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A ^{31}P AND ^{119}Sn NMR STUDY OF TRICHLOROSTANNATE DERIVATIVES OF SOME CHLORIDE-BRIDGED PALLADIUM(II) DIMERS

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Summary

The chloride-bridged dimers [Pd(μ-Cl)(SnCl$_3$)L]$_2$ (L = P(*p*-tolyl)$_3$, P(*p*-C$_6$H$_4$-OMe)$_3$, As(*p*-tolyl)$_3$, AsEt$_3$, PEt$_3$, PPr$_3^n$) have been synthesized and their ^{119}Sn and, where relevant, ^{31}P NMR spectra recorded. For the aryl phosphine and both arsine complexes the dimers exist as both the *sym-trans* and *sym-cis* isomers; however, for the PEt$_3$ and PPr$_3^n$ compounds, there is only one form, which we assign to the *sym-trans* structure. There is a geometric dependence of both ^4J(^{119}Sn, ^{117}Sn) and ^4J(^{119}Sn, ^{31}P). The dimeric complex with P(*p*-tolyl)$_3$ carbonylates 1-heptyne in the presence of excess SnCl$_2$, but is inactive in its absence.

Introduction

A large number of platinum-tin compounds have now been characterised [1], but there have been few reports of corresponding palladium-tin complexes. The products resulting from reaction of [PdCl$_4$]$^{2-}$ with SnCl$_2$ [2] have been identified and SnCl$_2$ derivatives of *trans*-[PdCl$_2$L$_2$] (L = tertiary phosphine or arsine) have also been characterised [3]. Indeed, *trans*-[PdCl$_2$L$_2$], in the presence of an excess of SnCl$_2$, is an active catalyst for the homogeneous carbonylation of alkynes [4]. We have now investigated the interaction of SnCl$_2$ with the chloride-bridged dimers *sym-*, *trans*-[Pd$_2$Cl$_4$L$_2$], where L is a tertiary phosphine or arsine ligand, and have made a preliminary study of the catalytic activity of one of the compounds formed.

Results and discussion

NMR spectroscopy

Treatment of CH$_2$Cl$_2$ solutions of *sym-*, *trans*-[Pd$_2$Cl$_4$L$_2$] (L = P(*p*-tolyl)$_3$, P(*p*-C$_6$H$_4$OMe)$_3$, As(*p*-tolyl)$_3$, AsEt$_3$, PEt$_3$, PPr$_3^n$) with two equivalents of SnCl$_2$ followed by the addition of diethyl ether leads to the isolation of crystalline solids with analyses consistent with the formula [PdCl(SnCl$_3$)L]$_2$. The ^{119}Sn NMR spectra

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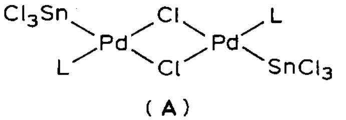
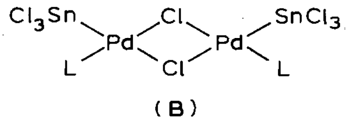
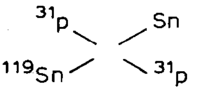
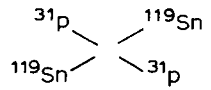
recorded with CH_2Cl_2/CD_2Cl_2 solutions of these solids show very broad resonances at ambient temperature, but below 213 K, these signals are sharp. NMR parameters for the complexes are given in Table 1. Figure 1 shows the ^{119}Sn NMR spectrum of the P(*p*-tolyl)$_3$ derivative recorded at 203 K, which comprises two sets of sharp signals consistent with the isomers **A** and **B**. We have assumed that the pattern at lower frequency is due to isomer **A**.


(A)


(B)

The ^{119}Sn NMR spectrum of this isomer comprises contributions from the three isotopomers containing ^{119}Sn, which we abbreviate as **1**–**3**, where Sn represents


