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Interaction of $[Pt_2Cl_4(PPr^n_3)_2]$ with some Simple Organic Molecules

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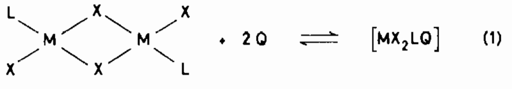
The reversible fission of the chloro-bridged complex $[Pt_2Cl_4(PPr^n_3)_2]$ by carbon monoxide, ethylene, phenylacetylene, methanol, water, tetrahydrofuran, phenol, acetone, cyclopentanone, benzophenone, acetaldehyde, benzaldehyde, acrolein, chloral, chloral hydrate, and methyl acetate is investigated by low-temperature ^{31}P n.m.r. spectroscopy.

Introduction

Halo-bridged complexes of the type $[M_2X_4L_2]$ (*1*) M = Pd or Pt; X = Cl, Br or I; L = PR_3, AsR_3, SR_2, Cl^- *etc.* are well known and much used in platinum and palladium chemistry [1–3]. One useful function is in the synthesis of mononuclear complexes of the type $[MX_2LQ]$ by the so-called bridge splitting reaction.



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With Q = amine the product is invariably of *trans*-configuration [4] but with Q = CO or olefin only *cis*-complexes, *cis*-$[PtX_2LQ]$ have been isolated [5, 6]. Halo-bridged complexes, $[M_2X_4L_2]$, have also been used as starting materials for the synthesis of various carbene–metal complexes [7–9].

In phosphine complexes $[M_2X_4(PR_3)_2]_2$ the greatly differing *trans*-influences of the tertiary phosphine- and the halo-ligands causes the bridging system (MX_2M) to be asymmetric. Thus with $[Pt_2Cl_4(PPr^n_3)_2]$ the Pt–Cl bond lengths are 242.5 pm (*trans* to phosphorus), 231.5 pm (bridging and *trans* to chlorine) and 227.9 pm (terminal) [10]. Because of the much greater *trans*-effect of tertiary phosphine over halide one would expect substitution (bridge splitting) in the *trans*-position to phosphorus to occur much more rapidly than *trans* to halide. Using ^{31}P and ^1H n.m.r. spectroscopy we have shown that molecules (Q) such as allyl alcohol, vinyl acetate, allyl acetate, etc. do indeed cause rapid bridge fission even at –90 °C to give *trans*-$[MX_2(PR_3)Q]$ and that in the bridge splitting reaction (1) the lower the temperature the more the R.H.S. is favoured [11, 12]. Thus in a typical experiment with Q = allyl alcohol conversion to *trans*-$[PtCl_2(PPr^n_3)(CH_2{=}CHCH_2OH)]$ was almost complete at –90 °C with the allyl alcohol ligand being bonded either through the double bond (major product) or the hydroxyl oxygen (minor product), whereas at 0 °C reversion back to the bridged complex $[Pt_2Cl_4(PPr^n_3)_2]$ was almost complete. Formation of bridge-split complexes of the type *cis*-$[MX_2LQ]$ occurs only slowly (hours or days) and reversibly even at ambient temperature.

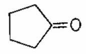
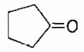
The observation that allyl alcohol and methanol can give O-bonded complexes with platinum(II) at low temperatures [11] prompted us to study bridge-splitting equilibria of type (1) with a variety of oxygen-donor and other ligands. The choice of a phosphine complex, $[Pt_2Cl_4(PPr^n_3)_2]$, enabled the reactions to be conveniently followed by ^{31}P n.m.r. and the presence of the ^{195}Pt nucleus is of great assistance in identifying the species present in solution.

Experimental

$[Pt_2Cl_4(PPr^n_3)_2]$ was prepared by the method of ref. [13] using *o*-dichlorobenzene as solvent, and purified by successive recrystallisations from hot methanol, benzene, and acetone. Aldehydes, ketones, and tetrahdrofuran were freshly distilled before use, if necessary after preliminary drying.

