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The Dynamic Behaviour of η^3-Allyl Palladium and Platinum Complexes Containing the $SnCl_3$ Ligand

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Abstract

The solution behaviour of [η^3-allylM(PR_3)$SnCl_3$] (M = Pd, Pt) has been studied. Dissociation of the Sn ligand (either $SnCl_2$ or $SnCl_3$) explains the dynamic behaviour observed by NMR. The M–Sn bond is stronger if an alkylphosphine is bound to the metal. According to the observed ^1J(Pt, C) values of the Pt–C bond *trans* to $SnCl_3$, tin ligand and olefin have comparable *trans* influence.

Introduction

Complexes containing the labile $SnCl_3$ ligand have been investigated by multinuclear NMR spectroscopy [1–3]. Much of the interest in these complexes stems from their importance in catalysis [4]. Among them the complexes containing the allyl group seem to have received much less attention. The X-ray structure of [η^3-allylPd(PPh_3)$SnCl_3$] (**1**) was reported by Mason and coworkers several years ago [5]. An interesting feature of the structure is the equal value (2.18 Å) of the two palladium terminal allyl carbon distances. As these carbon atoms are respectively *trans* to PPh_3 and $SnCl_3$, the *trans* influence of the ligands was considered similar. The ^{1}H NMR spectrum of **1** measured at room temperature displays two broad resonances associated with terminal allylic protons. As the band widths remain unchanged at −40 °C the broadening was attributed to coupling with other nuclei [5, 6]. Other authors [7] have found, in analogy with **1**, that the room temperature ^{1}H NMR spectra of [η^3-2-methylallylPd(PPh_3)$SnCl_3$] (**2**) and [η^3-2-methylallylPd(PPh_2Me)$SnCl_3$] (**3**) show two signals for the allylic protons which broaden at lower temperature. While the limiting spectrum was not reached for **2**, four broad resonances were observed at −57 °C ($CDCl_3$) for *syn* and *anti* protons of **3** as expected for a dissymetric coordination of the allyl group to the metal. The phosphorus allylic proton coupling constants of **3** could not be measured owing to the broadening of the peaks; thus the proposed assignment which places the signals of *syn* and *anti* protons *cis* to $SnCl_3$ at a lower field than *syn* and *anti* protons *cis* to PPh_2Me appears questionable. In order to obtain a better insight into the solution behaviour of π-allyl complexes containing the $SnCl_3$ ligand we have prepared and studied a number of Pd and Pt complexes by multinuclear NMR.

Results and Discussion

The complexes are readily prepared according to eqn. (1)

$$\eta^3\text{-allylM(L)Cl} + SnCl_2 \xrightarrow{CH_2Cl_2} \eta^3\text{-allylM(L)}SnCl_3 \quad (1)$$

L = PR_3, M = Pd, Pt

They are stable in the solid state as well as in solution although in some cases separations of slight quantities of insoluble material occurred.

The ^{1}H NMR spectra at 298 K of [η^3-2-methylallylPd(PEt_3)$SnCl_3$] (**4**) (Fig. 1) and [η^3-2-methylallylPd[P(i-C_3H_7)$_3$]$SnCl_3$] (**5**) in contrast to **1**–**3** show four separate signals for *syn* and *anti* protons of the allyl group thus these complexes have a rigid structure at room temperature. The assignment reported in Table I follows from the assumption that ^3J(H, P *trans*) > ^3J(H, P *cis*), and spin decoupling experiments. NOE difference experiments have proved that both *anti* protons resonate at a higher field than *syn* protons. For compound **4**, irradiation of the *anti* signal *trans* to phosphorus (δ 2.86, ^3J(H, P) 10.1 Hz) produces an enhancement of the integrated intensity of the signal at δ 4.67 which is therefore assigned to the geminal *syn* proton.