(1)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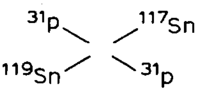
(3)

isotopes other than ^{117}Sn ($I = 1/2$, natural abundance 7.6%) and ^{119}Sn ($I = 1/2$, natural abundance 8.6%). The total relative intensities of the sub-spectra due to **1**, **2** and **3** are readily calculated as 83.8, 8.6, and 7.6% respectively. Strictly, the sub-spectrum due to **1** corresponds to the X part of an AA′X spectrum (assuming that tin isotope effects are negligible). However, since our ^{31}P NMR measurements show that $^4J(^{31}P, ^{31}P)$ is small * compared to the phosphorus–tin interactions, this sub-spectrum appears as a first-order doublet of doublets, and consequently values of $^2J(^{119}Sn, ^{31}P)$ and $^4J(^{119}Sn, ^{31}P)$ can be measured. The weaker lines in the spectrum are due to isotopomers **2** and **3**; analysis of the sub-spectrum due to **3** leads to a value for $^4J(^{119}Sn, ^{117}Sn)$. A similar analysis can be made of the spectrum of isomer **B**. NMR measurements on the analogous P(*p*-$C_6H_4OMe)_3$ compound show that this also exists as a mixture of isomers **A** and **B** in solution.

In contrast to the aryl phosphine derivatives, low temperature NMR measurements on the two alkyl phosphine compounds show that only one isomer is present in both cases. Surprisingly, the PPr^n_3 compound shows a very small two-bond tin–phosphorus coupling; in the case of the PEt_3 complex, ^{119}Sn–^{31}P coupling could not be resolved, even at 193 K where the ^{31}P and ^{119}Sn resonances are relatively sharp.

The ^{119}Sn NMR spectra of the two arsine derivatives both show two sharp resonances at 213 K. Each signal shows weak satellites consistent with coupling to ^{117}Sn arising from isotopomer **3** (e.g. see Fig. 2) and we conclude that these arsine compounds also exist as mixtures of the two isomers **A** and **B** in solution. The appearance of these ^{117}Sn satellites in both these spectra and those of the phosphine analogs support the view that the complexes are dimers in solution.

It will be seen from Table 2 that there are two markedly different magnitudes for

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* In theory, ^4J(PP) can be measured in the ^{31}P sub-spectra due to isotopomers containing a ^{119}Sn or a ^{117}Sn nucleus; however, at the temperature of our measurements the phosphorus line-width are such that we are unable to resolve this coupling, although we can assign to it an upper limit of ca. 5 Hz.

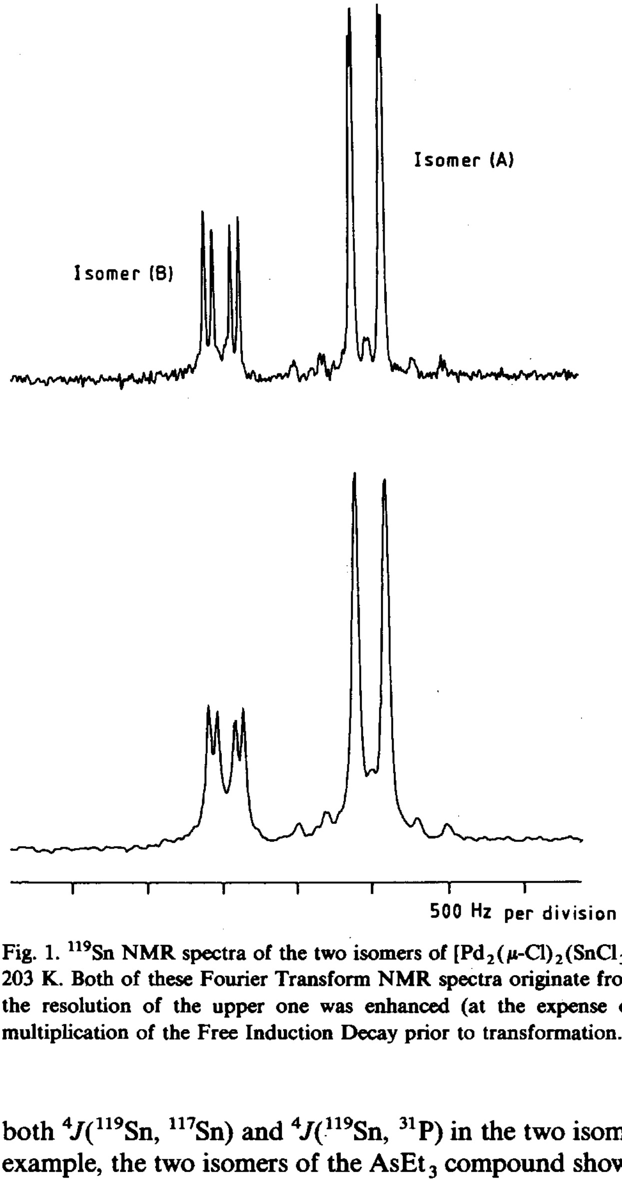


Fig. 1. ^{119}Sn NMR spectra of the two isomers of $[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]$ (L = P(*p*-tolyl)$_3$) recorded at 203 K. Both of these Fourier Transform NMR spectra originate from the same measurement. However, the resolution of the upper one was enhanced (at the expense of some signal/noise) by Gaussian multiplication of the Free Induction Decay prior to transformation.