^{31}P n.m.r. spectra were recorded on a JEOL FX100 n.m.r. spectrometer with broadband proton decoupling. A ^2D lock was provided either by the solvent in the case of $CDCl_3$ or by a capilliary containing $(CD_3)_2CO$ within the n.m.r. tube. Ratios of *trans*-$[PtCl_2(PPr^n_3)Q]$ to $[Pt_2Cl_4(PPr^n_3)_2]$ were measured by integration and in most cases the digital resolution was 0.61 Hz/channel. Care was taken in choosing pulse widths and repetition times to ensure that different spin–lattice relaxation times for the two species did not affect the integral; *ca.* 43° pulses at 1.68 s intervals were found to be satisfactory.

TABLE I. ^{31}P N.M.R. Parameters of *trans*-[$PtCl_2Q(PPr^n_3)$] Formed *in situ*.

Ligand (Q)	Conditions[a]	T/K	δ_P[b]	$^1J(PtP)$	Fraction of [$Pt_2Cl_4(PPr^n_3)_2$] converted to [$PtCl_2(PPr^n_3)Q$] for 1 mol Q per Pt atom
CO	Saturated in $CDCl_3$	243	5.7	3410	
C_2H_4	Saturated in $CDCl_3$	243	5.7	3408	
PhC≡CH	1.1*M* in $CDCl_3$[c]	213	6.1	3589	0.004
CH_3OH	Neat	243	–4.0	3976	0.3
CH_3OH	25% v/v in $CDCl_3$	243	–4.3	3927	
THF	Neat	243	–2.4	4086	0.03
$(CH_3)_2CO$	Neat	243	–4.8	4012	0.01
$(CH_3)_2CO$	25% v/v in $CDCl_3$	243	–4.7	3982	
	Neat	243	–4.6	4010	0.02
	25% v/v in $CDCl_3$	243	–4.9	3968	
Ph_2CO	1.6*M* in $CDCl_3$[d]	243	–3.9	[e]	<0.001
CH_3CHO	Neat	243	–2.7	4002	$\sim 10^{-3}$ [f]
PhCHO	Neat	243	–2.0	3984	0.002
$CH_2=CHCHO$	5*M* in $CDCl_3$	213	–1.8	3934	$\sim 10^{-3}$ [f]
CCl_3CHO[g]	60% v/v in $CDCl_3$	213	4.1	2803	$\sim 10^{-4}$
$CCl_3CH(OH)_2$[g]	Saturated in $CDCl_3$	223	18.4	3743	$\sim 10^{-3}$ [f]

[a] Total platinum concentration was 0.05 *M* except for [c] 0.1 *M* and [d] 0.07 *M*. [b] In p.p.m. to high frequency of H_3PO_4. [e] ^{195}Pt satellites not visible. [f] Not known accurately owing to precipitation of [$Pt_2Cl_4(PPr^n_3)_2$]. [g] Nature of species formed unknown (see text).

Results and Discussion

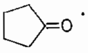
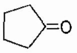
Table I lists ^{31}P n.m.r. data for those cases where the spectra indicated that some reaction had taken place. In all cases the products showed simple 1:4:1 triplets in the ^{31}P n.m.r. spectra and there was no indication of the formation of bridged species (a dimeric platinum complex would be expected to show long-range ^{31}P–^{195}Pt coupling and, S/N permitting, ^{195}Pt–^{195}Pt coupling) [14]. A general phenomenon was the broadening of the spectral lines above *ca.* 260 K owing to exchange with [$Pt_2Cl_4(PPr^n_3)_2$]. Lowering the temperature always increased the proportion of product in equilibrium with the bridged complex but in some cases this caused precipitation of [$Pt_2Cl_4(PPr^n_3)_2$] from the solution. Where possible we have chosen, somewhat arbitrarily, a temperature of 243 K at which to present data but in some of the less favourable cases we had to deviate from this temperature in order to obtain the best compromise between the position of equilibrium and solubility of the bridged complex.

On the basis of the position of equilibrium in equation (2), carbon monoxide and ethylene are much the strongest ligands, being the only ones for which the equilibrium lies well to the right. Indeed, in both cases isomerisation slowly occurred to give isolable *cis*-complexes previously reported [6]. In keeping with this, the values of $^1J(PtP)$ for *trans*-[$PtCl_2(PPr^n_3)_2Q$], Q = CO or C_2H_4, are substantially lower than for [$Pt_2Cl_4(PPr^n_3)_2$] (3765 Hz in $CDCl_3$ at 243 K) indicating that these two ligands have a higher *trans*-influence than bridging chloride. Phenylacetylene is evidently a much less effective ligand, and no corresponding *cis*-complex was observed in the spectra.

