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$Ga_2I_2[C(SiMe_3)_3]_2$ – an organogallium(II) halide containing a Ga–Ga single bond

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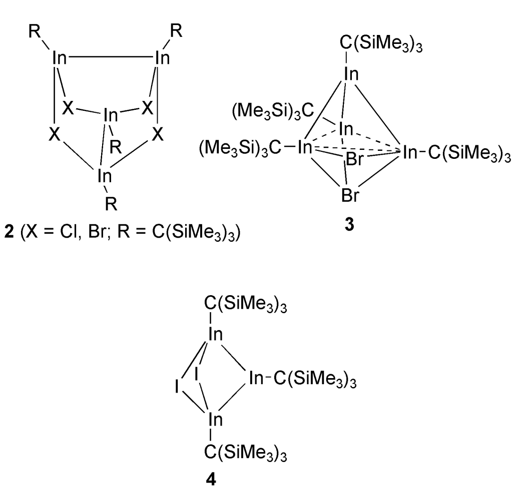
Treatment of the tetrahedral, tetranuclear gallium(I) cluster compound $Ga_4[C(SiMe_3)_3]_4$ (**5**) with a mixture of AlI_3 and ICl afforded in 58% yield the yellowish dinuclear digallium(II) compound $Ga_2I_2[C(SiMe_3)_3]_2$ (**6**), an X-ray crystallographic study of which has shown it to contain a nonplanar (symmetry C_2) $Ga_2I_2C_2$ skeleton and two three-coordinate gallium(II) atoms linked by a single gallium–gallium bond. DFT calculations on **6** and related compounds with alternative structures and the molecular structure of the organogallium(III) iodide, $Ga_2I_4[C(SiMe_3)_3]_2$ (**7**) are also described and discussed.

Introduction

The tetrahedral tetraindium(I) cluster compound $In_4[C(SiMe_3)_3]_4$[1] (**1**) is a facile starting material for the synthesis of organoelement subhalides of indium, which still have some direct In–In interactions and possess the indium atoms in unusual oxidation states.[2,3] Hexachloroethane or a mixture of Br_2 and $AlBr_3$ gave the oxidation of all indium atoms from +I to +II accompanied by the formation of In–In single bonds (**2**, Scheme 1).[2] The overall tetrahedral arrangement of four indium atoms was retained upon the reaction of **1** with 1,2-dibromoethane (**3**, Scheme 1), however, the In–In distances along the edges of the μ_3-bridged face of the cluster became rather long indicating no significant bonding interactions.[2] A chain of three indium atoms connected by In–In single bonds (**4**, Scheme 1) was obtained by the treatment of **1** with I_2/AlI_3.[3] Beside the fascinating structural variety of these organoindium subhalides their real importance may lie in their application in secondary reactions and in the generation of products containing indium atoms in unusual oxidation states by salt elimination. Up to now, a similar reactivity with the corresponding tetragallium cluster $Ga_4[C(SiMe_3)_3]_4$ **5** has not been observed,[4] and only inseparable mixtures of unknown products were formed when we treated **5** with halogens or halogen donors under conditions similar to those applied for the synthesis of compounds **2** to **4**. Here we report on the first successful experiment for the synthesis of an organogallium subhalide by the oxidation of **5**.



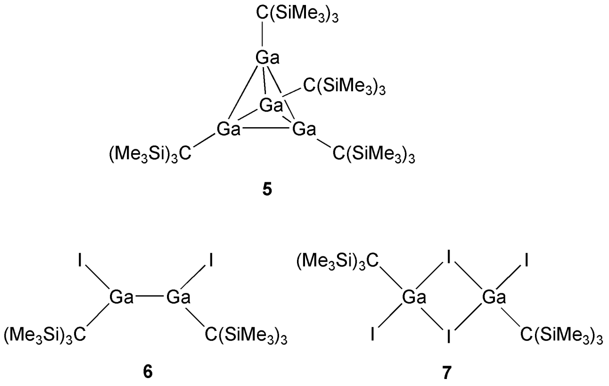
2 (X = Cl, Br; R = $C(SiMe_3)_3$)   **3**   **4**

