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PREPARATION AND CHARACTERIZATION OF SOME MIXED LIGAND COMPLEXES OF PLATINUM(II)

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Summary

The mixed ligand complexes $PtX_2(ER_3)L$ and $PtXY(ER_3)L$ (where $ER_3 = PR_3$ or $AsMe_3$; L = phosphine, arsine; X = Cl; Y = Cl, H or Me) have been prepared and characterized. Reaction of $PtMe_2(ER_3)L$ with HCl yields $PtMeCl(ER_3)L$, in exclusively one of three possible isomeric forms. Excess tetramethyltin reacts with $Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$ giving both *cis* and *trans* $Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$, as identified from the NMR spectra. Cleavage of $Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2$ with donor ligands such as $AsPh_3$, PMe_2Ph or pyridine, was useful as a synthetic route to the unsymmetrical methylchloro Pt^{II} derivatives. The reaction of *cis*-$[PtMe_2(PPh_3)(AsPh_3)]$ with excess dimethylacetylenedicarboxylate (DMA) yielded only one product, which was of the formula *trans*-$[Pt\{C(COOCH_3)=C(COOCH_3)CH_3\}_2(PPh_3)(AsPh_3)]$, with the alkenyl groups having the same geometry about the C=C bond. The use of diethylacetylene-dicarboxylate (DEA) rather than DMA gave a similar product. However, when *cis*-$[PtMe_2(PEt_3)(AsPh_3)]$ was allowed to react with DMA, two products of the formula *trans*-$[Pt\{C(COOCH_3)=C(COOCH_3)CH_3\}_2(PEt_3)(AsPh_3)]$ were obtained, with the stereochemistry of both alkenyl groups being either *cis* or *trans*.

Introduction

Metal complexes of low symmetry containing readily available ligands can be particularly useful in studies of (a) electronic and steric effects on the catalytic activity of complexes, and (b) asymmetric syntheses catalyzed by metal complexes [1]. Particularly for those species containing monodentate ligands, the tendency

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towards disproportionation to more symmetrical complexes has obviously deterred investigation, e.g. for Pt^{II}.

$$2\ PtLL'X_2 \rightarrow PtL_2X_2 + PtL'_2X_2$$

However, in a low symmetry species such as PtLL'XY, the ability to vary systematically just one ligand L' would open a unique method to study steric and electronic ligand effects, especially for those complexes which catalyze organic transformations and especially for Pt^{II} species where a variety of spectroscopic methods of investigation are available.

There have been only a few reports of such Pt^{II} compounds, most of which are dichlorides [2,3] and which frequently have been obtained only as impure products, e.g. the preparation of $Pt(P^nBu_3)(PEt_3)Cl_2$ [3]. However, more recently, a few mixed ligand aryl or aroyl chloroplatinum(II) complexes, $[PtRCl(PR'_3)L]$ (R = aryl or aroyl, L = neutral donor ligand), have been prepared and characterized [4,5]. In this paper, we describe the synthesis and some properties of not only mixed ligand Pt^{II} dichlorides, $PtLL'X_2$, but also of their methyl and hydrido derivatives, $PtLL'(CH_3)_2$, $PtLL'ClCH_3$ and PtLL'HCl, and thus demonstrate that a fairly extensive chemistry exists in which disproportionation plays only a minor role. A preliminary account of some of this work has appeared [6].

Results and discussion

The mixed ligand complexes were first prepared as the dichlorides, $PtCl_2LL'$, by reaction of the tetrachlorodiplatinum(II) complexes, $[Pt_2Cl_2(\mu\text{-}Cl)_2(ER_3)_2]$ (where $ER_3 = PEt_3$, PMe_2Ph, PPh_3, P(*p*-tolyl)$_3$ or $AsMe_3$) with another tertiary phosphine or arsine (L) in 2/1 molar stoichiometry in dichloromethane solution. The monomeric dichlorides were thus obtained as the *cis* isomers, *cis*-$PtCl_2(ER_3)L$, whose ^{31}P NMR spectra showed none of the resonances for the symmetrical species $PtCl_2L_2$ or $PtCl_2(ER_3)_2$, where L or $ER_3 = Pr_3$. The treatment of these monomeric dichlorides, *cis*-$PtCl_2(ER_3)L$ with excess methyllithium in ether or an ether/benzene mixture gave the dimethyl products usually in good yields.

