Inorganica Chimica Acta, 45 (1980) L51–L53
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A ^{117}Sn and ^{31}P NMR Study of *Trans*-[Pt(SnCl$_3$)$_n$-Cl$_{2-n}$(P(CH$_2$CH$_3$)$_3$)$_2$] (n = 1,2) in Acetone: the Effect of Solvent

B. R, KOCH*, G. V. FAZAKERLEY and E. DIJKSTRA

Department of Analytical Science, University of Cape Town, Rondebosch 7700, South Africa

Received March 13, 1890

Introduction

The binding of tin(II) halides to transition metals is well known and numerous compounds containing metal to tin bonds have been prepared [1]. In particular platinum(II, IV) salts bind to stannous halides forming characteristically coloured complexes, a phenomenon that has been exploited in the quantitative determination of platinum [2–5]. In addition platinum complexes containing the trichlorostannato moiety have been found to possess useful catalytic properties [6–8]. As part of a programme to investigate the structure and ^{117}Sn/^{119}Sn NMR parameters of tin(II) containing platinum(II) compounds, we have prepared *trans*-[Pt(SnCl$_3$)$_n$Cl$_{2-n}$(PEt$_3$)$_2$] (n = 1 or 2) complexes. Pregosin and Sze have recently studied similar complexes by means of ^{31}P and ^{195}Pt NMR in CDCl$_3$ and CD$_2$Cl$_2$ solutions [9]. Although ^{195}Pt chemical shifts of *trans*-[Pt(SnCl$_3$)$_n$-Cl$_{2-n}$(PEt$_3$)$_2$] (n = 1, 2) were reported, no ^{1}J(Sn–Pt) coupling constants were quoted, presumably due to low solubility of these complexes in CD$_2$Cl$_2$ at *ca.* 223 K. Very recently however, unusually large ^{2}J(Sn–H) coupling constants (1663 and 1740 Hz for ^{117}Sn and ^{119}Sn respectively) were reported for the complex *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] at 203 K [10].

We find that at 190 K the complexes *trans*-[Pt(SnCl$_3$)$_n$Cl$_{2-n}$(PEt$_3$)$_2$] are sufficiently soluble in acetone so that ^{1}J(Pt–Sn) coupling constants are readily observable in a reasonable time period. Nevertheless the title complexes were found to disproportionate extensively in acetone solution, and it is this process we wish to report here.

Experimental

Treatment of *cis/trans*-[PtCl$_2$(PEt$_3$)$_2$] in acetone with stoichiometric amounts of anhydrous SnCl$_2$, followed by heating under reflux for 10 min. yielded yellow [Pt(SnCl$_3$)Cl(PEt$_3$)$_2$] and orange [Pt(SnCl$_3$)$_2$-(PEt$_3$)$_2$] which were recrystallised from absolute ethanol. Only the *trans* isomers could be made. All operations were carried out under an atmosphere of dry N$_2$. Microanalysis data yielded 20.8% C, 4.3% H and 16.1% C, 3.4% H while C$_{12}$H$_{30}$P$_2$Cl$_4$SnPt and C$_{12}$H$_{30}$P$_2$Cl$_6$Sn$_2$Pt require 20.83% C, 4.37% H and 16.35% C, 3.43% H respectively.

^{31}P and ^{117}Sn NMR** spectra were measured in 10 mm tubes using a Brucker DS-90 spectrometer at 36.44 and 32.07 MHz respectively. ^{31}P and ^{117}Sn chemical shifts are quoted relative to external 85% H$_3$PO$_4$ in ^{2}H$_2$O and neat (CH$_3$)$_4$Sn at room temperature respectively. All solutions were freshly made using 1:1 mixtures of hexadeutero-acetone and ordinary acetone.

Results

The ^{31}P NMR spectrum of *trans*-[Pt(SnCl$_3$)Cl-(PEt$_3$)$_2$], (A), in acetone at room temperature, shows only a single sharp resonance flanked by two ^{1}J(Pt–P) satellites. No ^{2}J(Sn–P) coupling satellites are observed, indicating fast Pt–Sn bond breaking on the NMR time scale. On cooling to 190 K, the spectrum becomes quite complex and three major species are identifiable in solution. Additionally ^{2}J(Sn–Pt) coupling satellites become clearly visible around *two* of the three ^{31}P resonances. The corresponding ^{117}Sn NMR spectrum shows the presence of only two sets of resonances with unusually large ^{1}J(Pt–^{117}Sn) coupling constants. Table I collects the ^{31}P and ^{117}Sn NMR data for the title complexes.