Scheme 1

Results and discussion

Experimental work

Treatment of the tetragallium(I) compound $Ga_4[C(SiMe_3)_3]_4$ **1** with elemental iodine in a molar ratio of 1 to 2 in boiling *n*-hexane resulted in the formation of a mixture of compounds, from which after repeated recrystallization from toluene two products (**6** and **7**) were isolated in a pure form in small yields below 20%. In particular the work-up procedure proved to be quite difficult, and in some cases no pure product was isolated at all. Both compounds were characterized by crystal structure determinations (see below) and identified as $Ga_2I_2[C(SiMe_3)_3]_2$ **6** and $[I_2Ga–C(SiMe_3)_3]_2$ **7** (Scheme 2). **6** is the product of an oxidation of the gallium atoms from an oxidation state of +1 of **5** to +2 and possesses a Ga–Ga single bond, while the complete oxidation to +3 occurred with the formation of **7**. With respect to the application of compound **6** for secondary reactions its synthesis according to that procedure clearly is insufficient. In a series of experiments with different halogen donors we found that iodine monochloride in the presence of aluminum triiodide is suitable as an oxidant for the reproducible generation of the digallium derivative **6** in reasonable yields above 50%. A gray amorphous solid of unknown composition precipitated as a by-product. The reaction mechanism leading to the formation of **6** is unclear. AlI_3 may be required for the polarization of the interhalogen compound to enhance the selectivity of its attack on the cluster. That point has been discussed before in conjunction with the synthesis of the organoindium subhalides **2** to **4**.[2,3] Furthermore, the aluminum compound may act as an iodine transfer reagent, because by elemental



5   **6**   **7**

Scheme 2

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analysis chlorine has been detected in the product in trace amounts only.

The molecular structure of **6** is depicted in Fig. 1. The molecules are located on twofold crystallographic rotation axes which are perpendicular to the Ga–Ga single bonds. Each gallium atom is bonded to an iodine atom, the inner carbon atom of the tris(trimethylsilyl)methyl group and the second gallium. The iodine atoms do not occupy bridging positions between two digallium moieties, instead the dinuclear molecules remain monomeric even in the solid state with coordinatively and electronically unsaturated gallium atoms possessing an electron sextet only. Thus, that compound behaves different to the corresponding dialkyldiindium dihalides (**2**), which were discussed above and gave dimeric tetranuclear products *via* bridging halogen atoms possessing In_4X_4 cages (X = Cl, Br) and coordination numbers of four at the indium atoms. The formation of similar cages was also observed for the gallium compounds $Ga_2X_2[Si(SiMe_3)_3]_2$ (X = Cl, Br) and $Ga_2Cl_2[Si(CMe_3)_3]_2$,[5] which were synthesized on other routes not starting with the corresponding cluster derivatives. Dinuclear monomers were obtained by adduct formation with halide anions in the compounds $[R_2Ga_2X_4]^{2-}$ [R = $Si(SiMe_3)_3$, X = Br or I].[6] Two further monomeric digallium compounds similar to **6** containing three-coordinate gallium atoms are known with very bulky aryl groups [$C_6H_2(CMe_3)_3$ or $C_6H_3(C_6H_3iPr_2)_2$] attached to gallium.[7] As a remarkable difference to **6** they have planar molecular centers with the inner atoms $Ga_2C_2Cl_2$ lying in the molecular plane. Obviously, the effective steric shielding by the very bulky substituents causes the stabilization of these unusual molecules. As expected, the Ga–Ga distance in **6** (240.1 pm) is much shortened compared to the starting Ga_4 cluster with a delocalized bonding situation (268 pm[4]). It is also shorter than in tetraalkyl or tetraaryl digallium derivatives (>250 pm)[8] or in the tetranuclear halides cited above (250 pm on average). Compounds of the type $Ga_2I_4{\cdot}2L$[9] (L = donor ligands) have Ga–Ga bond lengths of 240 to 250 pm. The short Ga–Ga bond in **6** compared to those of other organoelement derivatives may be caused by the lower coordination numbers of the gallium atoms in **6** and the presence of the sterically less demanding iodine atoms. The Ga–I distance (258.7 pm) is in the characteristic range of terminal Ga–I bonds with tetracoordinated gallium atoms in an oxidation state of +2;[9] a Ga–I distance of 255 pm was detected in the compound I–Ga(Aryl)$_2$ [Aryl = $C_6H_3(C_6H_5)_2$][10] with an unsaturated, tricoordinated gallium atom. The Ga–I bonds of **6** stand almost ideally perpendicular to the Ga–Ga bond with Ga–Ga–I angles of 91.5°. Furthermore, they are almost perpendicular to one another with a torsion angle across the Ga–Ga bond (I–Ga–Ga–I) of 93.3°. That particular conformation may be favored by steric and electronic repulsion and by some contributions of hyperconjugative interaction which may result from the transfer of electron density from the Ga–I bond into the empty p-orbitals of the neighboring gallium atom (see below). Such an interaction across an element–element single bond has been verified before with the anion $[R_2Al(Br){-}AlR_2]^-$ [R = $CH(SiMe_3)_2$], in which the Al–Br bond is parallel to the empty p-orbital of the neighboring, coordinatively unsaturated aluminum atom.[11] In that case, the hyperconjugation strongly weakens the Al–Br bond and causes a very long Al–Br distance. Owing to the particular conformation of **6** the bulky substituents come into close contact. Large Ga–Ga–C angles (146.6°) result in order to minimize the steric repulsion.