These dimethyl derivatives can be characterized and their stereochemistry defined on the basis of their ^1H and ^{31}P NMR spectral data (Table 1). The ^1H NMR spectra of the symmetrical dimethyl compounds, *cis*-$PtMe_2L_2$, have been extensively studied previously [7–11], especially for L = tertiary phosphine. It is known that the ^1H spectra of such species are not first order but of the $AA'X_3X_3'$ spin type, further split owing to coupling to ^{195}Pt. It is also known that for ^3J(PPtCH), the *cis* couplings have the + sign and the *trans* couplings the − sign [7]. For example, in the complex $[PtMe_2(Ph_2PC_6H_4CH{=}CH_2)]$, which has the *cis* geometry but is not symmetrical, Bennett et al. [11] reported ^2J(PtCH) 86.5 (*cis*) and 67.0 (*trans*) Hz, and ^3J(PPtCH) $+7.5 \pm 0.3$ (*cis*) and -7.8 ± 0.3 (*trans*) Hz. For our mixed ligand-dimethyl compounds, the ^1H NMR spectra all display two doublets, each with ^{195}Pt satellites, for the Pt–CH_3 protons, consistent with a *cis* and not *trans* geometry (see Table 1 and Fig. 1). On comparing these data with those for *cis*-$[PtMe_2(PR_3)_2]$, *cis*-$[PtMeCl(PR_3)_2]$ and *trans*-$[PtMeCl(PR_3)_2]$ [12–15], we can assign these doublets on the basis of the magnitudes of the ^2J(PtH) and ^3J(PH); the Pt–Me resonance with the larger ^2J(PtH) (in the range 76–81 Hz) and also with the larger ^3J(PH) (7.9–9.1 Hz), we assign to the CH_3 group *cis* to the phosphine. The

TABLE 1

^{1}H AND ^{31}P{^{1}H} NMR DATA FOR MIXED LIGAND ORGANOPLATINUM(II) COMPLEXES AT ROOM TEMPERATURE (δ in ppm, J in Hz)

Complex	^{31}P{^{1}H} NMR		^{1}H NMR [a]					
			P–R			Pt–R		
	δ	^1J(Pt–P)	δ	^2J(P–H)	^3J(Pt–H)	δ	^2J(Pt–H)	^3J(P–H)
$[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	−10.7 [b]	4934	1.73(d)	11.0	50.0	0.50(d)	78.9	2.9
	−11.2 [c]	5003	1.70(d)	11.0	50.0	0.57(d)	76.7	2.8
cis-$[PtMe_2(PEt_3)(AsPh_3)]$	9.2	1922	1.38(q)	–	–	0.24(d)	63.5	6.7
			0.90(m)			0.80(d)	80.8	7.9
cis-$[PtMe_2(PMe_2Ph)(AsPh_3)]$	−10.0	1893	1.30(d)	7.5	19.5	0.41(d)	65.0	7.0
						0.85(d)	80.0	9.1
cis$[PtMe_2(T\text{-}p\text{-}tol_3)(AsPh_3)]$	25.8	2007	2.28 [d]	–	–	0.52(d)	66.7	6.7
						0.56(d)	81.0	8.8
cis-$[PtMe_2(PPh_3)(AsPh_3)]$	28.4	2012	–	–	–	0.56(d)	67.0	6.7
						0.55(d)	80	9.1
cis-$[PtMe_2(PPh_3)(AsMe_3)]$ [e]	27.3	1991	–	–	–	0.67(d)	67.3	6.8
						0.38(d)	77	8.6
cis-$[PtMe_2(P\text{-}p\text{-}tol_3)(AsMe_3)]$ [e]	25.0	2003	2.38 [d]	–	–	0.67(d)	66	7.0
						0.40(d)	76	8.0
$[PtMeCl(PEt_3)(AsPh_3)]$	15.1	3736	1.21(m)	–	–	0.23(d)	80.4	4.5
			1.98(m)					
$[PtMeCl(PMe_2Ph)(AsPh_3)]$	−3.8 [f]	3797	1.90(d)	10.5	38.5	0.12(d)	80.0	5.7
	−13.0 [g]	4317	1.44(d)	10.4	45	1.07(d)	66.8	4.5
trans-$[PtMeCl(PMe_2Ph)_2]$ [h]	−0.9	2896	1.80(t)	6.8	29.5	0.15	82	6.9
$[PtMeCl(PMe_2Ph)(py)]$ [h]	−16.7	4147	1.76(d)	10.9	41.0	0.86	78.2	3.0
$[PtHCl(PEt_3)(AsPh_3)]$	20.9	3531				−18.1(d)	1215	12

[a] Ligands containing phenyl groups displayed multiplet in the region 7.3 to 7.9 ppm; d = doublet, t = triplet, q = quintet, m = multiplet. [b] Due to *trans* isomer. [c] Due to *cis* isomer. [d] P-*p*-tol_3, Me group. [e] ^{31}P NMR spectrum showed small impurities in the complex, $AsMe_3$ δ(Me) 0.92 ppm, ^3J(Pt–H) 11 Hz. [f] Due to isomer C. [g] Due to isomer D; [h] From the dimer.

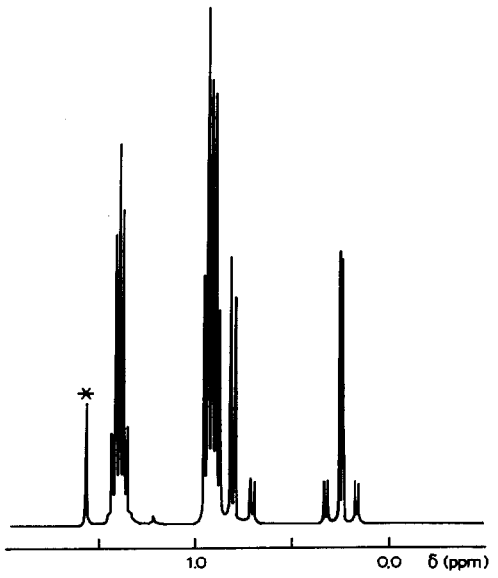


Fig. 1. ^{1}H NMR of $Me_2Pt(PEt_3)(AsPh_3)$.