both $^4J(^{119}Sn, ^{117}Sn)$ and $^4J(^{119}Sn, ^{31}P)$ in the two isomeric forms of our dimers. For example, the two isomers of the $AsEt_3$ compound show values for $^4J(^{119}Sn, ^{117}Sn)$ of 744 and 170 Hz, respectively. Similarly, the magnitudes of $^4J(^{119}Sn, ^{31}P)$ for the two isomers of the P(*p*-tolyl)$_3$ complex also differ significantly (15 and 58 Hz, respectively). Unfortunately, for these dimers the differences in the magnitudes of J do not indicate which coupling constants belong to which isomer. It has been shown that the analogous platinum compounds $[Pt(\mu\text{-}Cl)(SnCl_3)L]_2$ (L = PEt_3, P(*p*-tolyl)$_3$, or $AsEt_3$) exist solely as the *sym-*, *trans*-isomer in solution [2] and this assignment is supported by the solid-state structure of the PEt_3 complex [5]. However, no $^4J(^{119}Sn, ^{117}Sn)$ or $^4J(^{119}Sn, ^{31}P)$ data are available for comparison. Since our PPr^n_3 derivative also occurs as only one isomer in which we do not observe $^4J(^{119}Sn, ^{31}P)$ coupling and as no $^4J(^{119}Sn, ^{31}P)$ coupling is observed in the Pt-PEt_3 analog, we assume that it is the *sym-*, *trans*-form (i.e. isomer A). As species A has a value of 708

TABLE 1

NMR PARAMETERS FOR THE ISOMERS A AND B OF $[Pd_2(\mu\text{-Cl})_2(SnCl_3)_2L_2]$ [a]

L =	$P(p\text{-tolyl})_3$ [b]		$P(p\text{-}C_6H_4OMe)_3$ [c]		$As(p\text{-tolyl})_2$ [c]		$AsEt_3$ [c]		PEt_3 [d]	PPr^n_3 [d]
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**		
$\delta(^{31}P)$	36.0	35.4	33.3	34.4					45.6	36.3
$\delta(^{119}Sn)$	−239	−229	−238	−225	−277	−261	−2441	−250	−218	−195
$^2J(^{119}Sn, ^{31}P)$	195	174	202	189						35
$^4J(^{119}Sn, ^{31}P)$	15	58	18	55						
$^4J(^{119}Sn, ^{117}Sn)$	799	120 [e]	788	288 [e]	794	146	744	170		

[a] ^{31}P and ^{119}Sn shifts are quoted in ppm relative to 85% H_3PO_4 and $SnMe_4$, respectively; coupling constants are in Hz. [b] In CH_2Cl_2/CD_2Cl_2 at 213 K. [c] At 203 K. [d] At 193 K. [e] 20 Hz.

