Weak interactions induce asymmetry in the crystal structures of triaryl derivatives of group 14 elements

Paul D. Prince, G. Sean McGrady* and Jonathan W. Steed*

Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS. E-mail: jon.steed@kcl.ac.uk

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A search of the CSD shows that 42% of compounds of type Ph_3EX (E = group 14 element, X = halogen) possess more than one molecule in the asymmetric unit ($Z' > 1$). This phenomenon is rationalised in terms of CH···X hydrogen bonding and confirmed by the preparation of Ph_3GeI. A remarkable $Z' = 4$ structure of Ph_3GeCl is shown to arise from site-selective inclusion of Ph_3GeH impurity.

At the last systematic count, 8.3% of the entries in the Cambridge Structural Database (CSD) possessed more than one crystallographically independent molecule, that is more than one molecule in the asymmetric unit, with Z' values of 1/2, 1 and 2 making up 95.3% of all crystal structures.[1–6] The number of molecules in the asymmetric unit is represented by the parameter Z', which is strictly defined as the number of formula units in the unit cell (Z) divided by the number of independent general positions. Attempts to isolate the factors leading to non-crystallographic relationships between two or more molecules (*i.e.*, $Z' > 1$) have been frustrated by the extreme complexity of the problem, and by the difficulty in separating out the various intermolecular packing effects in the solid state. Interestingly, however, high Z' values do occur repeatedly within related series of compounds; notably, the incidence of $Z' > 1$ rises significantly (to *ca.* 40%) for mono-alcohols.[1,3] Similarly, we have recently shown that multiple hydrogen-bonded structures involving 15-crown-5 often display high Z' values, although the reasons for this are complex.[7] We believe that the study of intermolecular interactions in molecular crystals exhibiting $Z' > 1$ is of fundamental interest, since it represents a form of 'frustration' in which it is impossible to accommodate simultaneously the requirements of close packing and the tendency to indulge in stronger directional interactions such as hydrogen bonding. Hence, the degree to which non-crystallographic packing occurs should be a function of the importance of directional interactions in any one case.

One of the pitfalls in analysing high Z' structures is that mistakes in structure determination can artificially raise Z'. For example, simply assigning the uncommon space group $P1$ instead of the very common $P\bar{1}$ immediately doubles Z', and for this reason structures assigned to space group $P1$ without an obvious chemical cause (*e.g.*, resolved chiral material) must be treated with some suspicion.[8,9] Moreover, particularly for systems with very high Z' values, a modulated description is sometimes more appropriate than attempts to solve the structure based on an enlarged unit cell with multiple independent molecules.[10,11] In terms of the understanding of intermolecular forces, however, modulated structures are of equal relevance. Systems that crystallise in common—and, in particular, centrosymmetric—space groups where there is a clear chemical reason for the occurence of a high Z' value are of particular interest. Notable in this respect are compounds of type Ph_3EOH (E = Si, Ge); one example is triphenylsilanol, $Z' = 8$ ($P\bar{1}$), which comprises two motifs of four-membered hydrogen-bonded rings of Ph_3SiOH units linked by the hydroxyl groups. Each motif interacts edge-to-face in a non-crystallographically related fashion to its nearest neighbour.[12] The germanium analogue is isomorphous: clearly the hydroxyl functionality dominates the crystal packing in these materials. There has been much recent interest in crystal packing modes of triaryl derivatives in general (*e.g.*, complexes of triphenylphosphine), which display reproducible edge-to-face (EF) π–π interaction[12,13] motifs termed six-fold phenyl embrace (6PE), enlarged 6PE (E6PE) and four-fold aryl embrace (4AE).[14] Calculated intermolecular interaction energies are −14.0 kcal mol^{-1} per $(PAr_3)_2$ unit for each 6PE and −15.3 kcal mol^{-1} per $(PAr)_6$ unit in the E6PE in $[Cu\{P(C_6H_4\text{-}4\text{-}OCH_3)_3\}_3]ClO_4$, for example.[15,16]

In this study, we have examined compounds with the Ph_3E functionality (E = group 14 element), and have sought to establish the presence or absence of a link between the EF packing mode and Z' in the absence of other strongly interacting groups such as the hydroxyl functionality. In particular, we have chosen to study compounds of type Ph_3EX (X = halogen). Systems of type Ph_3EH crystallise in a remarkable series of polymorphs; we have subjected these to a detailed study, the results of which will be reported elsewhere.

