www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 598 (2000) 276–285

Mesitylpseudohalogermanes $Mes_2Ge(CN)_2$ and Mes_3GeX ($X = CN$, NCS, N_3, NCO and OH; Mes = 2,4,6-trimethylphenyl): syntheses, crystal and molecular structures

Goro Hihara [a,1], Rosemary C. Hynes [a], Anne-Marie Lebuis [a], Monique Rivière-Baudet [b], Ivor Wharf* [a,2], Mario Onyszchuk* [a,3]

[a] *Department of Chemistry, McGill University, Montreal, Québec, H3A 2K6, Canada*
[b] *Laboratoire Hétérochemie Fondamentale et Appliquée, UPRES(A) no 5069 du CNRS, Université Paul Sabatier, F-31062 Toulouse Cédex, France*

Received 22 October 1999; received in revised form 21 November 1999

Abstract

The crystal and molecular structures of the mesitylpseudohalogermanes, $Mes_2Ge(CN)_2$ (Mes = 2,4,6-trimethylphenyl) and Mes_3GeX ($X = CN$, NCS, N_3, NCO, or OH), have been determined by X-ray diffraction methods; the isocyanate and hydroxide crystallise as a 1:1 hydrogen-bonded complex. All are covalent monomers free from pseudohalogen bridging, and all except the cyanides and hydroxide are N-bonded to germanium. Each Ge atom is four-coordinate in a distorted tetrahedral geometry, as evident from (mes)–Ge–(mes) angles between 112 and 120°, which are attributed to the sterically demanding mesityl groups. The greatest distortion is displayed by $Mes_2Ge(CN)_2$, for which the NC–Ge–CN angle of 97.8(3)° and (mes)–Ge–(mes) angle of 119.8(3)° are also consistent with the bulky mesityl groups and the small steric requirements of the cyano groups. The Ge–N–Y angles show a distinctive trend, decreasing from 173.3(5)° for the isothiocyanate (Y = CS), through 153.5(5)° for the isocyanate (Y = CO), to 119.0(7)° for the azide (Y = NN), an effect attributed to differences in electronic structure of the pseudohalo ligands. The geometries of the compounds examined here are compared with those of some other tri- and dimesityl-Group 14 metal derivatives as well as related phenylgermanium compounds. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organogermanium; Pseudohalides; Mesityl; Bulky ligand; Crystal structures; Molecular structures; Syntheses

1. Introduction

In contrast to the wealth of information on organogermanium halides, rather less is known about the corresponding pseudohalides [1–3]. More recently our interest in organogermanium pseudohalides was piqued through a study of the reactions of Mes_3GeNH_2 ($Mes = 2,4,6-(CH_3)_3C_6H_2$) [4], following which we reported the synthesis of several Mes_3GeX (X = NCS, NCO, N_3) [5]. Bulky mesityl groups on Ge shield the germanium atom from attack and thus tend to stabilise small molecules that otherwise are thought to be unstable or exist only as transient species [6–8]. Of equal interest are the effects of bulky mesityl groups on molecular conformations as exemplified by the structures of Mes_3SiH and Mes_3GeH [9]. Moreover when the unhindered phenyl analogs of mesityl compounds also exist, the steric crowding of the *o*-CH_3 groups of the mesityls attached to the central metal atom can cause significant changes in geometry, as was found when comparing the structures of Mes_3SnI and Ph_3SnI [10]. Here we report the structures of Mes_3GeX (X = CN, NCS, N_3, NCO, OH), and $Mes_2Ge(CN)_2$ and compare them with those of related organo-silicon and -germanium compounds.

---

[1] Permanent address: Department of Chemistry, Josai University, Saitama, Japan.

[2] *Corresponding author. Tel.: + 1-514-398-6233; fax: + 1-514-398-3797; wharf@chemistry.mcgill.ca

[3] *Corresponding author. Tel.: + 1-514-398-6233; fax: + 1-514-398-3797.

PII: S0022-328X(99)00725-1

2. Results and discussion

2.1. Syntheses

Although silver thiocyanate easily converts Mes_3GeCl to Mes_3GeNCS in high yield [4], we found that AgCN would not react with Mes_3GeCl or Mes_2GeCl_2 under a variety of conditions. Instead, exchange reactions between Mes_3SiCN and Mes_3GeCl or Mes_2GeCl_2 were required to obtain the corresponding mesitylgermyl cyanides in good yield. The other trimesitylgermyl pseudohalides, i.e. the azide, isocyanate and isothiocyanate, were obtained earlier [5] by the reaction of Mes_3GeCl with NaN_3, KOCN, and KSCN, respectively, in a mixture of 18-crown-6-ether and *n*-hexane at 60°. Recrystallising Mes_3GeCN from THF gave X-ray-quality crystals of the solvate $Mes_3GeCN\cdot(1/2)THF$ but the isocyanate was only obtained as single-crystals from diethyl ether as the 1:1 hydrogen-bonded adduct, $Mes_3GeNCO\cdot Mes_3GeOH$ in spite of using 'dried' ether.

2.2. Single-crystal X-ray diffraction studies

Crystal data are listed in Table 1 while selected structural parameters are summarised in Table 2; the Platon [11] plots (without H-atoms) giving the numbering schemes are shown in Figs. 1–5 for Mes_3GeCN (**A**), Mes_3GeNCS (**B**), Mes_3GeN_3 (**C**), $Mes_3GeNCO\cdot Mes_3GeOH$ (**D**) and $Mes_2Ge(CN)_2$ (**E**), respectively (see Section 5).