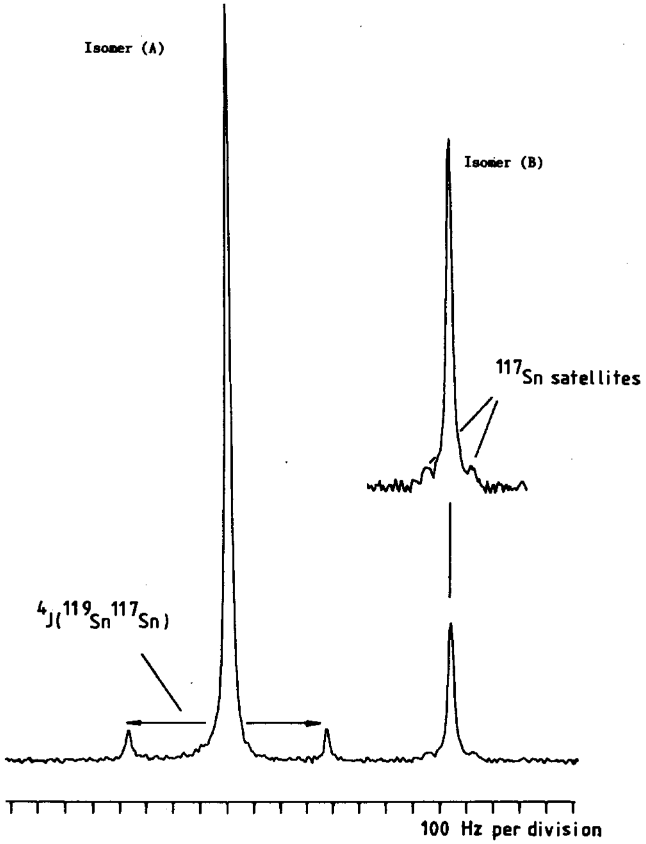


Fig. 2. ^{119}Sn NMR spectrum of the two isomers of $[Pd(\mu\text{-}Cl)(SnCl_3)(AsEt_3)]_2$ recorded at 213 K.

Hz for $^4J(^{119}Sn, ^{117}Sn)$, we are now in a position to assign the resonances for the isomers of the other compounds: e.g. we have assigned the *sym-,trans*-isomer of the $AsEt_3$ derivative as the one with the tin–tin coupling of 744 Hz.

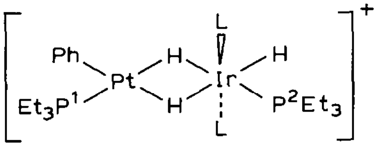
TABLE 2

ANALYTICAL DATA FOR THE COMPLEXES $[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]$ [a]

L	Found (calcd.) (%)			Yield (%)
	C	H	Cl	
$P(p\text{-tolyl})_3$	37.70 (37.57)	3.19 (3.16)	21.29 (21.12)	85
$P(p\text{-}C_6H_4OMe)_3$	35.11 (35.06)	3.00 (2.95)	-	71
PPr^n_3	20.38 (20.48)	3.62 (4.02)		68
$AsEt_3$	13.59 (13.62)	2.84 (2.86)	27.21 (26.80)	73
PEt_3	15.02 (14.86)	2.95 (3.12)		71

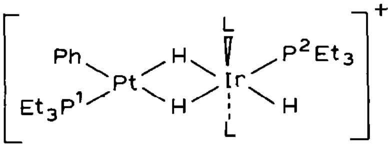
This appears to be the first report of the observation of four-bond tin–tin interactions. Values in excess of 700 Hz for $^{4}J(^{119}\mathrm{Sn}, ^{117}\mathrm{Sn})$ are not necessarily surprising when it is considered that two-bond couplings for two $SnCl_3$ ligands mediated by a transition metal can be greater than 40000 Hz [6]. The value of $^{3}J(^{119}\mathrm{Sn}, ^{117}\mathrm{Sn})$ can vary from several hundred to greater than one thousand Hz [7]. As we assume the two ends of these palladium dimers to be sterically independent, the existence of two isomeric forms when L is $P(p\text{-tolyl})_3$, $P(p\text{-}C_6H_4OMe)_3$, $AsEt_3$, or $As(p\text{-tolyl})_3$, but only one form when L is PEt_3 or PPr_3^n, appears to be a function of the donor/acceptor capacity of L.

In principle, the geometric dependence of either $^{n}J(^{119}\mathrm{Sn}, ^{117}\mathrm{Sn})$ [8], or a four-bond coupling constant is not new. The isomeric binuclear cationic complexes **4** and **5** show a geometric dependence of $^{4}J(P^1, P^1)$ [11].



(4)

$^{4}J(P^1,P^2)$ 43 Hz



(5)

not observed

However, the magnitude of $^{4}J(^{119}\mathrm{Sn}, ^{117}\mathrm{Sn})$ is somewhat unexpected. Since the $SnCl_3$ ligand is a partner in the production of (a) $^{2}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ values of > 1000 Hz [1b,9]; (b) > 4000 Hz $^{2}J(^{119}\mathrm{Sn}, ^{31}\mathrm{P})$ interactions [10], and (c) $^{2}J(^{199}\mathrm{Hg}, ^{119}\mathrm{Sn})$ values [12] of > 40000 Hz, this ligand is clearly somewhat unique.

