Co-ordination Chemistry of Bivalent Group 4B Heavy Metal Donors $M[N(SiMe_3)_2]_2$ (M = Ge or Pb) or $Ge[CH(SiMe_3)_2]_2$; and the Crystal and Molecular Structure of $[Cr(CO)_5(Ge\{CH(SiMe_3)_2\}_2)]$†

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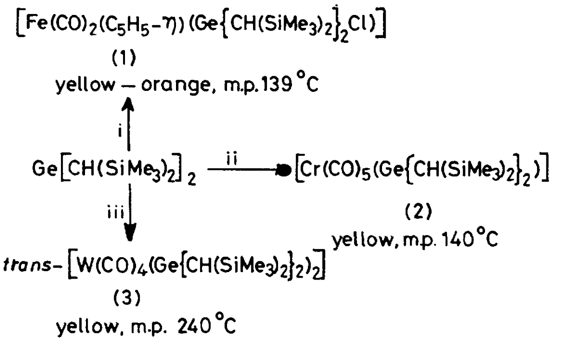
Summary The hydrocarbon-soluble Group 4 metal ligands $\ddot{M}X_2$ [M = Ge, X = $(Me_3Si)_2CH$; or M = Ge or Pb, X = $(Me_3Si)_2N$] form stable transition metal complexes (**1**)—(**7**) by nucleophilic attack at a transition metal centre causing (i) neutral ligand displacement, (ii) μ-dichlorodipalladium(II) bridge-splitting, or (iii) M'^{II}–Cl (M′ = Fe or Pt) insertion; the germanio(II)- or plumbio(II)-complexes (**2**)—(**4**), (**6**), and (**7**) have Ge or Pb in a 3-co-ordinate planar environment as confirmed for one complex (**2**) by single crystal *X*-ray diffraction.

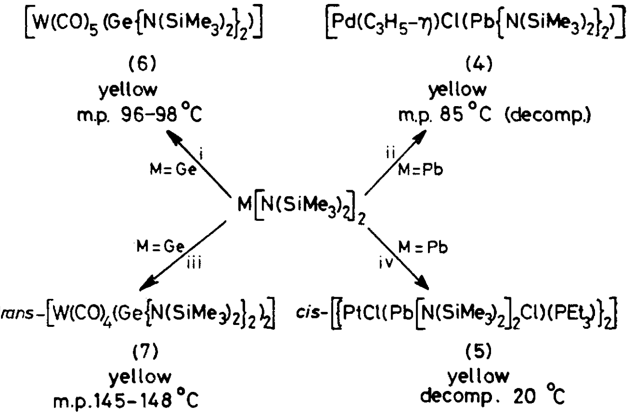
WE briefly describe significant extensions to that rare class of molecule, the bivalent Group 4 metal ligand. Schemes 1 and 2 summarise a selection of relevant data on respectively a germanium(II) alkyl[1] and disilylamides of Ge^{II} and Pb^{II}.[2]

For the alkyl there are precedents in the behaviour of the tin and lead analogues $M[CH(SiMe_3)_2]_2$,[3] but the latter have energetically much more accessible metal lone pair orbitals.[4] Similarly, the ability of the amides to act as effective donors is unexpected, because their first ionisation potentials are more than 1 eV higher than those of the isoelectronic alkyls.[4] Two compounds related to (**2**), $[Cr(CO)_5\{Ge(SR)_2\}]$, obtained from $[Cr(CO)_5\{GeCl_2(thf)\}]$ (thf = tetrahydrofuran) have been reported.[5]



SCHEME 1. i, $[Fe(CO)_2(C_5H_5\text{-}\eta)Cl]$, $n\text{-}C_6H_{14}$, 20 °C; ii, $[Cr(CO)_6]$, OEt_2, $h\nu$, 20 °C; iii, $[W(CO)_4(\text{norbornadiene})]$, PhMe, 100 °C.

The five germanio- and two plumbio-transition metal complexes shown in Schemes 1 and 2 were characterised by elemental analysis and i.r. and n.m.r. spectroscopy; and, in one case, $[Cr(CO)_5(Ge\{CH(SiMe_3)_2\}_2)]$, (**2**), by *X*-ray diffraction. The complexes are further of interest because they (i) show the main group divalent element M in the unusual three-co-ordinate environment and (ii) they shed light on the nature of the M–transition metal bond. It is interesting that the plumbio-palladium complex is thermally quite robust in view of the photo- and thermal-sensitivity of the parent ligand; this is probably a thermodynamic effect because decomposition involves a redox process leading to Pd^0 and the unfavourable Pb^{IV}.