A similar set of ^{31}P and ^{117}Sn NMR spectra is obtained from an acetone solution of *trans*-[Pt(Sn-Cl$_3$)$_2$(PEt$_3$)$_2$], (B), although the relative intensities of the three sets of ^{31}P and two ^{117}Sn resonances differed somewhat from those observed in the spectra of (A). It was, however, not possible to estimate the relative intensities reliably. Addition of further portions of anhydrous SnCl$_2$ to solutions of either (A) or (B) showed that once Sn(II) to Pt(II) ratios of *ca.* 5:1 are attained, only one set of ^{31}P and ^{117}Sn resonances is observed. Identical results are obtained whether the *cis*- or *trans*-[PtCl$_2$(PEt$_3$)$_2$] complex is used as starting material. Of the many possible species that may be postulated to exist in solution, the only satisfactory model that is consistent with these experiments may be given as follows:

---

*Author to whom correspondence should be addressed.

**Due to instrumental difficulties we achieved slightly better quality spectra for ^{117}Sn as compared to ^{119}Sn nuclei even though the latter is *ca.* 1% more abundant. Other workers have normally used the ^{119}Sn isotope. However use of ^{117}Sn nuclei in no way affects the conclusion reached.

TABLE I. ^{117}Sn and ^{31}P NMR Parameters[a] for the Title Complexes in Acetone ($R = CH_2CH_3$).

Compound	T/K	$\delta^{31}P$	$\delta^{117}Sn$	$\lvert{}^1J({}^{195}Pt–{}^{31}P)\rvert$	$\lvert{}^1J({}^{195}Pt–{}^{117}Sn)\rvert$	$\lvert{}^2J({}^{117,119}Sn–{}^{31}P)\rvert$
cis-$[PtCl_2(PR_3)_2]$	ambient	12.2	–	3125	–	–
trans-$[PtCl_2(PR_3)_2]$	ambient	15.6	–	2418	–	–
trans-$[Pt(SnCl_3)Cl(PR_3)_2]$	ambient	17.6	b	2068	–	–
	190	14.8	−270.0[g]	2069	29180	246[d]
		13.7		3481	–	c
		−10.4	−84.9[g]	1454	19670	266, 277[e]
trans-$[Pt(SnCl_3)_2(PR_3)_2]$	ambient	~18[f]	b	~2070	–	
	200	15.4	−235.7[g]	2065	29180	239, 250
		13.9	–	3480	–	c
		−7.4	−88.4[g]	1453	19670	265, 276
trans-$[Pt(SnCl_3)_2(PR_3)_2]$ + excess $SnCl_2$	200	−6.7	−88.7	1452	19500	265, 276
trans-$[Pt(SnCl_3)Cl(PR_3)_2]$[h]	223	13.4	–	2042	28954[i]	227, 237
trans-$[Pt(SnCl_3)_2(PR_3)_2]$[h]	223	8.4	–	1873	20410[i]	227, 246

[a] Coupling constants in Hz estimated to ±2.5 Hz for J(PtP) and ±25 Hz for J(PtSn). Chemical shifts in ppm relative to 85% H_3PO_4 and neat $(CH_3)_4Sn$, ±0.1 ppm. [b] Resonance not observed, excessively broad. [c] No $^2J(SnP)$ could be detected. [d] Average of ^{117}Sn and ^{119}Sn coupling constants. [e] ^{117}Sn and ^{119}Sn couplings resolved, ratio $^{119}Sn:^{117}Sn = 1.04$ close to theoretically expected value. [f] Resonances very broad. [g] Chemical shift concentration dependent. [h] From ref. [9], solvent CH_2Cl_2. [i] From ref. [13], $^1J(^{195}Pt–^{119}Sn)$.

$$cis/trans\text{-}[PtCl_2(PEt_3)_2] + n\ SnCl_2 \xrightarrow{\text{acetone}}$$

$$trans\text{-}[Pt(SnCl_3)_nCl_{2-n}(PEt_3)_2] \qquad (1)$$

$$trans\text{-}[Pt(SnCl_3)Cl(PEt_3)_2] \xrightleftharpoons{\text{acetone}}$$

$$cis\text{-}[PtCl_2(PEt_3)_2] + SnCl_2 \qquad (2)$$

$$SnCl_2 + trans\text{-}[Pt(SnCl_3)Cl(PEt_3)_2] \xrightleftharpoons{\text{acetone}}$$

