Synthesis and Characterization of Complexes with $Pt_3(\mu_3\text{-}SnX_3)$ Groups including the First SnF_3^- Complex; Possible Models for Heterogeneous Pt–Sn Catalysts

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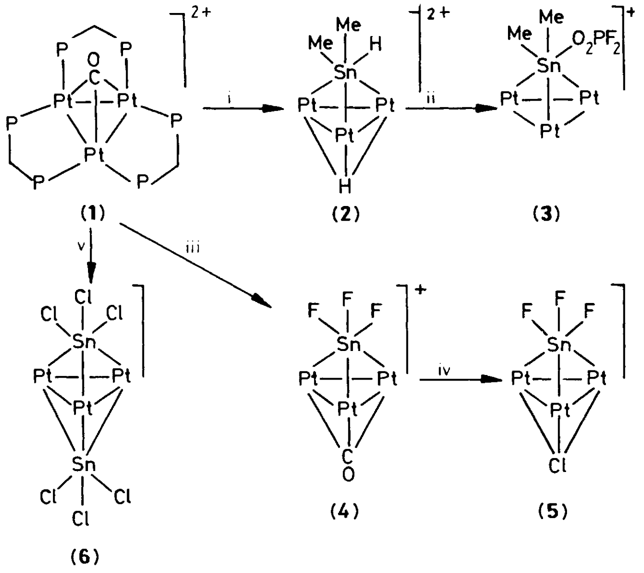
Novel complexes containing Pt_3 (μ_3-SnX_3) groups have been prepared by reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ (dppm = $Ph_2PCH_2PPh_2$) with organotin hydrides or with SnX_3^- and are of interest as possible models for heterogeneous Pt–Sn/support catalysts; the structures of $[Pt_3\{\mu_3\text{-}SnMe_2(PO_2F_2)\}$ $(\mu\text{-dppm})_3]^+$ and disordered $\{[Pt_3(\mu_3\text{-}SnF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]\}_{0.75}$ $[Pt_3(\mu_3\text{-}SnF_3)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3]_{0.25}$ are determined, the latter being the first SnF_3^- complex to be crystallographically characterized.

Pt–Sn complexes and Pt–Sn/support combinations are very useful in homogeneous and heterogeneous catalysis, respectively.[1,2] In the heterogeneous system there is much tin(II)[3] as well as tin(0) and this prompted a study of how tin(II) fragments might interact with the co-ordinatively unsaturated cluster cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, (**1**) (dppm = $Ph_2PCH_2PPh_2$), which can mimic some properties of a Pt surface.[4] The only structurally characterized Pt_3Sn complexes appear to be $[Pt_3(\mu_3\text{-}SnCl_3)_2(cod)_3]$ (cod = cyclo-octa-1,5-diene)[5,6] and the μ_2-Sn species $[Pt_3(CO)_3\{\mu_2\text{-}Sn(NR_2)_2\}_3]$ (R = $SiMe_3$).[7] Some results are given in Scheme 1.

Initially, reactions of (**1**), as the PF_6^- salt, with organotin hydrides were attempted. Reaction with Me_2SnH_2 gave (**2**), which could be characterized spectroscopically.[†] In particular, in the ^1H n.m.r. spectrum, the presence of a μ_3-H group was confirmed by the characteristic intensities of the ^{195}Pt satellite spectra and the $SnMe_2H$ group was identified by the septet and doublet splittings for the SnH and SnMe resonances, respectively, due to HH coupling. However, (**2**) had low thermal stability and slow crystallization yielded (**3**), clearly involving partial reaction of a PF_6^- group to give $PO_2F_2^-$ and loss of both PtH and SnH groups. Complex (**3**) was characterized crystallographically[‡] (Figure 1) and spectroscopically.[†] In (**3**) the cations retain the virtually equilateral triangle of platinum atoms present in (**1**), and the μ_3-CO ligand is replaced by a μ_3-$SnMe_2(PO_2F_2)$ group. Two methyl substituents and a $PO_2F_2^-$ unit, whose presence was confirmed by n.m.r.,[†] complete the roughly octahedral co-ordination about the tin atom.