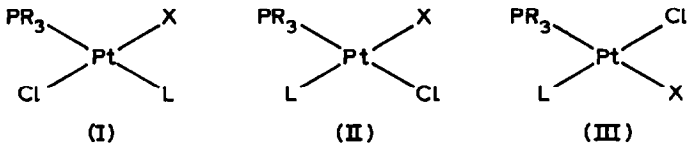
other resonance, with ^2J(PtH) values in the range 63–67 Hz and ^3J(PH) ~ 7 Hz, we assign to the CH_3 group *trans* to the phosphine ligand. A typical ^{1}H NMR spectrum, that for *cis*-[$PtMe_2(PEt_3)(AsPh_3)$] is shown in Fig. 1 *. These assignments are also consistent with the observation that a phosphine such as PEt_3 with a larger *trans* influence [16] than say $AsPh_3$, will induce a smaller ^2J(PtH) in the CH_3 group *trans* to the phosphine.

The ^{31}P NMR spectra of our complexes [$PtMe_2(LL')$] (where L = PEt_3, PMe_2Ph, P(*p*-tolyl)$_3$ or PPh_3) display, as expected, just a single resonance with ^{195}Pt coupling. The magnitudes of ^1J(PtP) lie in the range 1893–2012 Hz and are consistent with a *cis* geometry, i.e. with phosphine *trans* to CH_3. By comparison, *cis*-$PtMe_2(PEt_3)_2$ shows ^1J(PtP) 1856 Hz [9].

Treatment of the dimethyl compounds with one equivalent of hydrogen chloride in ether/benzene yielded the unsymmetrical methylchloro derivatives, PtMeCl(PR_3)L. The corresponding hydrido analogues, PtHCl(PR_3)L, can equally easily be obtained by reduction of the dichlorides, $PtCl_2(PR_3)L$, with sodium borohydride. In both types of reaction, the yields are again good (well over 60%) and provided PR_3 and L are sufficiently different (e.g. L = $AsPh_3$ but not a tertiary phosphine), there is no evidence of disproportionation to the symmetrical products $PtXClL_2$ and $PtXCl(PR_3)_2$ (X = CH_3 or H).

Such complexes can exist in any one of three different isomeric forms, I–III, which can be differentiated on the basis of the ^1J(PtP) values. The following order of ^1J(PtP) is usually observed: I, PR_3 *trans* to tertiary donor ligand L, ~ 2800 Hz; II, PR_3 *trans* to Cl, ~ 4000 Hz; III, PR_3 *trans* to CH_3 or H, ~ 1800–2000 Hz. Since, in our asymmetric complexes, we observe (Table 1) ^1J(PtP) to lie in the range

* In our preliminary report [6], we erroneously reported a single Pt–CH_3 resonance for this compound.



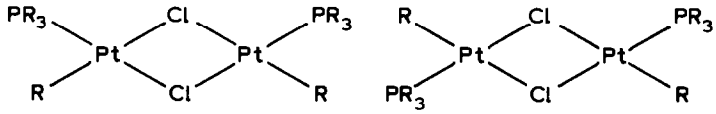
3500–4325 Hz, isomer III can be eliminated. Moreover, the crystal structure of $PtMeCl(PEt_3)(AsPh_3)$ has recently been determined [17] and shown to be of the type I, with PEt_3 and $AsPh_3$ *trans* to each other. The large value of ^1J(PtP), 3736 Hz (cf. 3738 Hz, ref. 17) is consistent with a low *trans* influence [16] for $AsPh_3$, producing a relatively short strong Pt–P bond. By comparison, in *trans*-$[PtMeCl(PMe_2Ph)_2]$, ^1J(PtP) is 2896 Hz (Table 1), consistent with the phosphine having a much larger influence than $AsPh_3$. The complex $[PtMeCl(PMe_2Ph)(AsPh_3)]$ prepared either from the reaction of *cis*-$[PtMe_2(PMe_2Ph)(AsPh_3)]$ with HCl, or by the bridge cleavage reaction of $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with $AsPh_3$ (see later) gave a two-line ^{31}P NMR spectrum, each showing ^{195}Pt satellites with ^1J(PtP) values of 3797 and 4317 Hz. Similarly, the ^1H NMR spectra of samples from the two methods of preparation displayed two Pt–Me resonances with different ^2J(PtH) values. The resonance of higher field showed a ^2J(PtH) value of 80 Hz and represented ca. 80% of the mixture and from its intensity corresponded to the ^{31}P resonance at lower field with ^1J(PtP) 3797 Hz. In view of the similarity of this latter value to the ^1J(PtP) value of 3736 Hz observed in $PtMeCl(PEt_3)(AsPh_3)$, we assign structure I to the more abundant product. The remaining ^{31}P resonance at higher field with ^1J(PtP) of 4317 Hz is coupled with lower field resonance in the ^1H NMR spectrum with ^2J(PtH) of 66.8 Hz; on the basis of these parameters, the isomer present in about 20% abundance must be assigned structure II, i.e. PMe_2Ph *trans* to Cl. Similarly, $PtHCl(PEt_3)(AsPh_3)$ with ^1J(PtP) 3531 Hz is assigned structure I; on the other hand, for $PtMeCl(PMe_2Ph)py$ (for preparation, see later) the ^1J(PtP) value of 4147 Hz does not allow an easy distinction to be made between structures I and II.