2.2.1. Mes_3GeX ($X = CN$, NCS, N_3) and $Mes_3GeNCO\cdot Mes_3GeOH$

The pseudohalides **A**–**C** are clearly monomeric and there is no evidence of intermolecular interactions as the shortest non-bonding contacts are all greater than the sum of the relevant van der Waals radii. Moreover the central Ge atom in each compound is four-coordinate but with a configuration seriously distorted from tetrahedral geometry. It is unlikely that crystal packing requirements are the main cause of the distortions in molecular geometry that are detailed below. The (mes)–Ge–(mes) bond angles lie in the range of 112.4(4)–118.7(4)° all significantly greater than the tetrahedral angle, while as expected the relevant (mes)–Ge–X angles are correspondingly less than tetrahedral, in the range 100.2(2)–104.4(4)°, perhaps aided by the low steric requirements of the N–Ge bond in these compounds. Similar distortions occur in Mes_3GeNH_2 [4] with (mes)–Ge–(mes) angles of 116.6(1), 113.0(1) and 112.0(1)°, and even more so for

Table 1
Crystal data and structure solution details

Compound	$Mes_3GeCN\cdot(1/2)THF$ (**A**)	Mes_3GeNCS (**B**)	Mes_3GeN_3 (**C**)	$Mes_3GeNCO\cdot Mes_3GeOH$ (**D**)	$Mes_2Ge(CN)_2$ (**E**)
Formula	$C_{30}H_{37}N_1O_{0.5}Ge$	$C_{28}H_{33}NSGe$	$C_{27}H_{33}N_3Ge$	$C_{55}H_{67}NO_2Ge_2$	$C_{20}H_{22}N_2Ge$
Formula weight	492.22	488.22	472.17	919.32	362.99
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$Pcan$
Z (Z')	8 (1)	4 (1)	4 (1)	2 (1)	4 (1/2)
Crystal size (mm)	0.33 × 0.33 × 0.08	0.33 × 0.30 × 0.30	0.40 × 0.25 × 0.10	0.40 × 0.15 × 0.13	0.33 × 0.25 × 0.10
a (Å)	40.384(15)	8.3034(20)	13.729(3)	8.2410(7)	9.523(2)
b (Å)	8.643(5)	22.847(5)	11.6125(14)	16.374(2)	11.037(2)
c (Å)	16.442(7)	13.7258(23)	15.714(3)	18.872(2)	17.250(3)
α (°)	90	90	90	97.668(10)	90
β (°)	108.99(3)	99.962(16)	94.856(16)	97.233(8)	90
γ (°)	90	90	90	100.352(9)	90
V (Å^3)	5427(4)	2564.6(9)	2496.3(8)	2453.0(5)	1813.0(6)
μ (mm^{-1})	1.13	1.27	1.23	1.78	1.67
Reflections measured	3619	3615	3016	15712	1347
Unique reflections	3556	3341	2859	7304	1186
R_{int}	0.044	0.011	0.028	0.052	0.026
Significant reflections	1796	2488	1644	5745	734
σ	2.5	2.5	2.5	2.0	2.5
Parameters used	287	290	281	542	105
[a] R_f	0.060	0.047	0.055	0.055	0.037
[b] R_w	0.059	0.050	0.053	0.051	0.040
Transmission range		0.7111 to 0.7535		0.5277 to 0.6458	0.5992 to 0.7523
Goodness-of-fit	1.82	2.11	1.79	2.29	1.79

[a] $R_f = \Sigma[|F_o| - |F_c|]/\Sigma[|F_o|]$.

[b] $R_w = \{\Sigma w[F_o - F_c]^2/\Sigma w F_o^2\}^{1/2}$; $w = [\sigma^2(F) + KF^2]^{-1}$.

Table 2
Selected structural parameters (e.s.d.) for Mes_3GeX (X = CN, NCS, N_3, NCO, and OH) and $Mes_2Ge(CN)_2$

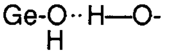
Bond distances (Å)	*Ge–X*	*Ge–Mes*	*Pseudohalide*
(**A**) Mes_3GeCN	1.975(11)	1.962(9); 1.979(8); 1.942(9)	CN, 1.149(15)
(**B**) Mes_3GeNCS	1.888(4)	1.957(5); 1.976(5); 1.961(5)	NC, 1.138(7); CS, 1.634(7)
(**C**) Mes_3GeN_3	1.895(9)	1.942(11); 1.913(10); 1.988(10)	N_1N_2, 1.210(15); N_2N_3, 1.171(16)
(**Da**) [a] Mes_3GeNCO	1.812(4)	1.960(5); 1.962(5); 1.962(5)	NC, 1.125(11); CO, 1.356(12)
(**Db**) [a] Mes_3GeOH	1.805(3)	1.973(5); 1.970(5); 1.974(5)	
(**E**) $Mes_2Ge(CN)_2$	1.944(6)	1.956(6)	CN, 1.121(10)
Bond angles (°)	*(mes)–Ge–(mes)*	*X–Ge–(mes)*	*Ge–(N–Y)*
(**A**) Mes_3GeCN	116.3(4); 115.7(4); 115.5(4)	103.0(4); 102.5(4); 100.4(4)	176.4(10) [b]
(**B**) Mes_3GeNCS	115.4(2); 116.7(2); 117.1(2)	101.79(21); 100.22(20); 101.18(21)	173.3(5) [Y = CS]
(**C**) Mes_3GeN_3	118.7(4); 115.7(4); 112.4(4)	104.4(4); 101.4(4); 100.9(4)	119.0(7) [Y = NN]
(**Da**) [a] Mes_3GeNCO	115.53(19); 115.17(19); 114.31(19) 101.8(2); 104.6(2); 103.1(2)	153.5(5) [Y = CO]	
(**Db**) [a] Mes_3GeOH	115.84(19); 113.44(19); 114.7(2)	105.12(18); 103.71(18);101.90(18)	
(**E**) $Mes_2Ge(CN)_2$	119.8(3); [97.8(3)] [c]	103.7(3); 115.0(3)	173.9(6) [b]

[a] As the $Mes_3GeNCO{\cdot}Mes_3GeOH$ hydrogen-bonded adduct.

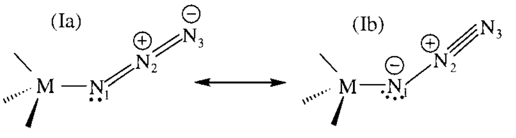
[b] Angle Ge–(C≡N).

[c] Angle (NC)–Ge–(CN).

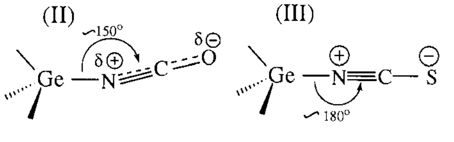
$Mes_3GeNHCOtBu$ [12] with (mes)–Ge–(mes) angles of 106.3(4), 117.0(4) and 117.8(4)°, while the same angles in $Mes_3GeN{=}C{=}NGeMes_3$ are 115.0(1), 114.7(1) and 113.3(1)° for Ge(1) and 115.0(1), 114.7(1) and 113.3(1)° for Ge(2) [13].

