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FURTHER STUDIES ON THE FLUXIONAL BEHAVIOUR OF TETRAMETHYLALLENE GROUPS BONDED TO BIVALENT PLATINUM*

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SUMMARY

The new compounds $LPtCl_2(TMA)$, where TMA = tetramethylallene and L = *p*-X-pyridine *N*-oxide, RNH_2, CH_3CONH_2, NH_2CONH_2 CD_3CN, CD_3OD and SPh_2, have been prepared from $[(TMA)PtCl_2]_2$ and the appropriate ligand L. From NMR studies it is concluded that these complexes, with the probable exception of the SPh_2 compound, have the same structure as the corresponding (Pyridine)-$PtCl_2(TMA)$ complexes.

A study of the fluxional behaviour of the TMA group shows that, as with the pyridine complexes, the rate of the intramolecular rearrangement increases with decreasing basicity of the ligand L. The complexes involving oxygen donor ligands, however, show much lower rates than would be expected from their p*K* values and an explanation of this is advanced.

INTRODUCTION

The mode of bonding of allenes bound to metal[1–3] atoms and the dynamic behaviour of the allene group have recently been subjects of discussion[4–7]. Fluxional behaviour of the tetramethylallene (TMA) group has been observed for $(TMA)Fe(CO)_4$[4], $[(TMA)PtCl_2]_2$[5], and $(p\text{-}X\text{-}C_6H_4N)PtCl_2(TMA)$[5], and involves migration of the metal atom from one double bond to the other. The influence of the pyridine ligand on the intramolecular rearrangement of the *trans* TMA group was studied kinetically by use of NMR and increasing σ-donor capacity in the pyridine ligand was found to cause a decrease in the rate of migration of the allene ligand, as shown by the linear correlation between log $(1/\tau)$ and the Hammett constants, σ_p.

In order to obtain a more detailed picture of the influence of the ligands on the intramolecular migrations of the tetramethylallene group, series of Pt^{II} compounds with N, O and S donor ligands *trans* to the tetramethylallene group in $LPtCl_2(TMA)$ have now been investigated. In addition, ligands such as carbon monoxide, ethylene and phosphines have been examined.

* For earlier studies see ref. 5.

RESULTS

Compounds $LPtCl_2(TMA)$

By reaction of $[TMA)PtCl_2]_2$[5] with the ligands, L, yellow to red compounds $LPtCl_2(TMA)$ were formed. These are listed with the corresponding ^1H NMR data in Table 1.

TABLE 1

^1H NMR DATA OF $LPtCl_2$ (TMA) IN $CDCl_3$

L	$\delta_{A,B}$, (*ppm*)[a]	$J(Pt-CH_3)$ (*Hz*)	δ_C (*ppm*)	δ_D (*ppm*)[a]	*pK* (*ppm*)[a]	$k(+9°)$ (sec^{-1})
p-$CH_3C_5H_4NO$	1.56,	49	2.16	2.57	1.3	3.3
C_5H_5NO	1.56	50	2.16	2.58	0.8	6.6
p-ClC_5H_4NO	1.55	50	2.17	2.57	0.4	7.2
p-$CH_3COC_5H_4NO$	1.61	51	2.23	2.63	−0.15	20
p-$NO_2C_5H_4NO$	1.58	51	2.23	2.63	−1.7	300
$C_6H_4CH_2NH_2$	1.83	40	2.18	2.53	9.35	70
p-$CH_3C_6H_4NH_2$	1.70	41	2.09	2.34	5.08	1.60
$C_6H_5NH_2$	1.66	42	2.05	2.29	4.60	4.60
p-$BrC_6H_4NH_2$	1.67	44	2.07	2.30	3.86	7.60
p-$NO_2C_6H_4NH_2$	1.70	46	2.12	2.32	1.00	1650
H_2NCN	1.70	46	2.13	2.50		
CD_3CN	1.81	54	2.23	2.59		≈25000
CH_2=$CHCN$	1.57	54	2.21	2.58		
CD_3OD	1.57	57	2.23	2.64	−2.2	1200
CH_3CONH_2	1.55	52		2.49		
NH_2CONH_2	1.58	48	2.15	2.50		

[a] δ in ppm from TMS.