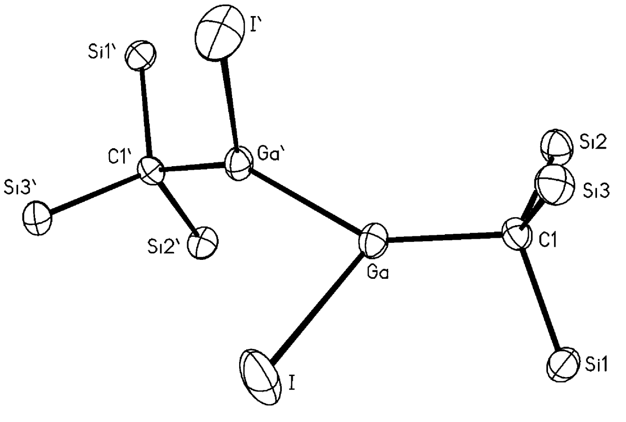

Fig. 1 Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (°): Ga–Ga′ 2.401(1), Ga–I 2.5867(8), Ga–C(1) 1.962(5); C(1)–Ga–Ga′ 146.6(2), C(1)–Ga–I 121.0(2), I–Ga–Ga′ 91.45(3); Ga′ generated by $-x, y, -z + 1/2$.

The gallium(III) compound $I_2Ga{-}C(SiMe_3)_3$ **7** was isolated in small quantities only by the reaction of **5** with elemental iodine. Some data of its characterization are given in the Experimental. Crystal structure determination revealed a dimeric formula unit with a central Ga_2I_2 heterocycle located on a crystallographic inversion center and one iodine atom and one alkyl group terminally attached to each gallium atom (Fig. 2). As expected, differing Ga–I distances (253.8 and 275.8 pm) were observed, the longer ones belong to the bridging groups. Similar observations were reported many times before for related organogallium dihalides [*e.g.* $(Cp^*GaI_2)_2$].[12]