In **A**–**C**, Ge–(mes) bond distances vary from 1.913(10) to 1.988(10) Å, similar to those in Mes_3GeNH_2 [4], $Mes_3GeNHCOtBu$ [12] and $Mes_3GeN{=}C{=}NGeMes_3$ [13], while **B** and **C** have Ge–N distances close to that found in $Mes_3GeNHCOtBu$ (1.899(6) Å). Angles formed by the linear pseudohalide groups with Ge (designated as Ge–C–N or Ge–N–Y in Table 2) are about 180° for **A** and **B** but in Mes_3GeN_3 the angle is 119.0(7)°. The more encumbered azide, $GeN_3[N(SiMe_3)_2][N(Mes)(SiMe_3)]_2$, has a Ge–N–N angle of 125.5(4)° [14], but interestingly its Ge–N(1), N(1)–N(2), and N(2)–N(3) bond distances are similar to those in Mes_3GeN_3. Trimesitylgermanium isocyanate (**Da**) and hydroxide (**Db**) are found as a 1:1 hydrogen bonded complex **D** (Fig. 4). Both **Da** and **Db** have bond lengths and angles similar to those of the other pseudohalides (Table 2) but the most distinctive feature is the unexpected hydrogen bonding between the two molecules. The oxygen to oxygen H-bond of 3.036(7) Å appears longer than the value (2.89(8) Å) found in the ostensibly analogous tin system, $Me_3SnNCO{\cdot}Me_3SnOH$, also formed by adventitious hydrolysis of the isocyanate [15]. However, in this adduct, chains of Me_3Sn groups are formed using alternating 1,1-isocyanate and hydroxide bridges, which are then connected by –NCO···H–O– hydrogen bonds. In **D** the weaker H-bond is between terminal isocyanate and hydroxide groups. In comparison, the  $Ge\text{-}\underset{H}{O}\cdots H\text{—}O\text{-}$ hydrogen bonds in Ph_3GeOH [16], average $d(O\cdots O) = 2.63(1)$ Å, are even stronger, showing that the O-atom of Ge–OH is a stronger H-bond acceptor than the end oxygen of a terminal isocyanate group.

The structure of **C** with $d(N_1N_2)$ apparently greater than $d(N_2N_3)$ and 119.0(7)° for the Ge–N_1–N_2 angle, is more like that of an organic azide [17–19] when compared with that of its silicon analog [20]. The bonding of covalent azides, R_3M–N_3, may be discussed in terms of two canonical forms (**Ia**) and (**Ib**), with the contribution of each form dependent on the R_3M moiety. For Mes_3SiN_3 with $d(N_1N_2)$ apparently less than $d(N_2N_3)$ and with angle Si–N_1–N_2 of 125.8(2)°, form **Ia** appears to contribute more than in the case of **C** or organic azides [20]. This is clearly one more example of the tendency of germanium to resemble carbon more than silicon [21]. The noted increase of the Ge–(N–Y) angle in Mes_3GeX as (N–Y)=N–NN is replaced by N–CO and then N–CS or C≡N, suggests that the following canonical forms determine the bond angles:



M = Si or Ge



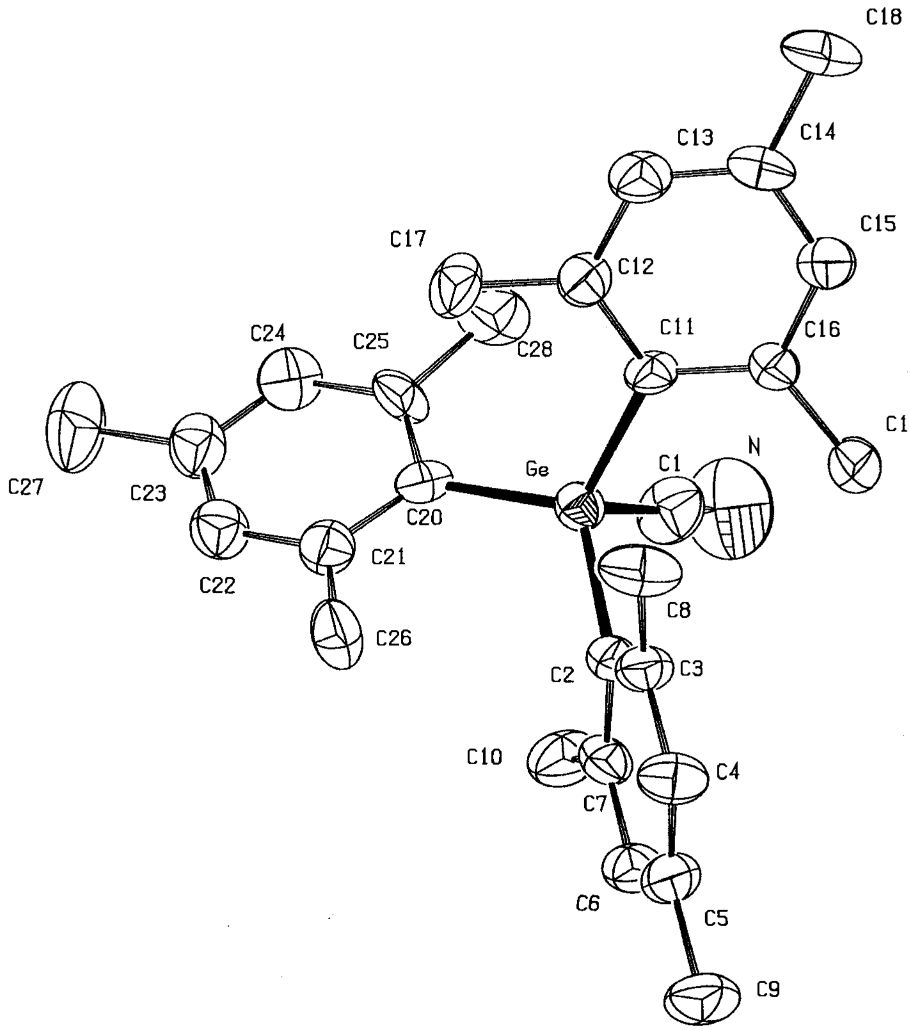
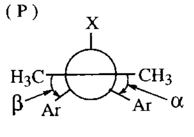


Fig. 1. Platon view of the molecule of **A** showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.