The alternative route to the methylchloro complexes, $PtMeCl(PR_3)L$, would involve the cleavage by L of dinuclear halogen-bridged Pt^{II} complexes $[Pt_2(\mu\text{-}Cl)_2R_2(PR_3)_2]$ for the case of $R = CH_3$. The comparable species for R = aryl or aroyl have been prepared very conveniently by Eaborn et al. [5] by the reactions of $[PtCl_2(C_2H_4)(PR_3)]$ or $[PtCl_2(CO)(PR_3)]$ with Me_3SnR. However, this method failed when it was employed in an attempt to make the methyl analogues, $[Pt_2(\mu\text{-}Cl)_2Me_2(PR_3)_2]$, by the comparable reactions with Me_4Sn. Puddephatt and Thompson [13] have prepared $[Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$ (IV) as a brown crystalline solid in 34% yield by the reaction of excess tetramethyltin with $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ in dichloromethane. We have carried out the same reaction in the hope of isolating IV, pure and in good yield, as a key intermediate for the synthesis of mixed ligand methylchloro Pt^{II} compounds. We find, however, that the reaction proceeds according to the equation:

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2] + \text{excess } Me_4Sn \rightarrow$$

$$\textit{cis}\text{- and } \textit{trans}\text{-IV} + \textit{trans}\text{-}PtCl_2(PMe_2Ph)_2 + Pt + Me_3SnCl$$

Reduction to Pt metal obviously occurs and is the cause of the reported brown colour of IV. Passage of the reaction mixture over a Florisil column gives a pale yellow solution from which after several recrystallizations a mixture of ca. 95% of IV (*cis* and *trans* isomers) and ca. 5% of *trans*-$PtCl_2(PMe_2Ph)_2$ is obtained. The existence of *cis* and *trans* isomers (i.e. V and VI) for such dinuclear complexes has been reported previously.



(V) (VI)

Thus, for R = aryl or aroyl, the complexes have been shown to exist as a mixture of *cis* and *trans* isomers [5,14,15]. For the methyl complex, IV, Puddephatt and Thompson [13] assigned a *cis* geometry in solution, based on dipole moment measurements; the NMR parameters which they reported indicated the presence of only one isomer, but did not distinguish between *cis* and *trans* geometries. The NMR spectra of our carefully purified IV can best be interpreted in terms of a mixture of *cis* and *trans* isomers. Its ^{31}P NMR spectrum displayed two Pt–P resonances with ^{195}Pt satellites (Fig. 2); we assign the resonance at δ −11.2 ppm with the larger ^1J(Pt–P) (5003 Hz) to the *cis* isomer and the other resonance at lower field with the smaller J(PtP) (4934 Hz) to the *trans* isomer. This assignment is consistent with previous assignments for $[Pt_2Cl_2(\mu\text{-}SR)_2(PR'_3)_2]$ [18], although

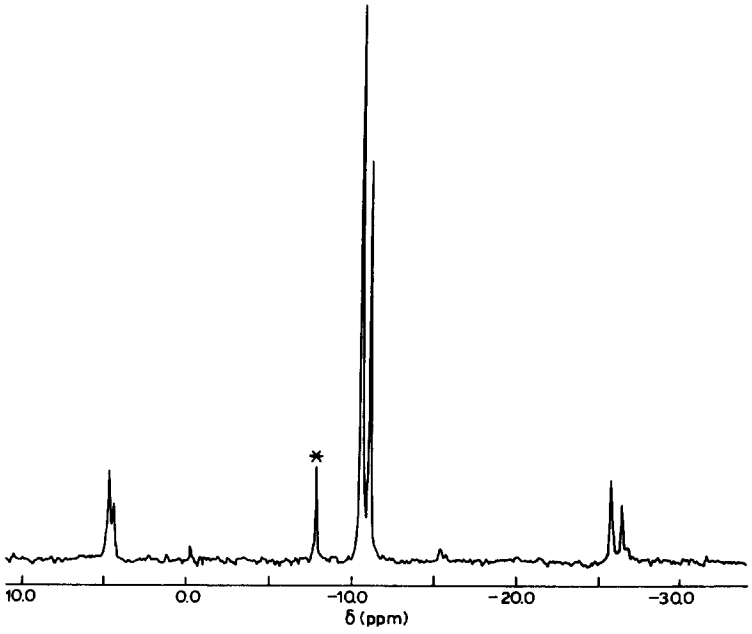


Fig. 2. $^{31}P\{^1H\}$ NMR of $Me_2Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$.