Scheme 1. μ-dppm ligands are omitted for clarity. *Reagents:* i, Me_2SnH_2, $-CO$; ii, recrystallization from CH_2Cl_2–pentane with counterion $[PF_6]^-$; iii, Ph_3SnH followed by recrystallization from CH_2Cl_2–pentane or, better, SnF_2–NaF; iv, CH_2Cl_2, see text; v, excess $SnCl_2$–NaCl.

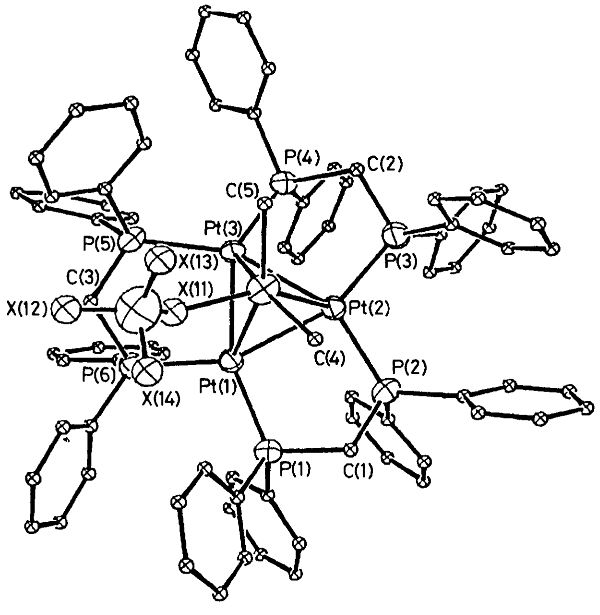


Figure 1. Structure of the cation (**3**). Hydrogen atoms are omitted and carbon atoms are presented by spheres of arbitrary size. Otherwise 50% probability ellipsoids are displayed. The O and F atoms of the $PO_2F_2^-$ substituent [atoms X(11)—X(14)] could not be distinguished from one another in the structure analysis and may be disordered; they were assigned F scattering factors. Selected distances are: Pt(1)–Pt(2) 2.609(1), Pt(1)–Pt(3) 2.615(1), Pt(2)–Pt(3) 2.635(1), Pt(1)–Sn 2.766(2), Pt(2)–Sn 2.739(2), Pt(3)–Sn 2.702(2), Sn–C(4) 2.08(3), Sn–C(5) 2.17(3), Sn–X(11) 2.12(2), P(7)–X(11) 1.53(2), P(7)–X(12) 1.49(3), P(7)–X(13) 1.50(3), P(7)–X(14) 1.48(3)Å.

Treatment of (**1**) with Ph_3SnH gave more extensive reactions and an unexpected crystalline product: a mixture of $[Pt_3(\mu_3\text{-}SnF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]$ and $[Pt_3(\mu_3\text{-}SnF_3)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3]$ in molar ratio 3 : 1. The presence of chloride was confirmed by *X*-ray fluorescence analysis using scanning electron microscopy on a single crystal. *X*-ray structure determination indicated that the cubic unit cell contains six complex cations (**4**), six $[PF_6]^-$ anions, and two neutral molecules (**5**) (Scheme 1).

Confirmation that the reaction of (**1**) with Ph_3SnH involves cleavage of all three phenyltin bonds was provided by the preparation of (**4**) in good yield directly from (**1**) and SnF_3^-

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[†] *Spectroscopic data*: n.m.r. data obtained using refs. $Me_4Si(^1H)$, $H_3PO_4(^{31}P)$, $K_2PtCl_4(^{195}Pt)$, $SnMe_4(^{119}Sn)$, $CFCl_3(^{19}F)$, multiplicities due to ^{195}Pt couplings not reported, *J* values in Hz. (**2**): $\delta(^{31}P)$ (acetone) -12.2 p.p.m. [s, $^1J(PtP)$ 3120, $^2J(PtP)$ 236, $^3J(PP)$ 116]; $\delta(^1H)$ 3.9 [sept., 1H, $^3J(HH)$ 6.1, $^1J(SnH)$ 122, Me_2SnH], 1.1 [d, 6H, $^3J(HH)$ 6.1, $(CH_3)_2SnH$], -3.5 [sept., 1H, $^2J(PH)$ 20, $^1J(PtH)$ 414, $Pt_3(\mu_3\text{-}H)$].

