# Syntheses, Characterization and Reactions of some Methyl Derivatives of Platinum(II). Part I.

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## Abstract

Reactions of [Pt(COD)(CH$_3$)$_2$] (where COD = 1,5-cyclooctadiene) with the mixed bidentate ligands, 8-(diphenylarsino)quinoline (N-As), 8-diphenyl-phosphino)quinoline (N-P), 1-thiomethyl-2-(diphenylarsino)ethane (S-As) and 1-(thiomethyl)-2-(diphenylphosphino)ethane (S-P), gave a series of dimethyl platinum(II) complexes, [Pt(L–L')(CH$_3$)$_2$] (where L–L' = N-As, N-P, S-As, S-P). Reaction of methyllithium with [Pt(L–L')Cl$_2$] (where L–L' = S-As, S-P) and [PtL$_2$Cl$_2$] (where L = diphenyl(2-phenylethyl)phosphine (PE), or diphenyl(1-naph-thyl)phosphine (PN)) gave the dimethyl complexes, [Pt(L–L')(CH$_3$)$_2$] and *cis*-[Pt(L)$_2$(CH$_3$)$_2$], respectively. Reactions of [Pt(L–L')(CH$_3$)$_2$] (where L–L' = S-As, S-P) with hydrogen chloride or hydrochloric acid have been investigated. The complexes were characterized by elemental analysis, IR, $^1$H NMR and $^{13}$C NMR spectral data; trends in the $^1$H NMR spectroscopic parameters are discussed.

## Introduction

Alkyl complexes of platinum(II) with various unidentate [1, 2] and symmetrical bidentate [1, 3] ligands have been prepared and studied. Recently [4, 5], there has been interest in the coordination chemistry of mixed donor ligands, with particular interest [6–9] given to the ligands that have aryl phosphine or aryl arsine at one end to stabilize the metal ion in low oxidation states, and a weakly coordinating site having a nitrogen or sulfur atom, that can be substituted by a $\pi$-acceptor ligand [7]. Examples of such ligands are: 8-(diphenylarsino)-quinoline (N-As), 8-(diphenylphosphino)quinoline (N-P), 1-thiomethyl)-2-(diphenylarsino)ethane (S-As), and 1-(thiomethyl)-2-(diphenylphosphino)ethane (S-P) [7, 9]. Although methyl complexes of plati-num with monodentate or symmetrical bidentate ligands have been extensively studied, complexes with mixed bidentate ligands have received little attention [10].

For the purpose of comparison, methyl platinum complexes of the monodentate ligands diphenyl(2-phenylethyl)phosphine (PE) and diphenyl(1-naph-thyl)phosphine (PN), which are structurally related to the above bidentate ligands, were prepared and studied.

## Experimental

All preparations were carried out in an atmosphere of purified nitrogen using standard techniques for air sensitive compounds [11]. Melting points (un-corrected) were determined on an electrothermal melting point apparatus. IR spectra were recorded (KBr and CsI pellets) on a Perkin-Elmer 577 spec-trometer. $^1$H NMR spectra were recorded on a Bruker WM-250 or a Varian T-60 A spectrometer. $^{13}$C NMR were recorded on a Bruker WM-250 instru-ment. Microanalyses were performed by Pascher, Microanalysis Laboratory, Bonn, F.R.G. or by Butterworth Laboratories, Teddington, U.K.

The ligands (N-As) [12], (N-P) [12], (S-As) [13] and (S-P) [14], and the complexes Pt(N-As)Cl$_2$ [6], Pt(N-P)Cl$_2$ [6] and Pt(S-P)Cl$_2$ [9] were prepared as previously described. The ligands (PE) [15] and (PN) [16], and the complex [Pt(COD)(CH$_3$)$_2$] [17] were prepared by published methods with minor modifications.

### Preparation of the Complexes

#### [Pt(S-As)Cl$_2$] (I)

To a filtered solution of K$_2$PtCl$_4$ (1.0 g, 2.41 mmol) in distilled water (20 ml) was added, with continuous stirring, a filtered solution of the ligand (S-As) (0.88 g, 2.9 mmol) in absolute ethanol (20 ml). Upon mixing, an off-white solid was sep-arated. Stirring was continued for 1 h, and the solid precipitate was filtered, washed with a mixture of acetone–water (1:1) and then with diethyl ether. The product was dried *in vacuo* at 50 °C (melting point (m.p.) 150 °C decomposition (dec.)).