Results

Database survey

A search of the Cambridge Structural Database (CSD),[17,18] Table 1, reveals a total of 24 unique compounds containing a four-coordinate group 14 central atom, a halogen and three aryl substituents. Of these, a total of 10 have $Z' > 1$, a remarkable 42% of the sample. The sample may be divided into four classes on the basis of crystal symmetry and Z' value: (1) trigonal space groups with $Z' = 1/3$ (3 structures); (2) trigonal with $Z' = 1\frac{1}{3}$ (1 structure, CSD code TPSNCL03); (3) monoclinic (P or C) or triclinic with $Z' = 1$ (11 structures); (4) monoclinic P or triclinic, $Z' = 2$ (9 structures).

The trigonal compounds of class 1 pack exclusively in an end-to-end fashion: all comprise systems containing *meta*-substituted aryl groups (*m*-xylyl, *m*-tolyl and *m*-anisole), and are hence less likely to form a 6PE type of interaction.[15] In contrast, both unique molecules in Ph_3SnCl (TPSNCL03, class 2) form a perfect 6PE, with one molecule situated on the

Table 1 CSD search unique hits along with Z' values and space group

CSD refcode	Compound	Z'	Space group
BARNUD	Ph_3SiCl	2	$P2_1/b$
BENQIU	Mes_3PbBr	2	$P\bar{1}$
BRTPSN	Ph_3PbBr	2	$P2_1/c$
CIPXUU	$(o\text{-Tol})_3SiF$	1	$P2_1/c$
FAVYIK	$(C_6Cl_5)SiCl$	1	$P2_1/n$
HAKQOZ	$C_{30}H_{27}S_3SiF$	1	$P2_1/c$
HATVIH	$(o\text{-}C_6H_4OMe)_3SnI$	1	$P2_1/n$
HERQUQ	$(9\text{-Anthr})_3SiF$	1	$P2_1/n$
HIBTAN	$(p\text{-}t\text{-}BuC_6H_4)_3SnCl$	1	$C2/c$
JIPROP	(*p*-Methiophenyl)SnCl	1	$P2_1/c$
LEHGEK	$(o\text{-}Me_2NCH_2C_6H_4)SiF$	1	$C2/c$
NIQZUI	$(m\text{-Tol})_3SnCl$	1/3	$R\bar{3}$
NIRBAR	$(m\text{-Xyl})_3SnCl$	1/3	$R\bar{3}c$
SEHROM	Mes_3SnF	2	$P2_1/n$
TICCAJ	$(m\text{-}C_6H_4OMe)_3SnCl$	1/3	$R\bar{3}$
TPGEBR	Ph_3GeBr	2	$P2_1/c$
TPSNCL	Ph_3SnCl	2	$P2_1/a$
TPSNCL03	Ph_3SnCl	1 1/3	$R\bar{3}$
VAFVUT	$(C_6Cl_5)GeCl$	1	$P\bar{1}$
WEHYUD	$Mes_3SnI{\cdot}CDCl_3$	2	$P\bar{1}$
WEHZAK	$Mes_3SnI{\cdot}PhMe$	2	$P\bar{1}$
WEHZEO	Ph_3SnI	2	$P\bar{1}$
WEHZEO01	Ph_3SnI	1	$P\bar{1}$
WEHZIS	$(p\text{-}C_6H_4OMe)_3SnI$	1	$P2_1/c$

crystallographic $\bar{3}$ axis and the other surrounding it on a general site, as shown in Fig. 1. However, it is not the existence of the 6PE interaction *per se* that leads to the presence of two unique molecules (or fragments), since the pair of molecules involved in the 6PE are related to one another by crystallographic inversion. The non-crystallographic interaction is similar to the 6PE, except that the position of two of the phenyl groups is occupied now by the chloro substituents. The interaction is characterised by two strong aryl CH···Cl interactions, with short H···Cl distances of 3.43 and 3.47 Å.