(**3**): $\delta(^{31}P)$ (acetone) -16.2 [s, 6P, $^1J(PtP)$ 3260, $^2J(PtP)$ 120, $^3J(PP)$ 140], -30.3 p.p.m. [t, 1P, $^1J(PF)$ 970, PO_2F_2]; $\delta(^1H)$ 0.46 [m, $^3J(PtH)$ 4.4, $^2J(SnH)$ 48, $(CH_3)_2Sn$]; $\delta(^{195}Pt)$ -2501 p.p.m. [br.t, $^1J(PtP)$ 3240]; i.r. (nujol): ν(P=O) 1312, ν(P–O) 1098 cm^{-1}, ν(P–F) 722 cm^{-1}.

(**4**): $\delta(^{31}P)$ (acetone) -1.1 p.p.m. [s, $^1J(PtP)$ 3684, $^3J(PP)$ 156]; $\delta(^{19}F)$ -71.6 [d, $^1J(PF)$ 707, PF_6], -74.3 p.p.m. [m, $^2J(PtF)$ 118, $^1J(^{117}SnF)$ 3961, $^1J(^{119}SnF)$ 4146, $Pt_3(\mu_3\text{-}SnF_3)$]; $\delta(^1H)$ 5.12 [d, $^2J(HH)$ 12, CH^aH^b], 5.96 [d, $^2J(HH)$ 12, $^3J(PtH)$ 84, CH^aH^b]; $\delta(^{195}Pt)$ -2575 p.p.m. [tq, $^1J(PtP)$ 3684, $^2J(PtF)$ 118]; $\delta(^{119}Sn)$ -320 p.p.m. [q, $^1J(^{119}SnF)$ 4146]; $\delta(^{13}C)$ 198 [m, $^1J(PtC)$ 650, CO]; i.r. (nujol): ν(CO) 1827 cm^{-1}. Some weakening of the Pt_3CO bonding occurs relative to (**1**) which has $^1J(PtC)$ 770 Hz and ν(CO) 1765 cm^{-1}.

(**6**): $\delta(^{31}P)$ (CD_2Cl_2) -7.6 p.p.m. [s, $^1J(PtP)$ 3240, $^3J(PP)$ 171]; $\delta(^1H)$ 6.0 [br.t., $^2J(PH) = 19$, CH_2]; Satisfactory elemental analysis was obtained.

[‡] *Crystal data* for (**3**)·$[PF_6]$: $C_{77}H_{72}F_8O_2P_8Pt_3Sn$, $M = 2133.2$, monoclinic, space group *C*2, $a = 24.808(5)$, $b = 12.136(3)$, $c = 26.890(6)$ Å, $\beta = 105.64(2)°$, $U = 7796(3)$ Å^3, $Z = 4$, $D_c = 1.817$ g cm^{-3}, $F(000) = 4104$, $\mu = 59.7$ cm^{-1}, purple plate, 0.76 × 0.48 × 0.20 mm. $R(R_w) = 0.043$ (0.057) for refinement of 314 parameters using 7959 unique, absorption-corrected intensities with $I \geqslant 3\sigma(I)$ and $2 \leqslant \theta \leqslant 27°$.