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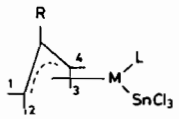
TABLE I. ^{1}H NMR Data[a] for Complexes



M	L	R		T (K)	δ_1	δ_2	δ_3	δ_4	R
Pd	PPh_3	H	1[b]	183	4.91	(3.1)[c]		4.55	5.52
Pd	PPh_3	CH_3	2[b]	193	4.65	3.03 J(H, P) 9.2	3.28	4.25	1.97
Pd	PEt_3	CH_3	4[d]	298	4.67 J(1, 4) 3.1 J(H, P) 4.0	2.86 J(H, P) 10.1	3.18	4.34	1.76
Pd	$P(i\text{-}C_3H_7)_3$	CH_3	5[b]	298	4.68 J(H, P) 3.9	2.83 J(H, P) 9.4	3.21	4.46	1.81
Pd	PMe_2Ph	CH_3	6[d]	273	4.66	2.95 J(H, P) 9.7	3.25	4.16	1.80
Pt	PPh_3	H	7[b]	193	4.85	(2.9)[c]		4.10	4.81
Pt	PMe_2Ph	H	8[d]	273	4.84	(2.8)[c]		4.18	4.78
Pt	$P(i\text{-}C_3H_7)_3$	H	9[d]	298	4.81	(2.6–2.7)[e]		4.35	4.61

[a]δ, ppm from TMS; J, Hz. The spectra were measured at 250.13, 200.13 and 80.13 MHz. [b]CD_2Cl_2. [c]Central shift of unresolved multiplet; J(H, P) not determined due to second order pattern. [d]$CDCl_3$. [e]Obscured by –CH of $i\text{-}C_3H_7$.

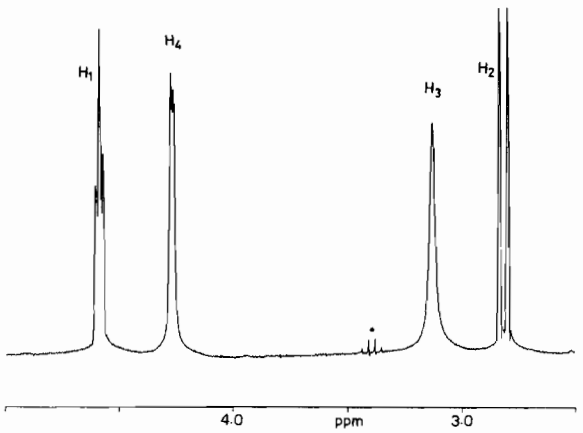


Fig. 1. ^{1}H NMR spectrum of [η^3-C_4H_7Pd(PEt_3)$SnCl_3$] (4) at 250.13 MHz, 299 K, $CDCl_3$. The signals are numbered as in Table I. *, Diethylether.

Accordingly irradiation of the *anti* proton *cis* to PEt_3 (δ 3.18, ^3J(P, H) ~ 0 Hz) enhances the signal at δ 4.34 which is then assigned to the *syn* proton *cis* to the tin ligand. The above assignment, *i.e.* both *syn* protons at a lower field than *anti* protons, is at variance with that previously proposed [7].

Our data confirm that at room temperature **1** and **2** are not rigid. We have been able to reach the limiting spectrum respectively at 183 K for **1** and 193 K for **2** at which four separate signals are observed for allyl protons. The variable temperature spectra of **2** are reported in Fig. 2. The static structure of [η^3-2-methylallylPd(PMe_2Ph)$SnCl_3$] (**6**) was reached at a higher temperature (273 K). The high temperature spectra of **1**–**3** and **6** are all consistent with a pairwise exchange of *syn* and *anti* protons [7, 8]. It is interesting to note that, as shown in Fig. 2, the averaged *anti* resonance reveals a phosphorus coupling.

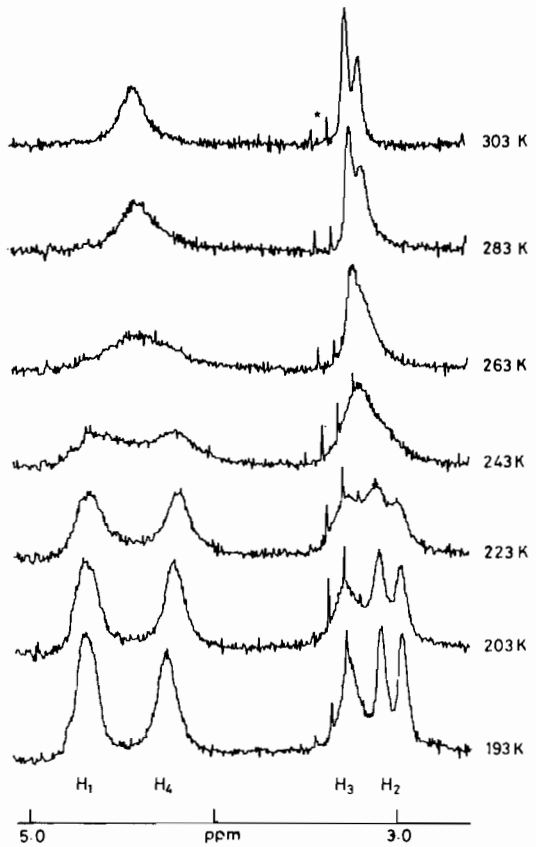


Fig. 2. Variable temperature ^{1}H NMR spectra of [η^3-C_4H_7-Pd(PPh_3)$SnCl_3$] (2) at 80.13 MHz, CD_2Cl_2. The signals are numbered as in Table I. *, Diethylether.

