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PHOSPHORUS-31, TIN-119 AND PLATINUM-195 NMR STUDIES ON SOME PLATINUM(II)-TIN BONDED COMPOUNDS

STUART CARR, RAY COLTON and DAINIS DAKTERNIEKS

Department of Inorganic Chemistry, University of Melbourne, Parkville 3052 (Australia)

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Summary

Phosphorus-31, tin-119 and platinum-195 NMR spectra have been measured for three series of compounds; *cis*-$Pt(PPh_3)_2(Ph)(Z)$ where Z = $SnPh_3$, $SnPh_2Cl$, $SnPhCl_2$, $SnCl_3$, $SnPh_2Br$, $SnPhBr_2$, $SnPh_2I$, $SnPh_2NCS$, $SnPh_2SPh$ and $SnPh_2SCH_2Ph$; *cis/trans*-$Pt(PPh_3)_2(Cl)(Q)$ where Q = $SnMe_2Cl$, $SnBu_2Cl$, $Sn(t\text{-}Bu)_2Cl$, $SnMeCl_2$, $SnBuCl_2$and $SnPhCl_2$; and *cis/trans*-$Pt(PPh_3)_2(Br)(Y)$ where Y = $SnMe_2Br$, $SnBu_2Br$, $SnMeBr_2$, $SnBuBr_2$, $SnPhBr_2$. The ^{195}Pt resonances cover a range of 450 ppm and the ^{119}Sn resonances a range of 300 ppm, with $^1J(Pt-^{119}Sn)$ varying between 7 and 20 kHz. Plots of ^1J(Pt–P*trans*) against $^1J(Pt-^{119}Sn)$ are approximately linear, indicating that the platinum–tin bond is predominantly σ in character.

Introduction

There have been several reports ([1] and ref. cited therein) of tin-119 (tin-117) and platinum-195 NMR spectra of platinum–tin bonded compounds of the types $Pt(PR_3)_2(Cl)_n(SnCl_3)_{2-n}$, $[Pt(PR_3)(SnCl_3)_3]^-$, $[Pt(PR_3)_3SnCl_3]^+$, $[Pt(PR_3)_2(SnCl_3)_3]^-$ and $[Pt(SnCl_3)_5]^{3-}$. Reported platinum–tin coupling constants range between 8000 and 30,000 Hz. These reports all describe compounds that are not easily related to each other in any systematic way, although they are all $SnCl_3^-$ derivatives. They have the disadvantages that they are relatively insoluble and the platinum–tin bond is generally labile on the NMR time-scale, even at low temperatures.

Pidcock et al. [2–4] have reported the preparation of a number of compounds of the type *cis*- and *trans*-$Pt(PPh_3)_2(R')(SnR'R''R''')$ (R′,R″,R‴ = alkyl, aryl, halide) which were prepared by the oxidative addition reaction (eq. 1). The group which

$$Pt^0(PPh_3)_2C_2H_4 + Sn^{IV}(R'_2R''R''') \rightarrow cis/trans\text{-}Pt^{II}(PPh_3)_2(R')(Sn^{II}R'R''R''') \quad (1)$$

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migrates from the tin to the platinum depends on the nature of the groups attached to the tin atom. In some cases, formation of both *cis* and *trans* isomers was revealed by the phosphorus-31 NMR spectra. These compounds are in general quite stable and soluble in organic solvents, and the platinum–tin bond is not labile at room temperature.

In this paper we report the ^{31}P, ^{119}Sn and ^{195}Pt NMR spectra of a related series of compounds of the form $Pt(PPh_3)_2(R')(SnR'R''R''')$, prepared by the oxidative addition reaction 1.

Results and discussion

The compounds (listed in Tables 1 and 2) were prepared either by stirring equimolar quantities of the tin compound and $Pt(PPh_3)_2C_2H_4$ in dry benzene under anaerobic conditions followed by precipitation with hexane, or by mixing the reactants in situ in an NMR tube in dry dichloromethane (eq. 1) [2–4]. New compounds were characterized by comparison of their NMR spectra with those of known compounds of similar formula. In some cases both *cis* and *trans* isomers are observed. The NMR data for all the compounds are listed in Tables 1, 2 and 3.

