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Dimeric Platinum Complexes with Trichlorostannato Ligands. Relationship between Pt–Sn Bond Lengths and $^1J(^{195}Pt, ^{119}Sn)$.

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The interest in trichlorostannate complexes of platinum(II) as intermediates in the homogeneous hydrogenation and hydroformylation of organic substrates is growing [1]. As part of our program in the area [2–6] we have studied the spin–spin coupling between ^{119}Sn and ^{195}Pt and found that this parameter can range from 5780–29242 Hz [7]. Since such large changes in one-bound platinum ligand coupling constants are sometimes indicative of changes in metal–ligand bond lengths [8, 9], we have begun parallel studies using X-ray diffraction and NMR methods and report here 1) an unusual structure for the dimeric complex *sym–trans*-$[Pt(SnCl_3)(\mu\text{-}Cl)(PEt_3)]_2$ and 2) a correlation of the Pt–Sn separation with $^1J(^{195}Pt, ^{119}Sn)$.

Reaction of *sym–trans*-$[PtCl(\mu\text{-}Cl)L]_2$, L = PEt_3, $P(p\text{-}CH_3C_6H_4)_3$, $AsEt_3$, with two equivalents of $SnCl_2$ affords the dimers $[Pt(SnCl_3)(\mu\text{-}Cl)L]_2$, (I), in which the $SnCl_3$ groups are terminal. In solution the ^{119}Sn NMR signals clearly reveal only a single $^1J(^{195}Pt, ^{119}Sn)$ coupling constant (there would be two such interactions if the tin were bridging). The values $^1J(^{195}Pt, ^{119}Sn)$ are significantly larger than previously reported [7] and this may be related to the small *trans* influence of the bridging halogen. There seems to be a small *cis* effect in that $^1J(^{195}Pt, ^{119}Sn)$ for L = $AsEt_3$ at 33691 Hz, is slightly smaller than that for L = PEt_3, 35309 Hz or $P(p\text{-}CH_3C_6H_4)_3$, 35278 Hz.

The structure for the PEt_3 complex was determined by X-ray diffraction and is shown in Fig. 1. The molecule consists of discrete chlorine bridged Pt dimers. Each Pt atom is bonded to $SnCl_3$ and PEt_3 groups which are *cis* with respect to each other, but the entire molecule has the *sym–trans* geometry. The coordination about the platinum is distorted square planar. Interstingly, the molecule is of the 'hinged' type, in contrast to the planar, *sym–trans*-$[Pt\text{-}Cl(\mu\text{-}Cl)(PPr_3)]_2$ [10]. We note that the separation between the two platinum atoms at 3.035(2) Å is reduced from the 3.54 Å value observed for planar dimers [8, 11], and in this connection that $^2J(^{195}Pt, ^{195}Pt)$ is 531 Hz, increased from the 200 Hz value found in $[PtCl(\mu\text{-}Cl)(PPr_3)]_2$ [11].

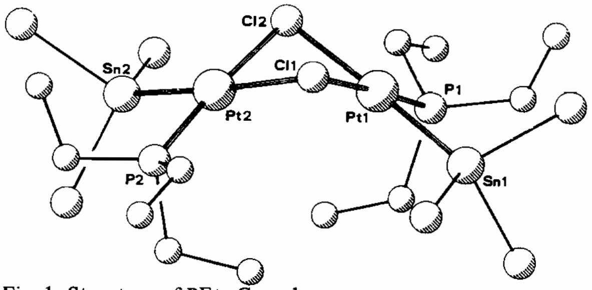

Fig. 1. Structure of PEt_3 Complex.

Of special interest are the Pt–Sn bond distances 2.478(3) and 2.487(3) Å, as these are rather short. The oxime complexe $[PtCl(SnCl_3)(PEt_3)(PhC(NH_2){=}NOH)]$ (II) (tin *trans* to chlorine) shows a Pt–Sn length of 2.501(1) Å; [12]; however, more representative are $[Pt(SnCl_3)_5]^{3-}$ (III) 2.553 Å (axial) 2.572 Å (equatorial) [13], $[Pd_2Cl(SnCl_3)(dpm)_2]$ 2.585 Å [14], $[Pt(SnCl_3)_3(AsMe_3)_2]^{2-}$, (IV) 2.602 Å [15], $[PtCl(SnCl_3)(DIOP)]$, (V), 2.598 Å [16] and $[Pt(SnCl_3)_2(P(OPh)_3)_2]$, (VI), 2.601 Å [17]. Although complexes (III) and (IV) are five-coordinate and not directly comparable to the square planar compounds (I), (II), (V) and (VI), the Pt–Sn distance is generally longer when the *trans* ligand has a substantial *trans* influence. It would seem then that the Pt–Sn bond length shows a dependence on the remaining ligands similar to that observed for Pt–P bond distances [8].