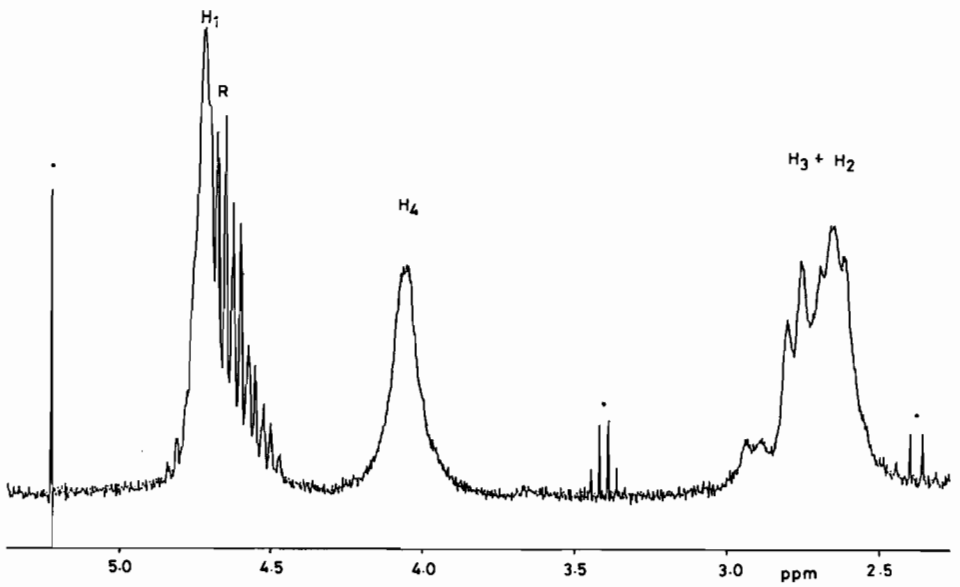


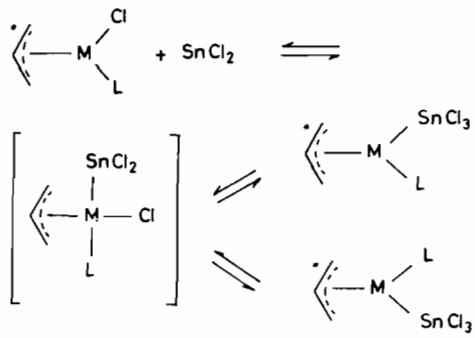
Fig. 3. ^{1}H NMR spectrum of $[\eta^3$-$C_3H_5Pt(PMe_2Ph)SnCl_3]$ (**8**) at 250.13 MHz, 273 K, $CDCl_3$. The signals are numbered as in Table I. *, Diethylether, CH_2Cl_2 and impurity.

Moreover comparing the variable temperature behaviour of **2**–**6** it appears that the process which exchanges respectively the *syn* and *anti* protons is slowed down if a more basic tertiary phosphine is bound to the metal.

In the Pt series the signals are less separated than in the Pd case. The ^{1}H limiting spectrum of all the examined Pt complexes displays a second order pattern at 250 MHz for the allylic *anti* protons, but distinct resonances can be observed for the *syn* protons (Fig. 3). The results obtained by dynamic NMR investigation parallel those observed in the Pd case. At room temperature the *syn* and *anti* protons of $[\eta^3$-allylPt$(PPh_3)SnCl_3]$ (**7**) and $[\eta^3$-allylPt$(PMe_2$-$Ph)SnCl_3]$ (**8**) exchange pairwise. The limiting spectra are reached at 193 K for **7** and 273 K for **8**. The structure of $[\eta^3$-allylPtP$(i$-$C_3H_7)_3SnCl_3]$ (**9**), as found for the corresponding Pd complexes (**5**) is rigid at room temperature. The variable temperature ^{1}H NMR spectra are in agreement with the mechanism previously proposed by Sakibara *et al.* [7]. Dissociation and successive insertion of $SnCl_2$ into the M–Cl bond (eqn. (2)) brings about *syn–syn* and *anti–anti* exchange of the allylic protons.

