Co-ordination Chemistry of Heavy-atom Group IV Donors, and the Crystal and Molecular Structure of $[(Me_3Si)_2CH]_2SnCr(CO)_5$

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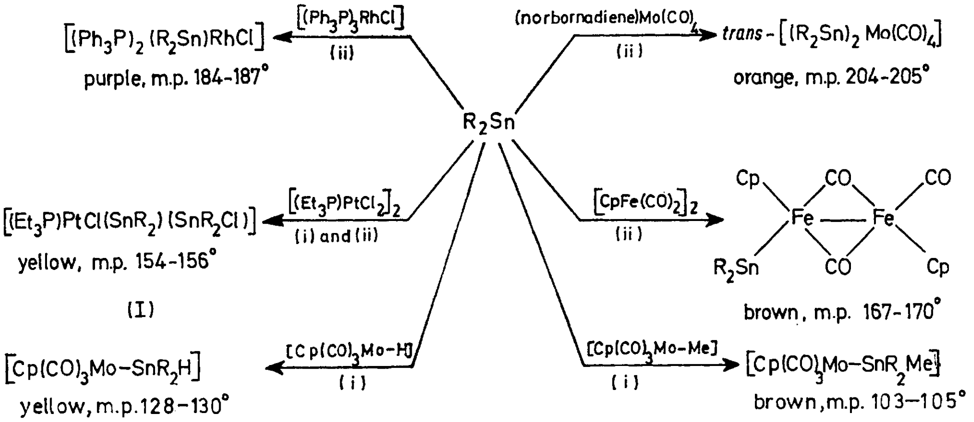
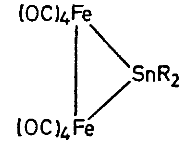
Summary A bulky monomeric tin(II) alkyl [R_2Sn, R = $(Me_3Si)_2CH$] is an example of a new type of ligand in which the ligating centre is a heavy Group IV atom; examples of new complexes include (i) tin(II) derivatives in which tin is three-co-ordinate in a planar environment, as confirmed (*X*-ray) for [$R_2SnCr(CO)_5$] and (ii) tin(IV) species resulting from R_2Sn insertion into M–H, M-alkyl, M–Cl, or M–M bonds, *e.g.*, [$R_2Sn\{Fe(CO)_4\}_2$].

THE co-ordination chemistry of stable neutral donors has mainly been restricted to that of carbon (CO, RNC, or nucleophilic carbenes) and elements of Groups V or VI (*e.g.*, NH_3, Ph_3P, or Et_2S). We now report a significant extension to the heavy Group IV atoms Sn and Pb.

The stable monomeric bivalent $R_2\ddot{M}$ [R = $(Me_3Si)_2CH$ and M = Sn or Pb][1] are the heavy-atom analogues of carbenes and have an extensive co-ordination chemistry. Some of the new complexes, and their synthesis, are illustrated for R_2Sn in the Scheme. (All the compounds gave satisfactory analytical and spectroscopic data.) We note that, unlike corresponding carbene complexes,[2] there is no necessity for a group R to be electron-rich (*e.g.*, alkoxy or dialkylamino). The stannylene or plumbylene, [*e.g.*, the yellow $R_2PbMo(CO)_5$, m.p. 93—94°] derivatives appear to have the Group IV atom in an unusual three-co-ordinate trigonal environment, as confirmed in one case by an *X*-ray analysis {of $[R_2SnCr(CO)_5]$,[1] *vide infra*}. Their stability, like that of the parent ligands, is probably kinetic in origin and derives from the bulk of the groups R. By contrast, with sterically less demanding groups, stability is achieved by incorporation of base: *e.g.*, in $[Bu^t_2(base)SnCr(CO)_5]$ or $[Bu^t_2(base)SnFe(CO)_4]$ (base = py or THF);[3] the tin atom now has the common co-ordination number four as demonstrated ultimately by an *X*-ray diffraction study of $[Bu^t_2(py)SnCr(CO)_5]$.[4]



