The Role of Bivalent Tin Compounds in Platinum Co-ordination Chemistry; *X*-Ray Structures of $[Pt\{Sn(NR'_2)_2\}_3]$, *trans*-$[(Pt(\mu\text{-}Cl)(PEt_3)\{SnCl(NR'_2)_2\})_2]$, and $(SnClR_2)_2$ $[R = CH(SiMe_3)_2, R' = SiMe_3]$†

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Bivalent tin compounds SnX_2 behave in one of three ways towards platinum substrates: (a) as neutral ligands, (b) as co-ordinatively unsaturated fragments by inserting into Pt–Cl bonds, and (c) as reducing agents; these features are illustrated, *inter alia*, by *X*-ray data on the three title compounds.

Tin(II) chloride has a significant place as a cocatalyst for alkene transformations in platinum chemistry, *e.g.*, with $H_2[PtCl_6]$ or $K_2[PtCl_4]$ in hydrogenation[1] or $[Pt(CO)Cl(H)(PPh_3)_2]$ in hydroformylation;[2] this is generally attributed to the creation of the labile $^{-}SnCl_3$ ligand. Numerous Pt^{II} complexes of this type have been identified.[3]

Recently a number of heavy main group 4b metal(II) carbene analogues $:MX_2$ (M = Ge, Sn, or Pb) have become available. They may prove to have an extensive transition-metal chemistry. Here we present some data on the structural chemistry of compounds obtained from SnR_2 or $Sn(NR'_2)_2$ $[R = CH(SiMe_3)_2, R' = SiMe_3]$ and certain Pt^0 or Pt^{II} complexes. These results illustrate that $:SnX_2$ may function as a ligand (a tertiary phosphine analogue), a source of $^{-}SnX_2Cl$ by insertion into a Pt–Cl bond, or a reducing agent which is oxidised to $(SnX_2Cl)_2$; for background literature see ref. 3.

Of particular interest is the yellow homoleptic, three-co-ordinate Pt^0 complex $[Pt\{Sn(NR'_2)_2\}_3]$, (**1**), Figure 1, obtained from $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) and an excess of $Sn(NR'_2)_2$ in toluene.

An alternative mode of Pt–Sn bonding is found in the yellow

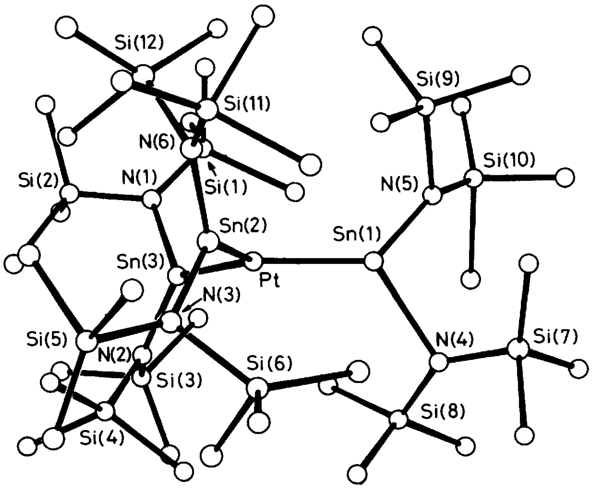

Figure 1. $[Pt\{Sn(NR'_2)_2\}_3]$, (**1**). The Pt, Sn, and N atoms are all trigonally planar co-ordinated. The SnN_2 planes are at *ca.* 85° to the $PtSn_3$ plane. Selected dimensions: Pt–Sn(1) 2.470(6), Pt–Sn(2) 2.487(6), Pt–Sn(3) 2.504(5), Sn–N (av.) 2.1(2), N–Si (av.) 1.8(2) Å; Sn(1)–Pt–Sn(2) 120.0(2), Sn(1)–Pt–Sn(3) 119.8(2), Sn(2)–Pt–Sn(3) 120.2(2)°.

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† No reprints available.

trans-$[(\mathrm{Pt}(\mu\text{-Cl})(\mathrm{PEt_3})\{\mathrm{Sn(NR'_2)_2Cl}\})_2]$, (**2**), Figure 2, prepared from $[\{\mathrm{PtCl}(\mu\text{-Cl})(\mathrm{PEt_3})\}_2]$ and an excess of $\mathrm{Sn(NR'_2)_2}$ in n-hexane.[3] This complex (30%) is now found to coexist with the *cis*-isomer, (**3**), (70%) when the freshly mixed n-C_6H_{14} solution is freed from solvent and the residue dissolved in C_6D_6; heating the mixture causes the isomerisation (**3**) → (**2**). The compounds are readily distinguished by ^{31}P n.m.r. spectroscopy [data for (**3**) in parentheses]: δ −133.7 (−132.5) p.p.m.; $^1J(^{195}\mathrm{Pt}^{31}\mathrm{P})$ 3 960 (4 109) Hz, $^2J(^{119}\mathrm{Sn}^{31}\mathrm{P})$ 170 (185.5) Hz.