The insertion of $SnCl_2$ into the M–Cl bond may occur through previous coordination of $SnCl_2$ to the metal in a five coordinate intermediate [9]. An alternative mechanism is a dissociation of the $SnCl_3$ group [10]. Unfortunately a study at variable concentration of $SnCl_2$ is hampered by the low solubility of $SnCl_2$ in the solvents used.

The ^{31}P NMR spectra of the complexes (Table II) are also consistent with the dissociation of the tin species (either $SnCl_2$ or $SnCl_3$) as ^2J(P, Sn) (200–400

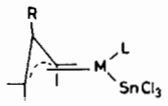


(2)

Hz) is observed only at the low temperature for **1**–**4** and **6**–**8**. Dissociation of the tertiary phosphine faster than the tin ligand is ruled out by the clear observation of J(Pt, P) both in the low and room temperature spectra (Table II). An interesting feature of the ^{31}P NMR spectrum of **7** is that ^1J(P, Pt) decreases by 382 Hz with respect to $[\eta^3$-allylPt$(PPh_3)Cl]$ (**10**) (^1J(P, Pt) 4454 Hz). Pregosin and coworkers [3] have found analogous behaviour for ^1J(P, Pt) on going from *trans*-$[PtCl_2(PEt_3)_2]$ to *trans*-$[PtCl(SnCl_3)$-$(PEt_3)_2]$. This has been associated with a weak σ-donor and potential π-acceptor ability of the $SnCl_3$ ligand. The variable temperature NMR data here reported are consistent with this view and indicate that the strength of the M–$SnCl_3$ bond increases in the same order as the increasing donor properties of the coordinated tertiary phosphine.

An interesting feature of the ^{13}C NMR spectra of the complexes is the very similar chemical shift for the terminal allyl carbon atoms (Table III). This is consistent with the comparable *trans* influence of the

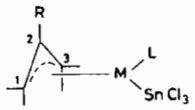
TABLE II. ^{31}P NMR Data[a] for Complexes



M	L	R		T (K)	δ	J(Sn, P)[b]	J(Pt, P)
Pd	PPh_3	H	1	299[c]	27.0		
				190[c]	27.3	427	
Pd	PPh_3	CH_3	2	299[c]	27.8		
				190[c]	28.3	414	
Pd	PEt_3	CH_3	4	299[d]	25.1		
				240[d]	24.6	448	
Pd	$P(i\text{-}C_3H_7)_3$	CH_3	5	299[c]	60.2	409	
Pd	PMe_2Ph	CH_3	6	289[d]	−5.4		
				220[d]	−5.0	432	
Pt	PPh_3	H	7	299[c]	21.0		4191
				190[c]	21.9	172	4191
Pt	PMe_2Ph	H	8	299[c]	−11.0		4006
				203[c]	−10.7	164	4006
Pt	$P(i\text{-}C_3H_7)_3$	H	9	299[d]	51.4	172	4072

[a]The spectra were measured at 101.26 MHz with random noise decoupling of the protons; δ, ppm referred to external H_3PO_4. [b]Average of ^{117}Sn and ^{119}Sn coupling. [c]CH_2Cl_2/CD_2Cl_2. [d]$CDCl_3$.

TABLE III. ^{13}C NMR Data[a] for Complexes



M	L	R		T (K)	δ_1	δ_2	δ_3	R
Pd	PPh_3	CH_3	2	220[b]	70.2	135.1	77.0	23.5
					J(C, P) 26.5			
Pd	PEt_3	CH_3	4	223[c]	70.4	133.9	70.1	23.9
					J(C, P) 24.5			
Pd	$P(i\text{-}C_3H_7)_3$	CH_3	5	299[b]	70.9	133.4	71.1	24.1
					J(C, P) 25.1			
Pd	PMe_2Ph	CH_3	6	223[b]	69.8	135.0	73.6	24.3
					J(C, P) 26.9			
Pt	PPh_3	H	7	220[b]	62.6	113.1	66.4	
					J(C, P) 25.9		J(C, Pt)[d]	
Pt	$P(i\text{-}C_3H_7)_3$	H	9	299[c]	63.1	110.1	59.2	
					J(C, P) 21.3			
					J(C, Pt) 35		J(C, Pt) 155.4	

