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REACTIONS OF TRI-ORGANOTIN COMPOUNDS WITH ETHYLENE BIS(TRIPHENYLPHOSPHINE)PLATINUM(0) *

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Summary

Additional evidence that the product from [Pt(C_2H_4)(PPh_3)$_2$] and $SnMe_3Cl$ is *cis*-[PtMe($SnMe_2Cl$)(PPh_3)$_2$] has been obtained from ^1H and ^{13}C-{^1H} NMR spectra. Similar insertion of platinum into the Sn—R bond has been demonstrated for a wide range of compounds SnR_3X including Sn_2Ph_6, but the compound $SnMe_3${N : C(CF_3)$_2$} undergoes insertion into the Sn—N bond. The ^{31}P-{^1H} NMR parameters of the complexes are reported.

Introduction

Evidence has been presented [1] that $SnMe_3Cl$ reacts with [Pt(C_2H_4)(PPh_3)$_2$] and other platinum(0) complexes of PPh_3 to form *cis*-[PtMe($SnMe_2Cl$)(PPh_3)$_2$] rather than [PtCl($SnMe_3$)(PPh_3)$_2$] as had been reported previously [2]. Thus, in the ^{31}P-{^1H} NMR spectrum the phosphorus identified as being *cis* to Sn from the magnitude of the coupling constant ^2J(SnPtP) gave a value of ^1J(Pt—P) of 2092 Hz, a value typical of PPh_3 *trans* to Me and very different from that expected for PPh_3 *trans* to Cl (ca. 4000 Hz). Also, in the ^1H NMR spectrum, in addition to a strong resonance at τ 10.1 from the $SnCH_3$ protons, a very weak pair of doublets was observed centred at τ 9.35 and this was assigned to the $PtCH_3$ protons split by coupling to the non-equivalent ^{31}P-nuclei. We now present some further spectroscopic characterisation of this complex and the results of examination by ^{31}P-{^1H} NMR spectroscopy of the products of reactions of [Pt(C_2H_4)(PPh_3)$_2$] with a variety of triorganotin compounds.

Results and discussion

Complex cis-[PtMe($SnMe_2Cl$)(PPh_3)$_2$]

The previously reported ^1H NMR spectrum of this complex was recorded on

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* No reprints available.

TABLE 1

^{31}P NMR PARAMETERS OF COMPLEXES [PtR(SnR$_2$X)(PPh$_3$)$_2$] FORMED FROM [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] AND SnR$_3$X [a]

R	X	Con-figura-	−δ (ppm) *trans* to Sn	^1J(Pt—P) (Hz)	^2J(^{119}Sn—P) (Hz)	^2J(^{117}Sn—P) (Hz)	−δ (ppm) *cis* to Sn	^1J(Pt—P) (Hz)	^2J(SnP) [b] (Hz)	^2J(PP) (Hz)
Me	Cl	*cis*	107.9	2474	2274	2174	118.4	2092	175	16
Me	Br	*cis*	108.5	2512	2283	2178	118.4	2080	181	16
Me	NMe$_2$	*cis*	107.9	2466	2275	2178	118.3	2087	193	16
Me	OAc	*cis*	108.6	2405	2130	2046	119.4	2108	185	16
Me	$\overline{\mathrm{N(CO)(CH_2)_2C}}\mathrm{O}$	*cis*	109.1	2422	2214	2109	119.4	2109	*c*	16
Me [d]	$\overline{\mathrm{N(CO)(CH_2)_2C}}\mathrm{O}$ [d]	*trans* [d]					114.9	2939	137	
Et	Cl	*cis*	108.4	2595	2058	1968	119.2	1892	*c*	14
Et	Br	*cis*	108.9	2666	*c*	*c*	119.1	1838	*c*	15
n-Bu	Cl	*cis*	108.2	2554	2128	2020	118.4	1948	*c*	15
n-Bu	Br	*cis*	108.8	2588	2064	1947	118.4	1938	*c*	15
n-C$_6$H$_{13}$	Cl	*cis*	108.2	2530	*c*	*c*	118.3	1948	*c*	15
CH$_2$Ph	Cl	*cis*	113.4	2771	2214	2117	121.4	2031	181	16
Ph	OMe	*cis*	112.8	2449	2195	2102	118.4	2097	151	15
Ph	OSnPh$_3$	*cis*	112.9	2446	2197	2065	118.5	2097	139	15
Ph	SnPh$_3$	*cis*	114.1	2471	1967	1885	119.9	2012	146	15
C$_6$H$_4$Cl-3	Cl	*cis*	115.1	2742	2417	2310	118.8	2121	156	15
C$_6$H$_4$Br-4	Br	*cis*	114.6	2744	2439	2319	118.7	2124	159	16
C$_6$H$_4$Me-2	I	*cis*	112.7	2383	*c*	*c*	119.8	2090	*c*	15
C$_6$H$_4$Cl-4	OSn(C$_6$H$_4$Cl-4)$_3$	*cis*	113.6	2493	2241	2139	119.8	2122	159	15