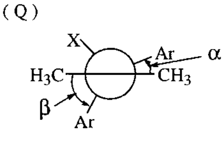
with **II** for **Da** intermediate between **Ia**–**b** for **C** and **III** for **B** which is equivalent to the expected structure of **A**. The similar Ge–NCO angles for **Da** and Ph_3GeNCO [150.7(9)°] [22], and **B** and Ph_3SiNCS (178.8(3)°) [23], would suggest that electronic effects of this type are the structure determinants rather than the steric effects of the distal *o*-CH_3 groups, which do not extend beyond the α-pseudohalide atom bound to M. When considering a given Ar_3MX pair (Ar = Ph or Mes) it was predicted earlier [24] that with M = C and X = H, the steric strain caused by replacing *ortho*-H atoms by methyl groups would result in larger values for *d*(M–C) and Ar–M–Ar angles. The effects of repulsions between *ortho*-methyls on adjacent mesityl groups in Mes_3MX systems may also be monitored by the dihedral angles defined by the plane of one ring and the C_i–M–C_i^* plane involving another ring*, and shown below as α and β in Newman projections **P**, **Q** and **R** [9].

(P)



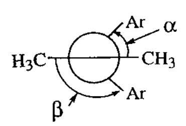
$\alpha = -30°$; $\beta = 30°$

(Q)



$\alpha = \phi - 30°$; $\beta = \phi + 30°$

(R)



$\alpha = 60°$; $\beta = 120°$

Ideally Ar_3MX systems are considered to have trigonal symmetry, with the two most symmetric arrangements having each ring plane perpendicular to the C_i–M–X plane **P** or rotated through 90° as seen in **R**. Both geometries give rise to extreme steric strain, which must be relieved by the rotation (ϕ) of each ring within the range 0–90°, giving the intermediate geometry seen in **Q**. In this case $\phi = (\alpha + 30°)$ or $(\beta - 30°)$. In fact, very few Ar_3MX systems have exact trigonal symmetry, so averaged values of the structural parameters listed above are given in Table 3 for the Mes_3GeX systems **A**–**Db** as well as for several other Mes_3MX (M = Si, Ge) **1**–**5** [9]. Indeed all Mes_3MX deviate so much from

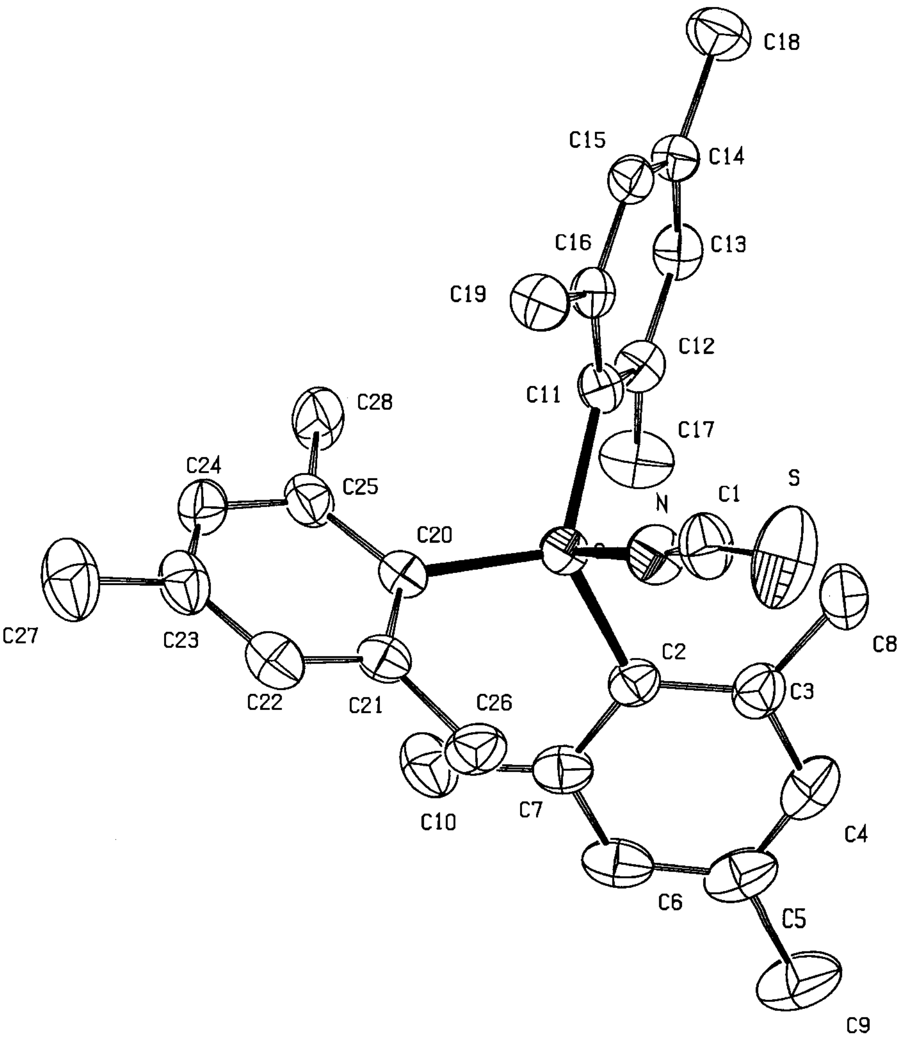


Fig. 2. Platon view of the molecule of **B** showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.

trigonal symmetry that $\bar{\alpha}$ and $\bar{\beta}$ provide two different numbers for the rotation ($\bar{\phi}$). Thus the average value, $\bar{\phi} = 0.5[(\bar{\alpha} + 30°) + (\bar{\beta} - 30°)]$ is listed instead.