$$[Pt_2Cl_4(PPr^n_3)_2] + 2Q \rightleftharpoons 2\ trans\text{-}[PtCl_2(PPr^n_3)Q] \qquad (2)$$

The oxygen-donor ligands differ from the three discussed above in having very high values of $^1J(PtP)$ (3927–4086 Hz) and much lower values of δ_P. In all cases the equilibrium lies to the left, with methanol by far the strongest ligand (except for water, see below). A phenomenon which puzzled us at first was the observation of *two* species in addition to [$Pt_2Cl_4(PPr^n_3)_2$] in the ^{31}P n.m.r. spectrum when the ligand was acetone, cyclopentanone, acetaldehyde, benzaldehyde, acrolein or tetrahydrofuran. The possibility of an enol-form being present in the case of the C=O derivatives is discounted since benzaldehyde showed two species. However, we found that drying the solvent (ligand) reduced the proportion of the species at lower δ_P while addition of water greatly increased it. A methanol solution

TABLE II. ^{31}P N.M.R. Parameters of *trans*-$[PtCl_2(H_2O)(PPr^n_3)]$ in Various Media.

Medium	T/K	δ_P[a]	$^1J(PtP)$
CH_3OH	243	–6.3	3926
THF	243	–6.2	4044
$(CH_3)_2CO$	243	–5.7	4020
25% $(CH_3)_2CO$ in $CDCl_3$ (v/v)	243	–5.7	3992
 ·	243	–5.4	4031
25%  in $CDCl_3$	243	–5.7	3986
CH_3CHO	243	–5.0	4006
PhCHO	243	–4.3	3997
5 *M* $CH_2{=}CHCHO$ in $CDCl_3$	213	–4.9	3946
CH_3COOCH_3	243	–5.4	4043

[a] In p.p.m. to high frequency of H_3PO_4.

of $[Pt_2Cl_4(PPr^n_3)_2]$ showed initially only one product, presumably *trans*-$[PtCl_2(PPr^n_3)(MeOH)]$, but addition of water gave a second species at lower frequency. These observations suggested that the species with lower δ_P was an aquo complex, *trans*-$[PtCl_2(PPr^n_3)(H_2O)]$. An alternative explanation for the aldehydes and ketones was that the second species contained a coordinated hemiacetal formed by attack of OH^- at carbon, but this was eliminated by the observation that mixtures of acetone and cyclopentanone, and cyclopentanone and methanol (with water added where necessary) gave only three species. Addition of water alone to a $CDCl_3$ solution of $[Pt_2Cl_4(PPr^n_3)_2]$ gave no aquo complex in the ^{31}P n.m.r. spectrum, no doubt owing to the low solubility of water in this medium, but the position of equilibrium in equation (2) for Q = H_2O was determined by adding known amounts of water to methanol and acetone solutions of $[Pt_2Cl_4(PPr^n_3)_2]$ and evaluating the ratio $[PtCl_2(PPr^n_3)(H_2O)]:[PtCl_2(PPr^n_3)Q]$ (Q = MeOH or Me_2CO). This showed that approximately half the amount of $[Pt_2Cl_4(PPr^n_3)_2]$ is converted to the aquo complex for 1 mol H_2O per platinum atom, *i.e.* water is a somewhat better ligand than methanol (see Table I).

Table II gives ^{31}P n.m.r. data for the aquo species in different media. It can be seen that although there is not much variation in the ^{31}P chemical shift, the values of $^1J(PtP)$ span a wide range. This is not unreasonable since the values of $^1J(PtP)$ for the species *trans*-$[PtCl_2(PPr^n_3)Q]$, Q = CH_3OH, $(CH_3)_2CO$ or cyclopentanone, are also medium-dependent (see Table I), and the coordinated water molecule might be expected to interact strongly with these polar solvents. Even for *trans*-$[PtCl_2(PBu^n_3)_2]$, which has no dipole moment and in which solvent-ligand interactions are probably less strong than with H_2O, $^1J(PtP)$ values span a range of 84 Hz in different solvents [15].