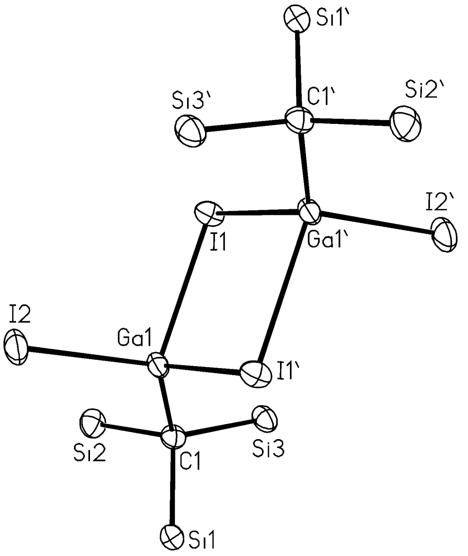

Fig. 2 Molecular structure of **7**. The thermal ellipsoids are drawn at the 40% probability level. Only the major occupied positions of the disordered molecule are shown. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (°) (figures of the disordered molecule with the smaller occupation factors in square brackets): Ga(1)–I(1) 2.7578(8) [2.736(2)], Ga(1)–I(1)′ 2.7163(8) [2.752(2)], Ga(1)–I(2) 2.5380(9) [2.520(2)], Ga(1)–C(1) 1.979(5) [1.964(5)]; I(1)–Ga(1)–C(1) 118.3(1) [119.9(1)], I(1)′–Ga(1)–C(1) 120.6(1) [119.7(2)], I(2)–Ga(1)–C(1) 119.8(1) [120.0(2)], I(1)–Ga(1)–I(1)′ 87.92(2) [87.65(4)], I(1)–Ga(1)–I(2) 103.07(3) [104.55(6)], I(1)′–Ga(1)–I(2) 101.36(3) [99.00(5)], Ga(1)–I(1)–Ga(1)′ 92.08(2) [92.35(4)]; Ga(1)′ and I(1)′ generated by $1 - x, -y, 1 - z$.

Theoretical calculations

We carried out quantum chemical DFT calculations of **6** and some model compounds in order to find out if the rather acute Ga–Ga–I angle of 91.5° is caused by hyperconjugative interactions across the Ga–Ga bond. Table 1 gives the most important results of the calculations.

We first optimized the geometries of the dihalogen parent molecules $Ga_2X_2H_2$ (X = F–I) with enforced planarity of the *trans* structure (C_s symmetry) in order to estimate the strength of the X⟶Ga π donation. The NBO analysis of the planar species shows that the donation of the lone-pair π orbitals of X into the empty gallium p(π) AO increases from 0.049 e (X = F) to 0.115 e (X = I) (Table 1). The increase of the π donor strength of the halogens F < Cl < Br < I has been found before.[13] The

Table 1 Calculated bond lengths *r* (Å), bond angles *α* (°) and torsion angles *τ* (°) of $Ga_2X_2R_2$ (X = halogen; X = H, C(SiMe$_3$)$_3$) molecules. Population of the p(π) AO at Ga and relative energies Δ*E* (kcal mol^{-1}) of the planar and perpendicular forms of the compounds

Molecule	Symmetry	*i*[a]	*r* (Ga–Ga)	*r* (Ga–X)	*r* (Ga–R)	*α* (X–Ga–Ga)	*α* (R–Ga–Ga)	*τ* (X–Ga–Ga–X)	Pop. p(π) Ga	Δ*E*
$Ga_2H_2F_2$ planar	C_{2h}	1 (23 i cm^{-1})	2.547	1.805	1.574	111.6	135.1	180.0	0.049	0.0
$Ga_2H_2F_2$ perp.	C_2	0	2.541	1.805	1.575	111.0	135.7	−118.4		−0.2
$Ga_2H_2Cl_2$ planar	C_{2h}	1 (19 i cm^{-1})	2.548	2.220	1.573	113.8	132.8	180.0	0.082	0.0
$Ga_2H_2Cl_2$ perp.	C_2	0	2.536	2.221	1.574	112.9	133.7	−111.1		−0.4
$Ga_2H_2Br_2$ planar	C_{2h}	1 (14 i cm^{-1})	2.550	2.356	1.575	114.6	131.5	180.0	0.098	0.0
$Ga_2H_2Br_2$ perp.	C_2	0	2.536	2.357	1.576	113.4	132.7	−109.3		−0.5
$Ga_2H_2I_2$ planar	C_{2h}	1 (13 i cm^{-1})	2.552	2.563	1.576	115.3	130.6	180.0	0.115	0.0
$Ga_2H_2I_2$ perp.	C_2	0	2.534	2.565	1.577	113.6	132.2	−107.9		−0.6
$Ga_2H_2I_2$ planar (constraint angle I–Ga–G*a* = 91.5°)	C_{2h}	–	2.525	2.640	1.568	91.5	146.6	180.0	0.122	10.9
$Ga_2H_2I_2$ perp. (constraint angle I–Ga–G*a* = 91.5°)	C_2	–	2.477	2.617	1.569	91.5	148.0	−97.8		3.9
Ga_2I_4 planar	D_{2h}	1 (6 i cm^{-1})	2.557	2.535	–	121.2	–	180.0	0.232	0.0
Ga_2I_4 perp.	D_{2d}	0	2.539	2.538	–	121.0	–	90.0	0.230	−0.9
$Ga_2I_2[C(SiMe_3)_3]_2$ planar [(**6**)]	C_{2h}	1 (17 i cm^{-1})	2.703	2.643	2.070	108.5	140.0	180.0	0.149	0.0
$Ga_2I_2[C(SiMe_3)_3]_2$ perp. [(**6**)]	C_2	0	2.546	2.646	2.039	98.5	140.3	−93.7		−13.3
$Ga_2I_2[C(SiMe_3)_3]_2$ perp. [(**6**)] (constraint angle I–Ga–G*a* = 91.5°)	C_2	–	2.530	2.672	2.033	91.5	146.2	−92.0		−12.5