Moving to classes 3 and 4, it appears again that the existence of a 6PE interaction is not a primary factor in determining class 3 or 4 behaviour. Thus, the two structures belonging to class 3 in space group $C2/c$, specifically $(o\text{-}C_6H_4CH_2NMe_2)_3SiF$ and $(p\text{-}C_6H_4Bu^t)_3SnCl$, each exhibit 6PE structures with $Z'=1$. Similarly, Ph_3SnI (CSD code WEHZEO01), which crystallises in space group $P\bar{1}$, exhibits a 6PE structure with $Z'=1$. Interestingly, however, this complex is polymorphic, forming a second $P\bar{1}$ structure with $Z'=2$ (WEHZEO), which contains two independent molecules, each of which forms 6PE interactions *via* a crystallographic inversion operation. The interaction between the two independent molecules is characterised by a single short *p*-arylCH···I contact, with an H···I distance of 3.356 Å. If the phenyl groups in this structure are replaced by mesityl, the same $Z'=2$ structure is obtained in two different cases with the inclusion of either enclathrated toluene or $CDCl_3$. The *p*-CH moiety close to the iodo substituent is replaced by the methyl group of an adjacent mesityl moiety.

The remaining class 3 structures exhibit a variety of interactions between molecules, none of which can be classified as embraces. In the case of $(C_6Cl_5)_3SiCl$ and $(o\text{-}C_6H_4OMe)_3SnI$, these take the form of offset face-to-face π–π stacking, while a small number of long edge-to-face interactions relate the sterically hindered molecules in $(o,o\text{-}C_6H_3Me_2)_3SiF$ and a bridged cyclophane (CSD code HAKQOZ). The class 4 structures with $Z'=2$ display a strong proclivity towards another type of embrace motif *via* a 2_1 screw axis in which one of the phenyl positions in a 6PE is supplanted by a halogen substituent (a five-fold phenyl embrace, *viz* Ph_3SiCl, Ph_3SnBr, Ph_3SnCl and Ph_3GeBr). The non-crystallographic relationship between unique molecules in these structures, however, involves short *p*-arylCH···X interactions characteristic of weak hydrogen bonds[19,20] (as in WEHZEO), such as Ph_3GeBr, in which H···Br is 3.094 Å and Ph_3SnCl with H···Cl equal to 2.949 Å. Even the sterically bulky mesityl substituents in $(o,o\text{-}C_6H_3Me_2)_3PbBr$ ($Z'=2$, $P\bar{1}$) exhibit a relatively close contact between a CH_3 proton and the bromo substituent, although an offset face-to-face π-stacking interaction may also play a part in this case. The only remaining structure, $(o,o\text{-}C_6H_3Me_2)_3SnF$, adopts a non-crystallographic packing mode related to TPSNCL03 (class 2), except that the bulky mesityl substituents prevent the close pairwise approach of the aryl CH unit and fluoro substituent. The interaction thus resembles an unsymmetrical four-fold phenyl embrace.

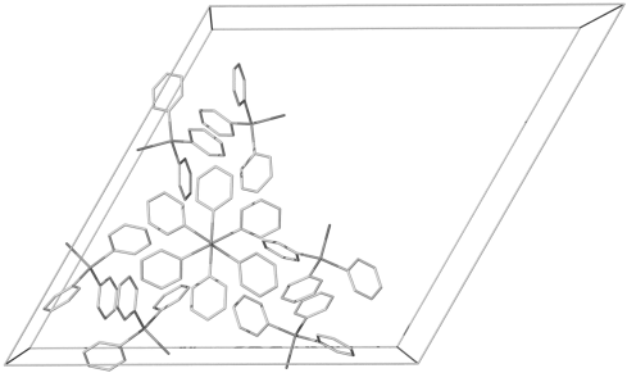

Fig. 1 The structure of crystalline Ph_3SnCl, showing the central six-fold phenyl embrace pair surrounded by three other similar (crystallographically unique) dimers.