The general appearance of the NMR spectra is similar for all the compounds. As an example, we consider the ^{31}P, ^{119}Sn and ^{195}Pt spectra of *cis*- and *trans*-$Pt(PPh_3)_2(Cl)(SnMe_2Cl)$. The ^{31}P spectrum of the *cis* isomer in dichloromethane is essentially the same as that previously reported [3], and consists of two main doublets (δ(P) 32.1 ppm δ(P) 21.5 ppm) arising from the inequivalent phosphines (^2J(P–P) 13 Hz). The doublet at higher frequency has two sets of satellites (^1J(Pt–P) 2211 Hz, ^2J(^{119}Sn–P) 2267 Hz) which is consistent with a phosphorus *trans* to a tin atom whereas the doublet at lower frequency has couplings (^1J(Pt–P) 2178 Hz, ^2J(^{119}Sn–P) 65 Hz) indicating a phosphorus *cis* to a tin atom. The ^{195}Pt spectrum (Fig. 1) has a central doublet of doublets, due to couplings to the two different

TABLE 1

THE ^{31}P, ^{119}Sn AND ^{195}Pt NMR PARAMETERS FOR *cis*-$Pt(PPh_3)_2(Ph)(Z)$ [a,b,c] AT 25°C IN CH_2Cl_2 (APPROXIMATE CONCENTRATION 0.13 *M*)

Compound	δ(Pt) (ppm)	^1J(Pt–P*cis*) (Hz)	^1J(Pt–P*trans*) (Hz)	$\delta(Sn_{(com)})$ [d] (ppm)	$\delta(Sn_{(lig)})$ [d] (ppm)
cis-$Pt(PPh_3)_2(Ph)(Z)$					
$Z = SnPh_3$	−4808	2030	2357	−106	−137
$Z = SnPh_2Cl$	−4780	2139	2690	32	−43
$Z = SnPhCl_2$	−4786	2055	3109	56	−33
$Z = SnCl_3$		1977	3710		
$Z = SnPh_2Br$	−4785	2139	2720	29	−40
$Z = SnPhBr_2$	−4788	2068	3143	47	−76
$Z = SnPh_2I$	−4797	2124	2747	2	−114
$Z = SnPh_2NCS$ [e]	−4796	2109	2774	−17	−124
$Z = SnPh_2SPh$	−4784	2093	2569	−4	−66
$Z = SnPh_2SCH_2Ph$	−4799	2062	2551	−7	−55

[a] δ(^{195}Pt) measured relative to external 1.0 *M* H_2PtCl_6 in conc. HCl; estimated error ±2 ppm δ(^{119}Sn) relative to Me_4Sn; estimated error ±2 ppm. δ(^{31}P) relative to 85% H_3PO_4; estimated error 0.1 ppm. [b] *cis*