[a] Number of imaginary frequencies.

geometry optimization of $Ga_2X_2H_2$ without symmetry constraints led to equilibrium structures with C_2 symmetry where the GaHX groups are orthogonal to each other. Table 1 shows that the energy differences between the C_s structures and the C_2 symmetric energy minima are very small, *i.e.* between 0.2 kcal mol^{-1} (X = F) and 0.6 kcal mol^{-1} (X = I). The small energy preference may be attributed to weak hyperconjugative interactions in $Ga_2X_2H_2$ which increases from X = F to I.[14] This interpretation concurs with the shortening of the Ga–Ga bond length in the orthogonal equilibrium structures which exhibit the trend F < Cl < Br < I (Table 1). However, the bond shortening and the slightly lower energy of the C_2 structures may also be explained with the steric repulsion between the vicinal hydrogen and halogen atoms of the two GaHX groups which becomes reduced in the orthogonal structures. Note that the bond angle X–Ga–Ga in the planar and orthogonal geometries is always much smaller than the H–Ga–Ga angle. This can be explained with Bent's rule which states that atomic s character concentrates in orbitals directed towards electropositive substituents.[17] The Ga–X should therefore have a higher % p character at gallium which leads to more acute bond angles. Table 1 shows that the bond angle X–Ga–Ga of planar and orthogonal $Ga_2X_2H_2$ increases when the halogens are less electronegative which is in agreement with Bent's rule. We want to point out that, in the perpendicular structures, the X–Ga–Ga bond angle is only slightly smaller and the Ga–Ga bond is a bit shorter than in the planar form. Thus, the study of the parent systems $Ga_2X_2H_2$ suggests that the hyperconjugative stabilization in the C_2 equilibrium structures is small if it exists at all.[14]

We also optimized the planar and perpendicular forms of $Ga_2I_2H_2$ with a frozen bond angle I–Ga–Ga = 91.45° which is the experimental value of **6**. Table 1 shows that the energy which is necessary to enforce the acute bond angle in the C_2 form is much less (4.5 kcal mol^{-1}) compared with the C_s structure (10.9 kcal mol^{-1}). This can also be explained with the increase of the Pauli repulsion between the vicinal substituents of the planar form and alternatively with enhanced hyperconjugation in the C_2 form.

The population analysis of $Ga_2X_2H_2$ does not lead to definite information about the extent of hyperconjugation in the perpendicular form because there is no mirror plane in the C_2 structures. Therefore it is not possible to compare *e.g.* the population of the Ga p(π) AO in the planar and orthogonal forms. We calculated the planar (D_{2h}) and perpendicular (D_{2d}) structures of Ga_2I_4 in order to address the question if the Ga–I bond is a potential hyperconjugative donor. Table 1 shows that the D_{2d} equilibrium geometry is 0.9 kcal mol^{-1} lower in energy than the D_{2h} form. The latter form has a shorter Ga–Ga bond (2.539 Å) than the former (2.557 Å) but the I–Ga–Ga bond angles in both forms (121.0 and 121.2°, respectively) are in the range of a normal bond angle of an sp^2-hybridized gallium atom. The most important result comes from the population analysis. Table 1 shows that the gallium atoms of the planar structure of Ga_2I_4 have a p(π) population of 0.232 e. The perpendicular form has nearly the same p(π) population at Ga (0.230 e) which means that the p(π) AO does not receive additional charge *via* hyperconjugative donation. This is yet another indication that the hyperconjugation of the Ga–I bond is negligibly weak.

