Journal of Organometallic Chemistry, 55 (1973) C45–C48
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The dynamic stereochemistry of the allylic ligand in a μ-allylic complex of platinum(II)

R.P. HUGHES and J. POWELL
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

(Received April 24th, 1973)

SUMMARY

^{1}H NMR studies of an equilibrium mixture of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-allylplatinum(II) [IA] and bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis-(μ-allyl)diplatinum(II) [IB] show that the μ-allylic ligands of (IB) exhibit temperature dependent tautomeric behaviour, giving rise to a site-exchange between protons on these ligands.

Only recently have allylic complexes of Pt^{II} been characterised by means of ^{1}H NMR spectroscopy and X-ray crystallography. In the solid state chloroallylplatinum(II) has been shown to be tetrameric and acetylacetonatoallylplatinum(II) to be dimeric[1]. Both complexes contain bridging μ-allyl ligands, but have proven too insoluble for ^{1}H NMR measurements[2]. Complexes of Pt^{II} containing substituted allylic ligands have been shown with one exception[3], to contain π-bonded allylic moieties[2].

1,1,1,5,5,5-Hexafluoropentane-2,4-dionatoallylplatinum(II) has recently been prepared in this laboratory as a stable, red, crystalline solid, soluble in common organic solvents. The ^{1}H NMR spectrum of this complex in CDCl$_3$ or toluene-d_8 solution at −25° clearly demonstrates the presence of an equilibrium mixture of monomer (IA), containing a symmetrically π-bonded allyl ligand, and dimer (IB), containing μ-allyl ligands (see Fig. 1 and Table 1)*.

On warming a solution of (IA) and (IB) in toluene-d_8 to +70° the AGMPX pattern of the μ-allyl ligand of (IB) collapses to a broad resonance. Further warming to +100° generates an AM$_2$X$_2$ pattern for the protons of the μ-allylic ligand, due to a site-exchange process which interconverts H^1 with H^4 and H^2 with H^3. The AM$_2$X$_2$ pattern of the π-bonded allylic protons of the monomer (IA) remains sharp and these resonances

---

*This equilibrium is also evident in the ^{13}C NMR spectrum, and in molecular weight observations.

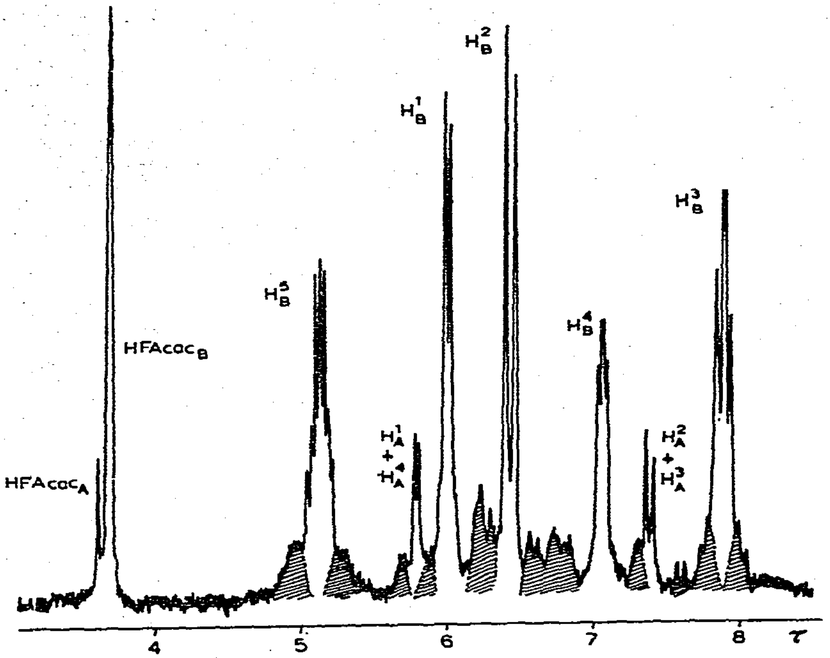


Fig. 1. ^{1}H NMR spectrum (220 MHz; $CDCl_3$; −20°) of 1,1,1,5,5,5-hexafluoroacetylacetonatoallylplatinum (II), showing an equilibrium mixture of (IA) and (IB). Notation of resonances; *e.g.* H_B^5 denotes H^5 in complex (IB). Shaded areas denote ^{195}Pt satellites.

TABLE 1

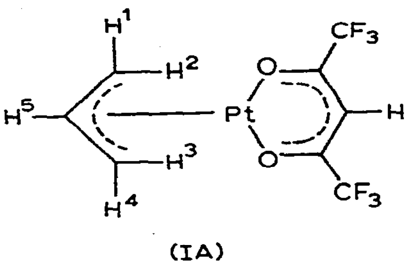
^{1}H NMR DATA (100 MHz; toluene-d_8; −25°) FOR COMPLEXES (IA) AND (IB)