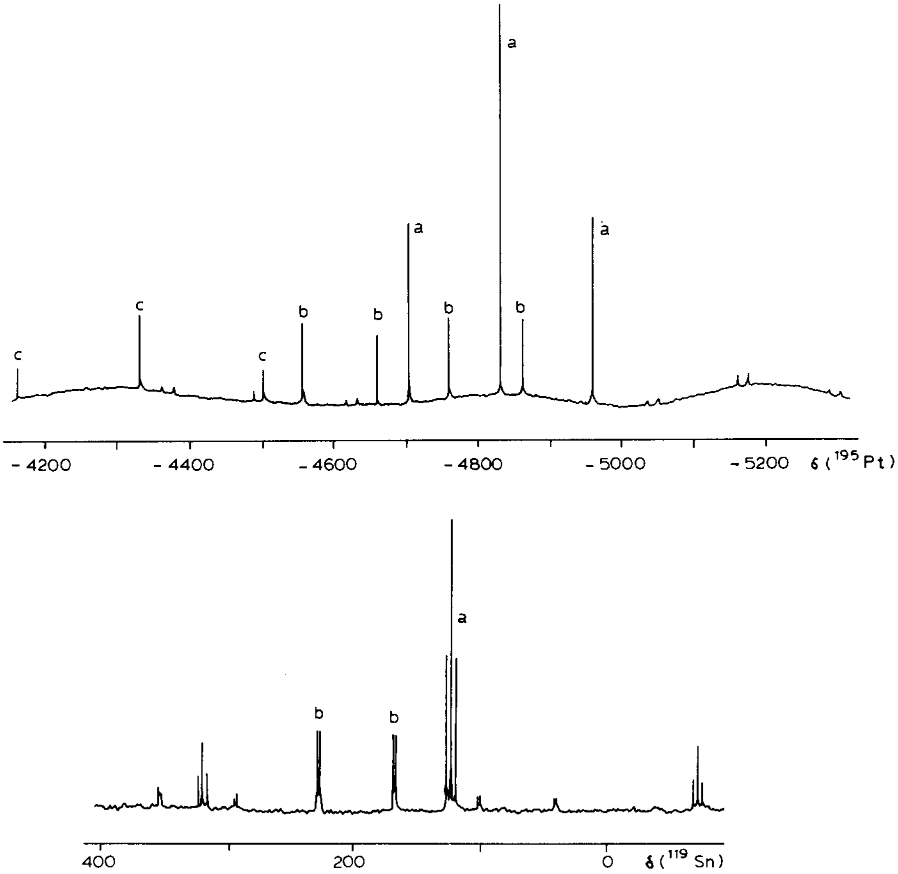

Fig. 1. ^{195}Pt and ^{119}Sn NMR spectra of a mixture of *trans*-Pt(PPh$_3$)$_2$(Cl)(SnMe$_2$Cl), (a), *cis*-Pt(PPh$_3$)$_2$(Cl)SnMe$_2$Cl, (b) and *trans*-Pt(PPh$_3$)$_2$(Me)(Cl) (c).

$\Delta(\delta(\mathrm{Sn}))$ [d] (ppm)	^2J(Sn–P*cis*) (Hz)	^2J(Sn–P*trans*) (Hz)	^1J(Pt–Sn) (Hz)	δ(P *trans*) (ppm)	δ(P *cis*) Pppm)	^2J(P–P) (Hz)
31	161	1934	12686	25.8	20.5	15
75	151	2398	14066	26.6	22.5	15
89	195	2959	16889	25.4	19.7	15
	240	3881		24.1	17.1	16
69	152	2398	13940	25.7	23.8	15
123	183	2954	16241	23.2	21.0	14
116	153	2380	13735	24.1	23.9	15
107	159	2375	14050	26.2	20.1	16
62	153	2185	13306	25.4	20.4	15
48	159	2167	13416	25.2	19.8	15

refers to phosphine adjacent to the tin. [c] Estimated error in all coupling constants is 5 Hz, except ^2J(P–P) where error is 1 Hz. [d] $\Delta(\delta(\mathrm{Sn})) = \delta(\mathrm{Sn}_{(\mathrm{com})}) - \delta(\mathrm{Sn}_{(\mathrm{lig})})$. [e] $^1J(\mathrm{Sn}-{}^{14}\mathrm{N}) = 170$ Hz.

TABLE 2

THE ^{31}P, ^{119}Sn AND ^{195}Pt NMR PARAMETERS[a] OF *cis*-$Pt(PPh_3)_2(Cl)(Q)$ AND *cis*-$Pt(PPh_3)_2(Br)(Y)$ IN CH_2Cl_2 AT 25°C (APPROXIMATE CONCENTRATION 0.13 *M*)