[a] In dichloromethane. With SnMe$_3${N : C(CF$_3$)$_2$} the products were *cis*-[Pt{N : C(CF$_3$)$_2$}(SnMe$_3$)(PPh$_3$)$_2$] δ (*trans* to Sn) 115.5 ppm, ^1J(Pt—P) 2021 Hz., ^2J(SnP) 1709 Hz, δ (*cis* to Sn) 124.7 ppm, ^1J(Pt—P) 2213 Hz, ^2J(SnP) 144 Hz, ^2J(PP) 15 Hz, and [Pt{HN : C(CF$_3$)$_2$}(PPh$_3$)$_2$] δ (*trans to N*) 118.6 ppm, ^1J(Pt—P) 4355 Hz, δ (*trans* to C) 119.6 ppm, ^1J(Pt—P) 3547 Hz, ^2J(PP) 17 Hz, ^4J(PF) 12 Hz. [b] Separate ^{119}Sn and ^{117}satellites were not resolved. [c] Signal to noise ratio insufficient for the observation of Sn satellites. [d] The structure of this product may be different from that stated (see text).

a continuous-wave instrument and the noise level precluded observation of satellites due to ${}^2J$(PtCH). Since the existence of such satellites would confirm the presence of the PtMe group we obtained a spectrum with much improved signal to noise ratio by use of a Fourier-transform spectrometer. The parameters of the spectrum (see Table 1) were substantially as reported previously, and the clearly displayed ^{195}Pt-satellites of the PtMe group are associated with a coupling constant ${}^2J$(PtCH) 57 Hz which is of similar magnitude to that in *cis*-[$PtMe_2(PPh_3)_2$] [${}^2J$(PtCH) 69 Hz] [3], where Me is also *trans* to PPh_3. The ^{13}C-{^{1}H} NMR spectrum after prolonged accumulation was also consistent with the presence of two kinds of methyl groups. The more intense resonance, assigned to the $SnMe_2$ group, was a doublet with ^{195}Pt satellites [${}^2J$(PtSnC) 102 Hz]; the doublet structure is presumed to be due to coupling with the phosphorus nucleus *trans* to Sn [${}^3J$(PPtSnC) 16 Hz]. The less intense resonance comprises a doublet of doublets due to the PtMe group coupled to two phosphorus nuclei [${}^2J$(PPtC) 76 Hz (P *trans* to Me) and 5 Hz (P *cis* to Me)]. These coupling constants are comparable with those of the PtMe group in *cis*-[$PtMe_2(PMe_2Ph)_2$] [${}^2J$(PPtC) 104 Hz (*trans* to Me) and 9 Hz (*cis* to Me)] [4]. The signal to noise ratio of the ^{13}C-{^{1}H} spectrum precluded the detection of the ^{195}Pt satellites of the Pt—Me group. Thus, all the spectroscopic results for this complex are consistent with the formula *cis*-[$PtMe(SnMe_2Cl)(PPh_3)_2$].