The wide ranges of average d(Ge–C) and Ar–Ge–Ar angles found for **A**–**Db** and **2** [1.95–1.98 Å and 113.9–116.4°] are effectively the same as those found for Ph_3GeX (X = Br [26], NCO [22], OH [16]), 1.93–1.95 Å and 118.6–112.6°. However, the comparison of average values of d(Si–C) and Ar–Si–Ar angles for **1** (1.89 Å, 114.0°) and **3** (1.91 Å, 112.9°) with data for Ph_3SiNCS [23] (1.85 Å, 112.4°) and Ph_3SiOH [27] (1.86 Å, 110.5°) shows the trends predicted by Mislow, the changes in angles being particularly significant. Together with these changes should also be observed a concomitant lengthening of the M–X bond and a significant lessening of the Ar–M–X angle and these trends were observed when comparing Mes_3SnI with Ph_3SnI [10]. The same trends in d(Ge–X) (Å) and average Ar–Ge–X angles (°) are also seen for the systems studied here. Thus we may compare Mes_3GeOH [1.805(3); 103.6(2)] with Ph_3GeOH [1.791(8); 107.1(4)] [16] and Mes_3GeNCO [1.812(4); 103.2(2)] with Ph_3GeNCO [1.83(2); 105.7(6)] [22], although for the second pair (X = NCO) only the angle change is significant at the error level of the triphenyl structure.

All compounds in Table 3 have very similar mean rotations ($\bar{\phi}$) ranging from 41.6 to 45.0°, the exceptions being **5** and **6**. For structures **A**–**Db** and **1** and **2** the average dihedral angles ($\bar{\alpha}$) and ($\bar{\beta}$) are all within narrow ranges, (21.0–22.7°) and (62.7–68.5°), respectively while the average deviations from trigonal symmetry given by $[\bar{\alpha} - (\bar{\phi} - 30°)]$ and $[\bar{\beta} - (\bar{\phi} + 30°)]$ are also very similar. Thus to relieve the interactions due to the *ortho*-methyls, the mesityl groups rotate and the molecules distort from trigonal symmetry, on average, by nearly the same amount regardless of the metal M or group X. Compound **3** is similar with less distortion, but **4** and **5** do not fit this picture at all. Thus while ($\bar{\phi}$) values are in the same range as before, the distortion from trigonal symmetry is the reverse of that noted

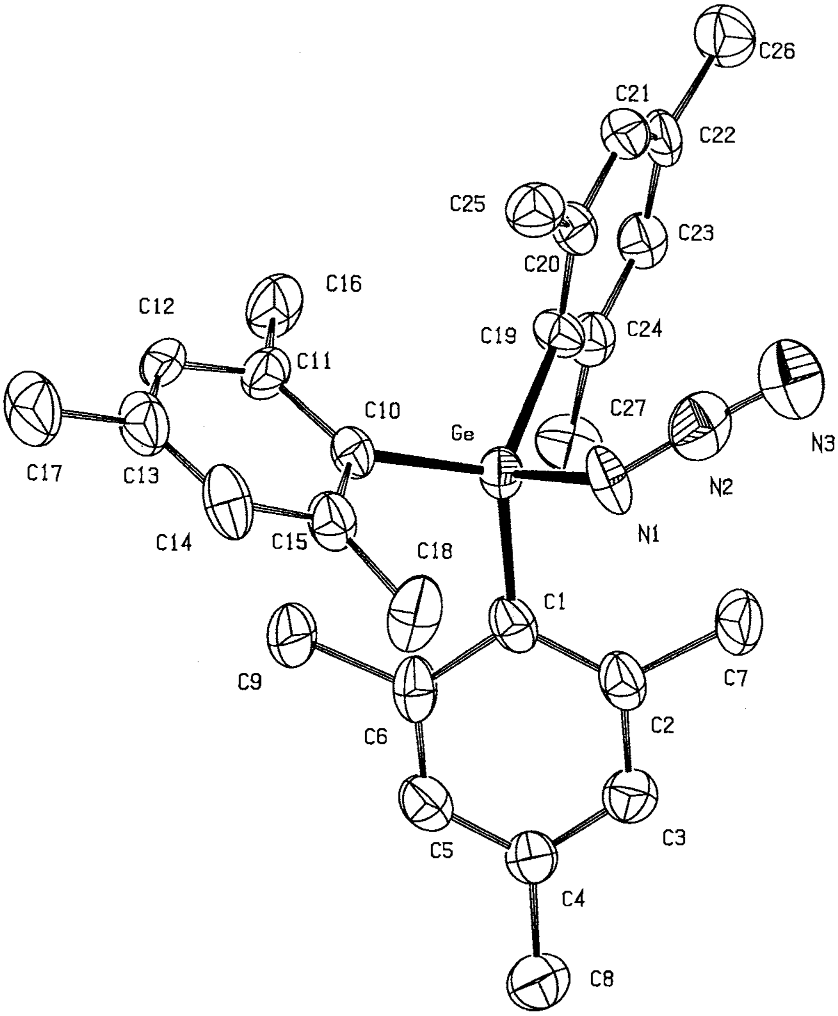
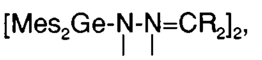


Fig. 3. Platon view of the molecule of **C** showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.

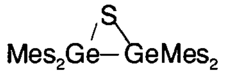
above. Furthermore the steric strain appears to be accommodated by a drastic increase in *d*(M–C) rather than any change in ArMAr angles. This is in contrast to the structure of Mes_3CH (**6**) [25], which is consistent with those of the other Mes_3MX in Table 3.