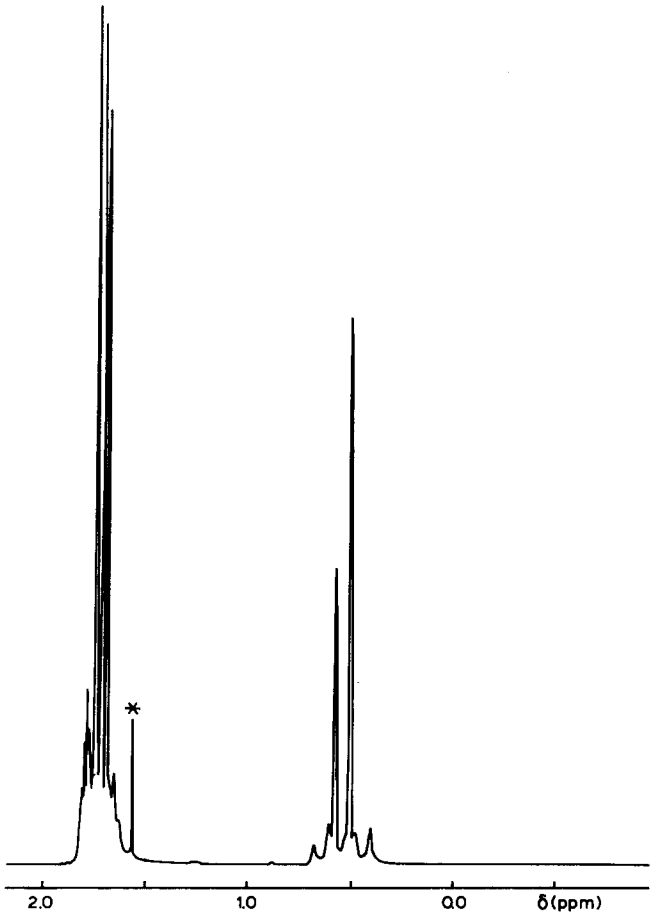


Fig. 3. ^{1}H NMR of $Me_2Pt_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$.

Eaborn et al. [5] assigned the larger value to $^{1}J(PtP)$ for $[Pt_2R_2(PR_3)_2(\mu\text{-}Cl)_2]$ (R = aryl or aroyl) to the *trans* isomer. The ^{1}H and ^{13}C NMR spectra each displayed two sets of resonances, each with ^{195}Pt satellites, for each of the Pt–Me and P–Me groups. The Pt–Me proton resonances, each coupled to ^{31}P, for the *cis* and *trans* isomers which on the basis of the ^{31}P NMR spectra are present in 3/2 ratio, can be identified from their relative intensities. Thus, a doublet appearing at lower field with $^{2}J(PtH)$ 76.7 Hz is assigned to the *trans* isomer while that at higher field with $^{2}J(PtH)$ 78.9 Hz must be due to the *cis* isomer (Fig. 3). The $^{3}J(PH)$ values for the two isomers are almost identical (Table 1). The ^{13}C NMR spectrum displayed two signals for the Pt–Me group with almost identical values for $^{1}J(PtC)$ of 703 ± 1 Hz, again consistent with the presence of both isomers. Again, this contrasts with the work of Puddephatt and Thompson who reported ^{13}C NMR data consistent with a single isomer.

As already indicated, we examined some cleavage reactions of $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with donor ligands, as a synthetic route to the unsymmetrical methylchloro Pt^{II} derivatives. Its reaction with triphenylarsine gave a mixture of

isomers I and II in a 4/1 ratio as discussed earlier. With dimethylphenylphosphine, only *trans*-$PtMeCl(PMe_2Ph)_2$ was obtained (i.e. isomer I); it seems likely that, as reported by Puddephatt and Thompson [13], a mixture of *cis* and *trans* (i.e. I and II) is initially formed but that *cis* to *trans* isomerization then occurs. With pyridine, only a single product is obtained as demonstrated by the single resonances for the Pt–Me and Pt–P observed in the ^1H and ^{31}P NMR spectra respectively. The relatively large value of J(PtP) 4147 Hz suggests structure I or II. A comparison of ^1J(PtP) for *trans*-$[PtCl_2(PR_3)_2]$ [19] as against *trans*-$[PtCl_2(PR_3)py]$ [20], shows that substitution of PR_3 by pyridine increases ^1J(PtP) significantly; this can be attributed to an increase in the covalency of the Pt–P bond due to the greater electronegativity of nitrogen. Hence, for $[PtMeCl(PMe_2Ph)py]$, on the basis of ^1J(PtP) value, we assign structure I (*trans*). Moreover, the magnitude of ^2J(PtH) (78.2 Hz) from the ^1H NMR spectrum indicates that the CH_3 group is *trans* to halogen, again consistent with structure I.