$$trans\text{-}[Pt(SnCl_3)_2(PEt_3)_2] \qquad (3)$$

Although it is not possible to state unambiguously whether the complex $[PtCl_2(PEt_3)_2]$ as postulated in eqn. (2) above is *cis* or *trans*, the $^1J(Pt–P) = 3480$ Hz as given in Table I strongly suggest the *cis* isomer. Two bond tin phosphorous coupling satellites were only evident about the ^{31}P resonances of both species (A) and (B), but not for third major resonance present in the spectrum. It might be expected that at Sn:Pt ratios of >2 an unbound $SnCl_2$(acetone) resonance is observable. A diligent search for such an unbound $SnCl_2$ resonance proved fruitless however. It appears that the ^{117}Sn resonance of unbound $SnCl_2$ at *ca.* 200 K is excessively broad and thus not observable under these conditions. Cooling an acetone solution of $SnCl_2$ indeed results in the progressive broadening of the sharp ^{117}Sn resonance observed at ambient temperatures. Further support for the proposed disproportionation lies in the observations of Wilkinson *et al.* in that $[Pt(SnCl_2)Cl(PPh_3)_2]$, prepared in ethanol, rapidly decomposes into $[PtCl_2(PPh_3)_2]$ and $SnCl_2$ in acetone solutions [11].

Turning to the exceptionally large $^1J(Pt–^{117}Sn)$ coupling constants of 29180 and 19670 Hz assigned to (A) and (B) respectively one notes that substituting a Cl^- for a $SnCl_3^-$ group results in a remarkably large change in the magnitude of $^1J(Pt–^{117}Sn)$. Generally the absolute magnitude of one bond coupling constants can be interpreted in terms of the Fermi contact expression [12]. This theory predicts J(Pt–Sn) to be proportional to (1) the product of gyromagnetic ratios of the coupling nuclei, (2) the products of the *s*-characters of the bonding orbitals and (3) the product of the *s*-electron spin density at the two nuclei. Although it is believed that the trichlorostannato moiety is strongly π-withdrawing [13], it is presently not possible to state whether the large difference in $^1J(Pt–Sn)$ values of (A) and (B) is due to changes in *s*-electron density at the Pt(II) nucleus and/or changes in the *s*-character of the bonding orbitals used. Very recently it has come to our attention that other workers have observed similarly large $^1J(Pt–^{119}Sn)$ coupling constants in *trans*-$[Pt(SnCl_3)_nCl_{2-n}(P(Et)_3)_2]$ of 28954 Hz (n = 1) and 20410 Hz (n = 2) [14].

In conclusion it may be stated that as in the case of ^{195}Pt NMR, ^{117}Sn or ^{119}Sn NMR shows itself to be a very useful tool in the understanding of transition metal complexes containing tin(II) bonds. The use of acetone as solvent is complicated by disproportionation that occurs, so that its excellent properties as a solvent are partly offset by such complications.

Acknowledgments

We thank the University of Cape Town and the Council for Scientific and Industrial Research for financial assistance.

References

1 F. G. A. Stone, New Pathways in Inorganic Chemistry', Cambridge University Press, Ch. 12, 283 (1968).
2 F. A. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers, London (1973).
3 E.B. Sandell, Colorimetric Determination of Trace Metals', Interscience Publishers, New York, p. 355, (1944).
4 F. Pantani and G. Piccardi, *Analytica Chim. Acta, 22,* 231 (1960).
5 M. A. Khattak and R. J. Magee, *Tantala, 12,* 733 (1965).
6 R. D. Cramer, E. L. Jenner, R. V. Lindsey Jr. and U. G. Stolberg, *J. Am. Chem. Soc., 85,* 1691 (1963).
7 I. Schwager and J. F. Knifton, *J. Catal., 45,* 256 (1976).
8 J. F. Knifton, *J. Org. Chem., 41,* 793 (1976).
9 P. S. Pregosin and S. N. Sze, *Helv. Chim. Acta, 61,* 1848 (1976).
10 K. A. Ostoja Starzewski, H. Ruegger and P. S. Pregosin, *Inorg. Chim. Acta, 36,* L445 (1979).
11 J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.,* 5176 (1964).
12 J. A. Pople and D. P. Santry, *Mol. Phys., 8,* 1 (1964).
13 J. D. Donaldson, *Prog. Inorg. Chem., 8,* 287 (1967).
14 K. A. Ostoja Starzowski and P. S. Pregosin, unpublished results, (1979).