Compound	δ(Pt) (ppm)	^1J(Pt–P*trans*) (Hz)	^1J(Pr–P*cis*) (Hz)	$(\delta Sn)_{com}$ (ppm)	$(\delta Sn)_{free}$ (ppm)	$\Delta(\delta(Sn))$ (ppm)
cis-Pt(PPh₃)₂(Cl)(Q)						
Q = $SnMe_2Cl$	−4715	2213	4355	196	137	+59
Q = $SnBu_2Cl$	−4750	2148	4479	116	126	−10
Q = Snt-Bu_2Cl	−4615	1923	4559	81	52	29
Q = $SnMeCl_2$	−4722	2551	3986	77	6	71
Q = $SnBuCl_2$	−4699	2520	4034	67	6	61
Q = $SnPhCl_2$	−4704	2630	3961	−31	−63	32
Q = $SnCl_3$[b]	−4718	3107	3634	−59	−140	89
cis-Pt(PPh₃)₂(Br)(Y)						
Y = $SnMe_2Br$	−4963	2293	4345	98	70	28
Y = $SnBu_2Br$	−4929	2240	4480	113	93	20
Y = $SnMeBr_2$	−4928	2618	4004	38	−170	208
Y = $SnBuBr_2$	−4880	2579	4063	44	−144	188
Y = $SnPhBr_2$	−4788	2680	3975	32	−227	259

[a] As in Table 1 footnotes *a*, *b*, *c* and *d*. [b] Phosphine is $(p\text{-tolyl})_3P$, cited from Helv. Chim. Acta 65 (1982) 785.

phosphorus atoms, but satellites due to coupling with ^{119}Sn (and ^{117}Sn) were not observed because of an insufficient signal to noise ratio. The ^{119}Sn spectrum (recorded in preference to the ^{117}Sn spectrum because of its higher sensitivity) also has a central doublet of doublets, corresponding to couplings with the two different

TABLE 3

THE ^{31}P, ^{119}Sn AND ^{195}Pt NMR PARAMETERS[a] OF *trans*-$Pt(PPh_3)_2(Cl)(Q)$ AND *trans*-$Pt(PPh_3)_2(Br)(Y)$ IN CH_2Cl_2 AT 25°C (APPROXIMATE CONCENTRATION 0.13 *M*)

Compound	δ(Pt) (ppm)	^1J(Pt–P*cis*) (Hz)	δ(Sn) (ppm)	^2J(Sn–P*cis*) (Hz)	^1J(Pt–Sn) (Hz)	δ(P) (ppm)
trans-Pt(PPh₃)₂(Cl)(Q)						
Q = $SnMe_2Cl$	−4837	2740	120	131	14788	23.8
Q = $SnBu_2Cl$	−4907	2789	81	119	13294	25.0
Q = $SnMeCl_2$	−4790	2527	−18	165	19982	19.3
Q = $SnBuCl_2$	−4779	2557	−2	155	18534	21.4
Q = $SnPhCl_2$	−4827	2844	60	244	8020	
Q = $SnCl_3$[b]		2327	−222	226	28052	17.5
trans-Pt(PPh₃)₂(Br)(Y)						
Y = $SnMe_2Br$	−5040	2734	29	128	14654	21.9
Y = $SnBu_2Br$	−5035	2795	78	116	13062	22.8
Y = $SnMeBr_2$	−4963	2533	−63	153	18361	18.5
Y = $SnBuBr_2$	−4913	2570	26	140	17877	19.5
Y = $SnPhBr_2$	−4977	2840	−57	223	7880	18.5

[a] As in Table 1, footnotes *a*, *b* and *c*. [b] Phosphine is $(p\text{-ClPh})_3P$ – cited from Helv. Chim. Acta 65 (1982) 785.

^2J(Sn–P*cis*) (Hz)	^2J(Sn–P *trans*) (Hz)	^1J(Pt–Sn) (Hz)	δ(P *trans*) (ppm)	δ(P *cis*) (ppm)	^2J(P–P) (Hz)
65	2267	8921	32.1	24.5	13
43	2044	8821	32.8	19.5	13
21	1853	8800	32.7	18.3	13
128	3119	13105	28.7	12.1	14
105	2911	12320	30.8	14.5	16
122	3223	13940	30.6	14.3	15
216	4298	16321	26.2	7.9	
49	2264	8928	28.2	19.6	13
24	2039	8191	28.8	20.8	13
104	3082	11896	24.0	15.1	15
80	2881	11156	28.3	16.4	15
101	3195	12361	24.8	15.7	16

phosphorus atoms, and symmetrically spaced ^{195}Pt satellites with ^2J(Pt–^{119}Sn) 8921 Hz (Fig. 1).