Table II shows coupling constant data for some $SnCl_3^-$ complexes for which solid state structural information is at hand. Clearly, where the Pt–Sn bond distance is relatively short, $^1J(^{195}Pt, ^{119}Sn)$ appears at the upper end of its range. Interestingly, the Pd–Sn separation of 2.473 Å, found in the $[PdCl_3(SnCl_3)]^-$ anion fits well with the observed coupling constant, 34,600 Hz, for the platinum analog [18]. To our knowledge, this is the first example of a metal–metal separation which correlates with its corresponding spin–spin coupling constant. A closer inspection of the data in Table II reveals that the $PtCl_2(SnCl_3)_2^{2-}$ anion does not quantitatively fit well with the remaining molecules. This is not disturbing since it does show a large $^1J(^{195}Pt, ^{119}Sn)$ value and a short Pt–Sn bond length and this qualitative trend is the most important. Further there is no theoretical reason to expect a linear relationship between these two observables; however, the qualitative trend is in keeping with the now accepted idea that coupling constants and bond lengths are relatable concepts [8, 9, 19]. We have observed that $^1J(^{195}Pt, ^{119}Sn)$ values for the compounds *trans*-$[PtH(SnCl_3)(PR_3)_2]$ fall in

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TABLE I. Some Relevant Bond Lengths (Å) and Bond Angles (°) for *sym–trans*-$[Pt(SnCl_3)(\mu\text{-}Cl)PEt_3)]_2$ [20] (e.s.d.s are given in parentheses).

Pt(1)–Pt(2)	3.036(2)	Pt–Cl–P[a]	80.5(3)
Pt–Cl[a]	2.35(1)	Cl(1)–Pt(1)–Cl(2)	84.1(2)
Pt(1)–Sn(1)	2.487(3)	Cl(1)–Pt(2)–Cl(2)	84.6(4)
Pt(1)–P(1)	2.20(1)	Sn(1)–Pt(1)–P(1)	93.8(3)
Pt(2)–Sn(2)	2.478(3)	Sn(2)–Pt(2)–P(2)	94.9(3)
Pt(2)–P(2)	2.18(1)		
Sn–Cl[a]	2.32(2)	Sn(2)–Pt(2)–Cl(2)	86.4(3)
		P(2)–Pt(2)–Cl(1)	94.1(4)
		Sn(1)–Pt(1)–Cl(1)	88.5(3)
		P(1)–Pt(1)–Cl(2)	94.1(4)
		Sn(1)–Pt(1)–Pt(2)–Sn(2)	135.0(8)
		P(1)–Pt(1)–Pt(2)–P(2)	–119.2(10)
		P(1)–Pt(2)–Cl(2)–Pt(1)	–177.3(9)

[a] Average value.

TABLE II. Pt–Sn Bond Distances and $^1J(^{195}Pt, ^{119}Sn)$ Values.

Compound	(Pt–Sn), Å	$^1J(^{195}Pt, ^{119}Sn)$Hz
$[PtCl_2(SnCl_3)_2]^{2-}$[a]	2.356	27640
$[Pt(SnCl_3)(\mu\text{-}Cl)(PEt_3)]_2$	2.482(3)	35309
$[PtCl(SnCl_3)(PEt_3)(PhC(NH_2){=}NOH)]$[b]	2.501(1)	32760
$[PtCl(SnCl_3)(DIOP)]$[c]	2.598	17057
$[Pt(SnCl_3)_5]^{3-}$[d]	2.572(1)	16030
$[Pt(SnCl_3)_3(AsMe_3)_2]^{-}$[e]	2.602(1)	19037
$[Pt(SnCl_3)_2(P(OPh)_3)_2]$[f]	2.601(2)	19043

[a] N. W. Alcock and J. H. Nelson, submitted for publication, *J. Chem. Soc. Dalton*, 1982. [b] Ref. 12. [c] Ref. 16. [d] Ref. 13. [e] Ref. 15. [f] Ref. 17.

the range 9067–11,512 Hz and, consequently, expect that the Pt–Sn lengths will be at the upper end of the observed range.

Experimental

Tin(II) dichloride (0.076 g, 0.040 mmol) was added to a solution of $[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ (0.154 g, 0.020 mmol) in 5 ml CH_2Cl_2 and the resulting suspension stirred until all of the solid had dissolved. Filtration was followed by careful treatment with pet. ether (30–60°)* such that the hydrocarbon forms a layer on the CH_2Cl_2. Storage at –20° for one week gave 0.216 g (94%) of product as yellow crystals. Calcd. (Found): C, 12.56 (12.75); H, 2.64 (2.55); Cl, 24.72 (24.61).

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*Yellow crystals of compound (Ia) suitable for an X-ray analysis were obtained with difficulty from CH_2Cl_2/petroleum ether (30–60°) solution, and are stable in the air. Compound (Ia) ($C_{12}H_{30}Pt_2Sn_2P_2Cl_3$, M.W. = 1147.50) is monoclinic, space group P2/C; a = 10.593(6), b = 23.473(8), c = 12.432(6), β = 77.9(4) (least squares refined values); Z = 4; V = 3032.7(4) Å^3; ρ = 2.51 g cm^{-3}; μ = 117.2 cm^{-1}. 4817 independent reflections were collected on a Philips PW 1100 four circle diffractometer using Mo-K$\bar{\alpha}$ graphite monochromated radiation up to $2\theta_{max}$ = 50.0° using an $\omega/2\sigma$ scan technique (scan speed 0.04° s^{-1}, scan width 1.0°). 3195 absorption corrected intensities were considered as observed (having $I_{net} > 3\sigma(I)$) and used for the structural determination. The structure was solved by the heavy atom method and refined by block diagonal least squares to the present agreement factor of 9.3% for the observed reflections, using anisotropic temperature factors for the Pt, Sn, P, Cl atoms, isotropic for the others.