Finally we calculated the real molecule $Ga_2I_2[C(SiMe_3)_3]_2$ (**6**) with enforced planar arrangement of the $Ga_2I_2C_2$ core atoms and with full geometry optimization. Table 1 shows that the planar form of **6** has a rather long Ga–Ga bond (2.703 Å) and that the p(π) population at Ga (0.149 e) is higher than in planar $Ga_2I_2H_2$ (0.115 e) which comes from the hyperconjugation of the C–Si bonds in **6**. Note that the I–Ga–Ga bond angle in planar **6** is still smaller (108.5°) than in planar $Ga_2I_2H_2$ (115.3°) which can be explained with the steric repulsion of the large C(SiMe$_3$)$_3$ groups. The perpendicular equilibrium structure of **6** has a significantly shorter Ga–Ga bond (2.530 Å) and a clearly more acute I–Ga–Ga bond angle (98.5°) than the planar form.

The driving force for these changes in geometry may partly come from hyperconjugative interaction in the energy minimum structure.[14] The results which have been obtained from the calculation of the model compounds suggest, however, that the steric repulsion of the $C(SiMe_3)_3$ groups and the hybridization in the Ga–I bond are the major driving forces for the acute I–Ga–Ga bond angles of **6**. This statement is made with some caution because there are significant differences between the calculated and experimental bond lengths and bond angles. The theoretical Ga–Ga, Ga–I and Ga–C bond lengths are 0.07–0.13 Å larger than the experimental values and the calculated I–Ga–Ga angle is 7° bigger than experimentally found. On the other hand the calculated C–Ga–Ga bond angle and the torsion angle across the Ga–Ga bond is in excellent agreement with experiment.

Experimental

All procedures were carried out under purified argon. *n*-Hexane was dried over $LiAlH_4$, pentafluorobenzene over molecular sieves. $Ga_4[C(SiMe_3)_3]_4$ (**5**) was obtained according to a literature procedure.[4] Commercially available AlI_3 was sublimed prior to use; ICl was distilled in vacuum for purification.

Synthesis of compound 6

A solution of iodine monochloride (55 mg, 0.339 mmol) in 5 ml of *n*-hexane was slowly added to a solution of 73 mg (0.179 mmol) of AlI_3 in 25 mL of *n*-hexane at room temperature. The mixture was stirred for 45 min. A solution of tetraalkyltetragallane(4), **5** (360 mg, 0.299 mmol), in 60 ml of *n*-hexane was added dropwise. The mixture was heated under reflux in a pre-warmed oil-bath (85 °C) for 1.5 h. The color changed from violet to yellow. After filtration the solvent was removed in vacuum. The yellow residue was dissolved in *n*-hexane. Yellowish crystals of compound **6** precipitated upon cooling to −70 °C for 2 d. Yield: 297 mg (58% based on **5**). Dec. (argon, sealed capillary): 162 °C. Anal. Calcd for $C_{20}H_{54}Si_6Ga_2I_2$ (856.41): C, 28.1; H, 6.4; Ga, 16.3; I, 29.6. Anal. Found: C, 28.4; H, 6.3; Ga, 16.0; I, 28.8; Cl, 0.16%. ^1H NMR (C_6D_6, 300 MHz): $\delta = 0.41$ ($SiMe_3$). ^{13}C NMR (C_6D_6, 125.8 MHz): $\delta = 25.5$ (InC), 5.8 ($SiMe_3$). IR (CsBr plates, paraffin, cm^{-1}): 1303 vw, 1264 s, 1252 s δCH_3; 1161 vw, 1042 vw; 852 vs, 717 m $\rho CH_3(Si)$; 676 m, 658 m $\nu_{as}SiC$; 642 w, 620 vw ν_sSiC. UV/vis (*n*-hexane): λ_{max} (nm) (log ε) = 280 (3.6), 325 (sh, 3.2), 345 (sh, 3.1).