2.2.2. $Mes_2Ge(CN)_2$

Like the preceding pseudohalides, $Mes_2Ge(CN)_2$ is four-coordinate in a highly (Fig. 5) distorted geometry but the molecule is symmetric since the Ge atom lies on a crystallographic twofold axis. The mesityl groups subtend an angle at Ge of 119.8(3)°, which is significantly larger than that found in other compounds having the Mes_2Ge unit, e.g. $Mes_2Ge{=}Par'$, 112.9(4)° [28],


$[Mes_2Ge\text{-}N\text{-}N{=}CR_2]_2$,

109.6(5)° [29], $Mes_2Ge(H)R^*$, 113.4(2) [30], and the cyclic oligomers $(Mes_2GeNCN)_3$, 115.9(2)° and $(Mes_2GeNCN)_4$, 112.5(3)° [31], as well as the three-membered ring compound



where the (mes)–Ge–(mes) angles of 110.6(3) and 109.4(1)° are almost tetrahedral [32]. The cyano groups in $Mes_2Ge(CN)_2$ subtend an angle of 97.8(3)° at Ge, which may be the result of crowding by the sterically demanding mesityl groups against the less bulky cyano groups. However, electronic effects should not be discounted since almost the same angles (Me–Ge–Me, 120.9(8)°; NC–Ge–CN, 100.9(7)°) are found in $Me_2Ge(CN)_2$ [33]. In this case, the distortion from tetrahedral geometry was ascribed to the relative electronegativities of the CH_3– and NC– groups as well as a weak intermolecular CN···Ge interaction (3.28(2) Å) causing an increase from 4- to 5-coordination for $Me_2Ge(CN)_2$. For **E**, the same intermolecular contact (5.397(7) Å) is too long to suggest bridging by cyano

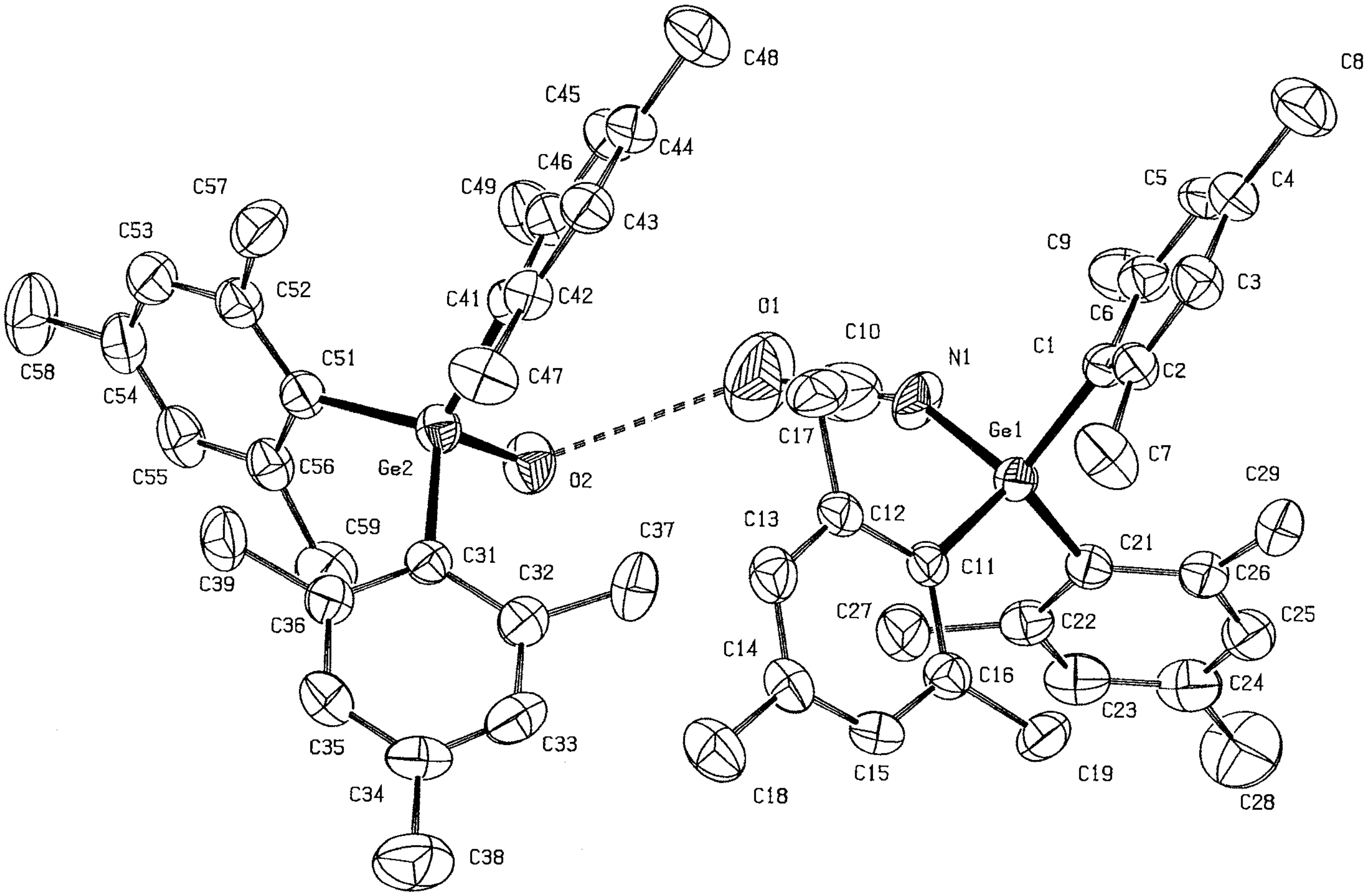


Fig. 4. Platon view of the hydrogen-bonded dinuclear molecule of **D** showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.