Since mono- and di-methyl derivatives of Pt^{II} with mixed ligands could be prepared, it seemed worthwhile to determine whether, without significant disproportionation to the symmetrical complexes, the chemistry could be carried one step further. We, therefore, investigated the reactions of $PtMe_2LL'$ with an activated acetylene, dimethylacetylene dicarboxylate (DMA). We have previously reported [21] that rapid reaction of hexafluorobut-2-yne occurs with *cis*-$PtMe_2L_2$, but that a mixture of products is obtained depending on the nature of L. For $L = AsMe_2Ph$, the principal product is that formed through insertion into only one Pt–Me bond (i.e. $PtMe(C_4F_6Me)L_2$), together with a small amount of the double insertion product (i.e. $Pt(C_4F_6Me)_2L_2$ alone, except at high acetylene concentrations when the Pt^0 complex, $Pt(C_4F_6)L_2$, was obtained). With such ligand dependence, and with two Pt–Me possible reaction sites, the system is complex and hence a good test of the tendency towards disproportionation.

The reaction of DMA with *cis*-$[PtMe_2(PPh_3)(AsPh_3)]$ in benzene yielded only one product; the ^1H NMR spectrum displayed a single peak at 1.39 ppm (due to alkenyl CH_3), two resonances at 2.99 and 3.24 ppm (due to $COOCH_3$) and a multiplet at 7.1–7.5 ppm (due to phenyl protons). The $^{31}P\{^1H\}$ spectrum revealed a single peak at 16.6 ppm with ^1J(PtP) 3683 Hz. These data, along with the analytical results (see Table 2) are consistent only with the formulation *trans*-$[Pt\{C(COOCH_3)=C(COOOH_3)CH_3\}_2(PPh_3)(AsPh_3)]$, where the DMA has inserted into both Pt–Me bonds and *cis* to *trans* isomerization has occurred. The *trans* geometry is indicated not only by the observation of a single magnetic environment for the two alkenyl groups but also by the magnitude of ^1J(PtP) which is consistent with phosphorous *trans* to $AsPh_3$ but not *trans* to σ-carbon. However, the NMR data are not adequate to distinguish between *cis* and *trans* alkenyl products, other than to establish that both alkenyl groups have the same geometry about the C=C bond.

The reaction of DMA with *cis*-$[PtMe_2(PEt_3)(AsPh_3)]$ was more complex; examination by ^1H NMR spectroscopy of the product obtained as described in the Experimental showed it to contain a number of compounds. The major component was isolated after several further recrystallizations from benzene/hexane, as a white solid whose ^1H NMR spectrum showed two peaks at 3.22 and 3.44 ppm (due to $COOCH_3$) and a singlet at 1.82 ppm (due to alkenyl CCH_3). In addition, multiplets at 1.08 and 2.06 ppm arise from CH_2 and CH_3 protons respectively of triethylphos-

phine. The $^{31}P\{^1H\}$ spectrum reveals a singlet at 6.6 ppm with $^1J(PtP)$ 3452 Hz. Again, therefore, these data are consistent only with the formulation *trans*-$[Pt\{(COOCH_3)C{=}C(COOCH_3)CH_3\}_2(PEt_3)(AsPh_3)]$ but with the stereochemistry of both alkenyl groups being either *cis* or *trans*.

The use of diethylacetylene dicarboxylate (DEA) with *cis*-$[PtMe_2(PPh_3)(AsPh_3)]$ also yielded only one product. The ^1H NMR spectrum displayed two triplets at 0.49 and 0.94 ppm (due to $COOCH_2CH_3$), two singlets at 1.40 and 1.57 ppm (due to alkenyl CH_3), a multiplet at 3.58 ppm (due to $COOCH_2CH_3$) and a multiplet at 7.2–7.6 ppm (due to phenyl protons). The $^{31}P\{^1H\}$ spectrum revealed a single peak at 17.0 ppm with $^1J(PtP)$ 3699 Hz. Similar to the use of DMA, these results are only consistent with the formulation *trans*-$[Pt\{C(COOC_2H_5){=}C(COOC_2H_5)CH_3\}_2(PPh_3)(AsPh_3)]$, where the DEA has inserted into both Pt–Me bonds and *cis* to *trans* isomerization has occurred.

These reactions show several interesting features. Firstly, the mixed ligand environment about the platinum centre appears to have had little qualitative effect on the rate of insertion; in both these cases and for the symmetrical compounds, $PtMe_2L_2$, [21], insertion into both Pt–CH_3 bonds is rapid. Secondly, there is an interesting contrast with the behaviour of *trans*-$PtH_2(PCy_3)_2$ (Cy = cyclohexyl) where insertion with DMA occurs into only one Pt–H bond [22]. Because of the bulk of the PCy_3 ligand, this has been attributed entirely to steric effects. The present rapid insertion of DMA into two Pt–CH_3 bonds with the smaller $AsPh_3$ and PR_3 ligands seems to be consistent with this. Thirdly, it is known that, with acetylene insertion into P–H bonds, the stereochemistry of the resulting alkenyl group may be indicative of the type of insertion mechanism involved [23]. It will, therefore, be worth investigating these reactions with other acetylenes such as C_4F_6 or $C_6H_5C{\equiv}CCF_3$ etc., where the NMR parameters of the products can help determine the alkenyl stereochemistry and perhaps provide some mechanistic insight.