The low temperature (−80 to −50°) limiting spectra for $LPtCl_2(TMA)$ consist of three absorptions in the intensity ratio 3/3/6 going from low to high field, as in the case of the pyridine compounds[5]. The high field signal of intensity 6 shows satellites due to coupling between the methyl protons and the ^{195}Pt nuclei. The high temperature limiting spectra consist of one signal at the weighted average of the low temperature chemical shifts. The coupling constant ranges from 20 to 27 Hz, showing that the TMA remains bonded to the metal atom over the whole temperature range of the coalescence.

Reaction of $[(TMA)PtCl_2]_2$ with SR_2(R = Me, Ph) in $CFCl_3$ gave complexes of the approximate composition $(R_2S)PtCl_2(TMA)$. In the case of the SMe_2 derivative it was not possible to obtain a clear low temperature limiting spectrum owing to some decomposition. The high temperature (20°) spectrum contains a methyl signal at δ 2.48 ppm due to the $S(CH_3)_2$ ligand, with $J(Pt-CH_3)$ 43 Hz, and one coalesced TMA signal at δ 2.05 ppm, with $J(Pt-CH_3)$ 23.0 Hz. A similar high temperature spectrum (20°) was observed for the SPh_2 compound, with the TMA coalesced signal at δ 1.97 ppm and $J(Pt-CH_3)$ 21.0 Hz. It is especially interesting that the low temperature limiting spectrum (−60°) is very different from the normal pattern. It

consists of three signals in the intensity ratios of 6/3/3 at δ 2.13, 1.90, and 1.83 ppm, respectively, the last two signals each having ^{195}Pt satellites with coupling constants of 50 and 54 Hz, respectively. The compound could only be prepared in $CFCl_3$, and contained, as shown by analysis and NMR, slightly more SPh_2 than expected. This is probably due to the presence of $(SPh_2)_2PtCl_2$, since in solution the compound slowly decomposes to give free tetramethylallene and $(SPh_2)_2PtCl_2$.

There is some uncertainty about the mode of bonding of H_2NCN, CH_3CONH_2 and NH_2CONH_2 to the platinum atom. In the first case the TMA signals and coupling constant seem to indicate that the H_2NCN ligand is bonded to Pt through the NH_2 group. In the case of CH_3CONH_2 and NH_2CONH_2 the TMA spectra are very similar, and it thus seems probable that both ligands are linked to the Pt atom through the same function. It is not clear, however, whether the bonding is through the oxygen or the nitrogen atom. Normally these ligands are linked to the Pt^{II} atom through the N atom as observed for $Pt(urea)_2Cl_2$[8].

Kinetic measurements (slow exchange limit) on the compounds in $CDCl_3$ solution showed that the rate of rearrangement for both the pyridine *N*-oxide and the monosubstituted amine series (RNH_2) increased with decreasing basicity of the ligands. Figure 1 shows that when $\log(1/\tau)$ (τ is the lifetime of protons C or D) is plotted against the p*K* (at +9°), there is a fairly good linear relationship, as for the pyridine series[5]; the plot for the latter series is included in Fig. 1 for purposes of comparison. Some pyridine derivations were remeasured to ensure that no temperature errors occurred, as the rates were measured on different NMR machines.

It can be seen that the rates of the amine and pyridine series are very similar, but in general are higher than those for the pyridine *N*-oxide series. The addition of an excess of the ligand had no effect on the rates.

Calculated activation energies were in the range of 10–14 kcal·mole^{-1}, while the frequency factor *A* had values between 10^{10} to 10^{14} sec^{-1}, but further details of these are not given since the *k* values are thought to be more reliable. Rates were also measured for L=CD_3CN and CD_3OD (the latter compound was not isolated). The p*K* value for CD_3CN is not known with any accuracy but is about −9. At +9° the extrapolated rate is very fast ($\approx$25000 sec^{-1}).

Finally, an attempt was made to prepare the compounds $LPtCl_2$(TMA) with L=CO, C_2H_4, PPh_3 and $PPhMe_2$. Bubbling CO or C_2H_4 gas through solutions of $[(TMA)PtCl_2]_2$ at −50° gave clear yellow solutions, in which the presence of $LPtCl_2$-(TMA) could be clearly demonstrated by NMR. The compounds could not be isolated however, or studied further since free TMA was formed above −20°. Treatment of $[(TMA)PtCl_2]_2$ with the phosphines afforded free TMA and L_2PtCl_2.