Synthesis and structure

The database survey reveals that within this class of compounds, structures with $Z'>1$ are more common for Ph_3EX (X = Cl, Br or I) species, suggesting that the observed CH···X interactions may be important. Accordingly, we decided to examine Ph_3GeF, Ph_3GeCl and Ph_3GeI, the structures of which were absent from the CSD. These compounds are commercially available, however, for reasons of economy they were prepared by reaction of the appropriate halide with either Ph_3GeBr or Ph_3GeH (see Experimental).

The X-ray crystal structure of Ph_3GeI (**1**) proved also to exhibit $Z'=2$ (space group $P\bar{1}$). Both unique molecules form full 6PE structures *via* crystallographic inversion. The interaction between the independent molecules consists of CH···I hydrogen bonds and a 4PE motif combined with a single EF interaction, isomorphous with Ph_3SnI (WEHZEO); Fig. 2. The fluoride, Ph_3GeF (**2**), exhibits a rather different structure, not analogous to those previously discussed, with $Z'=1$. The packing comprises slightly offset 6PE interactions (Fig. 3) between pairs of molecules with Ge···Ge distances of 5.75 Å. Each molecular pair interacts with surrounding molecules *via* two CH···F hydrogen bonds with C···F distances of 3.28 and 3.32 Å.

In our studies, Ph_3GeCl (**3**) was found to crystallise in the common monoclinic space group $P2_1/c$ with a total of *four* independent molecules (*i.e.*, $Z'=4$, $Z=16$). The structure closely resembles the bromide analogue (CSD code TPGEBR), and the unit cell parameters are likewise similar to the fivefold embrace found in Ph_3SiCl (BARNUD). Both TPGEBR and BARNUD exhibit $Z'=2$. In Ph_3GeCl the length of the *b* axis is approximately doubled, resulting in $Z'=4$, meaning that all four molecules of the two crystallographically unrelated 6PE pairs are unique. This, in turn, seems to be linked to the absence of inversion symmetry for one 6PE pair in particular,

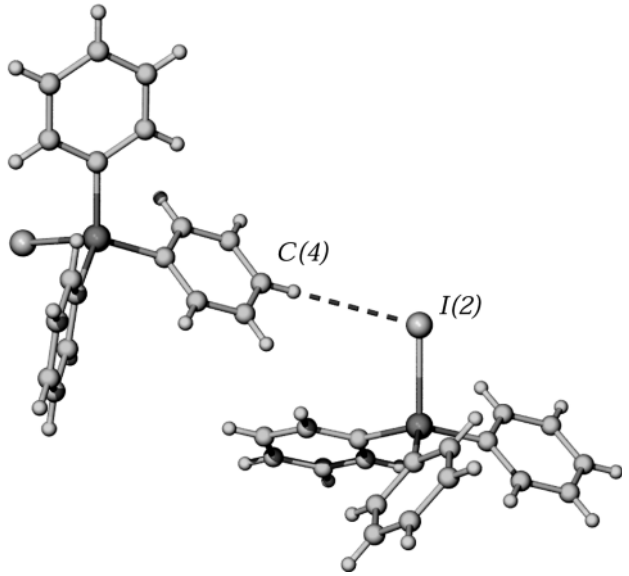

Fig. 2 The two crystallographically independent molecules in Ph_3GeI. The bromide analogue exhibits two similar independent six-fold phenyl embrace motifs with one half of each pair unique ($Z' = 2$). Selected intermolecular distances and angles: C(4)···I(2) 4.051 Å, H(4)···I(2) 3.28 Å, C(4)–H(4)···I(2) 140°, C(10)···I(1) 3.869 Å, H(10)···I(1) 3.33 Å, C(10)–H(10)···I(1) 118°.

centred on Ge(1) and Ge(2). The Ge···Ge distance in this 6PE pair is very short at 5.427 Å (Fig. 4), compared with 5.533 Å in the Ge(3)···Ge(4) pair, 5.565 Å in Ph_3SnCl and even longer distances in the bromide analogue. Most interestingly, it is the Ge(1)···Ge(2) pair that forms the least number of aryl CH···Cl interactions (only one appreciably short one—see figure caption), suggesting that in the absence of CH···Cl bonds the 6PE interaction becomes stronger and slightly less symmetrical (the lowered symmetry arising from slight torsional twists in the aryl rings).

