A Hexaco-ordinate Platinum Complex containing Four Pt–Sn Bonds, One of Them to Sn^II
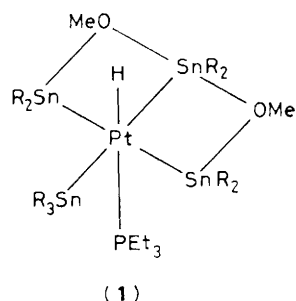
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The complex [Pt(CO₃)(SEt₂)(PEt₃)] reacts readily with SnR₃H (R = p-MeC₆H₄) in MeOH to give a hexaco-ordinate Pt^IV complex in which the ligands are PEt₃, H (these two being *trans* to one another), R₃Sn^IV, R₂Sn^II, and 2 × R₂(MeO)Sn^IV, with the OMe groups of the last ligands bridging to the R₂Sn^II centre; the four Sn and two O atoms lie approximately in a plane, with the Pt atom 0.48 Å out of this plane towards the PEt₃ ligand.

As part of a study of the use of [Pt(CO₃)(SEt₂)(PR₃)] (containing only one strongly bound ligand) as a source of the fragment PtPR₃, we treated the complex [Pt(CO₃)(SEt₂)-(PEt₃)] with 5 mol. equiv. of Sn(C₆H₄Me-p)₃H in MeOH. After stirring for 1 h at room temperature the pale yellow precipitate was filtered off, washed with MeOH, dried under vacuum, and shown to be (1), m.p. 180 °C (decomp.). Crystals used for an X-ray diffraction study were produced by diffusion of pentane vapour into a solution of (1) in Et₂O.† The structure of (1) is shown in Figure 1; the hydridic hydrogen atom was not located, but its presence is clearly revealed by i.r. [ν(PtH) 2060 cm⁻¹] and ¹H n.m.r. spectroscopy. It can be seen that (1) is a hexaco-ordinate Pt^IV species containing four Pt–Sn bonds, two to SnR₂OMe ligands (R = p-MeC₆H₄), one to an SnR₃ ligand, and one to a neutral R₂Sn^II ligand in which the tin is pentaco-ordinate as a result of bridging by the two OMe groups of the SnR₂OMe ligands. The four tin and the two oxygen atoms fairly accurately lie in a plane, with the platinum atom raised by 0.48 Å out of this plane in the direction of the PEt₃ ligand. The Pt–Sn^II bond length lies between those of the Pt–SnR₃ and Pt–SnR₂OMe bonds. The geometry around the Sn^II atom is that of a distorted bypyramid with the oxygen atoms at apical positions, and, as expected, these two Sn–O bonds are significantly longer than the other Sn–O bonds.

The ¹H and ³¹P {¹H} n.m.r. spectra are fully consistent with the structure of (1). The ³¹P {¹H} spectrum (in CH₂Cl₂ with C₆D₆ lock) shows a singlet (δ −169.1 p.p.m.) with ¹⁹⁵Pt side bands [¹J(Pt–P) 1960 Hz], and in addition each component shows Sn satellites [²J(Sn–P) 117.2 Hz];‡ there was no change in the spectrum from −50 to +50 °C. The ¹H n.m.r. spectrum (in CDCl₃) shows the expected peaks, the hydridic hydrogen giving a doublet due to coupling to phosphorus [δ −10.70 p.p.m.; ²J(P–H) 157.6 Hz] and satellite doublets due to ¹⁹⁵Pt [¹J(Pt–H) 501 Hz]. The ¹¹⁹Sn n.m.r. spectrum (in CDCl₃, relative to SnMe₄) shows the expected three sets of signals in 2:1:1 intensity ratio: δ 132.5 p.p.m., ¹J(Sn–Pt) 7034, ²J(Sn–P) 121 Hz; −17.5 p.p.m., ¹J(Sn–Pt) 5568, ²J(Sn–P) 116 Hz; −113.8 p.p.m., ¹J(Sn–Pt) 5952, ²J(Sn–P) 101 Hz. (Tin–tin couplings were also evident.)

