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The Reactivity of Organotin–Platinum Complexes

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The reactivity of $(Ph_2PCH_2)_2Pt(SnMe_3)_2$ *(II) towards air, base, acids, thiols, organic halides and some metal halides has been examined. Many reagents cleaved both Pt–Sn bonds, though "mixed" complexes e.g.* $(Ph_2PCH_2)_2Pt(SnMe_3)(SCOCH_3)$ *were also isolated. The thermal stability of (II) and the platinum(IV) complex* $(Ph_2PCH_2)_2PtH(SnMe_3)_3$ *have been examined.*

Introduction

Although various methods are available for forming platinum–tin bonds [1], little work has been reported on their chemical reactions beyond the recognition that they are stable to air and water [2–4]. Compounds of this type are known for both the +2 and +4 oxidation states of platinum, and for a variety of ligands bonded to tin, *e.g.* $SnCl_3$ [5], $SnClMe_2$ [6], $SnMe_3$ [2–4]. In this paper we describe a number of reactions of complex (II), prepared by the reactions:

$$\begin{array}{c} (Ph_2PCH_2)_2PtMe_2 + 3Me_3SnH \\ \downarrow \\ (Ph_2PCH_2)_2PtH(SnMe_3)_3 + 2CH_4 \\ \text{(I)} \\ \Big\downarrow\, C_6H_6 \\ (Ph_2PCH_2)_2Pt(SnMe_3)_2 + Me_3SnH \\ \text{(II)} \end{array}$$

Attempts to make a "mixed" complex, $(Ph_2PCH_2)_2$-$PtMe(SnMe_3)$, by this method were unsuccessful: equimolar ratios of reactants gave unreacted material and complex (II).

Experimental

$(Ph_2PCH_2)_2Pt(H)(SnMe_3)_3$ and $(Ph_2PCH_2)_2Pt(SnMe_3)2$

An excess of trimethyltin hydride (1 ml) and benzene (5 ml) were condensed onto $(Ph_2PCH_2)_2$-

TABLE I. Analytical Data.

Complex	M.Pt. °C	% Found C	% Found H	% Found N	% Calc. C	% Calc. H	% Calc. N
$L_2Pt(OCOCH_3)_2$		52.0	5.2		50.6	4.3	
$L_2Pt(OCOCF_3)_2$	222–226 (dec.)	44.0	3.0		44.0	2.9	
$L_2Pt(SnMe_3)(SCOCH_3)$	159–161 (dec.)	44.5	4.2		44.7	4.4	
$L_2Pt(SCOCH_3)_2$	188–190 (dec.)	48.5	4.1		48.4	4.1	
$L_2Pt(OCOCO_2H)_2$		45.8	3.7		46.7	3.4	
$L_2Pt(SCH_2)_2$	274–279 (dec.)	49.2	4.2		49.0	4.1	
$L_2Pt(SnMe_3)(SCH_2CH_2OH)$	164–166	44.6	4.9		44.6	4.6	
$L_2Pt(ONO_2)_2$	260–265	43.3	3.1	3.8	43.5	3.4	3.9
$L_2Pt(SCN)(NCS)$	260–262	46.9	3.4	4.0	47.4	3.4	3.9

TABLE II. Reactions of $(Ph_2PCH_2)_2Pt(SnMe_3)_2$.[a]

Reagent	Conditions	Reaction Products Isolated
10% NaOH	$H_2O/EtOH$, 20 °C, 2 weeks	No Reaction
$PhC:CH$	C_6H_6, 110 °C, 18h	$L_2Pt(C:CPh)(SnMe_3) + Me_3SnH$
CH_3CO_2H	C_6H_6, 80 °C, 15m	$L_2Pt(OAc)_2$
CF_3CO_2H	20 °C, 15m	$L_2Pt(OCOCF_3)_2 + CH_4 + Sn$
CH_3COSH	C_6H_6, 80 °C, 30m	$L_2Pt(SnMe_3)(SCOMe) + Me_3SnH$
CH_3OCSH	C_6H_6, 20 °C, 14h	$L_2Pt(SCOMe)_2 + Me_3SnH$
$(CO_2H)_2$	THF, 56 °C, 30m	$L_2Pt(OCOCO_2H)_2 + Me_3SnH$
$(CH_2SH)_2$	C_6H_6, 20 °C, 30m	$L_2Pt(SCH_2)_2 + Me_3SnH$
$HOCH_2CH_2SH$	C_6H_6, 20 °C, 20m	$L_2Pt(SCH_2CH_2OH)(SnMe_3) + Me_3SnH$
HCl	C_6H_6, 20 °C, 5m	$L_2PtCl_2 + Me_3SnCl + H_2 + CH_4$
Conc. HNO_3	20 °C, 10m	$L_2Pt(ONO_2)_2$
HgX_2 (X = Cl, Br, I, CN)	THF, 20 °C, 20m	$L_2PtX_2 + Me_3SnX + Hg$
$Hg(SCN)_2$	THF, 20 °C, 10m	$L_2Pt(SCN)(NCS) + Hg$
$SnCl_4$	C_6H_6, 20 °C, 5m	$L_2PtCl_2 + SnCl_2 + Me_3SnCl$
I_2	THF, 20°C, 5m	$L_2PtI_2 + Me_3SnI$
PX_3 (X = Cl, Br)	20°C, 12h	$L_2PtX_2 + Me_3SnX$
$(CH_2Br)_2$	20°C, 3w	$L_2PtBr_2 + Me_3SnBr + C_2H_4$
CH_3I	90°C, 2h	$L_2PtI_2 + Me_4Sn$
$CHCl_3$	20°C, 2w	$L_2PtCl_2 + Me_3SnCl$
CCl_4	40°C, 5m	$L_2PtCl_2 + Me_3SnCl$
H_2	C_5H_5N, 20 °C, 120 atm	No Reaction