During the course of this study the structure of a commercial sample of Ph_3GeCl was reported by Tiekink *et al.*[21] This independent work produced a structure closely related to that of **3**, except that the crystallographic *b* axis is halved, resulting in the more common $Z' = 2$, structure **4**. We were readily able

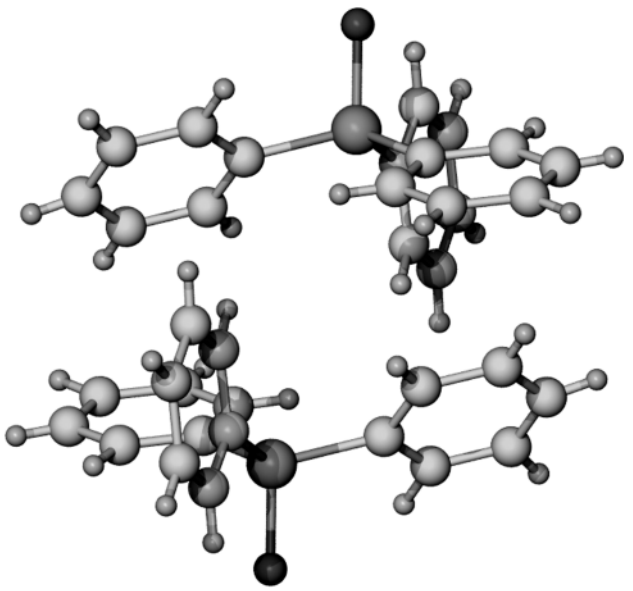

Fig. 3 The offset six-fold phenyl embrace between two crystallographically identical molecules in Ph_3GeF.

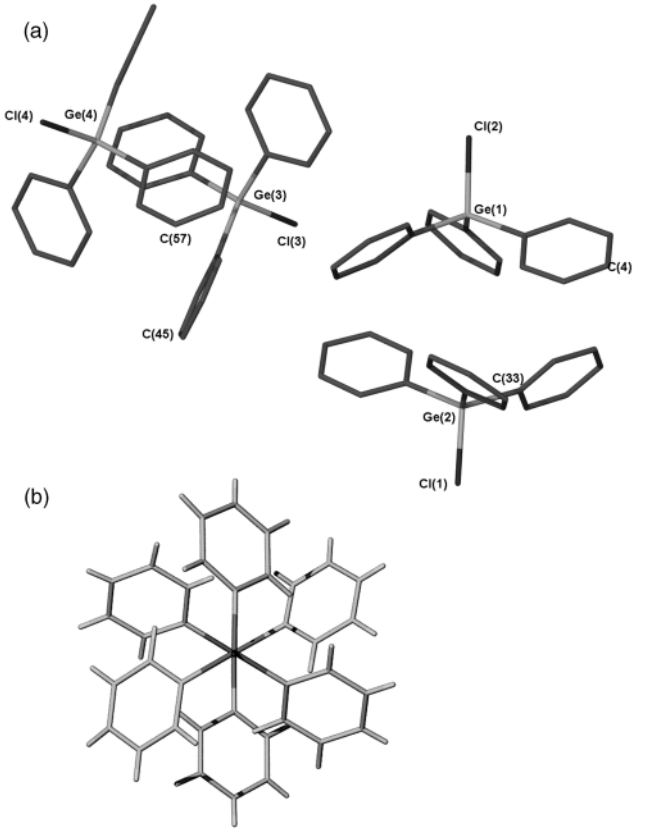

Fig. 4 (*a*) Two independent six-fold embrace pairs in the asymmetric unit of Ph_3GeCl doped with Ph_3GeH ($Z' = 4$). The Ge(1)···Ge(2) pair is highly compressed, resulting in loss of inversion symmetry. (*b*) Plane view of the Ge(1)···Ge(2) six-fold phenyl embrace. Selected intermolecular distances and angles: C(57)···Cl(1) 3.665 Å, H(57)···Cl(1) 3.01 Å, C(57)–H(57)···Cl(1) 130°; C(3)···Cl(3) 3.479 Å, H(3)···Cl(3) 2.91 Å, C(57)–H(57)···Cl(1) 120°; C(33)···Cl(4) 3.730 Å, H(33)···Cl(4) 3.04 Å, C(33)–H(33)···Cl(4) 138°; C(45)···Cl(4) 3.684 Å, H(45)···Cl(4) 3.07 Å, C(45)–H(45)···Cl(4) 127°.