Compounds (bidentate)PtCl(TMA)

Treatment of *N-trans*-glycine $Pt(C_2H_4)Cl$[9-11] with tetramethylallene gave lemon yellow crystals of (glycine)Pt(TMA)Cl. In CD_3OD at −60° the main isomer shows TMA peaks at δ 2.43, 2.10, 1.77 and 1.62 ppm; the last two signals have platinum satellites with $J(Pt-CH_3)$ of 42 and 32 Hz, respectively. Two further small methyl signals were observed at δ 1.82 and 2.18 ppm. It seems likely that the TMA molecule is *trans* to the N atom, since N has a higher *trans* effect than O. In the parent ethylene compound the ethylene was also *trans* to the N atom. No further analysis was carried out, since the NMR spectrum showed the correct ratios.

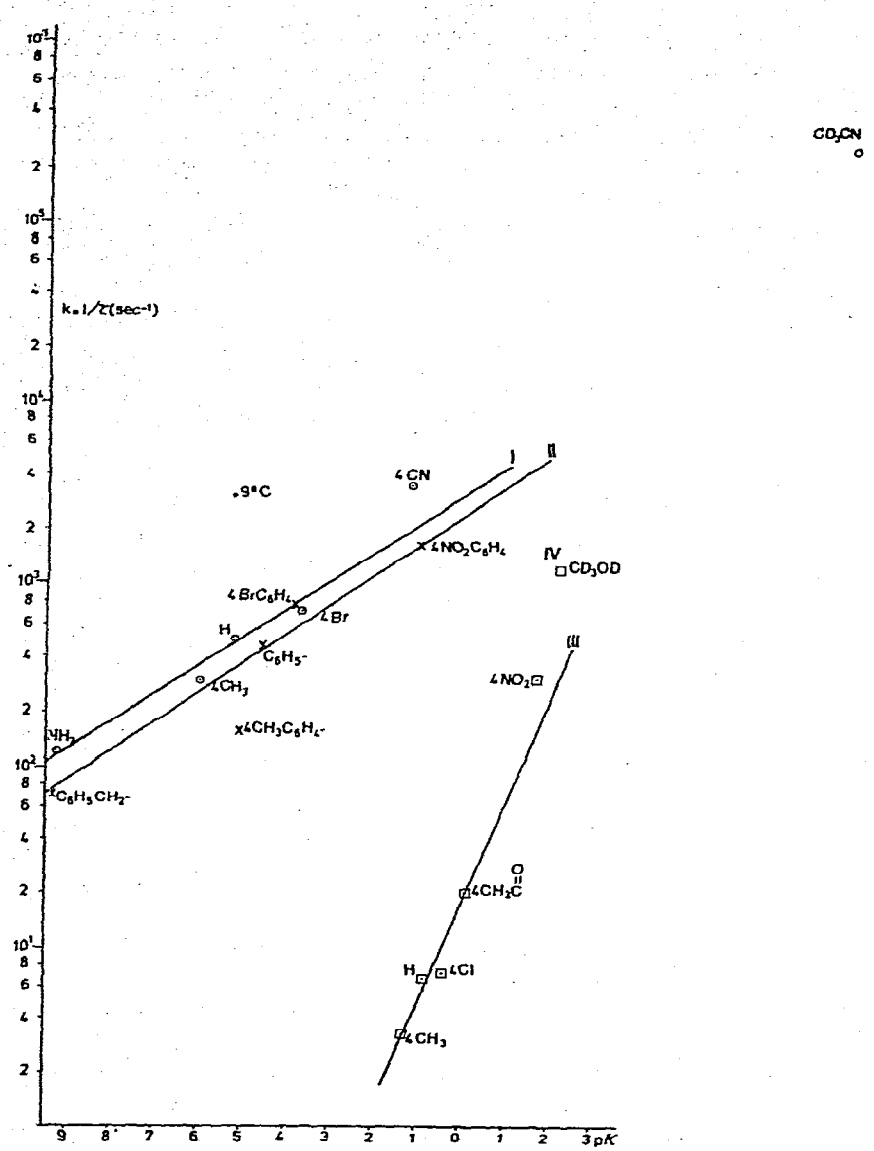

Fig. 1. log ($1/\tau$) *versus* pK for compounds $LPtCl_2(TMA)$. I: L = pyridine; II: L = RNH_2; III: L = pyridine *N*-oxide; IV: L = CD_3OD; V: L = CD_3CN.

Reactions with the alanine derivative and with $(Acac)PtCl(C_2H_4)$ gave no satisfactory products, although some reaction took place.