Reactions of [$Pt(C_2H_4)(PPh_3)_2$] with triorganotin compounds

The products of the reactions of the ethylene complex with $SnMe_3X$ [X = Br, NMe_2, OAc, $\overline{NC(O)(CH_2)_2C}(O)$] were examined in situ by ^{31}P-{^{1}H} NMR spectroscopy. In each instance the spectrum was of the same characteristic form as that for *cis*-[$PtMe(SnMe_2Cl)(PPh_3)_2$] and with parameters of similar magnitude (Table 1). These products are therefore formulated *cis*-[$PtMe(SnMe_2X)(PPh_3)_2$]. As expected, the coupling constants ${}^1J$(Pt—P) for PPh_3 *trans* to the changing $SnMe_2X$ ligand vary more (2405—2512 Hz) than those for PPh_3 *trans* to Me (2080—2109 Hz) (Table 1), and formulae involving Pt—X bonds are ruled out because the values of ${}^1J$(Pt—P) *trans* to such electronegative groups X would be in the region of 4000 Hz rather than the 2000 Hz observed. Whilst for X = Cl, Br, NMe_2, and OAc only this single product type was detected, the spectrum for X = $\overline{NC(O)(CH_2)_2C}(O)$ also displayed a singlet resonance with ^{195}Pt satellites [${}^1J$(Pt—P) 2939 Hz] and with combined ^{117}Sn and ^{119}Sn satellites [${}^2J$(SnPtP) 137 Hz] of relative intensity indicative of one Sn atom per molecule. The magnitude of ${}^1J$(Pt—P) is similar to that in several complexes containing mutually *trans* PPh_3 ligands, and consistently, the magnitude of ${}^2J$(SnPtP) shows that Sn is *cis* to the PPh_3 ligands (Table 1). Two possible formulae viz. *trans*-[PtMe{$SnMe_2[\overline{NC(O)(CH_2)_2C}(O)]$}($PPh_3)_2$], the *trans* isomer of the established product, and *trans*-[Pt{$\overline{NC(O)(CH_2)_2C}(O)$}($SnMe_3$)($PPh_3)_2$] are compatible with these results. Although *cis* and *trans* isomers are often produced from oxidative addition reactions, we have not observed any *trans* isomers as products of reactions with tin compounds where the ligands on platinum(II) are PPh_3, an organostannio ligand, and an alkyl or aryl group. *Trans* isomers have been found only where an ionizable ligand such as a halide is transferred to platinum; isomeric products can then presumably be formed by the normal process involving catalysis by traces of free PPh_3 [5]. This suggests that the product is more likely to be *trans*-$[Pt\{\overline{NC(O)(CH_2)_2C(O)}\}(SnMe_3)(PPh_3)_2]$, and the fact that the coupling ^2J(SnPtP) (137 Hz) is smaller than *cis* couplings between PPh_3 and $SnMe_2X$ (X = Cl, Br, NMe_2, OAc) (Table 1) is consistent with the presence of the less electronegative $SnMe_3$ group. However, these indirect couplings may be sensitive to the nature of the ligands *trans* to the coupled nuclei, in which case the above argument would be invalid, and this formulation of the product would imply an improbable near coincidence in the rates of reaction of this $SnMe_3X$ species to form products of insertion into the Sn—Me bond (*cis* product) or the Sn—X bond (*trans* product). The ^{1}H NMR spectrum of the product mixture was unfortunately inconclusive because the signals in the methyl region were further complicated by the presence of the free trimethyltin imide.

A related reaction between $SnMe_3\{N : C(CF_3)_2\}$ and $[Pt(PPh_3)_3]$ in benzene has been investigated previously with the conclusion that two products could be obtained, the platinum(II) complex $[Pt\{N : C(CF_3)_2\}(SnMe_3)(PPh_3)_2]$ resulting from insertion into the Sn—N bond, and the platinum(0) tris(phosphine) complex $[Pt\{HN : C(CF_3)_2\}(PPh_3)_3]$, which was presumed to be formed from $HN : C(CF_3)_2$ derived from $SnMe_3\{N : C(CF_3)_2\}$ [6]. We carried out a reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and an excess of $SnMe_3\{NC(CF_3)_2\}$ in CH_2Cl_2 and examined the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the product mixture (Table 1, footnote ^{a}). The spectrum shows the presence of two complexes A and B, each with a 1 : 1 ratio of non-equivalent PPh_3 ligands. For complex A one PPh_3 ligand is associated with a poorly resolved doublet with weak Sn-satellites [^2J(SnPtP) 1709 Hz] and ^1J(Pt—P) 2021 Hz and can be assigned to PPh_3 *trans* to Sn, and the second PPh_3 ligand appears as a sharp doublet with well defined satellites [^1J(Pt—P) 3313 Hz, ^2J(SnPtP) 144 Hz]. The coupling ^1J(Pt—P) is much larger than that expected for PPh_3 *trans* to Me, but is similar to that for PCy_3 (Cy = cyclohexyl) *trans* to N in *trans*-$[PtCl_2(NC_5H_5)(PCy_3)]$ [^1J(Pt—P) 3394 Hz] [7], so product A is assigned the formula *cis*-$[Pt\{N : C(CF_3)_2\}(SnMe_3)(PPh_3)_2]$. The poor resolution of the resonances for the PPh_3 ligand *trans* to Sn is an unusual feature and could be associated with ^{14}N quadrupolar effects, coupling to ^{19}F, or exchange of PPh_3. The ^{14}N quadrupolar effects would be expected to affect the more strongly coupled *trans* ligand to a greater extent than the *cis* ligand and this would also apply to ^{19}F coupling unless this is determined by a "through space" interaction.