[a] $L_2 = (Ph_2PCH_2)_2$.

$PtMe_2$ [7] (0.35 g, 0.56 mmol) in an evacuated tube fitted with a teflon tap. After 12 h methane (1.00 mmol) was separated. The white solid residue [2] of $(Ph_2PCH_2)_2Pt(H)(SnMe_3)_3$ (ν(Pt–H), 1960 cm^{-1}) was dissolved in hot benzene (50 ml); addition of methanol (100 ml) gave $(Ph_2PCH_2)_2Pt(SnMe_3)_2$ as pale yellow microcrystals (0.44 g, 85%), m.p. 204–206 °C (Found: C, 41.67; H, 4.65. Calc. for $C_{32}H_{42}P_2PtSn_2$, C, 41.68; H, 4.60%).

Reactions of $(Ph_2PCH_2)_2Pt(SnMe_3)_2$

With PhC≡CH

Complex (II) (0.40 g), benzene (5 ml) and PhC_2H (1.0 g) were heated in an evacuated break-seal tube at 110 °C for 18 h. Removal of volatile components including Me_3SnH (δ, 0.76 ppm) left the monoethynyl complex, $(Ph_2PCH_2)_2Pt(C:CPh)(SnMe_3)$ (III) as a bright yellow solid (0.32 g); m.p. 198–200 °C (decomp.) (Found: C, 51.50; H, 4.27. $C_{37}H_{38}P_2PtSn$ requires: C, 51.76; H, 4.47%). Its i.r. spectrum showed a strong sharp band at 2100 cm^{-1} which was unchanged by carrying out the reaction with PhC:CD.

With other reagents

In general, the reactants were treated as indicated in Table II maintaining an inert (N_2) atmosphere throughout. Analytical data on new compounds are listed in Table I.

The i.r. spectrum of (III) contained a sharp band at 2100 cm^{-1}, due to ν(C≡C) rather than ν(Pt–H) since the i.r. spectrum was unaffected by carrying out the reaction with PhC:CD. It was stable in air as the solid but slowly decomposed in $CDCl_3$ solution to unidentified brown products. Attempts to replace the second $SnMe_3$ group by phenylethynyl were unsuccessful: using neat PhC:CH at 155 °C produced an intractable tar, methane and a metallic mirror. The simplicity of the reaction of (II) with phenylacetylene contrasts strikingly with the behaviour of the trimethylsilyl-platinum complex [8], *trans*-$(Et_3P)_2PtCl(SiMe_3)$, and suggests that (III) is formed by initial π-bonding of phenylacetylene to platinum rather than via an oxidative addition intermediate. The ^1H n.m.r. of the methyl protons in (III) (δ, –0.22 ppm) showed the couplings $^2J(HSn) \approx 42$; $^3J(HPt)$, 8.7; ^4J(HP *trans*), 1.5 Hz. In the similar compound with *trans*-phosphines [4], *trans*-$(Ph_3P)_2Pt(SnMe_3)(C:CPh)$, $^4J(HP)$ was not observed, but complex (II) also failed to show this coupling [2].