For the ketones and aldehydes, the amount of *trans*-$[PtCl_2(PPr^n_3)Q]$ present at equilibrium decreases in the order cyclopentanone > acetone >> acetaldehyde, benzaldehyde >> benzophenone. This order might be anticipated since electron-withdrawing substituents should decrease the availability of the oxygen lone pairs. We also attempted to evaluate the coordinating ability of esters by treating $[Pt_2Cl_4(PPr^n_3)_2]$ with methyl acetate, both neat and as a mixture with $CDCl_3$. Unfortunately the bridged complex was so insoluble in these media (and also in ethyl acetate) at low temperatures that the experiment was rather unsatisfactory. We observed lines due to $[Pt_2Cl_4(PPr^n_3)_2]$ and *trans*-$[PtCl_2(PPr^n_3)(H_2O)]$* in the ^{31}P spectra; another peak at –3.4 p.p.m. (in neat methyl acetate at 243 K) was observed and is presumably due to *trans*-$[PtCl_2(PPr^n_3)(CH_3COOCH_3)]$ but the concentration of this species was too low for ^{195}Pt satellites to be detected. We also investigated the reaction of $[Pt_2Cl_4(PPr^n_3)_2]$ with phenol in $CDCl_3$. No ^{31}P features were observed apart from those of the bridged complex, from which we can estimate the fraction of $[PtCl_2(PPr^n_3)(PhOH)]$ generated per mol phenol at 243 K as $<10^{-4}$.

The molecule $CH_2{=}CHCHO$ (acrolein) has two possible coordination sites. The n.m.r. parameters of the bridge-split product *trans*-$[PtCl_2(PPr^n_3)(CH_2{=}CHCHO)]$ and their similarity to those of the aquo species which was also observed (Tables I and II) strongly suggests that the molecule preferentially coordinates via oxygen. However there was also a weak peak at 10.5 p.p.m. which probably relates to the π-bonded form; unfortunately we could not detect its ^{195}Pt satellites (the solubility of $[Pt_2Cl_4(PPr^n_3)_2]$ is rather low in this medium).

Finally, two of the results in Table I seemed anomalous. The value of $^1J(PtP)$ for the product with chloral, CCl_3CHO, is abnormally low and suggests a ligand of fairly high *trans*-influence *trans* to the phosphine. We think it most unlikely that this species is *trans*-$[PtCl_2(PPr^n_3)(CCl_3CHO)]$ and suggest that some other reaction has taken place, *e.g.* an oxidative addition {a Pt(IV) complex would also give a low value of $^1J(PtP)$}. We also found two other peaks in the ^{31}P n.m.r. spectrum, one at 5.8 p.p.m. having about a third of the intensity of the main product, and another very weak line at 14.0 p.p.m. (in neither case were ^{195}Pt satellites identified). The same applies to the product with chloral hydrate, $CCl_3CH(OH)_2$, where the value of $^1J(PtP)$ is somewhat lower than in the other O-bonded complexes and the value of δ_P is abnormally high. A weak peak at 14.0 p.p.m. was observed in this spectrum also.

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*In a previous paper [12] we wrongly identified this species as *trans*-$[PtCl_2(PPr^n_3)(CH_3COOCH_3)]$.

Stable complexes containing neutral oxygen donor ligands are rare in platinum chemistry. The few such complexes which have been isolated are mostly cationic, *e.g.* *trans*-[Pt(CH_3)(acetone)(PMe_2Ph)$_2$]-[PF_6] [16], *trans*-[PtH(acetone)(PMe_2Ph)$_2$] [PF_6] [17], *trans*-[PtH(CH_3OH)(PCy_3)$_2$] [18], and [Pt{(F_3C)CHC(CF_3)=C(CH_3)CH_2OCH_3}(PEt_3)$_2$]-[PF_6] [19]. Aquo species are particularly rare and are generally present only as equilibrium components of mixtures in aqueous solution, *e.g.* $[PtCl_3(H_2O)]^-$ which has been detected in aqueous $K_2[PtCl_4]$ both spectrophotometrically [20] and by ^{195}Pt n.m.r. [21]. As methanol was the strongest ligand (apart from water) of those oxygen donors which we investigated, we attempted the isolation of *trans*-[$PtCl_2$-(PPr^n_3)(CH_3OH)] by evaporating a methanol solution of [Pt_2Cl_4(PPr^n_3)$_2$] at −78 °C under vacuum. The resulting yellow plates were much paler than the bridged starting material, but they did not analyse particularly well (probably the complex slowly loses methanol) and have not been further characterised.

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