Characterization of compound 7

Dec. (argon, sealed capillary): 174 °C. ^1H NMR (C_6D_6, 200 MHz): $\delta = 0.33$ ($SiMe_3$). ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 5.7$ ($SiMe_3$), InC not detected. IR (CsBr plates, paraffin, cm^{-1}): 1309 vw, 1262 m δCH_3; 854 vs, 722 s $\rho CH_3(Si)$; 674 m, 660 m $\nu_{as}SiC$; 640 vw, 620 vw ν_sSiC.

Crystal structure determinations of 6 and 7

Single crystals of **6** and **7** were obtained on cooling of saturated solutions in pentafluorobenzene to 0 °C. The crystallographic data were collected with a CAD-4 diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97[18] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 2. With the exception of the atoms I1 and C1 the whole molecule of **7** showed a disorder which could clearly be resolved. The atoms of the disordered part of the molecule were refined on split positions with occupation factors of 0.66 and 0.34. The carbon atoms of the disordered methyl groups were refined with isotropic displacement parameters.

CCDC reference numbers 199310 (**6**) and 199311 (**7**).

See http://www.rsc.org/suppdata/dt/b2/b212144c/ for crystallographic data in CIF or other electronic format.

Table 2 Crystal data, data collection parameters, and structure refinement details for **6** and **7**

	6	**7**
Formula	$C_{20}H_{54}Ga_2I_2Si_6$	$C_{10}H_{27}GaI_2Si_3$
Crystal system	monoclinic	orthorhombic
Space group	*C*2/*c* (No. 15)[19]	*P*bca (No. 61)[19]
Z	4	8
a/Å	9.308(1)	13.4567(9)
b/Å	15.405(2)	11.788(1)
c/Å	25.564(3)	24.308(2)
β/°	96.95(1)	90
$V/10^{-30}$ m³	3638.7(7)	3855.9(5)
T/K	193(2)	193(2)
μ/mm^{-1}	3.384	4.797
Unique rflns (R_{int})	3069 (0.0410)	3773 (0.0594)
R_1 (reflns $I > 2\sigma(I)$)	0.0456	0.0441
wR_2 (all data)	0.1163	0.1292

Quantum chemical calculations

The geometries of the molecules have been optimized according to gradient corrected density functional theory (DFT) using Becke's three-parameter hybrid method B3LYP.[20] For all atoms except hydrogen and iodine we used a quasi-relativistic ECPs with valence basis sets (31/31/1).[21] A quasi-relativistic ECP but with a slightly larger valence basis set (31/311/1) was employed for iodine[21] while a (31) valence basis set was used for H.[22] The nature of the stationary points on the PES was investigated by calculation of the Hessian matrices. The calculations have been carried out using GAUSSIAN 98.[23]

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References and notes

1 (*a*) W. Uhl, R. Graupner, M. Layh and U. Schütz, *J. Organomet. Chem.*, 1995, **493**, C1; (*b*) W. Uhl, A. Jantschak, W. Saak, M. Kaupp and R. Wartchow, *Organometallics*, 1998, **17**, 5009.

2 W. Uhl and S. Melle, *Chem. Eur. J.*, 2001, **7**, 4216.

3 W. Uhl, S. Melle, G. Geiseler and K. Harms, *Organometallics*, 2001, **20**, 3355.

4 (*a*) W. Uhl, W. Hiller, M. Layh and W. Schwarz, *Angew. Chem.*, 1992, **104**, 1378; W. Uhl, W. Hiller, M. Layh and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1364 (molecular structure); (*b*) W. Uhl and A. Jantschak, *J. Organomet. Chem.*, 1998, **555**, 263 (synthesis).

5 (*a*) A. Schnepf, E. Weckert, G. Linti and H. Schnöckel, *Angew. Chem.*, 1999, **111**, 3578; A. Schnepf, E. Weckert, G. Linti and H. Schnöckel, *Angew. Chem., Int. Ed.*, 1999, **38**, 3381; (*b*) G. Linti and W. Köstler, *Angew. Chem.*, 1996, **108**, 593; G. Linti and W. Köstler, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 550; (*c*) N. Wiberg, T. Blank, M. Westerhausen, S. Schneiderbauer, H. Schnöckel, I. Krossing and A. Schnepf, *Eur. J. Inorg. Chem.*, 2002, 351.