The ^{31}P NMR spectrum of the *trans* isomer [3] consists of a single main resonance at 23.8 ppm with ^{195}Pt satellites (^1J(Pt–P) 2739 Hz)) and ^{119}Sn satellites (^2J(^{119}Sn–P) 131 Hz) indicating a tin atom *cis* to the two phosphines. The ^{195}Pt spectrum (Fig. 1) consists of a central triplet, due to coupling with two equivalent phosphorus atoms, with tin satellites equally spaced about this triplet (^1J(Pt–^{119}Sn) = 14788 Hz). The ^{119}Sn spectrum (Fig. 1) consists of a central triplet accompanied by equally spaced platinum-195 satellites which have the same value of the coupling constant (^1J(Pt–^{119}Sn)) as observed in the ^{195}Pt spectrum. In all the spectra the intensities of the satellites are in correct proportion with respect to the central multiplets and, where applicable, both ^{119}Sn and ^{117}Sn satellites were observed. The couplings to ^{119}Sn and ^{117}Sn were found to be in proportion to the magnetogyric ratio of the ^{119}Sn and ^{117}Sn nuclei (1.13).

For compounds of the type *cis*-Pt(PPh$_3$)$_2$(Ph)(Z) (Table 1) the platinum-195 frequency does not alter significantly upon variation of substituents attached to the tin atom. However, the tin-119 frequencies of the complexes do vary considerably (Table 1). The relationship between the ^{119}Sn data and the other NMR parameters measured may be better understood if the parameter $\Delta(\delta(\text{Sn}))$ is considered, where $\Delta(\delta(\text{Sn})) = \delta(\text{Sn(complex)}) - \delta(\text{Sn(ligand)})$ and δ(Sn(ligand)) represents the chemical shift of the compound used for the oxidative addition reaction (eq. 1). For example, in the series where Z = SnPh$_3$, SnPh$_2$Cl, SnPhCl$_2$ and SnCl$_3$, $\Delta(\delta(\text{Sn}))$ moves to higher frequency and ^1J(Pt–P*trans*), ^2J(Sn–P*trans*) and ^1J(Pt–Sn) all increase.

The trends described above are also apparent in the series where Z = SnPh$_3$,

$SnPh_2Br$, $SnPhBr_2$ and in the sequence in which the halogen is changed, i.e. Z = $SnPh_2Cl$, $SnPh_2Br$ and $SnPh_2I$. Little variation in ^2J(Sn–P*cis*) and ^1J(Pt–P*cis*) values is observed, which is consistent with the observation that a PR_3 group *trans* to a carbon σ-donor is resistant to perturbation [5]. When the halogen substituents are replaced by thiocyanate or thiol donors the coupling constant data and the tin-119 NMR shifts are of similar magnitudes to those of the compounds described above. Interestingly, for *cis*-$Pt(PPh_3)_2(Ph)(SnPh_2NCS)$ a coupling $^1J(^{119}Sn-^{14}N)$ of 170 Hz is observed.

In the related series of compounds *cis*-$Pt(PPh_3)_2(Cl)(Q)$ and *cis*-$Pt(PPh_3)_2(Br)(Y)$ (Q and Y as specified in Table 2) variations in $\Delta(\delta(Sn))$, ^1J(Pt–P*trans*), ^2J(Sn–P*trans*) and $^1J(Pt-^{119}Sn)$ correlate as described above for the compounds *cis*-$Pt(PPh_3)_2(Ph)(Z)$. In *cis*-$Pt(PPh_3)_2(Cl)(Q)$ and *cis*-$Pt(PPh_3)_2(Br)(Y)$ there is a more pronounced effect on ^1J(Pt–P*cis*) and $^2J(^{119}$Sn–P*cis*) as the groups attached to tin are changed. Values for ^2J(Sn–P*cis*) increase as $\Delta(\delta(Sn))$ increases while ^1J(Pt–P*cis*) decreases. In the series of compounds *trans*-$Pt(PPh_3)_2(Cl)(Q)$ and *trans*-$Pt(PPh_3)_2(Br)(Y)$ the same trend is shown, with ^2J(Sn–P*cis*) increasing and ^1J(Pt–P*cis*) decreasing as a function of increasing $\Delta(\delta(Sn))$.