DISCUSSION

From the preparative results, and the properties of the complexes it is clear that stable compounds $LPtCl_2(TMA)$ are formed when L is a fairly strong σ-donor and a poor π-acceptor such as the pyridines, amines and pyridine *N*-oxides. Unstable

compounds are formed when the ligands L are poor σ-donors and good π-acceptors, such as CO and C_2H_4, as evidenced by the ready dissociation of TMA at low temperatures in solution. The phosphines would be expected to give stable compounds; but disproportionation occurs because of the easy formation of L_2PtCl_2, and this was also found to some degree with SR_2 ligands.

From Table 1 it is clear that the compounds $LPtCl_2$(TMA) have the same structure as the corresponding pyridine compounds, which were shown to have the ligand L *trans* to the TMA group. This group itself is bonded to the metal by one of its double bonds; the other double bond being bent away from the metal atom. The structure of $(SPh_2)PtCl_2$(TMA), which unfortunately could not be studied more thoroughly because of its instability, appears to be different, in view of its different NMR pattern, from which one must conclude that there is no plane of symmetry perpendicular to the plane of the molecule through the L–Pt bond. Possibly the allene molecule is asymmetrically bonded to the Pt atom because of steric hindrance arising from the phenyl groups of the SPh_2 ligand.

Another possibility is that the phenyl groups exercise a direct through-space effect on the methyl chemical shift, while a third possibility is that the complex is a *cis* isomer, but this seems unlikely in view of the bulky nature of the SR_2 group and the *trans* directing effect of the allene group itself.

An example of a situation in which there is also no plane of symmetry perpendicular to the plane of the complex is (glycine)Pt(TMA)Cl. In this case four peaks are observed, analogous to those found with the dimer $[(TMA)PtCl_2]_2$[5], and quite different from the pattern shown by $(SPh_2)PtCl_2$(TMA).

The NMR kinetic measurements showed that, as with the pyridine compounds, the amine and pyridine *N*-oxide series exhibited a linear relationship between log $(1/\tau)$ and the p*K* of the ligand concerned. Of interest is the fact that, while the pyridine and amine series showed similar rates, as expected on basis of their similar p*K* values, the pyridine *N*-oxide series of compounds showed much lower rates than would be expected in view of their weak basicities. The rate of rearrangement of the deuterated methanol platinum compound falls in the range found for the pyridine *N*-oxides; CD_3OD also has a low basicity. On the other hand, it was found that the rate for $(CD_3CN)PtCl_2$(TMA) is very fast indeed; although the p*K* of CD_3CN is not known, it is thought to possess a very low basicity (p*K* -9).

It is clear that in the case of the oxygen ligands examined there is, in addition to basicity, another factor which causes the rates of rearrangement of the TMA group to be abnormally low. In this respect it is helpful to refer to the structure of (*p*-methoxypyridine *N*-oxide)$PtCl_2$(CO), in which the Pt–O–N angle is 120°, while the PyO ring is almost at right angles to the plane of the Pt atom and the four groups bonded to it[12]. Orchin and Schmidt[12] pointed out that the oxygen lone pair(s) may interact with the relevant Pt orbitals; this interaction involves a donor action to the Pt atom and consequently an increase in the π-backbonding to the groups trans to the pyridine *N*-oxide. If the influence of the free electron pair(s) on the oxygen atom is taken into account, a factor also relevant in the case of alcohols, the abnormally low rate of rearrangement can be accounted for.

In view of the above, it is noteworthy that the CO stretching frequencies in $LPtCl_2$(CO) are lower for L = *p*-X-pyridine *N*-oxide ($\approx$2120 cm^{-1}) than for L = *p*-X-pyridine and L = *p*-X-aniline (both at about 2130 cm^{-1}). Once again the pyridine

and aniline series are similar, while the lower CO frequencies for the pyridine *N*-oxide series indicate a stronger donor action for these ligands, although the basicity is lower. It is relevant to mention that in all three series the CO frequencies show little or no change on variation of the *para* substituents. In the allene compounds the *para* substituent has a very important effect on the rates; the infrared frequencies, however, give information only about the *trans* influence, *i.e.* the situation in the initial state, while the rates for the allene compounds are determined both by the initial state and the transition state. As a result one cannot carry the analogy between the two sets of data too far*.

From Fig. 1, it can further be seen that the slope for the pyridine *N*-oxide series is steeper than that for the nitrogen-donor series. It seems reasonable to suggest that a change in *para* substituent will affect both the basicity and the donor action of the free electron pairs, and the change in the total donor action can be expected to be greater for the oxide than for the N-donor series.