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*cis-[Pt(PE)₂Cl₂] (IIIa) and trans-[Pt(PN)₂Cl₂] (IV)*

To a filtered solution of K₂PtCl₄ (0.5 g, 1.22 mmol) in distilled water (15 ml) was added, with continuous stirring, a filtered solution of the ligand (2.5 mmol) in absolute ethanol (15 ml). During the addition, a white solid started to precipitate. The mixture was stirred for 1 h at room temperature and the solid precipitate was filtered, washed with distilled water, ethanol and finally was dried *in vacuo* at 50 °C (IIIa: m.p. 114–116 °C, IV: m.p. 219 °C dec.).

*trans-[Pt(PE)₂Cl₂] (IIIb)*

A sample of *cis*-[Pt(PE)₂Cl₂] (0.3 g, 0.35 mmol) was heated at 240 °C for 10 min. The resultant glassy material was washed with acetone and dried *in vacuo* at 50 °C (m.p. 265 °C dec.).

*[Pt(N-As)(CH₃)₂] (V), [Pt(N-P)(CH₃)₂] (VI), [Pt(S-As)(CH₃)₂] (VII) and [Pt(S-P)(CH₃)₂] (VIII)*

To a filtered solution of [Pt(COD)(CH₃)₂] (0.2 g, 0.6 mmol) in acetone (10 ml) was added dropwise a filtered solution of the ligand (0.6 mmol) in acetone (10 ml). The solution was heated with continuous stirring at 50 °C for 1 h and then stirred at room temperature for 4 h. Solvent was evaporated to the point of crystallization (5 ml) and the product was separated upon addition of n-pentane. The product was filtered, dried *in vacuo* and finally stored in a vacuum desiccator (V: m.p. 145 °C dec.; VI: m.p. 158 °C dec.; VII: m.p. 90 °C dec.; VIII: m.p. 115 °C dec.).

*[Pt(S-As)(CH₃)₂] (VII) and [Pt(S-P)(CH₃)₂] (VIII)*

To an ice-cooled suspension of the dichloro complex, [Pt(L–L′)Cl₂] (where (L–L′ = S-As or S-P) (1.9 mmol) in dry ether (50 ml) was added dropwise (30 min) a solution of methyllithium (1.6 M, 15 mmol). The mixture was stirred at room temperature for 2 h. During this time, the solution changed colour from light brown to colourless. The mixture was hydrolyzed at 0 °C with a saturated solution of aqueous ammonium chloride (50 ml). The ether layer was separated, dried (MgSO₄) and decolourized over activated charcoal. The filtrate was reduced to *c.* 15 ml and then cooled to −20 °C to give a white microcrystalline solid. The product was filtered, dried *in vacuo* and finally stored in a vacuum desiccator (VII: m.p. 90 °C dec.; VIII: m.p. 115 °C dec.). These compounds were found to be identical with those prepared in the above procedure.

*cis-[Pt(PE)₂(CH₃)₂] (IX) and cis-[Pt(PN)₂(CH₃)₂] (X)*

The general procedure used above for the preparation of VII and VIII was utilized here. A sample

of the dichloro complex, Pt(L)₂Cl₂ (where L = PE or PN) (0.59 mmol) in dry ether (50 ml) was allowed to react with methyllithium (1.6 M. 5.9 mmol). The mixture was stirred for *c.* 20 h. The compounds were isolated as shown in the above procedure (IX: m.p. 146 °C dec.; X: m.p. 189 °C dec.).

*[Pt(S-As)(CH₃)(Cl)] (XI) and [Pt(S-P)(CH₃)(Cl)] (XII)*

(a) From the reaction of [Pt(L–L′)(CH₃)₂] (where L- L′ = S-As or S-P) and hydrogen chloride (generated *in situ*).

To a filtered solution of the dimethyl complex (0.38 mmol) in CH₂Cl₂ (5 ml) was added, with continuous stirring, a solution of acetyl chloride (0.35 µl, 0.5 mmol) in CH₂Cl₂ (4 ml) containing methanol (1.5 ml). The solution was stirred for 10 h before the solvent was evaporated. The residue was dissolved in CH₂Cl₂ and the product was reprecipitated with ether. It was then filtered and dried *in vacuo* at 40 °C (XI: m.p. 143 °C dec.; XII: m.p. 140 °C dec.).