to reproduce this structure from a variety of solvents (toluene, chloroform, dichloromethane) using a sample of Ph_3GeCl purchased from Aldrich. However, numerous independent syntheses and crystallisations of Ph_3GeCl prepared from Ph_3GeH reliably gave the $Z' = 4$ structure, compound **3**. We considered the possibility that the *b* axis in compound **3** was erroneously doubled, resulting in absent data for $k \neq 2n$ on *hkl*. The data was examined using the program Layer;[22] however, data for both even and odd *k* values were present and strong, demonstrating that the doubled unit cell is indeed the correct one.

A reduction in temperature can cause phase transitions to lower symmetry structures.[7,23] Accordingly, a crystal of **4** ($Z' = 2$) was cooled on the diffractometer to 120 K (the temperature of our study of the structure of **3**). No doubling in unit cell volume was observed, although the possibility of a kinetically slow phase change cannot be ruled out. An alternative explanation for the occurrence of the two structures is the inclusion on crystallisation of small amounts of Ph_3GeH into crystalline **3** as a result of the synthetic route adopted. ^1H NMR analysis of the crystalline $Z' = 4$ structure did indeed reveal the presence of significant amounts of hydride, while close examination of the anisotropic displacement parameters for the four independent chloro substituents shows them to be slightly larger than might be expected at 120 K, particularly in the case of Cl(3) and Cl(4). Moreover, the crystallographically determined Ge–Cl distances in **3**, which range from 2.1377(16) to 2.1734(14) Å, are markedly shorter than those obtained from the commercial sample [2.184(2)–2.191(2) Å[21]].

The shortest distance is to Cl(3), which also exhibits the largest anisotropic displacement parameters. It is likely, therefore, that Ph_3GeH acts as a crystal-growth modifier and is actually included upon crystallisation in small quantities (up to *ca.* 25% from analysis of the chloride ellipsoids), resulting in an interesting variation of the $Z' = 2$ structure; a phenomenon reminiscent of the now discredited "bond stretch isomerism".[24] This is further confirmed by the depressed melting point of the sample at 105–108 °C (*cf.* 114–115 °C for the commercial sample). It is remarkable, however, that one 6PE pair within the asymmetric unit is more susceptible to replacement by triphenyl germane than the other, suggesting the importance of CH···ClGe and CH···HGe interactions in controlling the supramolecular architecture during crystal growth.

Conclusions

Two common types of intermolecular interactions are found in compounds of type Ph_3EX, namely CH···X hydrogen bonding and EF interactions. The π–π interactions are generally compatible with crystallographic symmetry, whereas the presence of significant CH···X bonding may be a factor leading to an increased Z' value, particularly in cases where it is necessary to simultaneously satisfy the EF and CH···X bonding requirements. The structure of **3** shows that small quantities of impurities, either present in the mother liquor or doped within the crystal, may have a significant effect on the Z' value. This observation has wider implications for the occurrence of polymorphism in general.

Experimental

Instrumental

Mass spectra were recorded at King's College London on a Jeol AX505W spectrometer in EI mode in a thioglycerol matrix. NMR spectra were recorded on a Bruker ARX-360 spectrometer operating at 360.1 MHz. IR spectra were recorded in the form of nujol mulls on a PE Paragon 100 FTIR spectrometer. Microanalyses were performed at The University of North London.