Carbonylation of hept-1-yne

Knifton has shown that *trans*-$[PdCl_2L_2]/SnCl_2$ mixtures (L = tertiary phosphine) catalyse the regioselective carbonylation of alkynes [4]; in particular, when L is $P(p\text{-tolyl})_3$, hept-1-yne can be carbonylated under ambient conditions, and with a selectivity in excess of 92 mol%. It was therefore of interest to assess the performance of $[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]$ (L = $P(p\text{-tolyl})_3$) in catalysing the same reaction. In relation to this, studies by Clark and co-workers [13] have shown that complexes such as *cis*-$[PtCl_2L(PR_3)]$ (L = CO, R = alkyl or aryl) and *sym*-, *trans*-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (i.e. complexes with one phosphine ligand per Pt) in the presence of $SnCl_2$ are much better catalyst precursors for alkene hydroformylation than the bis-phosphine systems *cis*-$[PtCl_2(PR_3)_2]/SnCl_2$.

The catalysed reaction we chose for study was the acetylene carbonylation described by Knifton [4], viz. eq. 1:

$$RC{\equiv}CH + CO + R'OH \rightarrow RCH{=}CHCOOR' \qquad (1)$$

$$(R = CH_3(CH_2)_4,\ R' = CH_3)$$

The catalyst mixtures studied were (a) *trans*-$[PdCl_2L_2]/5SnCl_2$, (b) $[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]$, and (c) $[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]/8SnCl_2$ (0.04 mmol complex based on Pd, L = $P(p\text{-tolyl})_3$]. These were stirred in a mixture of isobutyl methyl ketone (2.5 ml), methanol (0.5 ml), and hept-1-yne (0.26 ml, 2 mmol) until all the solid had dissolved (ca. 5 min). Carbon monoxide gas was then gently bubbled through the solution for 4 h, after which the ^{13}C NMR spectrum of the mixture was recorded (benzene-d_6 was added to stabilize the magnetic field).

Our results for mixture (a) are similar to those reported by Knifton [4], i.e. only moderate alkyne conversion (ca. 50 mol%), but highly selective formation of methyl 2-octenoate (~ 90 mol%). Mixture (c) also showed high selectivity, but a considerably lower alkyne conversion (ca. 25 mol%). In contrast, mixture (b) showed essentially no catalytic activity. The results demonstrate that (i), a high $SnCl_2$ concentration is required for catalytic activity, and (ii), a Pd/phosphine ratio of 1/2 gives better conversion than a ratio of 1/1. It is noteworthy in connection with points (i) and (ii) that ^{31}P NMR data show that mixture (c) contains bis-phosphine complexes of palladium so that some disproportionation has taken place. Possibly, the lower activity of catalyst (c) is related to the decrease in concentration of the active complex as a consequence of the smaller phosphine/palladium ratio.

Experimental

Complexes of the type $[Pd(\mu\text{-}Cl)(SnCl_3)L]_2$ ($L = PEt_3$, PPr^n_3, $P(p\text{-tolyl})_3$, $P(p\text{-}C_6H_4OMe)_3$, $As(p\text{-tolyl})_3$, or $AsEt_3$) were prepared by the following general methods:

A CH_2Cl_2 solution of *sym-*, *trans-*$[Pd_2Cl_4L_2]$ was stirred with 2 equiv. of $SnCl_2$ for 2 h until all the solid had dissolved. During this time, some decomposition to palladium metal occurred, but filtration through Celite gave a pale-orange solution from which a sample of $[Pd_2Cl_2(SnCl_3)_2L_2]$ was isolated in good yield by addition of diethyl ether. Analytical data for some of the products are given in Table 2. The PEt_3 complex was prepared as follows: $[Pd_2Cl_4(PEt_3)_2]$ (196 mg, 0.34 mmol) and $SnCl_2$ (193 mg, 1.02 mmol) were stirred in CH_2Cl_2 for 2.5 h. Filtration to remove excess $SnCl_2$ was followed by removal of the solvent. Recrystallization from CH_2Cl_2/petroleum ether gave 230 mg of the product as orange crystals.

^{31}P and ^{119}Sn NMR spectra were measured using a Bruker WM-250 instrument as reported previously [1–3] and shifts are quoted with respect to external H_3PO_4 and Me_4Sn, respectively.

Acknowledgement

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