standing.

B. Preparation of $[Pt(CH_3)_3BipyX]ClO_4$

(*a*). $X = H_2O$. $[Pt(CH_3)_3]_2SO_4 \cdot 4\ H_2O$ (0.178 g) and 0.086 g of 2,2′-bipyridine were added to 3 ml water. When both compounds had dissolved, the solution was filtered and ca. 1 ml of saturated $NaClO_4$ solution was added slowly. The white precipitate which formed was filtered off, washed and dried over $CaCl_2$. Yield 90%.

(b). X = NH_3, CH_3NH_2, $C_2H_5NH_2$, piperidine and pyridine. $[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$ was dissolved in water with a two-fold excess of 2,2′-bipyridine, and then excess base X was added to the solution. Dropwise addition of saturated $NaClO_4$ solution gave in each case a white precipitate which was filtered, washed with water and dried over $CaCl_2$. Yield 90%.

(c). X = PPh_3. The above procedure was followed except that an acetone/water mixture was used to allow dissolution of the PPh_3. The product again precipitated as a white solid on addition of saturated $NaClO_4$ solution. Yield 90%.

Properties. The compounds $[Pt(CH_3)_3BipyX]ClO_4$ are all white solids, soluble in nitrobenzene, dioxane, and acetone. Conductance measurements in nitrobenzene, showed these compounds to be 1/1 electrolytes.

C. Preparation of $Pt(CH_3)_3A_2X$.

(a). A = pyridine, X = Cl, Br and I; A = lutidine (3,5-dimethylpyridine), X = I. The compounds $Pt(CH_3)_3Py_2Cl$ and $Pt(CH_3)_3Py_2I$ have been prepared previously[15,29]. The bromo analogue was prepared similarly: $[Pt(CH_3)_3Br]_4$ in benzene was treated with a slight excess of pyridine and the solvent evaporated off until crystals were deposited. The compound $Pt(CH_3)_3Lut_2I$ was prepared in like manner except that it was precipitated with n-hexane. Yield 90–95%.

(b). A = lutidine, X = NO_3 and CH_3COO. The compounds $Pt(CH_3)_3Lut_2X$ were prepared similarly to the bipyridine compounds. A chloroform solution of $Pt(CH_3)_3Lut_2I$ was treated with excess solid AgX, the solution was filtered, the filtrate concentrated to a small volume and the product precipitated with n-hexane. Yield 70–80%. In the case of the acetato compound an analytically pure sample could not be obtained due to loss of lutidine.

(c). A = lutidine, X = NO_2, NCS, NCO, CN, Cl and Br. An aqueous solution of $[Pt(CH_3)_3]_2SO_4 \cdot 4\,H_2O$ was treated with an excess of 3,5-lutidine. An aqueous solution containing excess KX was added, giving either a white precipitate or an oil. The mixture was extracted with chloroform, the chloroform layer washed with water, dried over Na_2SO_4, and concentrated to a small volume. Addition of n-hexane precipitated the product as colorless crystals. Yield 80–90%. $Pt(CH_3)_3Lut_2NCS$ is fairly stable in the solid state but decomposes rapidly in chloroform solution to yield the dimer $[Pt(CH_3)_3LutNCS]_2$ (Found: Pt, 47.9. Calcd.: Pt, 48.1%.) The cyano species decomposes with loss of lutidine in the solid state and has not been obtained in a pure form.

(d). A = pyridine, X = CH_3. An attempt was made to prepare $Pt(CH_3)_4Py_2$, in a manner analogous to that of $Pt(CH_3)_4Bipy$. A benzene slurry of 1.30 g of $Pt(CH_3)_3$-Py_2I in 20 ml of benzene was treated with excess 2 *M* CH_3Li in ether, the flask being kept at ice-temperature with the reaction mixture under dry nitrogen throughout. After stirring for one hour the excess CH_3Li was hydrolysed with 10% $HClO_4$ in crushed ice and the organic layer decanted off. The aqueous layer was extracted twice with small portions of benzene. The benzene layer and the combined extracts were dried with anhydrous Na_2SO_4, filtered, and evaporated to dryness. Attempts to recrystallise the substance were unsuccessful since the compound decomposed in solution. Analyses of this crude product were not good and the infrared spectrum indicated that $[Pt(CH_3)_3OH]_4$ was present. However, as mentioned elsewhere in this paper, both the infrared and NMR spectra contained features very similar to

those obtained for $Pt(CH_3)_4Bipy$.