For complex B both coupling constants ^1J(Pt—P) are relatively large (Table 1, footnote ^{a}) and are indicative of a platinum(0) complex $[Pt\{HN : C(CF_3)_2\}(PPh_3)_2]$ in which the N : C moiety coordinates to platinum. The phosphorus *trans* to carbon is associated with coupling to fluorine [J(PF) 12 Hz], a result previously reported for a complex of this formula by Ashley-Smith et al. [9]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum gave no evidence for the presence in solution of the the tris(phosphine) complex $[Pt\{HN : C(CF_3)_2\}(PPh_3)_3]$ [6].

Thus, with the established exception of $SnMe_3\{N : C(CF_3)_2\}$ and the possible exception of $SnMe_3\{\overline{N(CO)(CH_2)_2C(O)}\}$ all the triorganotin derivatives examined (Table 1 and ref. 1) react with $[Pt(C_2H_4)(PPh_3)_2]$ to give products of insertion into the Sn—alkyl or Sn—aryl bonds [with Sn—Ph reacting in preference to Sn—Me in $SnMePh_2Cl$ and $SnMe_2PhCl$] even when such reactive bonds as Sn—Cl, Sn—I, and Sn—Sn are also present. This behaviour of the tin compounds towards platinum(0) complexes contrasts with the behaviour of triorganotin chlorides towards the platinum(II) complex $[PtMe_2(bipy)]$ (bipy = 2,2′-bipyridyl) where there is unambiguous evidence for oxidative addition by the Sn—Cl bonds [10]. It is likely that the two oxidation-states of platinum react with the tin compounds by different mechanisms rather than, for example, by different steric control of a single mechanism. Possible mechanisms for oxidative addition are radical processes involving release of tin or carbon centred radicals, nucleophilic attack by Pt on Sn, or three-centre mechanisms involving Pt and either Sn—X or Sn—C bonds. We have made a variety of attempts to detect radicals in the reactions of SnR_3X with $[Pt(C_2H_4)(PPh_3)_2]$ [5], but since these have been so far unsuccessful and the mechanism of the reactions of the platinum(II) bipyridyl complexes has not been studied, discussion of the contrasting modes of reaction would be premature.

Experimental

All the solvents were dry and oxygen-free, and reactions were carried out under nitrogen. The ^{31}P-$\{^1H\}$ NMR spectra were recorded at 40.48 MHz on a JEOL PFT 100 instrument. Solutions in dichloromethane in 8 mm outside-diameter tubes were used. The field was locked to the ^2H resonance of trimethyl phosphite in deuteriobenzene which served as external reference. The ^{13}C-$\{^1H\}$ and ^1H NMR spectra were recorded on the same instrument using dichloromethane as solvent and tetramethylsilane as internal standard. Positive chemical shifts are to high frequency of the reference. Tin compounds were available in this laboratory and $[Pt(C_2H_4)(PPh_3)_4]$ was prepared by a published method [11].

cis-[PtMe(SnMe₂Cl)(PPh₃)₂]. A solution of $SnMe_3Cl$ (0.106 g) in diethyl ether (2 cm^3) was added to $[Pt(C_2H_4)(PPh_3)_2]$ (0.4 g) in benzene (2 cm^3), and the mixture stirred at room temperature. After 2 h the solid was filtered off and washed with ether to give a white product, m.p. 240°C (dec.) (lit. [1] 240—242°C). Analysis found: C, 51.2; H, 4.5. $C_{39}H_{39}ClP_2PtSn$ calcd.: C, 51.0; H, 4.3%. ^1H NMR: $PtCH_3$, δ 0.77 ppm, $^2J(PtH)$ 57 Hz, $^3J(PH)$ (*trans*) 11 Hz, $^3J(PH)$ (*cis*) 6 Hz; $SnCH_3$, δ 0.02 ppm, $^2J(SnH)$ 34 Hz. ^{13}C-$\{^1H\}$ NMR: Pt—CH_3 δ —2.3 ppm, $^2J(PC)$ (*trans*) 76 Hz, $^2J(PC)$ (*cis*) 4.9 Hz; $SnCH_3$, δ 1.43 ppm, $^2J(PtC)$ 103 Hz, $^3J(PC)$ (*trans*) 16 Hz.

Other complexes. The remaining complexes were obtained in situ by addition of an excess of tin compound to be a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (ca. 0.05 g) in dichloromethane (1 cm^3). The mixture was shaken vigorously in the NMR tube for ca. 5 min, during which evolution of ethylene occurred. The mixture was then put aside for ca. 30 min before being placed in the NMR probe.

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