(b) From the reaction of [Pt(L–L′)(CH₃)₂] (where L–L′ = S-As or S-P) and hydrochloric acid.

To a filtered solution of the dimethyl complex (0.38 mmol) in ether containing CH₂Cl₂ (2 ml) was slowly added an aqueous solution of HCl (1.10 ml, 0.25 M). The solution was refluxed for 10 h and then dried over anhydrous MgSO₄. The solvent was evaporated to dryness and the residue was digested in petroleum ether (b.p. 40–60 °C). The precipitated monomethyl derivative was further purified by dissolving it in CH₂Cl₂ and then reprecipitating with ether. It was then filtered and dried *in vacuo* at 40 °C. The products were shown by their melting points and spectral data to be identical with those isolated in the procedure (a) above.

When these monomethyl derivatives were further allowed to react with hydrogen chloride or hydrochloric acid as shown in procedures (a) or (b) above, the corresponding dichloro complexes [Pt(L–L′)Cl₂] were obtained (I: m.p. 150 °C dec.; II: m.p. 153 °C dec.).

## Results and Discussion

### Dimethyl Complexes

#### Preparation of the complexes

The dimethyl complexes of platinum were prepared by two different methods. The first method involves displacement of 1,5-cyclooctadiene (COD) from [Pt(COD)(CH₃)₂] by the desired ligand(s) [17]. In the second method, direct alkylation of the corresponding dichloro complexes, [Pt(L–L′)Cl₂] (I: L–L′ = S-As; II: L–L′ = S-P [9]), *cis*-[Pt(PE)₂-Cl₂] (IIIa), *trans*-[Pt(PE)₂Cl₂] (IIIb) and *trans*-[Pt(PN)₂Cl₂] (IV), was employed [1].

The reaction of [Pt(COD)(CH$_3$)$_2$] with the mixed bidentate ligands (N-As), (N-P), (S-As) and (S-P) probably proceeds by addition of the ligand to the dimethyl complex, followed by breakage of one of the Pt–olefin bonds facilitated by the strong *trans* influence of the methyl group. Finally, the second Pt–olefin bond is broken to give the chelates **V, VI, VII** and **VIII**, respectively (eqn. (1)).
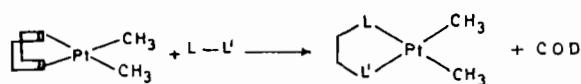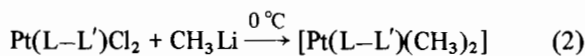


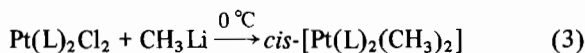**V**: L–L' = N-As      **VII**: L–L' = S-As
**VI**: L–L' = N-P       **VIII**: L–L' = S-P

However, the dimethyl complexes, [Pt(L–L')(CH$_3$)$_2$] (where L–L' = S-As, S-P) and *cis*-[Pt(L)$_2$(CH$_3$)$_2$] (where L = PE, PN) were prepared by the direct reaction of methyllithium with the corresponding dichloro complexes (eqns. (2) and (3)).

$$Pt(L-L')Cl_2 + CH_3Li \xrightarrow{0\,°C} [Pt(L-L')(CH_3)_2] \qquad (2)$$

**VII**: L–L' = S-As
**VIII**: L–L' = S-P

$$Pt(L)_2Cl_2 + CH_3Li \xrightarrow{0\,°C} cis\text{-}[Pt(L)_2(CH_3)_2] \qquad (3)$$

**IX**: L = PE
**X**: L = PN

Attempts to prepare complexes **V** and **VI** by the direct alkylation of the dichloro complexes, [Pt(N-As)Cl$_2$] or [Pt(N-P)Cl$_2$], were unsuccessful. This behavior may be attributed to the high energy gap between the ground state and the five-coordinated transition state [18] as a consequence of the ligand rigidity that resists changes required by the substitution to attain the five-coordinated trigonal bipyramidal transition state [19]. The reaction of *cis*- or *trans*-[Pt(PE)$_2$Cl$_2$] with excess methyllithium affords the corresponding *cis*-dimethyl complex (**IX**). Such substitution reactions are believed to proceed with steric retention through a five-coordinated trigonal-bipyramidal intermediate [20]. However, the loss of steric retention in the reaction of the *trans*-isomer (*trans*-[Pt(PN)$_2$Cl$_2$]) could be attributed to the *trans–cis* isomerism of the finally formed product in the presence of methyllithium [21].