6 M. Kehrwald, W. Köstler, A. Rodig, G. Linti, T. Blank and N. Wiberg, *Organometallics*, 2001, **20**, 860.

7 (*a*) A. H. Cowley, A. Decken and C. A. Olazábal, *J. Organomet. Chem.*, 1996, **524**, 271; (*b*) N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, *Angew. Chem.*, 2002, **114**, 2966; N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, *Angew. Chem., Int. Ed.*, 2002, **41**, 2842.

8 (*a*) W. Uhl, M. Layh and T. Hildenbrand, *J. Organomet. Chem.*, 1989, **364**, 289; (*b*) X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon and P. P. Power, *Angew. Chem.*, 1993, **105**, 761; X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 717.

9 (*a*) G. Gerlach, W. Hönle and A. Simon, *Z. Anorg. Allg. Chem.*, 1982, **486**, 7; (*b*) B. Beagley, S. M. Godfrey, K. J. Kelly, S. Kungwankunakorn, C. A. McAuliffe and R. G. Pritchard, *Chem.

Commun., 1996, 2179; (*c*) A. Schnepf, C. Doriat, E. Möllhausen and H. Schnöckel, *Chem. Commun.*, 1997, 2111; (*d*) C. U. Doriat, M. Friesen, E. Baum, A. Ecker and H. Schnöckel, *Angew. Chem.*, 1997, **109**, 2057; C. U. Doriat, M. Friesen, E. Baum, A. Ecker and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1969; (*e*) W. Hönle, G. Miller and A. Simon, *J. Solid State Chem.*, 1988, **75**, 147.

10 R. C. Crittendon, B. C. Beck, J. Su, X.-W. Li and G. H. Robinson, *Organometallics*, 1999, **18**, 156.

11 W. Uhl, U. Schütz, S. Pohl and W. Saak, *Z. Naturforsch.*, 1994, **49b**, 637.

12 (*a*) P. Jutzi, B. Neumann, G. Reumann and H. G. Stammler, *Organometallics*, 1998, **17**, 1305; (*b*) M. Wilkinson and I. J. Worrall, *J. Organomet. Chem.*, 1975, **93**, 39.

13 G. Frenking, S. Fau, C. M. Marchand and H. Grützmacher, *J. Am. Chem. Soc.*, 1997, **119**, 6648.

14 In a recent theoretical study of B_2X_4 (X = H, F, Cl, Br, I) it was found that the B–I bond is a slightly stronger hyperconjugative donor than the B–H bond.[15] Each B–I bond stabilizes the orthogonal (D_{2d}) equilibrium structure by 4.5 kcal mol^{-1} while the B–H bond yields a stabilization of only 4.0 kcal mol^{-1}. However, the planar (D_{2h}) form of B_2I_4 is stabilized by p(π) charge donation from the iodine lone-pair orbitals into the formally empty p(π) orbitals of boron. This is the reason why the energy difference between the D_{2d}, and D_{2h} forms of B_2I_4 is less than that of B_2H_4. Thus, the activation barrier for rotation about the B–B bond should not be used as a probe for the strength of hyperconjugative interactions. The same situation was found for the Ga_2X_4 system but the absolute numbers of the strength of hyperconjugation, and p(π) charge donation are much less.[16] Both studies showed also that the bond angles do not correlate with the hyperconjugation.

15 M. Lein, A. Szabó, A. Kovács and G. Frenking, *Faraday Discuss.*, in press.

16 A. Szabó, A. Kovács and G. Frenking, unpublished work.

17 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

18 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

19 *International Tables for Crystallography, Space-Group Symmetry*, vol. A, ed. T. Hahn, Kluwer Academic Publishers, Dordrecht–Boston–London, 1989.

20 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

21 (*a*) A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431; (*b*) W. Küchle, M. Dolg, H. Stoll and H. Preuss, *Mol. Phys.*, 1991, **74**, 1431.

22 (*a*) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98 (Revision A.3), Gaussian, Inc., Pittsburgh, PA, 1998.