SCHEME 2. i, $[W(CO)_6]$, $n\text{-}C_6H_{14}$, $h\nu$, 20 °C; ii, $[\{Pd(C_3H_5\text{-}\eta)Cl\}_2]$, $n\text{-}C_6H_{14}$, 20 °C; iii, $[W(CO)_4(\text{norbornadiene})]$, $n\text{-}C_6H_{14}$, reflux; iv, $[\{PtCl_2(PEt_3)\}_2]$, $n\text{-}C_6H_{14}$, 20 °C.

Orange needles of $[Cr(CO)_5(Ge\{CH(SiMe_3)_2\})]$, (**2**), obtained by crystallisation from hexane at −30 °C, were found to be monoclinic with $a = 9{\cdot}386(2)$, $b = 13{\cdot}113(3)$, $c = 24{\cdot}089(7)$ Å, $\beta = 90{\cdot}39(4)^\circ$, $U = 3010{\cdot}0$ Å^3, $Z = 4$, $D_c = 1{\cdot}287$ g cm^{-3}, $F(000) = 1216$, space group $P2_1/c$ (No. 14; C_{2h}). Mo-K_α radiation, $\lambda = 0{\cdot}71069$, $\mu(\text{Mo-}K_\alpha) = 16{\cdot}11$ cm^{-1}. Intensity data for 3925 independent reflections ($2\theta \leqslant 45^\circ$) were obtained on a GE XRD-6 automated diffractometer and 2791 with significant [$I \geqslant 3\sigma(I)$] intensities were used for the structure determination. Solution by heavy-atom techniques and full-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms gave an R of 0·047. The C–H hydrogen atom positions were located, but not refined. The overall stereochemistry and important bond lengths and angles are shown in the Figure.‡

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† No reprints available.

‡ 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.

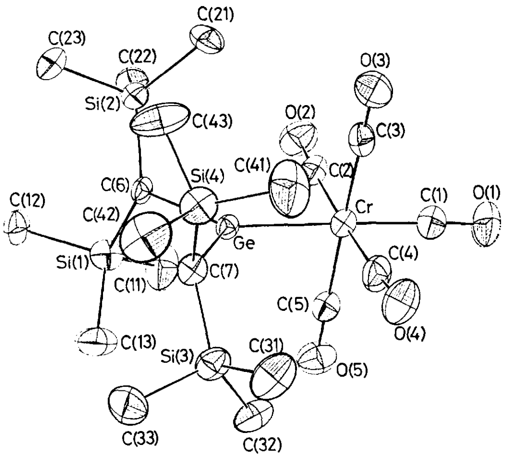

FIGURE. A perspective view of the molecular structure of [Cr(CO)$_5$(Ge{CH(SiMe$_3$)$_2$}$_2$)] showing the atomic labelling. Important bond lengths and angles are: Cr–C(1), 1·881(9); Cr–C(2), 1·878(8); Cr–C(3), 1·891(8); Cr–C(4), 1·893(8); Cr–C(5), 1·888(7); Ge–C(6), 1·989(6); and Ge–C(7), 1·984(7) Å; ∠C(6)–Ge–Cr, 128·4(1) and ∠C(7)–Ge–Cr, 128·1(1)°. Important intramolecular contacts are: O(2) · · · C(22), 3·40(1)° and O(5) · · · C(32), 3·44(1)°.

Significant stereochemical differences are evident between [Cr(CO)$_5$(Ge{CH(SiMe$_3$)$_2$}$_2$)] and the (nucleophilic) carbene complexes [Cr(CO)$_5$(carbene)]. The orientation of the germanio-group is such that the atoms Ge, Cr, C(1), O(1), C(2), O(2), C(4), O(4), C(6), C(7), H(1), and H(2) [H(1) and H(2) being attached to C(6) and C(7) respectively] are essentially coplanar, whereas the equatorial CO groups in [Cr(CO)$_5$(carbene)] are not coplanar with the carbene ligand.[6] Additionally, the Cr–C(1) (*trans* to Ge) bond length [1·881(9) Å] is not significantly different from the Cr–CO (equatorial) (av. 1·888 Å) bond lengths and the C(6)–Ge–C(7) angle [102·8(2)°] lies between the corresponding angles in [Cr(CO)$_5$(Sn{CH(SiMe$_3$)$_2$}$_2$)] (98·2°)[1] and [Cr(CO)$_5$(carbene)] (*ca.* 108—114°).[6] These differences may be accounted for in terms of (i) steric effects (C > Ge > Sn), (ii) decreasing *s*-character in the Cr–M bond in the sequence M = Sn > Ge > C (*cf.* Bent's Rule), (iii) decreasing *trans*-influence in the order M = Sn $\sim$ Ge > C, and (iv) greater π-acceptor character of the heavier atom Group 4 donors.

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