Finally, this paper clearly establishes that Pt^{II} mixed ligand complexes of considerable stability can be readily prepared and that they can exhibit an extensive chemistry unimpaired by any tendency to disproportionate.

Experimental

The following chemicals were obtained commercially and were used without further purification; all tertiary phosphines and arsines from Strem Chemicals Inc., methyllithium and dimethylacetylene dicarboxylate from Aldrich Chemical Co., and potassium tetrachloroplatinate(II) and platinum(II) chloride from Johnson Matthey and Mallory.

All reactions were carried out in spectrograde solvents under a nitrogen atmosphere. The chloro-bridged dimers $(PR_3)_2Pt_2Cl_2(\mu\text{-}Cl)_2$ and $(AsMe_3)_2Pt_2Cl_2(\mu\text{-}Cl)_2$ were prepared by the literature methods [24,25]. As described previously [6], the bridge-cleavage reactions of these dimers with L (L = phosphine, or $AsPh_3$) in dichloromethane gave the pale yellow products *trans*-$[PtCl_2LL']$ from which the *cis* isomers could be prepared by adding catalytic amounts of L; this isomerization was usually complete 2–3 h to give 95–100% yields. For all of these products, the ^{31}P NMR spectra showed that no observable disproportionation had occurred to PtL_2Cl_2 and PtL'_2Cl_2.

The ^{1}H and ^{31}P NMR spectra were recorded on Bruker WP-60 and WH-400 spectrometers operating in Fourier transform mode at 60 and 400 MHz for protons and 24.3 and 161.98 MHz for ^{31}P respectively. The ^{13}C NMR spectra were recorded on a Bruker WH-400 spectrometer. Chemical shifts are relative to external TMS for ^{1}H and ^{13}C and 85% H_3PO_4 for ^{31}P, with more positive shifts representing deshielding. Microanalyses were performed by Guelph Chemical Laboratories; melting points were determined by the capillary method and are uncorrected.

Preparation of cis-Pt(CH_3)$_2$(PEt_3)($AsPh_3$)

To an ethereal suspension of *cis*-$PtCl_2(PEt_3)(AsPh_3)$ (841 mg in ca. 30 ml), excess of methyllithium in ether was added slowly under a nitrogen atmosphere with stirring. After 30 min of stirring, the reaction mixture became clear and was hydrolyzed with a saturated solution of ammonium chloride at 5°C. The organic layer was separated and washed with water. The aqueous layer was extracted three times with 15 ml portions of diethyl ether, which were then added to the original ether layer and the total ether volume was dried over anhydrous $MgSO_4$. On evaporation, colourless crystals were obtained which were recrystallized from benzene/hexane (yield 618 mg, 78%). Similarly, other dimethyl compounds of the type *cis*[$PtMe_2LL'$] were prepared, and pertinent analytical and other data are given in Table 2.

Preparation of [PtMeCl(PMe_2Ph)($AsPh_3$)]

To the diethyl ether/benzene (1/1 v/v) solution of *cis*-[$PtMe_2(PMe_2Ph)(AsPh_3)$] (163 mg), a solution of hydrogen chloride in ether (0.2 ml, 1.23 *N*) was added dropwise with vigorous stirring. The desired product was precipitated, and after a further 15 min of stirring, the solvent was evaporated to give a white solid which was recrystallized from benzene/hexane mixture (108 mg, 64% yield).

Other compounds of the type [$PtMeCl(PR_3)(AsPh_3)$] were prepared similarly, with relevant characterization data given in Table 2.

Preparation of [PtHCl(PEt_3)($AsPh_3$)]

To a stirred suspension of *cis*-[$PtCl_2(PEt_3)(AsPh_3)$] (220 mg) in THF (ca. 5 ml) at 0°C was added dropwise under a nitrogen atmosphere a suspension of sodium borohydride (28 mg) in anhydrous ethanol (5 ml). After the addition was complete, the yellow-brown reaction mixture was stirred at room temperature for 30 min and then slightly acidified with dilute HCl (0.5 ml, 11.6 *M* HCl in 5 ml ethanol). After 1 h of stirring, the solvent was evaporated under vacuum and the residue extracted with benzene (5 ml × 3). The volume of the benzene extract was reduced to 1 ml and hexane (ca. 3 ml) was added, the precipitate out a pale-yellow compound which was washed with hexane and dried under vacuum (yield 150 mg, 71%).

