

Chemistry, Including the X-Ray Structure, of Bis[bis(trimethylsilyl)methyl]germanium(II), R_2GeGeR_2 [$R = CH(SiMe_3)_2$], a Stable Compound having a Metal–Metal ‘Double Bond,’ a Dimetallene†

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Reaction of $MgClR(OEt_2)$ [$R = CH(SiMe_3)_2$] with $GeCl_2$ ·dioxane in OEt_2 yields the bright yellow crystalline Ge_2R_4 [having a *trans*-folded C_{2h} Ge_2C_4 framework with a fold angle of 32° , a germanium environment intermediate between pyramidal and planar (sum of angles at Ge = 348°), and a GeGe bond length of $2.347(2)$ Å (ca. 4% shorter than in elemental germanium)], which behaves chemically as a singlet germylene $\dot{G}eR_2$.

There has been much recent interest in thermally stable compounds having a ‘double bond’ between two main group atoms other than carbon, nitrogen, or a chalcogen, the *dimetallenes*. We define these as the heavy atom congeners of the olefins $R'_2C=CR'_2$, azo compounds $R'_2N=NR'_2$, or Schiff bases $R'_2C=NR''$. They are thus binuclear molecules of formula $R'_2MMR'_2$ ($M = Si, Ge, Sn, \text{ or } Pb$) or $R'MMR'$ ($M = P, As, Sb, \text{ or } Bi$), or heterobinuclear analogues, which are diamagnetic and hence in a singlet rather than a triplet electronic ground state. The nature of the M–M bond remains an open question, but relevant parameters are (a) structural and (b) chemical. As to (b), a crucial point relates to whether in chemical reactions of the dimetallene the M–M framework maintains its integrity or whether fragmentation with M–M scission occurs. We now present such results for (a) (Figure 1)

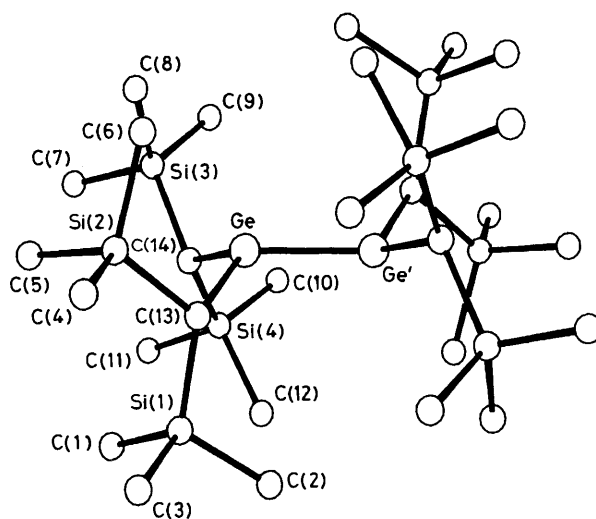
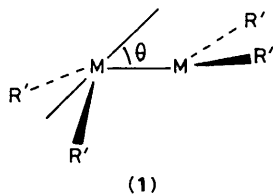
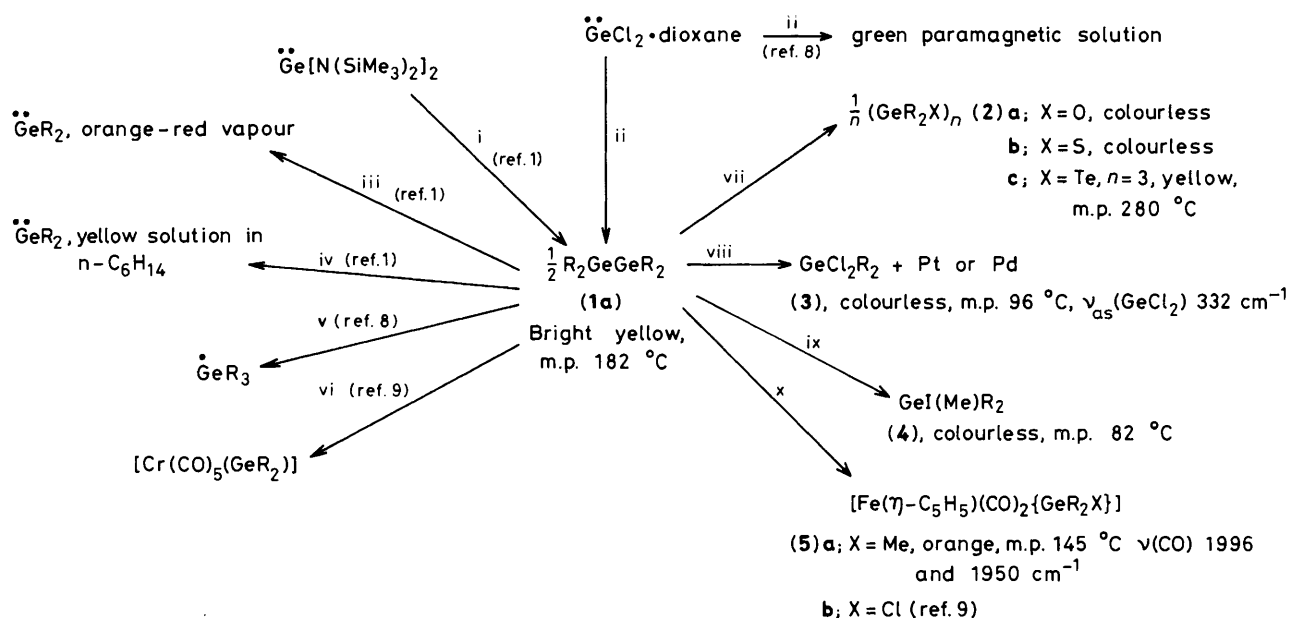