TABLE 2

ANALYTICAL DATA FOR TETRAMETHYLALLENE COMPOUNDS OF PLATINUM(II), $LPtCl_2$ (TMA)

Ligand L	*Analysis, found (calcd.) (%)*					
	Pt	*C*	*H*	*C*	*Cl*	*S*
C_5H_5NO	44.79	31.46	3.80	3.26	15.54	
	(42.67)	(31.51)	(3.72)	(3.06)	(15.51)	
p-$CH_3C_5H_4NO$	41.39	33.19	4.13	3.07	14.98	
	(41.40)	(33.12)	(4.03)	(2.97)	(15.07)	
p-ClC_5H_4NO	40.80	30.14	3.38	3.32	22.04	
	(39.67)	(29.30)	3.26	(2.85)	(21.67)	
p-$CH_3COC_5H_4NO$	39.23	33.57	3.90	2.90	14.29	
	(39.38)	(33.67)	(3.81)	(2.81)	(14.23)	
p-$NO_2C_5H_4NO$	33.58	28.50	3.19	5.61	14.23	
	(38.84)	(28.68)	(3.19)	(5.58)	(14.14)	
p-$CH_3C_6H_4NH_2$	41.63	35.73	4.38			
	(41.58)	(35.82)	(4.48)			
$C_6H_5NH_2$	42.78	34.32	4.08			
	(42.86)	(34.29)	(4.18)			
p-$BrC_6H_4NH_2$	38.45	29.37	3.76			
	(36.52)	(29.21)	(3.37)			
p-$NO_2C_6H_4NH_2$	36.77	30.46	3.42			
	(39.00)	(31.20)	(3.60)			
$C_6H_5CH_2NH_2$	40.49	38.16	4.88			
	(41.58)	(35.82)	(4.48)			
H_2NCN	48.05	23.53	3.36			
	(48.27)	(23.76)	(3.44)			
CD_3CN	48.42	26.69	4.51			
	(48.03)	(26.60)	(4.43)			
SPh_2	32.57	43.35	3.69		12.10	9.20
	(35.58)	(43.43)	(4.01)		(12.96)	(5.84)

* Infrared and Raman studies will be described later.

EXPERIMENTAL

The compounds $LPtCl_2(TMA)$ were usually prepared by adding the required amount of ligand L to the dimer $[(TMA)PtCl_2]_2$. As a typical example the preparation of $(p\text{-}CH_3COC_5H_4NO)PtCl_2(TMA)$ is given as follows.

$[(TMA)PtCl_2]_2$ (0.543 g) was mixed with $p\text{-}CH_3COC_5H_4NO$ (0.206 g) in 5 ml of $C_2H_2Cl_2$ at 0° under nitrogen. The bright orange solution was stirred for half an hour at 0°, and subsequently stored at −30°. Some solvent was later removed under vacuum to promote crystallisation. The orange crystalline product was washed with pentane and dried.

The diphenyl sulphide compound $(Ph_2S)PtCl_2(TMA)$ was formed by mixing 0.539 g $[(TMA)PtCl_2]_2$ with 0.294 g Ph_2S in 15 ml $CFCl_3$ at −20°. After 2 h stirring, the mixture was allowed to stand until the $CFCl_3$ had evaporated off and the bath had reached room temperature. The yellow-orange solid deposited on the walls of the flask was collected, the darker orange solid below being discarded.

The glycine complex was prepared by adding 0.2 ml tetramethylallene to a suspension of 0.115 g (*N-trans*-glycine)$Pt(C_2H_4)Cl$ in 5 ml acetone at 50° with stirring. Within a few minutes a steady stream of C_2H_4 gas began to be evolved, and the solid dissolved to give a yellow solution. After approximately 15 min the solvent was evaporated under vacuum to leave a bright yellow solid, which was washed with pentane and dried.

Table 2 shows the analytical data for the tetramethylallene compounds.

Molecular weights were measured with a Mechrolab Vapour Pressure Osmometer Model 201 A with $CHCl_3$ as solvent. The results are not listed because all the compounds were monomolecular, like the pyridine compounds.

Spectroscopic measurements

The NMR spectra of the platinum complexes were recorded on a Varian HA 100 spectrometer with $CDCl_3$ as solvent. Low temperatures were obtained with variable Varian Dewar inserts.

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