*Spectral data*

The dimethyl complexes isolated in this study were characterized by their elemental analyses (Table 1) and spectral data (Tables 2 and 3). The IR spectra of the dimethyl complexes of both types, [Pt(L–L')(CH$_3$)$_2$] and [Pt(L)$_2$(CH$_3$)$_2$], show methyl $\nu$(C–H)

in the range 2800–2930 cm$^{-1}$ and $\delta$(C–H) in the range 1135–1230 cm$^{-1}$. The bands due to Pt–CH$_3$ stretching vibrations (530–550 cm$^{-1}$) [22] were clearly characterized in the IR spectra of complexes **VII** and **VIII**, but were obscured by ligand absorptions in other complexes.

These complexes were further characterized by $^1$H NMR spectroscopy. The $^1$H NMR spectra of [Pt(N-As)(CH$_3$)$_2$] and [Pt(S-As)(CH$_3$)$_2$] show two singlets, flanked by satellites ($J(^{195}$Pt–CH$_3$)) arising from coupling with $^{195}$Pt ($I = 1/2$, 33.6% abundance). For example, the $^1$H NMR spectrum of Pt(N-As)(CH$_3$)$_2$ shows two singlets at 1.03 ($J(^{195}$Pt–CH$_3$) = 77.1 Hz) and 1.17 ppm ($J(^{195}$Pt–CH$_3$) = 89.0 Hz), assigned to the methyl groups *trans* to arsenic and nitrogen, respectively. The chemical shifts as well as the platinum coupling constants are consistent with the *trans* influence order: As > N.

The $^1$H NMR spectra of the analogous complexes having bidentate ligands with phosphorus donor atoms instead of arsenic, [Pt(N-P)(CH$_3$)$_2$] and [Pt(S-P)(CH$_3$)$_2$], show two doublets flanked by satellites arising from Pt coupling. For example, the $^1$H NMR spectrum of Pt(S-P)(CH$_3$)$_2$ shows two doublets centered at 0.48 ($J(^{31}$P–Pt–CH$_3$) = 8.0 Hz) and 0.77 ($J(^{31}$P–Pt–CH$_3$) = 7.0 Hz) ppm, assigned to the methyl groups *trans* to the phosphorus and sulfur atoms, respectively. These doublets were coupled with $^{195}$Pt with coupling constants of 70.0 and 79.0 Hz, respectively. The chemical shifts and their coupling constants are also consistent with the *trans* influence order: P > S.

The $^1$H NMR spectra of the *cis*-complexes, [Pt(PE)$_2$(CH$_3$)$_2$] and [Pt(PN)$_2$(CH$_3$)$_2$], show the Pt–CH$_3$ resonances as a quartet with two satellite quartets due to coupling with $^{195}$Pt. The quartet in the spectrum of *cis*-[Pt(PN)$_2$(CH$_3$)$_2$] appears at 0.42 ppm with $J(^{195}$Pt–CH$_3$) = 70.1 Hz. Similar spectra have been reported for complexes of the same type. For example, the complexes, *cis*-[Pt(PR$_3$)$_2$(CH$_3$)$_2$] (where R = C$_6$H$_5$ [23], CH$_3$ [24]) and the complexes **IX** and **X** show common features in their $^1$H NMR spectra. Such spectra have been interpreted by Goodfellow *et al.* on the basis of the spin system [AR$_3$X$_n$]$_2$ [24]. The $^{13}$C NMR spectrum of [Pt(S-As)(CH$_3$)$_2$] (in CDCl$_3$) shows two absorptions at 2.56 and 4.16 ppm, assigned to the methyl groups *trans* to arsenic and sulfur atoms, respectively. It also shows absorptions at 15.75 ($\delta$(S–C)) and at 36.45 and 35.49 ppm ($\delta$(As–C–C–S)). In agreement with the $^1$H NMR results, the $^{13}$C chemical shifts of the methyl groups decrease with increasing *trans* influence of the *trans* donor atoms [25]. Unfortunately, the $^{13}$C NMR spectrum of the analogous complex, [Pt(S-P)(CH$_3$)$_2$] (in (CD$_3$)$_2$CO), which is expected to show two doublets for the methyl groups, shows only one doublet centered at 1.44 ppm ($J(^{31}$P–Pt–C) = 6.0 Hz) indicating a complete