Preparations

Ph_3GeI (1). Sodium iodide (1.56 g, 10.4 mmol) was added to acetone (20 cm^3) with stirring according to the published procedure.[25] Triphenylgermanium bromide (0.9 g, 2.3 mmol) was dissolved in acetone (30 cm^3), added to the sodium iodide acetone mixture and refluxed overnight. Cold hexane (0 °C, 100 cm^3) was then added and the mixture was filtered to remove excess NaI and NaBr. The solvent was removed by evaporation to give the product as a yellow white powder. The product was recrystallised from diethyl ether. Yield 0.60 g, 1.4 mmol, 61%. ^{1}H NMR ($CDCl_3$, δ) 7.62–7.59 (m, 2H), 7.44–7.41 (m, 3H). M.p. 154–156 °C (lit. mp 157 °C[26]). Anal calcd: C, 50.18; H, 3.51%. Found: C, 50.25; H, 3.58%.

Ph_3GeF (2). Triphenylgermanium bromide (0.92 g, 2.6 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and added dropwise to a stirred solution of $(NMe_4)F$ (0.3 g, 3.0 mmol) in CH_2Cl_2 (15 cm^3), resulting in the immediate formation of a white precipitate. The mixture was refluxed for 2 h after which time distilled water (30 cm^3) was added. The organic layer was separated and the aqueous portion was washed with 3×20 cm^3 portions of CH_2Cl_2. The organic portions were combined and the solvent removed under vacuum. The final product was obtained from recrystallisation from petroleum spirit (bp 60–80 °C). Yield 0.77 g, 2.4 mmol, 92%. ^{19}F NMR ($CDCl_3$, δ) −202.2. ^{1}H NMR ($CDCl_3$, δ) 7.28–7.38 (m, 9H), 7.51–7.55 (m, 6H). M.p. 77–78 °C (lit. mp 76.6 °C[26]). Anal. calcd: C, 66.94; H 4.68%. Found: C 67.00; H, 4.81%.

Ph_3GeCl (3). Triphenylgermane (0.075 g, 0.2 mmol) was refluxed in $CHCl_3$ (25 cm^3) for 90 h. The resulting crystalline product (0.076 g) was found to be a mixture of Ph_3GeCl (45% conversion, from ^{1}H NMR) and Ph_3GeH. Slow evaporation of a $CHCl_3$ solution of this product gave colourless crystals of predominantly the chloride although contaminated with *ca.* 20% of the hydride. ^{1}H NMR ($CDCl_3$, δ): 5.71 (s, 1H), 7.3–7.7 (m, 27H). IR: ν(Ge–H) 2034 cm^{-1}. MS (EI): m/z (relative intensity/%): 340 (1), 338 (1), 336 (0.7), 305 (14), 303 (11), 228 (100). M.p. 105–108 °C (lit. mp 114–115 °C[27]).

Crystallography

Crystals were mounted using a fast setting epoxy resin on the end of a glass fibre and cooled on the diffractometer. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using ϕ rotations with 2° frames and a detector-to-crystal distance of 30 mm. Integration was carried out by the program DENZO-SMN.[28] Data sets were corrected for Lorentz and polarisation effects and for the effects of absorption using the program Scalepack.[28] Structures were solved using the direct methods option of SHELXS-97[29a] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97)[29b] with the aid of XSeed.[30] All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealised positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. All calculations were carried out either on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer.

$GeIPh_3$ (1). $C_{18}H_{15}GeI$, M 430.79 g mol^{-1}, $P\bar{1}$, $a = 9.5925(4)$, $b = 9.6743(3)$, $c = 18.3085(8)$ Å, $\alpha = 83.959(3)°$, $\beta = 78.664(2)°$, $\gamma = 77.060(2)°$, $U = 1620.26(11)$ Å^3, $Z = 4$, 5696 unique data ($2\theta \leqslant 50°$), 361 parameters, R_1 [$F^2 > 2\sigma(F^2)$] = 0.033, wR_2 (all data) = 0.082.

$GeFPh_3$ (2). $C_{18}H_{15}GeF$, M 322.89 g mol^{-1}, $P2_1/c$, $a = 10.3444(8)$, $b = 11.7723(7)$, $c = 13.0869(11)$ Å, $\beta = 110.328(4)°$, $U = 1494.43(19)$ Å^3, $Z = 4$, 2621 unique data ($2\theta \leqslant 50°$), 242 parameters, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0619, wR_2 (all data) = 0.1714.