The trends for the platinum–phosphorus and tin–phosphorus couplings can be explained in terms of simple σ-bonding. It is generally accepted that metal–phosphorus couplings are dominated by the Fermi contact term and that coupling

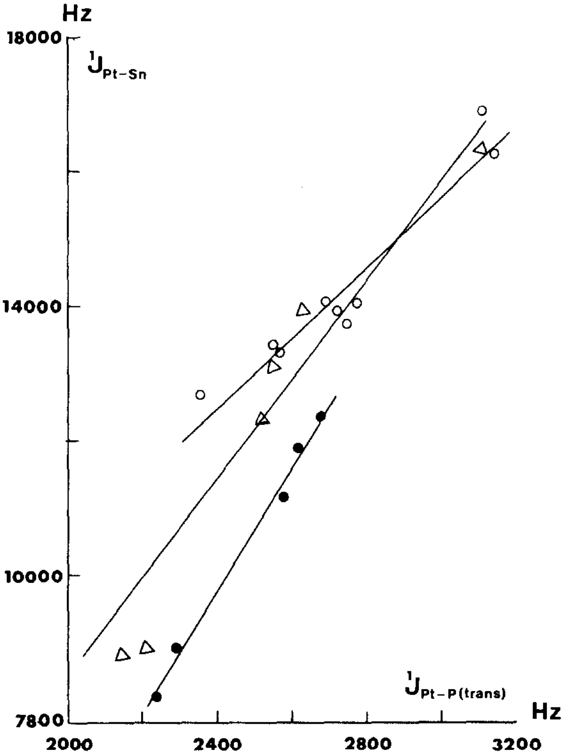

Fig. 2. Plots of ^1J(Pt–Sn) versus ^1J(Pt–P*trans*) for *cis*-$Pt(PPh_3)_2(Ph)(Z)$, ○, (Correlation coefficient, $R = 0.95$); *cis*-$Pt(PPh_3)_2(Cl)(Q)$, △, ($R = 0.95$) and *cis*-$Pt(PPh_3)_2(Br)(Y)$, ●, ($R = 0.93$).

constants can be expressed by the relationship:

$$J(\mathrm{M{-}P}) \propto \gamma_{\mathrm{M}}\gamma_{\mathrm{P}}(\Delta E^{-1})|\psi_{\mathrm{M}(ns)}(\mathrm{O})|^2|\psi_{\mathrm{P}(3s)}(\mathrm{O})|^2\alpha^2_{\mathrm{M}}\alpha^2_{\mathrm{P}}$$

where ΔE is the average singlet-triplet excitation energy, $|\psi_{\mathrm{M}(ns)}(\mathrm{O})|$, $|\psi_{\mathrm{P}(3s)}(\mathrm{O})|$ are the s-valence shell densities at the nuclei and α_{M},α_{P} are the proportions of s character in the bonding orbitals used by the respective atoms in the M–P bond, and γ_{M},γ_{P} are the magnetogyric ratios of the respective nuclei. Platinum–phosphorus one bond coupling constants ^1J(Pt–P) are thought to be dominated by the $\alpha^2_{\mathrm{Pt}}\alpha^2_{\mathrm{P}}$ term with α^2_{Pt} being the more important variable [6,7]. Two bond tin–phosphorus couplings, J(Sn–P), may also be described in terms of the above equation by addition of a constant to allow for an intervening atom, in this case platinum [8]. Tin–phosphorus couplings are dominated by the α^2_{Sn} term since $|\psi_{\mathrm{Sn}(5s)}(\mathrm{O})|$ will be approximately constant [7] and the term $\alpha^2_{\mathrm{P}}|\psi_{\mathrm{P}(3s)}(\mathrm{O})|$ will remain approximately constant throughout a series of structurally similar compounds [6]. This argument shows the magnitude of the platinum–phosphorus and tin–phosphorus coupling constants are dominated by the α^2_{Pt} and α^2_{Sn} terms respectively, and are thus predominantly σ in character.