TABLE 1. Physical data and elemental analyses for the complexes

| No. | Complex | Colour | Melting point[a] (°C) | Calculated (found) (%) | | | |
|-----|---------|--------|----------------------|------|------|------|------|
| | | | | C | H | N | S |
| I | Pt(S-As)Cl$_2$ | off-white | 150 dec. | 31.59 | 3.00 | | 5.62 |
| | | | | 31.88 | 3.07 | | 5.62 |
| II | Pt(S-P)Cl$_2$ | off-white | 153 dec. | 34.23 | 3.26 | | 6.09 |
| | | | | 33.94 | 3.19 | | 5.65 |
| IIIa | cis-Pt(PE)$_2$Cl$_2$ | white | 114–116 | 56.74 | 4.52 | | |
| | | | | 56.70 | 4.79 | | |
| IIIb | trans-Pt(PE)$_2$Cl$_2$ | white | 265 dec. | 56.74 | 4.52 | | |
| | | | | 56.85 | 4.56 | | |
| IV | trans-Pt(PN)$_2$Cl$_2$ | white | 219 dec. | 59.33 | 3.84 | | |
| | | | | 58.45 | 3.81 | | |
| V | Pt(N-As)(CH$_3$)$_2$ | yellow | 145 dec. | 47.43 | 3.81 | 2.40 | |
| | | | | 47.57 | 3.66 | 2.71 | |
| VI | Pt(N-P)(CH$_3$)$_2$ | yellow | 158 dec. | 51.30 | 4.12 | 2.60 | |
| | | | | 51.11 | 4.06 | 2.66 | |
| VII | Pt(S-As)(CH$_3$)$_2$ | white | 90 dec. | 38.57 | 4.37 | | 6.05 |
| | | | | 38.64 | 4.31 | | 5.64 |
| VIII | Pt(S-P)(CH$_3$)$_2$ | white | 115 dec. | 42.06 | 4.78 | | 6.60 |
| | | | | 41.91 | 4.85 | | 6.31 |
| IX | cis-Pt(PE)$_2$(CH$_3$)$_2$ | white | 146 dec. | 62.60 | 5.50 | | |
| | | | | 62.37 | 5.69 | | |
| X | cis-Pt(PN)$_2$(CH$_3$)$_2$ | white | 189 dec. | 65.01 | 4.74 | | |
| | | | | 64.77 | 4.92 | | |
| XI | Pt(S-As)(CH$_3$)Cl | white | 143 dec. | 34.95 | 3.67 | | 5.83 |
| | | | | 34.88 | 3.46 | | 5.57 |
| XII | Pt(S-P)(CH$_3$)Cl | off-white | 140 dec. | 37.99 | 3.98 | | 6.34 |
| | | | | 37.69 | 3.76 | | 5.86 |

[a]dec. = decomposition

decomposition* of the complex to a solvated mono-methyl derivative [26]. It also shows $\delta$(S–C) at 20.03 ppm and $\delta$(P–C–C–S) at 36.90 ($J(^{31}$P–C–C–S) = 13.28 Hz) and 30.62 ($J(^{31}$P–C–C–S) = 15.31 Hz) ppm.

*Monomethyl Complexes*

Reaction of equimolar amounts of the dimethyl complexes, [Pt(L–L′)(CH$_3$)$_2$] (where L–L′ = S-As, S-P), with hydrogen chloride or hydrochloric acid affords the monomethyl derivatives, Pt(L–L′)(CH$_3$)-Cl. These compounds were characterized by their elemental analyses, IR and $^1$H NMR spectra. The IR spectra of both complexes show, in addition to the characteristic absorption bands due to $\nu$(C–H) and $\delta$(C–H), only one absorption band in the range 290–310 cm$^{-1}$ assigned to $\nu$(Pt–Cl). The $^1$H NMR

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*The decomposition was mainly due to the long time necessary to record the $^{13}$C NMR spectra.

spectrum of [Pt(S-As)CH$_3$)Cl] exhibits a singlet at 0.73 ppm (($J(^{195}$Pt–CH$_3$) = 68.9 Hz) attributed to the methyl group. As expected, the $^1$H NMR spectrum of [Pt(S-P)(CH$_3$)Cl] shows a doublet centered at 0.56 ppm ($J(^{195}$Pt–CH$_3$) = 4.0 Hz) flanked by satellites (($J(^{195}$Pt–CH$_3$) = 70.0 Hz). Although the values of $\delta$(Pt–CH$_3$) and $J$(Pt–CH$_3$) do not indicate which of the two possible positions is occupied by the methyl group, it is believed that the methyl group is *trans* to the donor atom with the lower *trans* influence, that is *trans* to the sulfur atom.