For (**4**)·$[PF_6]_{0.75}$·(**5**)$_{0.25}$: $C_{75.75}H_{66}O_{0.75}F_{7.5}P_{6.75}Sn_1Pt_3Cl_{0.25}$, $M = 2052.7$, cubic, space group $P\bar{4}3n$ (No. 218), $a = 26.242(5)$ Å, $U = 18071(6)$ Å^3, $Z = 8$, $D_c = 1.509$ g cm^{-3}, $F(000) = 7868$, $\mu = 51.3$ cm^{-1}, orange parallelopiped, 0.12 × 0.24 × 0.24 mm. $R(R_w) = 0.042$ (0.059) for refinement of 109 parameters using 1069 unique, absorption-corrected intensities with $I \geqslant 3\sigma(I)$ and $2 \leqslant \theta \leqslant 25°$. Full-matrix least-squares refinement of 109 parameters (phenyl rings as rigid groups) gave $R = 0.0424$, $R_w = 0.0589$.

Crystallographic measurements were made with Mo-K_α *X*-rays ($\lambda = 0.71069$ Å) at 297 K on an Enraf-Nonius CAD4F diffractometer. Both structures were solved by direct methods and refined by full-matrix least-squares. Phenyl rings were treated as rigid groups. Atomic parameters, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

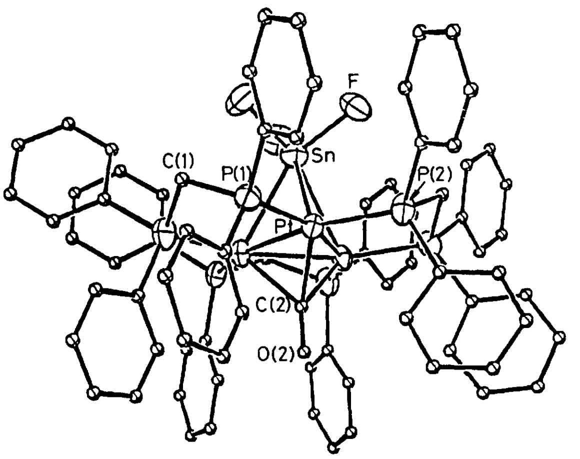

Figure 2. Structure of the cation (**4**). The atoms Sn, C(2), and O(2) lie on a crystallographic three-fold axis. 50% Probability ellipsoids are displayed, except for C and O atoms which are represented by spheres of arbitrary size. Selected distances are: Pt–Pt 2.639(3), Pt–Sn 2.805(2), Sn–F 1.96(3), Pt–C(2) 2.16(5)Å.

(prepared *in situ* by reaction of NaF with SnF_2 in acetone). Similarly, the slower reaction of (**1**) with excess $SnCl_3^-$ gave the neutral complex $[Pt_3(\mu_3\text{-}SnCl_3)_2(\mu\text{-dppm})_3]$,† (**6**), analogous to the known complex $[Pt_3(\mu_3\text{-}SnCl_3)_2(cod)_3]$.[5] Complex (**6**) has a plane of symmetry containing the $Pt_3(\mu\text{-dppm})_3$ groups and so has only a singlet for the CH_2P_2 protons in the ^1H n.m.r. spectrum, whereas unsymmetrical complexes such as (**4**) give an AB multiplet for the $CH^aH^bP_2$ protons.

This work has demonstrated the generality of the $Pt_3(\mu_3\text{-}SnX_3)$ group, which is most favourable with electronegative substituents X on tin. The electron count at platinum may be 42e [complex (**2**) or (**3**)] or 44e [complex (**4**) or (**6**)]. The ease of formation and stability of complex (**4**) strongly suggests that SnF_3^- should be a particularly good ligand for stabilizing low oxidation state Pt–Sn complexes, presumably as a result of its backbonding ability (compare PR_3 and PF_3 for example). We are not aware of any other metal–SnF_3 complexes.[6] Finally, these model compounds suggest that Pt–Sn/support catalysts[2,3] may contain $Pt_3(\mu_3\text{-}SnX_3)$ groups, where the X groups may be oxygen atoms of the surface tin(II) aluminate support material.[3]

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