Carboxylic acids cleaved both Pt–$SnMe_3$ bonds in (II); the reactivity being a function of acid strength, hence oxalic acid did not chelate to platinum. Thioacetic acid selectively cleaved either one or both Pt–Sn bonds in (II) under mild conditions, whereas 1,2-

ethanedithiol yielded the pale yellow crystalline chelate complex, $(Ph_2PCH_2)_2Pt(SCH_2)_2$, with some evidence for the formation of the intermediate, $(Ph_2PCH_2)_2Pt(SnMe_3)(SCH_2CH_2SH)$. With 2-mercaptoethanol the sole product was the complex $(Ph_2PCH_2)_2Pt(SnMe_3)(SCH_2CH_2OH)$. Mineral acids (HCl, HNO_3), as expected, cleaved both Pt–Sn bonds and, depending on the conditions, cleavage of Sn–Me bonds also occurred yielding methane. $(Ph_2PCH_2)_2Pt(NO_3)_2$, a white crystalline solid is one of the few binitrato platinum complexes. Its i.r. and Raman spectra suggest that the nitrato groups are not ionic, and in view of the known chemistry of Pt(II) they are most likely to be unidentate, $Pt–ONO_2$ (I.r. bands at 1492 s br, 1277 s, 985 s, 800 m cm^{-1}. The region in which the remaining two NO_3 fundamentals were expected for C_{2v} symmetry (750–700 cm^{-1}) was complicated by bands due to the phosphine. Concentrated sulphuric acid reacted with (II), liberating much methane; phosphoric acid was unreactive either cold or hot; HBF_4 cleaved the Pt–Sn bonds but the products were not adequately characterised.

Mercury(II) di-halides and pseudohalides all cleaved the Pt–Sn bonds in (II) yielding $(Ph_2PCH_2)_2PtX_2$, Me_3SnX and mercury – this parallels the behaviour of $Pt–GePh_3$ complexes [9]. Rather unexpectedly, because of its insolubility, Hg_2Cl_2 reacted in a similar way. Like most of the acid cleavage reactions these could not be stopped at the half-way stage. Mercury(II) dithiocyanate was reduced to mercury and the vibrational spectrum of the platinum product strongly suggests the presence of one S- and one N-bonded thiocyanato group [10], $((Ph_2PCH_2)_2Pt(SCN)(NCS)$, [ν(CN) of PtSCN at 2120 cm^{-1} (sharp, i.r. and Raman); ν(CN) of Pt-NCS at 2080 cm^{-1} (broad, i.r. and Raman)].

Tin(IV) chloride has previously been shown to cleave the Au–Ge bond in $Ph_3GeAuPPh_3$ [11] and it reacted rapidly at room temperature with (II) to give probably $(Ph_2PCH_2)_2Pt(SnCl_3)_2$ which, like related compounds [5], readily decomposed on attempted purification into $SnCl_2$ and $(Ph_2PCH_2)_2PtCl_2$. Phosphorus-trichloride and -tribromide behaved similarly, though the phosphorus-containing products were not identified. Organic halides of various types cleaved the Pt–Sn bonds in (II), often rapidly and under mild conditions. Of these the most unexpected were the reactions with CCl_4 and $CHCl_3$ both of which gave $(Ph_2PCH_2)_2PtCl_2$ and Me_3SnCl.

Whereas Pt–Si and Pt–Ge complexes reacted extremely readily with dihydrogen [2, 8] complex (II) was unaffected. This could be because the equilibrium $L_2Pt(SnMe_3)_2 + H_2 \rightleftharpoons L_2PtH(SnMe_3) + Me_3SnH$ lies well to the left, but no reaction occurred in pyridine which would have catalysed the decomposition of any Me_3SnH formed to Me_6Sn_2. The failure of (II) to react with H_2 seems more probably due to the combined effect of stronger Pt–Sn and weaker H–Sn bonds relative to Si and Ge analogues.

Results and Discussion

Complex (II) was stable in moist air at room temperature, and was even unaffected in air at 150 °C over 3 weeks. Some decomposition occurred over 3 weeks in an evacuated tube at 185–200 °C when the solid turned black as methane was formed, but solvent extraction gave 82% unreacted material. The platinum(IV) complex (I) decomposed over 24 h at 200 °C forming methane (1 mol) and a golden-brown solid which showed no ν(Pt–H) and could not be obtained in a crystalline form. Both (I) and (II) were stable to 10% aqueous–ethanolic sodium hydroxide in contrast to analogous trimethylsilyl- and trimethylgermyl-complexes [8], but many protic reagents cleaved either one or both of the Pt–Sn bonds in (II) (Table II). Phenylacetylene in slight excess reacted with (II) only slowly in refluxing benzene, but over 18 hours at 110 °C in a sealed tube one Me_3Sn group was replaced:

$$(II) + PhC{:}CH \rightarrow \underset{(III)}{(Ph_2PCH_2)_2Pt(C{:}CPh)(SnMe_3)} + Me_3SnH$$

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