When these monomethyl complexes are further allowed to react with hydrogen chloride, another oxidative-addition/reductive-elimination reaction occurs, yielding the dichloro complexes, Pt(L–L′)-Cl$_2$. These complexes were characterized by their melting points and IR spectra, and found to be identical with authentic samples prepared from K$_2$PtCl$_4$ and (L–L′) [9].

TABLE 2. Infrared spectra of the complexes[a]

| No. | Complex | Aliphatic | | $\nu$(As—Ph) or $\nu$(P—Ph) | $\nu$(Pt—Cl) |
|---|---|---|---|---|---|
| | | $\nu$(C—H) | $\delta$(C—H) | | |
| I | Pt(S-As)Cl$_2$ | 2922(wb) | | 1434(mb) 996(m) | 325(m) 312(s) |
| II | Pt(S-P)Cl$_2$ | 2915(wb) | | 1436(m) 995(m) | 330(m) 310(s) |
| IIIa | cis-Pt(PE)$_2$Cl$_2$ | 2920(wb) 2850(wb) | | 1430(s) 994(m) | 310(s) 294(s) |
| IIIb | trans-Pt(PE)$_2$Cl$_2$ | 2930(wb) 2868(w) | | 1430(s) 994(m) | 338(s) |
| IV | trans-Pt(PN)$_2$Cl$_2$ | | | 1430(m) 998(mb) | 338(mb) |
| V | Pt(N-As)(CH$_3$)$_2$[b] | 2920(wb) 2874(mb) | 1135(wb) | 1434(m) 998(mb) | |
| VI | Pt(N-P)(CH$_3$)$_2$[b] | 2900(w) 2865(mb) | 1154(wb) | 1432(m) 996(w) | |
| VII | Pt(S-As)(CH$_3$)$_2$[c] | 2915(mb) 2860(mb) | 1210(wb) | 1434(m) 998(m) | |
| VIII | Pt(S-P)(CH$_3$)$_2$[d] | 2910(mb) 2860(mb) | 1212(m) | 1432(m) 998(wb) | |
| IX | cis-Pt(PE)$_2$(CH$_3$)$_2$[b] | 2920(mb) 2875(mb) | 1140(w) | 1430(m) 996(w) | |
| X | cis-Pt(PN)$_2$(CH$_3$)$_2$[b] | 2920(mb) 2882(mb) | 1143(m) | 1436(s) 998(m) | |
| XI | Pt(S-As)(CH$_3$)Cl[b] | 2896(m) | 1208(m) | 1432(m) 996(mb) | 302(mb) |
| XII | Pt(S-P)(CH$_3$)Cl[b] | 2920(mb) 2880(wb) | 1210(mb) | 1430(m) 994(mb) | 292(mb) |

[a]All absorptions are in cm$^{-1}$; s, strong; m, medium; w, weak; b, broad.  [b]$\nu$(Pt—CH$_3$) are obscured by ligand absoprtions. [c]$\nu$(Pt—CH$_3$) = 550(wb), 532(m).   [d]$\nu$(Pt—CH$_3$) = 542(w).

## Carbonylation Reactions

The reaction of carbon monoxide with the dimethyl complexes, [Pt(L- L')(CH$_3$)$_2$] (where L- L' = S-As, S-P), is expected to give the acyl derivatives, [Pt(L—L')(COCH$_3$)$_2$], which are important intermediates in some catalytic reactions [27]. In this study, carbon monoxide was bubbled through a toluene solution of [Pt(S-As)(CH$_3$)$_2$] under atmospheric pressure and at 30 °C. The solution changed colour from colourless to yellow. The IR spectrum of this solution shows weak bands in the terminal (2020, 1935 cm$^{-1}$) and bridging (1850, 1790, 1736 cm$^{-1}$) carbonyl regions [28]. When the solvent was evaporated, a red—brown oily residue was obtained, which showed only one IR band in the bridging carbonyl region at about 1725 cm$^{-1}$. Platinum clusters of the type, [Pt$_3$(CO)$_n$(L)$_4$] ($n$ = 3, 4), may have been formed [28], but were not fully characterized.