Figure 1. X-Ray structure of Ge_2R_4 [$R = CH(SiMe_3)_2$] and atom labelling scheme. Selected bond lengths (Å) and angles ($^\circ$) are Ge–Ge' $2.347(2)$, Ge–C(14) $1.979(9)$, Ge–C(13), $2.042(8)$ Å, Ge'–Ge–C(13) $113.7(3)$, C(13)–Ge–C(14) $112.5(3)$, and Ge'–Ge–C(14) $122.3(2)^\circ$.

†No reprints available.



Scheme 1. Abbreviations: R = CH(SiMe₃)₂, thf = tetrahydrofuran. Reagents and conditions: i, LiR, OEt₂, 0 °C; ii, $\frac{2}{n}$ [MgClR(OEt₂)_n], OEt₂, 25 °C, ca. 12 h; iii, 110 °C at 10⁻³ Torr; iv, cyclo-C₆H₁₂, 20 °C; v, C₆H₆, hv, 20 °C; vi, [Cr(CO)₆], OEt₂, hv, 20 °C; vii, air, n-C₆H₁₄, 20 °C (a), or S₈, PhMe, 20 °C (b), or Te, PhMe, 108 °C, 3 h (c); viii, $\frac{1}{2}$ [MCl(μ-Cl)(PEt₃)₂] (M = Pd or Pt), n-C₆H₁₄, 20 °C, 5 h; ix, MeI, n-C₆H₁₄, 20 °C; x, [Fe(η-C₅H₅)(CO)₂X], n-C₆H₁₄, 20 °C. Characterisation: Compounds (2), (3), (4), and (5) gave satisfactory microanalytical and molecular weight (2c) and (3)] results, as well as i.r., ¹H and ¹³C n.m.r. spectra (for e.s.r. data GeR₃, see ref. 2); for X-ray data on compound (1), see Figure 1 {and are available³ on [Cr(CO)₅(GeR₂)]}.

Table 1. Some structural parameters for crystalline group 4 dimetallenes M₂R'₄

M, R'	C, Ph ^a	Si, C ₆ H ₂ Me _{3-2,4,6} ^b	Ge, CH(SiMe ₃) ₂ ^c	Sn, CH(SiMe ₃) ₂ ^d
Sum of angles, Σ, at M ^o	360	355.3	348.5	342
Fold angle, θ ^o	0	18	32	41
Twist angle I ^o	8.4	5	0	0
<C(sp ² or sp ³)-M>/Å	1.494	1.88	2.00	2.28
M-M/Å	1.356	2.160	2.347(2)	2.764(2)
M-M In tetrahedral M _∞ /Å ^c	1.545	2.352	2.445	2.810
M-M Bond shortening in M ₂ R' ₄ compared with M _∞ , %	12	8	4	2

^a From A. Hoekstra and A. Vos, *Acta Crystallogr., Sect. B*, 1975, **31**, 1722. ^b From ref. 2. ^c This work. ^d From ref. 1. ^e From 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, Vols. 1 and 2.

and (b) (Scheme 1) for the first stable crystalline digermene Ge₂R₄ [R = CH(SiMe₃)₂], (**1a**); these are available for comparison with isoleptic C, Si, and Sn compounds [for (a), see Table 1].