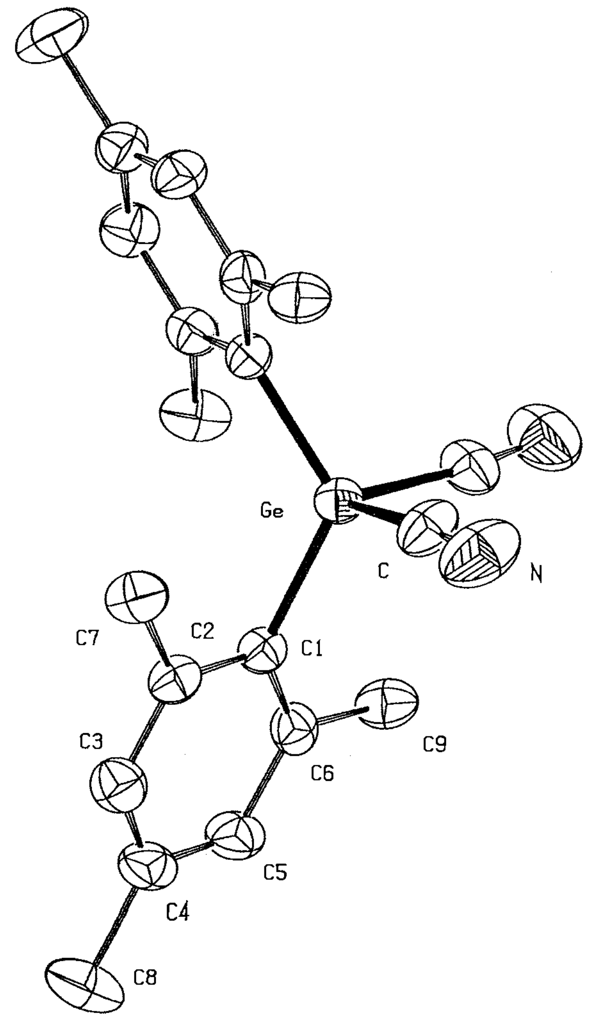


Fig. 5. Platon view of the molecule of **E** showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.

groups. A similar comparison of averaged angles can be made between **A** [Mes–Ge–Mes, 115.9(4)°; NC–Ge–CN, 102.0(4)°] and Me$_3$Ge(CN) [34] with Me–Ge–Me = 116(2)° and NC–Ge–CN = 103(2)°. In the latter compound there is a relatively short intermolecular CN···Ge interaction (3.57 Å) which suggests an incipient interaction might be there, but in **A** the same datum is 5.53(3) Å, again too long to suggest bridging by the cyano group.

3. Experimental

3.1. Syntheses

All manipulations were done under nitrogen using standard Schlenk techniques. Solvents were degassed, dried with Na–K alloy and distilled, stored over molecular sieves, and distilled again immediately before use. Proton and ^{13}C-NMR data (δ ppm) were obtained on either Bruker AC 80 or AC 200 instruments. Infared spectra were measured on a Perkin–Elmer 451, while mass spectra were obtained with a Nermag R10-10H instrument. Elemental analyses were done by the Analytical Services Laboratory of Josai University (Japan).

Literature procedures were used to prepare Mes$_3$GeCl [34], Mes$_2$GeCl$_2$ [35], as well as colourless crystals of Mes$_3$GeNCS (**B**) [5], and Mes$_3$GeN$_3$ (**C**) [5,36]. Since Mes$_3$GeCN and Mes$_3$GeNCO were obtained by new methods and Mes$_2$Ge(CN)$_2$ is a new compound, the preparation and characterization of these three is described in detail below.

3.1.1. Preparation of Mes$_3$GeCN (*A*)

Cyanotrimethylsilane (1.31 g; 13.1 mmol) was added slowly to a stirred solution of Mes$_3$GeCl (0.968 g; 2.08 mmol) in THF (100 ml) and the mixture was refluxed at 60°C for 48 h, then cooled to 0°C and solid product filtered; yield, 64%; m.p. 215–216°C. Anal. Calc. for C$_{28}$H$_{33}$NGe: C, 73.73; H, 7.29; N, 3.00; Found: C, 73.93; H, 7.53; N, 2.91%. IR [ν(CN)]: 2225 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 80 MHz): 2.23 (s, 18H, *o*-Me); 2.27 (s, 6H, *p*-Me); 6.85 (s, 6H, CH$_{ar}$). ^{13}C-NMR (CDCl$_3$, 50.3 MHz): 24.18 (*o*-Me); 21.09 (*p*-Me); 131.58 (C1); 139.89 (C2); 129.84 (C3); 143.58 (C4); 128.48 (C≡N). MS (DCi–CH$_4$: *m*/*z*,%): 456 [M$^+$ − 1, 19]; 338 [M$^+$ − mes, 50]; 431 [M$^+$ − CN, 100]. Colourless single crystals of the hemi-solvate resulted from the filtrate kept at ambient temperature in a Petri dish.

3.1.2. Preparation of Mes$_3$GeNCO (***Da***)

Silver cyanate (0.500 g; 1.07 mmol) was added slowly to a stirred solution of Mes$_3$GeCl (0.161 g; 1.07 mmol) in THF (8 ml). Since the reaction was incomplete after 16 h, an excess of AgNCO was added. The mixture was agitated for another 20 h after which the liquid phase was cannulated and the THF evaporated, leaving white crystals of Mes$_3$GeNCO; yield 83%; m.p. 161–164°C. IR [ν_{as}(NCO)]: 2268 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 80 MHz): 2.27 (s, 18H, *o*-Me); 2.21 (s, 6H, *p*-Me); 6.83 (s, 6H, CH$_{ar}$); in C$_6$D$_6$: 2.30 (s, 18H, *o*-Me); 2.05 (s, 6H, *p*-Me); 6.68 (s, 6H, CH$_{ar}$). ^{13}C-NMR (CDCl$_3$, 50.3 MHz): 23.78 (*o*-Me); 21.07 (*p*-Me); 134.96 (C1); 148.19 (C2); 129.77 (C3); 139.58 (C4); 124.30 (NCO). MS (EI: *m*/*z*,%) 472 [M$^+$ + 1]; 431 [M$^+$ − NCO]; 353 [M$^+$ − Mes]. Recrystallising the sample from diethyl ether gave twinned crystals. A second recrystallisation produced colourless single crystals suitable for X-ray diffraction measurements, which revealed the crystals to be the 1:1 H-bonded adduct, Mes$_3$GeNCO·Mes$_3$GeOH (**D**), presumably due to traces of water remaining in the dried diethyl ether.

Table 3
Summary of averaged structural parameters for various Mes_3MX

	M	X	d(M–C$_i$) (Å)	<ArMAr (°)	$(\bar{\alpha})$ [a] (°)	$(\bar{\beta})$ [a] (°)	$(\bar{\phi})$ [a] (°)
A	Ge	CN	1.961	115.8	21.0	62.7	41.8
B	Ge	NCS	1.965	116.4	22.7	62.7	42.7
C	Ge	N_3	1.948	115.6	22.7	64.7	43.7
Da	Ge	NCO	1.961	115.0	22.3	65.3	43.8
Db	Ge	OH	1.972	114.6	21.3	68.0	44.6
1 [b]	Si	N_3	1.889	114.0	21.8	68.1	45.0
2 [b]	Ge	NH_2	1.978	113.9	19.1	68.5	43.8
3 [b]	Si	CH_2R [c]	1.909	112.9	14.2	69.0	41.6
4 [b]	Ge	H	2.047	109.0	3.0	81.8	42.4
5 [b]	Si	H	2.02	105	9	87	48
6 [d]	C	H	1.539	115.9	22.3	82.3	52.3

[a] See text.