Preparation of [Pt_2Me_2(μ-Cl)$_2$(PMe_2Ph)$_2$]

Excess tetramethyltin (0.5 ml) was added to a dichloromethane solution (ca. 20 ml) of $Pt_2Cl_2(\mu\text{-}Cl)_2(PtMe_2Ph)_2$ (0.55 g) and the mixture was stirred for about 48 h at room temperature (reaction is incomplete after 20 h). Solvent was evaporated from the resulting brown solution, and the residue was washed with portions of diethyl ether (5 ml × 3) and then dried. It was re-dissolved in dichloromethane (ca. 10 ml), treated with activated charcoal and filtered, following which the solvent was

TABLE 2

PHYSICAL AND ANALYTICAL DATA OF MIXED LIGAND COMPLEXES OF PLATINUM(II)

Complex	Solvent of recrystallization (Colour)	M.p. (°C)	Anal. (Found (calc)(%))	
			C	H
$[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	Benzene/hexane (cream)	142–143	28.03 (28.17)	3.87 (3.68)
$[PtMe_2(PEt_3)(AsPh_3)]$	Benzene/hexane (colourless)	147–149	48.22 (48.08)	5.50 (5.59)
$[PtMe_2(PMe_2Ph)(AsPh_3)]$	Benzene/hexane (white)	170–173 [a]	50.93 (50.23)	4.99 (4.82)
$[PtMe_2(P\text{-}p\text{-}tol_3)(AsPh_3)]$	Benzene/hexane (white)	200–204 [a]	58.61 (58.92)	5.75 (5.06)
$[PtMe_2(PPh_3)(AsPh_3)]$	Chloroform/ether (white)	190–200 [a]	56.97 (57.50)	5.03 (4.57)
$[PtMe_2(PPh_3)(AsMe_3)]$	Benzene/hexane (white)	146–149	45.82 (45.47)	5.22 (4.98)
$[PtMe_2(P\text{-}p\text{-}tol_3)(AsMe_3)]$	Benzene/hexane (white)	170–172 [a]	48.10 (48.08)	5.72 (5.59)
$[PtMeCl(PEt_3)(AsPh_3)]$	Chloroform/hexane (white)	126–128	44.74 (44.82)	4.97 (4.96)
$[PtMeCl(PMe_2Ph)(AsPh_3)]$	Chloroform/hexane (white)	166–170	46.72 (47.00)	4.04 (4.24)
$[PtHCl(PEt_3)(AsPh_3)]$	Benzene/hexane (pale yellow)	122–123 [a]	44.38 (43.94)	4.98 (4.76)
$[Pt\{C(COOMe)=C(COOMe)Me\}_2(PEt_3)(AsPh)_3)]$	Benzene/hexane (white)	145–149	49.12 (48.88)	5.22 (5.18)
$[Pt\{C(COOMe)=C(COOMe)Me\}_2(PPh_3)(AsPh_3)]$	Chloroform/hexane (white)	137–140	55.68 (55.71)	4.37 (4.49)
$[Pt\{C(COOEt)=C(COOEt)Me\}_2(PPh_3)(AsPh_3)]$	Chloroform/hexane (white)	130–134	57.41 (57.20)	5.19 (4.98)

[a] Decomposes with or without melting.

evaporated off, the residue was dissolved in benzene and the benzene solution passed through a Florisil column. The resulting pale-yellow benzene solution was reduced to 3 ml and hexane was added to precipitate pale-yellow crystals which on repeated crystallizations by this same procedure gave $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ in about 95% purity. Yield 23%. ^1H and ^{31}P NMR spectroscopic and analytical data are given in Tables 1 and 2, respectively. ^{13}C NMR in $CDCl_3$: δ (PtMe) -13.1 (^1J(PtC) 704 Hz) and -14.3 (^1J(PtC) 702 Hz); δ(PMe) 13.4(d) (^1J(PC) 43, ^2J(PtC) 55 Hz), and 13.4(d), ^1J(PC) 42.6, ^2J(PtC) 55 Hz).

Bridge cleavage reactions of $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$

(i) With $AsPh_3$. A $CDCl_3$ solution (1 ml) of triphenylarsine (64 mg) was added dropwise to a stirred solution (2 ml) of $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (81 mg). The solution was stirred at room temperature for 30 min and then examined spectroscopically. The reaction with PMe_2Ph was studied similarly.

(ii) Reaction with pyridine. Excess pyridine (0.1 ml) was added to a solution of $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (42 mg) in benzene (4 ml) and the solution was stirred

at room temperature for 30 min. The solvent was removed under vacuum leaving a pasty mass which was recrystallized from benzene/hexane to give white crystals (yield 25 mg).

Reactions with dimethylacetylene dicarboxylate (DMA)

Typically, an excess of DMA (3-fold) in benzene (2 ml) was added dropwise to a benzene solution (5 ml) of *cis*-[$PtMe_2(PPh_3)(AsPh_3)$] (75 mg). The reaction mixture was stirred at room temperature overnight. Hexane was added to precipitate a white solid which was recrystallized from chloroform/hexane to give *trans*-[{C-($COOCH_3$)=C($COOCH_3$)CH_3}$_2$Pt(PPh_3)($AsPh_3$)] (55 mg, 51% yield). Similarly, the reaction of *cis*-[$PtMe_2(PEt_3)(AsPh_3)$] with DMA was carried out.

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