When (1) is isolated from the reaction mixture by other methods it sometimes contains a second species (seemingly very closely related) with very similar n.m.r. parameters
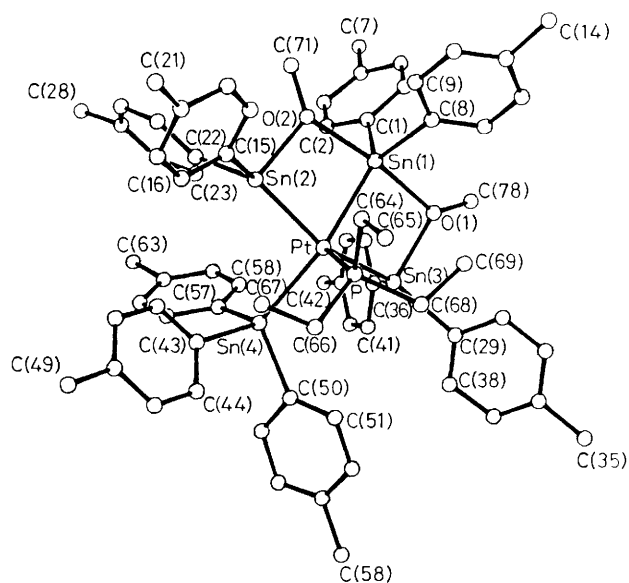

(1)

Figure 1. Molecular structure of (1), with H atoms omitted. Important dimensions: Pt–Sn(1) 2.626(1), Pt–Sn(2) 2.585(1), Pt–Sn(3) 2.595(1), Pt–Sn(4) 2.645(1), Sn(1)–O(1) 2.344(7), Sn(1)–O(2) 2.276(7), Sn(2)–O(2) 2.096(7), Sn(3)–O(1) 2.101(7), and Pt–P 2.337(3) Å; Sn(1)–Pt–Sn(2) 80.27(3), Sn(1)–Pt–Sn(3) 80.88(3), Sn(2)–Pt–Sn(4) 96.95(3), Sn(3)–Pt–Sn(4) 94.30(3), C(1)–Sn(1)–C(8) 106.9(4), C(1)–Sn(1)–Pt 122.2(3), C(8)–Sn(1)–Pt 130.9(4), and O(1)–Sn(1)–O(2) 171.3(2)°.

‡ In principle several different ²J(Sn–P) values should be observed because of the presence of ¹¹⁷Sn and ¹¹⁹Sn isotopes and three chemically distinct tin environments, but these were not resolved in our spectra and the quoted ²J(Sn–P) values are averages.

[^{31}P {^{1}H}, δ -167.9 p.p.m., ^{2}J(Pt–P) 1957, ^{1}J(Sn–P) 118.4 Hz; ^{1}H (hydride) δ -10.56 p.p.m., ^{2}J(P–H) 158.8, ^{1}J(Pt–H) 503 Hz], and this species is also formed when a solution of (1) in CH_2Cl_2 or similar solvents is kept at room temperature. This second species is immediately converted into (1) upon addition of even a very small amount of MeOH.§

Similar results have been obtained from other [Pt(CO$_3$)-(SEt$_2$)(PR$'_3$)] complexes and other triaryltin hydrides.

Complex (1) is formed from [Pt(CO$_3$)(SEt$_2$)(PEt$_3$)] in yields which are remarkably high (75%) in view of the complex sequence of bond-breaking and bond-making processes which must be involved. We are studying this sequence, and for the present note only that reactions of triorganotin hydrides with [Pt(CO$_3$)(PR$'_3$)$_2$] or [Pt(CO$_3$)(bipy)] (bipy $=$ 2,2'-bipyridyl) complexes to give hexaco-ordinate complexes have been

described previously,[1] as has the loss of aryl groups from tin by transfer to platinum.[2] The potential of [Pt(CO$_3$)(SEt$_2$)-(PR$'_3$)] complexes as sources of other novel platinum derivatives is an additional feature of interest.

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§ *Added in proof.* The second species is now thought to contain OH in place of one of the OMe bridging groups.

References

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