$[\mathrm{Pt}\{\mathrm{Sn(NR'_2)_2}\}_3]$
(**1**)

$[(\mathrm{Pt}(\mu\text{-Cl})(\mathrm{PEt_3})\{\mathrm{Sn(NR'_2)_2Cl}\})_2]$
(**2**), *trans*
(**3**), *cis*

$[(\mathrm{Pt}(\mu\text{-Cl})(\mathrm{PEt_3})\{\mathrm{SnR_2Cl}\})_2]$
(**4**), *trans*

$[\mathrm{PtCl(PEt_3)(SnR_2)(SnR_2Cl)}]$
(**5**), *cis*
(**6**), *trans*

$[(\mathrm{SnClR_2})_2]$
(**7**)

Treatment of the same $\mathrm{Pt^{II}}$ substrate $[\{\mathrm{PtCl}(\mu\text{-Cl})(\mathrm{PEt_3})\}_2]$ with an excess of $\mathrm{SnR_2}$ yields (**4**), the $\mathrm{SnR_2Cl}$ analogue of (**2**), as well as *cis*-(**5**)[4] and *trans*-(**6**) $[\mathrm{PtCl(PEt_3)(SnR_2)(SnR_2Cl)}]$ (the designations *cis* and *trans* refer to the relative disposition of the Sn-containing ligands); a by-product was crystalline $[(\mathrm{SnClR_2})_2]$, (**7**), Figure 3. ^{31}P N.m.r. data for (**4**), (**5**), and (**6**) are: δ −133.5, −125.0, and −127.6 p.p.m.; $^1J(^{195}\mathrm{Pt}^{31}\mathrm{P})$ 4 304, 2 490, and 4 497 Hz; $^2J(^{119}\mathrm{Sn}^{31}\mathrm{P})$ 80, obscured, and 129.4 ($\mathrm{SnR_2}$ or $\mathrm{SnR_2Cl}$) and 34.3 ($\mathrm{SnR_2Cl}$ or $\mathrm{SnR_2}$) Hz. Compound (**7**) is notable also for being the dichloro adduct of $\mathrm{R_2Sn{=}SnR_2}$ [which has a SnSn bond length of 2.764(2) Å].[4]

The *X*-ray structures of complexes (**1**), (**2**), and (**7**) are illustrated in Figures 1—3 and crystal data and refinement parameters are in Table 1. There are *X*-ray data in the literature for a number of transition-metal complexes having the $^-\mathrm{SnCl_3}$ ligand or a simple analogue, but only four for $\mathrm{SnR_2}$ or $\mathrm{Sn(NR'_2)_2}$ derived compounds: $[\mathrm{Cr(CO)_5(SnR_2)}]$,[4] $[\mathrm{Os_3SnH_2(CO)_{10}R_2}]$,[5] $[\mathrm{Os_3Sn}(\mu\text{-H})\{\mu\text{-RC(OS){=}O(SN)}\}\mathrm{(CO)_9R}]$,[6] and $[\mathrm{Os_3Sn(CO)_9}\{\mu_2,\eta^1\text{-C(CO_2Me)CH_2C{=}O(Os)OMe}\}\mathrm{R_2}]$. The complex $[\mathrm{PtH(PEt_3)(SnR''_2OMe)_2(SnR''_2)(SnR''_3)}]$ (R'' = *p*-$\mathrm{C_6H_4Me}$) has a base-stabilised $\mathrm{SnR''_2}$ ligand,[7] while $[\mathrm{Pt(PPh_3)_2}\{\mathrm{Sn}(\eta^2\text{-acac})_2\}_2]$ and $[\mathrm{Pt_2}\{\mu_2\text{-Sn}(\eta^2\text{-}$

