Homoleptic, Three-co-ordinate Group 8c Noble Metal(0) Complexes having Ge^{II} or Sn^{II} Ligands, $[M\{M'(NR_2)_2\}_3]$ (M = Pd or Pt, M′ = Ge or Sn, R = $SiMe_3$), and the *X*-Ray Structure of One of Them (M = Pd, M′ = Sn)†

Peter B. Hitchcock, Michael F. Lappert, and Mohan C. Misra

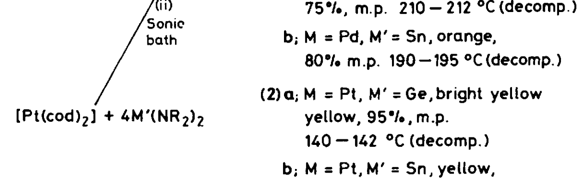
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Homoleptic bis(amido)-germylene and -stannylene d^{10} complexes of Pd and Pt $[M\{M'(NR_2)_2\}_3]$, obtained from an excess of $M'(NR_2)_2$ and $[Pd(cod)Cl_2]$ or $[Pt(cod)_2]$ (M = Pd or Pt, M′ = Ge or Sn, R = $SiMe_3$, cod = cyclo-octa-1,5-diene), yield with CO the heterobimetallic trinuclear clusters $[(M\{\mu\text{-}M'(NR_2)_2\}CO)_3]$; $[Pd(Sn\{N(SiMe_3)_2\}_2)_3]$ has a trigonal planar environment at each of Pd, Sn, and N, with <Pd–Sn> 2.53(1) Å and the parameters for the $Sn(NR_2)_2$ moieties little changed from those in the free ligand.

We report on an interesting family of homoleptic noble metal d^{10} complexes of formula $[M\{M'(NR_2)_2\}_3]$ (M = Pd or Pt, M′ = Ge or Sn, R = $SiMe_3$).

High yield syntheses are summarised in Scheme 1 (cod = cyclo-octa-1,5-diene); the shown stoicheiometries represent optimal conditions. In these reactions the main group 4 metal(II) amides behave as two electron σ-donors (tertiary phosphine analogues) and in the Pd systems also as reducing agents; there are precedents for the dechlorinating ability of Sn^{II} alkyls[1] or amides.[2]

The formation of the Pd^0 complexes (**1**) under the mild conditions of Scheme 1 is surprising. Formation of a $[Pd(cod)\{Sn(NR_2)_2Cl\}_2]$ intermediate, (**3**), is likely, by analogy with the observed product[3] from the reaction of $[Pt(cod)Cl_2]$ and excess of $Sn(NR_2)_2$. Compound (**3**) must be unstable with respect to reductive elimination under the influence of an excess of the tin(II) amide. Whether $[M'(NR_2)_2Cl]_2$ is the coproduct in reaction (i) of Scheme 1



Scheme 1

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† No reprints available.

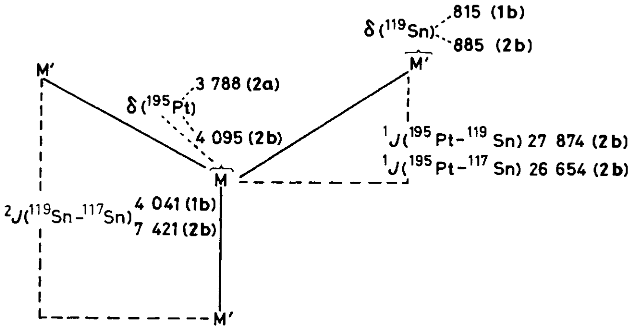

Figure 1. Some n.m.r. chemical shifts {δ in p.p.m., ^{195}Pt relative to $K_2[PtCl_4]$ (recorded at 77 MHz) and ^{119}Sn relative to $SnMe_4$ (recorded at 134 MHz)} and coupling constants (*J* in Hz) for complexes (**1b**), (**2a**), and (**2b**), in C_6D_6 at 70 °C.

has not yet been ascertained, but the isoelectronic $[Sn\{CH(SiMe_3)_2\}_2Cl]_2$ is known; *X*-ray structures both of this compound and (**2b**) are established.[1]

Complexes (**1**) and (**2**) are exceedingly sensitive to air: Pd > Pt and Sn > Ge, sequences which reflect the inverse orders of M–X or M′–X bond strengths.

$$[Pd(cod)\{Sn(NR_2)_2Cl\}_2]$$
(**3**)

Multinuclear n.m.r. spectroscopic data are summarised in Figure 1 for complexes (**1b**), (**2a**), and (**2b**). The ^{119}Sn chemical shifts for compounds (**1b**) and (**2b**) show little difference from that of the free tin(II) amide $Sn(NR_2)_2$, 770 p.p.m. The high coupling constants $J(^{195}Pt–^{117/119}Sn)$ are comparable to those in several Pt^{II}–$SnCl_3$ complexes, *e.g.*, 35 309 Hz in *trans*-$[\{Pt(\mu\text{-}Cl)(PEt_3)(SnCl_3)\}_2]^4$ [which has <Pt–Sn> 2.482(3) Å; it was suggested[5] that large *J* values in $SnCl_3$–Pt^{II} complexes correlate with short Pt–Sn distances].