	τ, J(Hz)[a]					
Complex	H^1	H^2	H^3	H^4	H^5	*HFAcac*
IA	6.60	8.22	8.22	6.60	~5.5[b]	3.91
	$J_{1,5}$ 6	$J_{2,5}$ 11	$J_{3,5}$ 11	$J_{4,5}$ 6		
	J(Pt–H)40	J(Pt–H)94	J(Pt–H)94	J(Pt–H)40		J(Pt–H)8
IB	6.51	7.14	8.46	7.46	5.31	4.28
	$J_{1,5}$ 7	$J_{2,5}$ 13	$J_{3,5}$ 12	$J_{4,5}$ 5	$J_{5,1}$ 7	
					$J_{5,2}$ 13	
			$J_{3,4}$ 9	$J_{4,3}$ 9	$J_{5,3}$ 12	
					$J_{5,4}$ 5	
	J(Pt–H)90	J(Pt–H)70	J(Pt–H)104	J(Pt–H)49	J(Pt–H)82	J(Pt–H)5

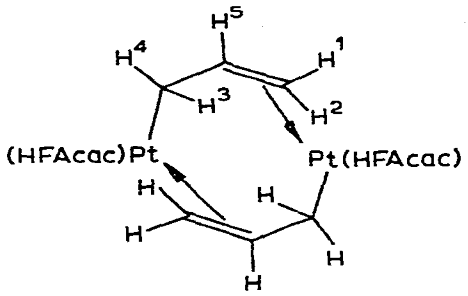
[a] J(H–H) and J(Pt–H) were confirmed by running spectra at 60 MHz ($CDCl_3$ and toluene-d_8) and 220 MHz ($CDCl_3$) (*e.g.* see Fig. 1).
[b] Obscured by H^5 resonance of complex (IB).

retain their coupling to ^{195}Pt throughout the above temperature range, indicating that the exchange process occurring in (IB) cannot be proceeding via the intermediacy of (IA). Furthermore the individual resonances of the γ-proton of the hexafluoropentane-2,4-dionato (HFAcac) ligand in both (IA) and (IB) remain sharp and coupled to ^{195}Pt throughout the exchange process, showing that HFAcac dissociation is not a requirement for the exchange*. At +70° (close to T_C) the shape of the coalescence envelope for the μ-allylic protons of (IB) is not affected by dilution, nor by addition of methanol (1 mol. per Pt atom), indicating that the exchange process is intramolecular and is probably not a solvolytic partial bridge-cleavage reaction**. Partial solvolysis of (IB) would be expected to result in either an $AGMX_2$ or AX_4 pattern for the allylic protons rather than the observed AM_2X_2 pattern.

The above data suggest the mechanism for the proton site-exchange process to be that shown in Fig. 2, a tautomeric rearrangement via a symmetrical bridging intermediate accounting for the site-interconversion of H^1 with H^4 and H^2 with H^3 ***. This represents



(IA)



(IB)

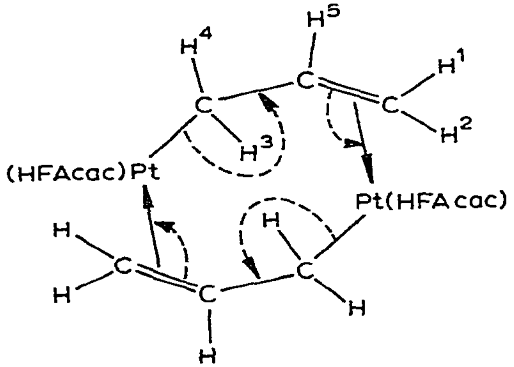


Fig. 2. Mechanism of proton site-exchange in complex (IB).

---

* Observation of discrete resonances for the HFAcac ligand in (IA) and (IB) allows the equilibrium constant (*K*) for the dimer (IB) ⇌ 2 monomer (IA) system to be evaluated by integration. $\log_{10}K$ varies linearly with $1/T$ from +50° to +100°; ΔH +6.3 kcal·mol^{-1} and ΔS +16.8 e.u.

** Methanol is an efficient nucleophilic reagent for increasing the rate of solvolysis of carboxylate bridging ligands in Pd^{II} and Pt^{II} systems[4].

***Preliminary calculations indicate the free-energy of activation for this exchange to be of the order of 16 kcal·mol^{-1}. Symmetrically bridging μ-allyl ligands have been reported in the case of $Cr_2(allyl)_4$[5] and $(allyl)Pd_2(PPh_3)_2I$[6].

a novel process in the dynamic stereochemistry of allylic transition metal systems and is of undoubted significance in the intermetallic transfer reactions of allylic ligands which have been reported in recent years[7]. The tautomeric rearrangement of the μ-allyl ligand may also be considered as a possible model for olefin isomerization reactions on metal surfaces.

ACKNOWLEDGEMENT

This work was supported by the National Research Council of Canada.

REFERENCES

1 G. Raper and W.S. McDonald, *J. Chem. Soc. Dalton*, (1972) 265.
2 B.E. Mann, B.L. Shaw and G. Shaw, *J. Chem. Soc. A*, (1971) 3536.
3 R. Mason, G.B. Robertson and P.O. Whimp, *J. Chem. Soc. A*, (1970) 535.
4 T. Jack and J. Powell, *Inorg. Chem.*, 11 (1972) 1039.
5 T. Aoki, A. Furusaki, Y. Tomiie, K. Ono and K. Tanaka, *Bull. Chem. Soc. Japan*, 42 (1969) 545.
6 Y. Kobayashi, Y. Itaka and H. Yamazaki, *Acta Cryst.*, B, 28 (1972) 899.
7 See for example: A.N. Nesmeyanov, S.P. Gubin and A.Z. Rubezhov, *J. Organometal. Chem.*, 16 (1969) 163; R.F. Heck, *J. Amer. Chem. Soc.*, 90 (1968) 317.