The field of stable dimetallenes was inaugurated in 1976, when the X-ray structure of the crystalline brickred distannene Sn₂R₄ was disclosed.¹ The synthesis of the bright orange-yellow disilene Si₂(C₆H₂Me_{3-2,4,6})₄ appeared in 1981 and X-ray data followed in 1983.² Both molecules adopt the C_{2h} M₂C₄ skeletal conformation, (**1**), *i.e.*, a *trans*-folded arrangement (θ = fold angle) (see Table 1). Other stable group 4b compounds reported are the tetrakis(2,6-xylyl)dimetallenes [(**1**), R' = C₆H₃Me_{2-2,6}, and M = Si³ or (less stable) Ge^{4a}] or (**1**), M = Si, R' = Bu^t,^{4b,4c} Prⁱ,^{4d} or CH₂Bu^t.^{4e}

Syntheses of dimetallenes have been based on either M^{II} (Scheme 1) or M^{IV} precursors; as for the latter, these have involved photolysis of a trisilane,² a cyclotrimetallane (Si^{3,4e} or Ge^{4a}), cyclotetrasilane,^{4d} or 2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene [1,4-dihydro-1,4-(disilaethano)naphthalene],^{4b} or reductive elimination from Si(C₆H₂Me_{3-2,4,6})₂Cl₂,⁵ [SiCl(CH₂Bu^t)₂]₂,^{4c} or

Sn[CH(SiMe₃)₂]₂Cl₂.⁶ Although the synthesis (i in Scheme 1; this involves a cumbersome separation procedure) and characterisation of the bright-yellow germanium analogue (**1a**) of Sn₂R₄ (as well as of the purple lead compound) were described in our 1976 paper,¹ previous attempts to obtain X-ray quality crystals of the digermene (**1a**) have failed. Our success now is, in part, due to the discovery of a superior method of synthesis, ii in Scheme 1, using GeCl₂·dioxane and the new⁷ Grignard reagent MgClR(OEt₂); the corresponding reaction¹ with LiR did not give compound (**1a**).

From Scheme 1 it is clear that the chemical properties of crystalline Ge₂R₄ are those of the monomer GeR₂, with GeR₂ behaving as (a) a Lewis base (vi in Scheme 1); (b) a substrate for valence expansion to yield a tetravalent Ge adduct (vii-x); or (c) a substrate for disproportionation (v). It is also evident that in properties (a)-(c) Ge₂R₄ resembles Sn₂R₄, and that the M-M bond for both these compounds is exceedingly labile.

The structural trends in the dimetallene series M₂R'₄ show that (i) whereas M is trigonally planar for M = C, there is increasing tendency for pyramidity with increasing atomic number of M (*cf.*, Σ in Table 1), as predicted by M.O.

calculations;⁶ and (ii) the % bond shortening of the M-M bond length in the $M_2R'_4$ compared with that in the diamond form of the element M [taken as our standard $M(sp^3)-M(sp^3)$ single bond] decreases in the sequence $C > Si > Ge > Sn$.

Crystal data: $C_{28}H_{76}Ge_2Si_8$, $M = 782.8$, triclinic, $a = 9.612(2)$, $b = 11.982(4)$, $c = 11.983(3)$ Å, $\alpha = 67.62(2)$, $\beta = 70.35(2)$, $\gamma = 65.40(2)^\circ$, $U = 1134$ Å³, space group $P\bar{1}$, $Z = 1$, $D_c = 1.15$ g cm⁻³, $F(000) = 420$, $\lambda(Mo-K\alpha) = 0.71069$ Å, $\mu = 16.2$ cm⁻¹. Data were measured on an Enraf-Nonius CAD-4 diffractometer.

The structure was solved, using 1497 'observed' reflections, by routine heavy atom methods and refined by full-matrix least-squares to a current $R = 0.083$, $R' = 0.087$.[‡]

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References

- 1 D. E. Goldberg, D. H. Harris, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 261; P. J. Davidson, D. H. Harris, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
- 2 M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, and J. Michl, *J. Chem. Soc., Chem. Commun.*, 1983, 1010. [In this paper the compound $Sn\{N(SiMe_3)_2\}_2$ was cited as being an Sn-Sn-bonded dimer; this is an error, the tin(II) amide being a monomer in both crystal and vapour (T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639), but *n.b.*,¹ Sn_2R_4].
- 3 S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, *J. Am. Chem. Soc.*, 1982, **104**, 1150.
- 4 (a) S. Masamune, Y. Hanzawa, and D. J. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 6136; (b) S. Masamune, S. Murakami, and H. Tobita, *Organometallics*, 1983, **2**, 1464; (c) M. Weidenbruch, A. Schäfer, and K. L. Thom, *Z. Naturforsch., Teil B*, 1983, **39**, 1695; (d) H. Watanabe, Y. Kougo, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1984, 66; (e) H. Watanabe, T. Okawa, M. Kato, and Y. Nagai, *ibid.*, 1983, 781.
- 5 P. Boudjuk, B.-H. Han, and K. R. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 4992.
- 6 T. Fjeldberg, A. Haaland, M. F. Lappert, B. E. R. Schilling, R. Seip, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1982, 1407.
- 7 J. Jeffery and M. F. Lappert, unpublished work.
- 8 A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1976, 2369.
- 9 M. F. Lappert, S. J. Miles, P. P. Power, A. J. Carty, and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1977, 458.

[‡] 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.