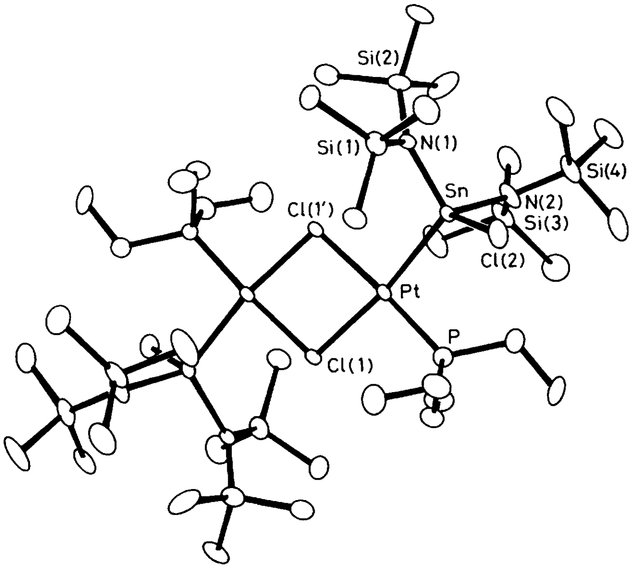

Figure 2. *trans*-$[(\mathrm{Pt}(\mu\text{-Cl})(\mathrm{PEt_3})\{\mathrm{Sn(NR'_2)_2Cl}\})_2]$, (**2**). Selected dimensions: Pt-Sn 2.534(1), Pt-Cl(1) 2.430(3), Pt-Cl(1') 2.370(3), Pt-P 2.202(3), Sn-Cl(2) 2.401(3), Sn-N(1) 2.066(8), Sn-N(2) 2.088(8) Å; P-Pt-Sn 94.8(1)°.

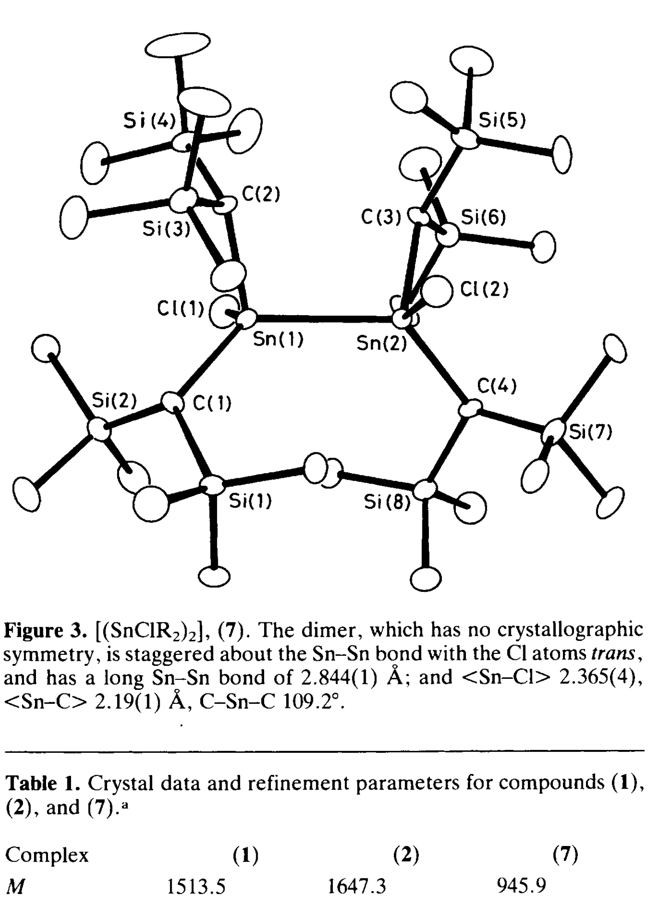

Figure 3. $[(\mathrm{SnClR_2})_2]$, (**7**). The dimer, which has no crystallographic symmetry, is staggered about the Sn–Sn bond with the Cl atoms *trans*, and has a long Sn–Sn bond of 2.844(1) Å; and <Sn–Cl> 2.365(4), <Sn–C> 2.19(1) Å, C–Sn–C 109.2°.

Table 1. Crystal data and refinement parameters for compounds (**1**), (**2**), and (**7**).[a]

Complex	(**1**)	(**2**)	(**7**)
M	1513.5	1647.3	945.9
Crystal system	Triclinic	Monoclinic	Triclinic
a/Å	13.927(17)	11.501(1)	9.093(2)
b/Å	13.823(5)	17.975(2)	12.017(3)
c/Å	19.545(9)	17.244(1)	23.869(4)
α/°	78.78(3)		98.32(1)
β/°	86.99(6)	105.20(1)	90.08(1)
γ/°	74.36(6)		110.58(1)
U/Å^3	3556.4	3440.1	2412.2
Z	2	2	2
D_c/g cm^{-3}	1.41	1.59	1.30
F(000)	1524	1624	980
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
μ(Mo-K_α)/cm^{-1} [b]	33.3	53.5	13.6
2θ limits/°	15	25	20
Reflections used in refinement $I > \sigma(I)$	1395	3722	2943
R	0.13	0.07	0.06
R'	0.13	0.08	0.07

[a] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. [b] λ(Mo-K_α) = 0.71069 Å.

acac)$_2$}$_3$(PPh$_3$)$_2$][8] (Hacac = acetylacetone) are Pt^0–Sn^{II} complexes having different co-ordination numbers for Pt and Sn (4 and 5, respectively) than complex (**1**).

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