## Further Discussion of the $^1H$ NMR Data

It has been observed that the platinum—methyl coupling constants ($J(^{195}$Pt—CH$_3$) Hz) in the complexes, cis-[Pt(L)$_2$(CH$_3$)$_2$], are sensitive to the ligand, (L), and decrease in the order: COD (83.4) [17] > As(CH$_3$)$_2$(C$_6$H$_5$) (79.0) [29] > As(CH$_3$)$_3$ (77.6) [30] > P((C$_6$H$_5$)$_3$ (69.0) [23] > P(CH$_3$)$_2$(C$_6$H$_5$) (67.0) [22] > P(CH$_3$)$_2$ (65.4) [24]. This order is the inverse of the trans influence of the donor atoms (P > As > N ⩾ S) [31]. However, the published data about the effect of the trans influence on the chemical shifts of the methyl groups is limited to a few examples [29].

In this study, the effect of the trans influence on $J(^{195}$Pt—CH$_3$), as well as on the methyl chemical shifts has been observed within the same complex. The methyl signals are shifted upfield, and their Pt coupling constants are decreased, with increasing trans influence (Fig. 1). This may be explained in

TABLE 3. $^1H$ NMR spectral data of the complexes[a]

| No. | Complex | $\delta(Pt-CH_3)$ | $J(^{195}Pt-CH_3)$ $[J(^{31}P-Pt-CH_3)]$ | $J(^{195}Pt-N-C-H)$ $[J(^{195}Pt-N-C-H)]$ | $\delta(S-CH_3)$ |
|---|---|---|---|---|---|
| V | $Pt(N-As)(CH_3)_2$[b] | 1.03(3H,s) | 77.1 | 9.72(1H,dd) [21.0] | |
| | | 1.17(3H,s) | 89.0 | | |
| VI | $Pt(N-P)(CH_3)_2$[b] | 0.87(3H,d) | 65.2 [7.60] | 9.72(1H,dd) [20.3] | |
| | | 1.06(3H,s) | 88.2 [7.84] | | |
| VII | $Pt(S-As)(CH_3)_2$[c] | 0.65(3H,s) | 82.0 | | 2.40(3H,s) |
| | | 0.85(3H,s) | 85.0 | | |
| VIII | $Pt(S-P)(CH_3)_2$[c] | 0.48(3H,d) | 70.0 [8.00] | | 2.47(3H,s) |
| | | 0.77(3H,d) | 79.0 [7.00] | | |
| IX | $cis$-$Pt(PE)_2(CH_3)_2$[b] | 0.59(6H,q) | 65.0 | | |
| X | $cis$-$Pt(PN)_2(CH_3)_2$[b] | 0.42(6H,q) | 70.1 | | |
| XI | $Pt(S-As)(CH_3)Cl$[c] | 0.73(3H,s) | 68.4 | | 2.55(3H,s) |
| XII | $Pt(S-P)(CH_3)Cl$[c] | 0.56(3H,d) | 70.0 [4.0] | | 2.60(3H,s) |

[a]$J$ values are in Hz. Chemical shifts are in ppm relative to TMS as internal standard. Multiplicity abbreviations are: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet.  [b]Spectra were recorded in $CDCl_3$ solutions.  [c]Spectra were recorded in $(CD_3)_2CO$.



L = As, V
L = P VI
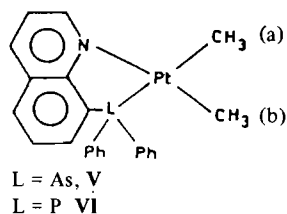
| | $\delta(CH_3)$ (ppm) | $J(^{195}Pt-CH_3)$ (Hz) | |
|---|---|---|---|
| L = As | 1.03 | 77.1 | a |
| L = P | 0.87 | 65.2 | |
| L = As | 1.17 | 89.0 | b |
| L = P | 1.06 | 88.2 | |

Fig. 1. Methyl chemical shifts and platinum coupling constants in the complexes V and VI.

terms of the weakening effect caused by the donor atom on the $Pt-CH_3$ bond *trans* to it. Consequently due to the difference in electronegativity between the Pt atom and the $CH_3$ group, this will lead to an increase in the 'ionic character' of the $Pt-CH_3$ bond: $L-Pt^{\delta+}-CH_3^{\delta-}$. The shielding caused by increasing the electron density on the methyl group is reflected in its chemical shifts.

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