When ^1J(Pt–^{119}Sn) is plotted against ^{1}J(Pt–P*trans*) (or ^2J(Sn–P*trans*) for the

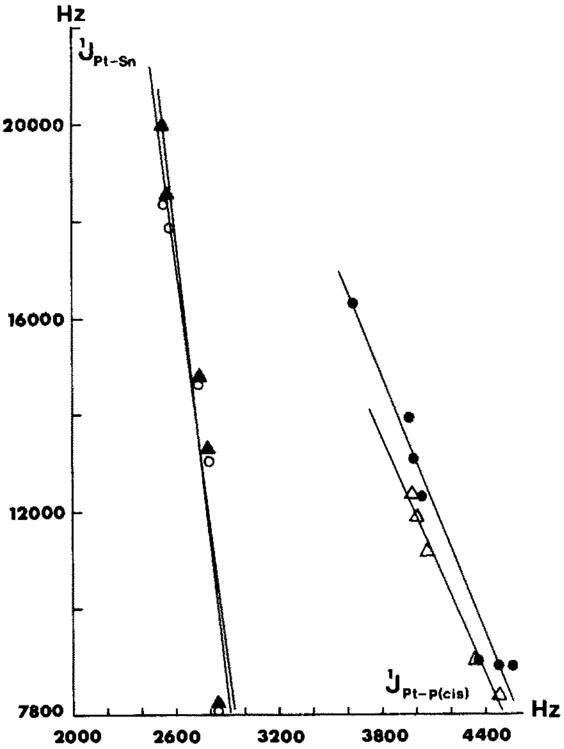

Fig. 3. Plots of linear correlations between ^1J(Pt–Sn) and ^1J(Pt–P*cis*) for *cis*-Pt(PPh$_3$)$_2$(Cl)(Q), ●, ($R = 0.95$), *cis*-Pt(PPh$_3$)$_2$(Br)(Y), △, ($r = 0.99$), *trans*-Pt(PPh$_3$)$_2$(Cl)(Q), ▲, ($R = 0.98$) and *trans*-Pt(PPh$_3$)$_2$(Br)(Y), ○, ($R = 0.93$). The point for *trans*-Pt(PPh$_3$)$_2$(Cl)(SnCl$_3$) is not shown but is included in the correlation coefficient.

compounds *cis*-Pt$(PPh_3)_2$(Ph)(Z), *cis*-Pt$(PPh_3)_2$(Cl)(Q) and *cis*-Pt$(PPh_3)_2$(Br)(Y) an approximately linear correlation is observed (Fig. 2). This correlation suggests that similar factors influence the magnitude of these couplings, and consequently it can be stated that the platinum–tin bond is also predominantly σ in character. Further evidence that the platinum–tin bonds are predominantly σ in character is obtained from the complexes *cis/trans*-Pt$(PPh_3)_2$(Cl)(Q) and *cis/trans*-Pt$(PPh_3)_2$(Br)(Y) where the coupling constant $^1J(Pt-^{119}Sn)$ is a linearly decreasing function of $^1J(Pt-P_{cis})$ (Fig. 3) and consequently a linearly increasing function of $^2J(^{119}Sn-P_{cis})$. These observations are as expected for operations of the *trans* effect in platinum(II) compounds [9].

Experimental

All solvents were dry and the reactions were carried out under dry nitrogen. The organotin compounds were prepared by the literature method [10] or obtained commercially. Compounds $Pt(PPh_3)_2C_2H_4$ [11] and $Pt(PPh_3)_2(R')(SnR'R''R''')$ were prepared by literature methods [2–4].

NMR spectra were recorded in CH_2Cl_2 using an external ^7Li lock on JEOL FX100 spectrometer at 2.3T. The references used were external 85% H_3PO_4, external 1 *M* H_2PtCl_6 in concentrated HCl and external $SnMe_4$. High frequency positive convention is used. Phosphorus-31 spectra were typically recorded after 500 transients whereas ^{195}Pt and ^{119}Sn required about 60000 transients to achieve sufficient signal to noise. Tris(acetylacetonato)chromium(III) was used as a paramagnetic relaxation agent.

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