$GeClPh_3$ (3). $C_{18}H_{15}ClGe$, M 339.34 g mol^{-1}, $P2_1/c$, $a = 18.637(4)$, $b = 18.317(4)$, $c = 18.129(4)$ Å, $\beta = 98.38(3)°$, $U = 6122(2)$ Å^3, $Z = 16$, 12 004 unique data ($2\theta \leqslant 52°$), 722 parameters, R_1 [$F^2 > 2\sigma(F^2)$] = 0.055, wR_2 (all data) = 0.131.

CCDC reference numbers 179372–179374. See http://www.rsc.org/suppdata/nj/b1/b105457k/ for crystallographic data in CIF or other electronic format.

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References

1 C. P. Brock and L. L. Duncan, *Chem. Mater*., 1994, **6**, 1307.
2 C. P. Brock and J. D. Dunitz, *Chem. Mater*., 1994, **6**, 1118.
3 C. P. Brock, *J. Res. Natl. Inst. Stand. Technol*., 1996, **101**, 321.
4 A. J. C. Wilson, *Acta Crystallogr., Sect. A*, 1993, **49**, 795.
5 N. Padmaja, S. Ramakumar and M. A. Viswamitra, *Acta Crystallogr., Sect. A*, 1990, **46**, 730.
6 T. Steiner, *Acta Crystallogr., Sect. B*, 2000, **56**, 673.
7 J. W. Steed, E. Sakellariou, P. C. Junk and M. Smith, *Chem. Eur. J*., 2000, **7**, 1240.
8 H. Jacobsen, H. W. Schmalle, A. Messmer and H. Berke, *Inorg. Chim. Acta*, 2000, **306**, 153.
9 R. E. Marsh, *Acta Crystallogr., Sect. B*, 1999, **55**, 931.
10 M. Meyer, W. A. Paciorek, K. J. Schenk, G. Chapuis and W. Depmeier, *Acta Crystallogr., Sect. B*, 1994, **50**, 333.
11 W. Paciorek, V. B. Gaillard, K. Schenk and G. Chapuis, *Acta Crystallogr., Sect. A*, 1996, **52**, 349.
12 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc*., 1990, **112**, 5525.
13 H. Takahashi, S. Tsuboyama, Y. Umezawa, K. Honda and M. Nishiro, *Tetrahedron*, 2000, **56**, 6185.
14 C. Horn, M. Scudder and I. Dance, *Cryst. Eng. Comm*., 2001, 2.
15 M. Scudder and I. Dance, *J. Chem. Soc., Dalton Trans*., 2000, 2909.
16 M. Scudder and I. Dance, *Cryst. Eng. Comm*., 2001, 12.
17 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
18 Cambridge Structural Database, April 2001 release, 233 218 entries.
19 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press/IUPAC, Oxford, UK, 1999.
20 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, UK, 1997.
21 D. Dakternieks, A. E. K. Lim, B. Zobel and E. R. T. Tiekink, *Main Group Met. Chem*., 2000, **23**, 789.
22 L. J. Barbour, Layer–A program for the Display and Analysis of Crystallographic Reflection Data, University of Missouri, Columbia, MO, USA, 1995.
23 J. D. Dunitz, G. Fillippini and A. Gavezzotti, *Helv. Chim. Acta*, 2000, **83**, 2317.
24 (*a*) V. C. Gibson and M. McPartlin, *J. Chem. Soc., Dalton Trans*., 1992, 947; (*b*) G. Parkin, *Chem. Rev*., 1993, **93**, 887.
25 R. Fuchs and H. Gilman, *J. Org. Chem*., 1958, **23**, 911.
26 C. A. Kraus and L. S. Foster, *J. Am. Chem. Soc*., 1927, **49**, 457.
27 *Aldrich Handbook of Fine Chemicals*, Aldrich Chemical Co., Gillingham, UK, 2000–01, p. 1747
28 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, London, 1996, vol. 276, pp. 307–326.
29 (*a*) G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
30 L. J. Barbour, XSeed, A Program for the Manipulation and Display of Crystallographic Models, University of Missouri, Columbia, MO, USA, 1999.