Scheme

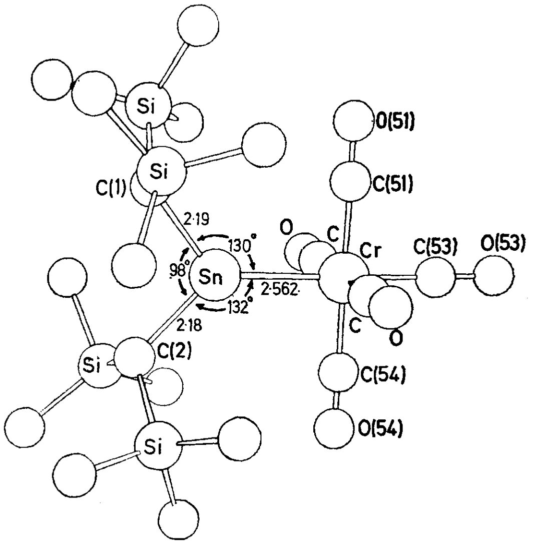


orange, m.p. 139-141° (decomp.)

(II)

It will be noted (see Scheme) that R_2Sn is a good nucleophile, being able to displace CO or R'_3P from metal complexes or to cleave the chloride bridges of a binuclear Pt^{II} species to yield (I). However, as this shows R_2Sn has a more complicated co-ordination chemistry than a tertiary phosphine because of its greater tendency to achieve a higher valence state while still able to bond to a metal (*e.g.*, Pt^{II}) site. Other such reactions involve insertions into M–H, M–alkyl, M–Cl, or M–M bonds [*e.g.*, (II) from R_2Sn and $Fe_2(CO)_9$]. As well as (i) such oxidative addition reactions ($Sn^{II} \rightarrow Sn^{IV}$) and (ii) its Lewis base properties, R_2Sn is (iii) a weak Lewis acid,[1] capable (iv) of disproportionation upon photolysis [$2Sn^{II} \rightarrow Sn^{III} + (Sn^{I}?)$],[5] or of undergoing (v) other Sn–C cleavage reactions.

Orange needles of $[R_2SnCr(CO)_5]$, obtained by crystallisation from toluene at −30°, were found to be monoclinic with $a = 9{\cdot}340(4)$, $b = 13{\cdot}548(8)$, $c = 24{\cdot}272(10)$ Å; $\beta = 90{\cdot}33(1)°$, space group $P2_1/c$, $Z = 4$, $D_c = 1{\cdot}362$ g cm^{-3}. Intensity data for 1591 independent reflections, having $I_{obs} \geqslant 3\sigma\ (I_{obs})$ and $4° \leqslant 2\theta \leqslant 40°$, were obtained on a Hilger and Watts Y290 four-circle diffractometer with Mo-K_α radiation, and the structure solved by conventional heavy atom techniques. Least-squares refinement of the positional parameters of all non-hydrogen atoms with anisotropic temperature factors for the Sn, Cr, and Si, and isotropic Debye temperature factors for the C and O atoms, converged to $R = 0{\cdot}071$. The e.s.d.'s for the Sn–Cr and Sn–C bond lengths are 0·005 and 0·02 Å, respectively The overall stereochemistry and important bond lengths are shown in the Figure.



Figure

The structure consists of well separated molecules with approximate C_2 symmetry. The atoms C(1), C(2), Cr and Sn are coplanar, and there are no intermolecular contacts with the tin atom at less than 5 Å. The Sn–Cr bond length [2·562(5) Å] is significantly shorter than that in $[Bu^t_2(py)SnCr(CO)_5]$ [2·654(3) Å].[4] While this shortening may simply reflect the change in hybridisation on the tin atom, the orientation of the R_2Sn group, which is essentially coplanar with Cr, C(51), C(53), C(54), O(51), O(53), and O(54), raises the additional possibility of π-interaction between the Cr 3*d*-orbitals and the vacant 5*p*-orbital on Sn. The C(1)–Sn–C(2) bond angle (98°) is surprisingly low.

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