[a]δ, ppm downfield from TMS; J, Hz; the spectra were measured at 62.9 MHz with random noise decoupling of the protons. [b]CD_2Cl_2. [c]$CDCl_3$. [d]Not observed, owing to the low solubility of the compound.

tertiary phosphine and $SnCl_3$ ligand as suggested by X-ray data [5]. Moreover the ^{13}C NMR spectra of the Pt complexes (Table III) allow an evaluation of the *trans* influence of the $SnCl_3$ ligand by observing the *trans* one bond platinum–carbon coupling constant. The observed value of 155 Hz in **9** is 100 Hz less than the corresponding value in **10** (*J*(C, Pt) 251 Hz) and compares well with that found in $[\eta^3\text{-}C_4H_7Pt(COD)]^+$ (*J*(C, Pt) 154 Hz) [11]. A strong *trans* influence of the ligand has been associated with a decrease in the *trans* spin–spin coupling constant [12, 13]. Our results confirm those found by Pregosin *et al.* [3], that $SnCl_3$ has a *trans* influence similar to that of an olefin. On the other hand the X-ray crystal structure determination of **1** suggests that PPh_3 and $SnCl_3$ have a comparable *trans* influence. Therefore considering the qualitative sequence of the *trans* influence: anionic carbon ligand > tertiary phosphine >

olefin > halogen, the $SnCl_3$ ligand should have a *trans* influence intermediate between a tertiary phosphine and an olefin.

The catalytic properties of π-allylic complexes of the Ni group containing $SnCl_3$ are being investigated and will be reported later.

Experimental

The NMR spectra were recorded on Bruker WP-80, AC-200 and AC-250 instruments. The NMR tubes were prepared using vacuum-line techniques. ^{13}C and ^{31}P NMR spectra were measured under conditions of broad-band ^1H decoupling. Chemical shifts are in ppm relative to TMS for ^1H, ^{13}C and external H_3PO_4 85% for ^{31}P. The coupling constants, in Hz, were determined with an accuracy of ±0.1, ±0.5 and ±2 Hz for ^1H, ^{13}C and ^{31}P measurements respectively. The sample temperature was controlled by the inlet of cooled N_2 into the probe and is estimated to be accurate to ±2°. Solvents and further details are given in Tables I–III.

Elemental analyses were performed at Dipartimento di Chimica Organica, Università di Milano.

The preparation of the complexes was performed under dinitrogen purified by passage through BASF catalyst R3-11. Solvents were dried and degassed prior to use.

All the Pd and Pt complexes were prepared by following the procedure below described for the P(i-$C_3H_7)_3$ complexes. Satisfactory elemental analyses were obtained for all the isolated complexes.

{η^3-2-methylallylPd[P-i-$C_3H_7)_3$]$SnCl_3$} (5)

P(i-$C_3H_7)_3$ (0.169 g, 1.05 mmol) was added to (η^3-$C_4H_7PdCl)_2$ (0.205 g, 0.52 mmol) dissolved in CH_2Cl_2 (10 ml). $SnCl_2$ (0.198 g, 1.05 mmol) was added to the pale yellow solution. The mixture was magnetically stirred until the $SnCl_2$ disappeared. The solution was then concentrated (2.5 ml) and diethylether (2.5 ml) was added. On cooling **5** separated out as a pale yellow material. The solid material was filtered off, washed with ether and dried (0.280 g, 51% yield). *Anal.* Calc. for $C_{13}H_{28}PPdSnCl_3$: C, 28.54; H, 5.12. Found: C, 28.66; H, 5.08%.

{η^3-allylPt[P(i-$C_3H_7)_3$]$SnCl_3$} (9)

P(i-$C_3H_7)_3$ (0.090 g, 0.56 mmol) was added to a suspension of $(C_3H_5PtCl)_4$ (0.153 g, 0.14 mmol) in CH_2Cl_2 (5 ml). The mixture was magnetically stirred for 3 h. $SnCl_2$ (0.106 g, 0.56 mmol) was then added. After stirring for 1.5 h the mixture was filtered to eliminate small quantities of solid material. The solution was concentrated (2.5 ml) and diethylether was added. **9** separated out as a white solid. The material was filtered off, washed with ether and dried (0.140 g, 39% yield). *Anal.* Calc. for $C_{12}H_{26}PPtSnCl_3$: C, 23.18; H, 4.18. Found: C, 23.38; H, 4.16%.

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