Treatment of any one of compounds (**1**) or (**2**) with carbon monoxide in toluene under ambient conditions rapidly affords the appropriate cluster complex (**4**) (for characterisation, see ref. 6), which undergo reversible and facile one electron reduction in tetrahydrofuran.[6]

$$[(M\{\mu\text{-}M'(NR_2)_2\}CO)_3]$$
(**4**)

a; M = Pd, M′ = Ge, bright yellow, 80%, m.p. 160—164 °C
b; M = Pd, M′ = Sn, yellow, 90%, m.p. 195—199 °C (decomp.)
c; M = Pt, M′ = Ge, bright orange, 80%, m.p. > 360 °C (decomp.)
d; M = Pt, M′ = Sn, red, 85%, m.p. 80—84 °C (decomp.)

Crystal data for (**1b**): $C_{36}H_{108}N_6PdSi_{12}Sn_3$, $M = 1\,424.8$, triclinic, space group $P\bar{1}$, $a = 13.953(5)$, $b = 13.868(8)$, $c = 19.519(10)$ Å, $\alpha = 78.71(4)$, $\beta = 87.23(4)$, $\gamma = 74.11(4)$°, $U = 3\,562.3$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}. The structure of (**1b**) (Figure 2) was solved, using 5 073 reflections with $I > \sigma(I)$ (measured on a CAD-4 diffractometer with Mo-K_α radiation), by routine heavy atom methods and refined for non-hydrogen atoms by full-matrix least squares to $R = 0.098$, $R' = 0.123$.‡ Compounds (**1b**) and (**2b**) [<Pt–Sn> 2.49(1) Å][1] are isomorphous; the $Sn(NR_2)_2$ ligands have the following <Sn–N> bond lengths and <NSnN> angles [data for (**2b**) in parentheses]: 2.08(2) [2.1(2)] Å and 107(1) [104(1)]°; *cf.* ref. 7, 2.092(4) Å and 104.7(2)° in $Sn(NR_2)_2$. Three other Pt^0–Sn^{II} compounds are known: $[Pt(PPh_3)_2\{Sn(\eta^2\text{-}acac)_2\}_2]$ [δ(^{119}Sn) −601 p.p.m., $^1J(^{195}Pt–^{119}Sn)$ 12 891 Hz, <Pt–Sn> 2.558(1) Å] and $[Pt_2\{\mu_3\text{-}Sn(\eta^2\text{-}acac)_2\}_3(PPh_3)_2]$ [δ(^{119}Sn) −563 p.p.m., <Pt–Sn> 2.680(1) Å] [acacH = $MeCOCH_2COMe$; δ (^{119}Sn) in $Sn(acac)_2$ −702 p.p.m.], in which Pt and Sn are 4- and 5-co-ordinate, respectively;[8] and $[PtH(SnCl_3)_2(PEt_3)_2]^{3-}$ [δ(^{119}Sn) −122 p.p.m., δ(^{195}Pt) −5 396 p.p.m., $^1J(^{195}Pt–^{119}Sn)$ 4 488 Hz, and $^2J(^{119}Sn–^{117}Sn)$ 2 356 Hz].[9]

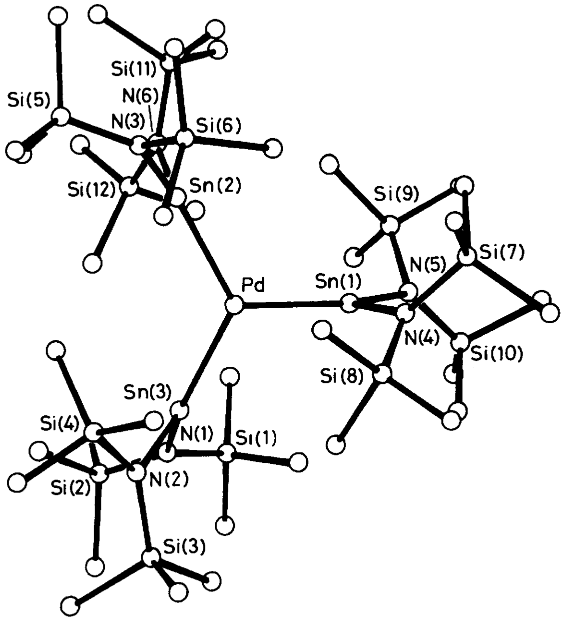

Figure 2. The molecular structure and atom numbering scheme for $[Pd\{Sn(NR_2)_2\}_3]$, (**1b**). The Pd, Sn, and N atoms are all trigonally planar co-ordinated. The SnN_2 planes are at *ca.* 90° to the $PdSn_3$ plane. Selected dimensions: Pd–Sn(1) 2.533(1), Pd–Sn(2) 2.540(1), Pd–Sn(3) 2.517(1) Å; Sn(1)–Pd–Sn(2) 118.82(4), Sn(1)–Pd–Sn(3) 120.78(4), Sn(2)–Pd–Sn(3) 120.40(4)°.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.