Properties. All the compounds $Pt(CH_3)_3Py_2X$ and $Pt(CH_3)_3Lut_2X]$ are colorless to pale yellow solids. They are soluble in organic solvents such as chloroform, benzene, acetone, and nitrobenzene.

D. *Preparation of* $[Pt(CH_3)_3LI]$ *(L = a substituted 2,2'-bipyridine or 1,10-phenanthroline)*

These compounds were prepared by mixing together stoichiometric (1/1) quantities of $[Pt(CH_3)_3I]_4$ and the ligand, both dissolved in benzene. Usually the product crystallized out after a short period of time, although in some case concentration and cooling were necessary. The compounds are pale yellow and are soluble in nitrobenzene.

Nuclear magnetic resonance spectra

NMR spectra were recorded at 60 MHz on a Varian A60 NMR spectrometer at a sample temperature of $34 \pm 2°$. The complexes were studied in saturated or near-saturated solutions on sweep width of 500 Hz using tert-butanol as internal reference. τ values were obtained using τ(t-BuOH) 8.72 ppm for $CDCl_3$ and 8.68 ppm for nitrobenzene. Spin–spin coupling constants are considered accurate to ±0.5 Hz, and τ values to ±0.01 ppm.

Infrared spectra

IR spectra were recorded from 4000 to 400 cm^{-1} on a Perkin–Elmer Model 457 Spectrometer as Nujol and hexachlorobutadiene mulls between KBr discs. Frequencies are considered accurate to $\pm 2\ cm^{-1}$.

ACKNOWLEDGEMENT

One of us (G.A.S.) acknowledges the award of a Commonwealth Post-Graduate Scholarship.

REFERENCES

1 S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 90 (1968) 6669, and references cited therein.
2 R. J. Goodfellow, P. L. Goggin and D. A. Duddell, *J. Chem. Soc. A*, (1968) 504.
3 J. Powell and B. L. Shaw, *J. Chem. Soc.*, (1965) 3879.
4 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, (1970) 1938.
5 F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, (1968) 2700.
6 F. H. Allen, A. Pidcock and C. R. Waterhouse, *J. Chem. Soc. A*, (1970) 2087.
7 J. A. Pople and D. P. Santry, *Mol. Phys.*, 8 (1964) 1.
8 G. W. Smith, *J. Chem. Phys.*, 39 (1963) 2031.
9 G. W. Smith, *J. Chem. Phys.*, 42 (1965) 435.
10 J. A. S. Smith, *J. Chem. Soc.*, (1962) 4736.
11 K. Kite, J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, (1966) 1744.
12 D. E. Clegg and J. R. Hall, *Aust. J. Chem.*, 20 (1967) 2025.
13 D. E. Clegg, J. R. Hall and N. S. Ham, *Aust. J. Chem.*, 23 (1970) 1981.
14 M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, (1951) 299.
15 O. M. Ivanova and A. D. Gel'man, *Zhur. Neorg. Khim.*, 3 (1958) 1334.
16 A. G. Swallow and M. R. Truter, *Proc. Roy. Soc, Ser. A*, 256 (1962) 527.

17 J. R. Hall and G. A. Swile, *J. Organometal. Chem.*, 21 (1970) 237.
18 J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.*, (1965) 6740.
19 J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, (1969) 2801.
20 J. V. Hatton, W. G. Schneider and W. Siebrand, *J. Chem. Phys.*, 39 (1963) 1330.
21 A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. A*, (1966) 1707.
22 J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, (1969) 2964.
23 C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 29 (1958) 1012.
24 D. E. Clegg and J. R. Hall, *J. Organometal. Chem.*, 22 (1970) 491.
25 D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, 23A (1967) 263.
26 D. M. Adams, J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1960) 2047.
27 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, N.Y., 2nd Ed., 1970.
28 D. M. Adams, *Metal–Ligand and Related Vibrations*, Arnold, London, 1967.
29 W. J. Lile and R. C. Menzies, *J. Chem. Soc.*, (1949) 1168.
30 J. Bjerrum, *Chem. Rev.*, 46 (1950) 381.