[b] Ref. [9].

[c] –R = –CH=CH$_2$.

[d] Ref. [26].

3.1.3. Preparation of $Mes_2Ge(CN)_2$ (**E**)

To Mes_2GeCl_2 (1.185 g; 3.10 mmol) dissolved in THF (10 ml) was added $(CH_3)_3SiCN$ 7(1.699 g; 17.1 mmol) and the mixture was refluxed for 24 h before it was cooled to 0°C and the precipitate filtered; yield, 100%. Colourless crystals for analysis were obtained from toluene; m.p. 239°C. Anal. Calc. for $C_{20}H_{22}N_2Ge$: C, 66.18; H, 6.11; N, 7.72; Found: C, 65.92; H, 6.20; N, 7.62%. IR [ν(CN)]: 2186 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 80 MHz): 2.30 (s, 6H, p-Me); 2.48 (s, 12H, o-Me); 6.94 (s, 4H, CH$_{ar}$). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 23.75 (o-Me); 21.14 (p-Me); 123.66 (C$_1$); 143.30 (C$_2$); 130.35 (C$_3$); 142.37 (C$_4$); 122.00 (C≡N). MS (DCi,CH$_4$: m/z,%) 365 ($M^+ + 1$, 20); 393 ($M^+ + 29$, 5); 405 ($M^+ + 41$, 2); 338 ($M^+ - $CN, 100).

3.2. X-ray structure analysis

X-ray crystallographic measurements were made on a Rigaku AFC6S diffractometer using the ω–2θ scan mode at 21 ± 1°C; **D** was measured using Cu–K$_\alpha$ radiation ($\lambda = 1.54056$ Å), all others used Mo–K$_\alpha$ radiation ($\lambda = 0.70930$ Å). Structures were solved by direct methods; hydrogens were included in calculated positions while all non-hydrogen atoms were refined anisotropically. Computations were done with NRCVAX [37]; absorption corrections were done using ψ-scans. The sulfur atom of the NCS unit in **B** is disordered in two positions at 50% occupancy each. Compound **A** has four THF molecules per unit cell, each disordered about the twofold axis; each THF molecule exhibits multiple orientations, presumably due to tumbling of the solvent molecule in the cell cavity, thus the disorder was not modelled further.

4. Conclusions

Single-crystal X-ray diffraction measurements show that Mes_3GeX (X = CN, NCS, N_3, NCO and OH) and $Mes_2Ge(CN)_2$ are molecular, free from pseudohalo-bridging, and with Ge atoms four-coordinate in a distorted tetrahedral geometry. Distortions are assigned to steric hindrance by the bulky mesityl groups. Angles formed by the linear pseudohalides with Ge decrease from about 180 to 120° in the order –NCS > –NCO > –N_3, an effect attributed to differences in electronic structures of the pseudohalides. The H-bonded adduct $Mes_3GeNCO \cdot Mes_3GeOH$ was obtained when Mes_3GeNCO was recrystallized from diethyl ether that was not sufficiently dry. In each unit of the adduct, (mes)–Ge–(mes) bond angles and Ge–(mes) bond distances are similar to those of the other pseudohalides, confirming that the H-bonded components retain their molecularity in the adduct.

5. Supplementary material

Crystallographic material has been deposited with the Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, UK; CCDC no. 136047, **E**; 136048, **A**; 136049, **B**; 136050, **C**; and 136051, **D**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The financial support of the Ministère de l'Education du Québec (Fonds FCAR) and of the CNRS (France) is gratefully acknowledged, as is a major equipment grant in 1989 from the Natural Sciences and Engineering Research Council of Canada for the purchase of X-ray equipment. G.H. is especially grateful to Josai University (Japan) for sabbatical leave at McGill University, and M.O. thanks McGill University (Montreal) for sabbatical leave at Université Paul Sabatier (Toulouse).

References

[1] M. Lesbre, P. Mazerolles, J. Satgé, The Organic Compounds of Germanium, Wiley, London, 1971, Chapters 5 and 8.

[2] J.J. Zuckerman, in: A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV elements, Vol. 2, Part II, Marcel Dekker, New York, 1972, Chapter 2.

[3] B.J. Aylett, Organometallic Compounds, 4th edition, Vol. 1, Part 2, Chapman and Hall, London, 1979, Chapter 3.

[4] M. Rivière-Baudet, A. Morère, J.F. Britten, M. Onyszchuk, J. Organomet. Chem. 423 (1992) C5. M. Rivière-Baudet, A. Morère, M. Onyszchuk, J. Satgé, Phosphorus, Sulfur and Silicon 70 (1992) 75.

[5] G. Hihara, M. Nakamura, H. Kobayashi, H. Miyamae, I. Wharf, M. Onyszchuk, P. Rivière, M. Rivière, Chromatography 16 (1995) 31.

[6] J. Barrau, J. Escudié, J. Satgé, Chem. Rev. 90 (1990) 283.

[7] J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, J. Coord. Chem. 130 (1994) 427.

[8] P. Rivière, M. Rivière-Baudet, J. Satgé, in: E.W. Abel, F.G.A. Stone, G. Wilkinson, A.G. Davies (Eds.), Comprehensive Organometallic Chemistry, 2nd edition, Vol. 2, Pergamon, Oxford, 1995, chaper 5.

[9] J.B. Lambert, C.L. Stern, Y. Zhao, W.C. Tse, C.E. Shawl, K.T. Lentz, L. Kania, J. Organomet. Chem. 568 (1998) 21.

[10] M.G. Simard, I. Wharf, Acta Crystallogr. Sect. C 50 (1994) 397.

[11] A.L. Spek, Platon — A multipurpose crystallographic tool, Acta Crystallogr. Sect. A 50 (1990) C-34; Version 190499.

[12] A. Morère, M. Rivière-Baudet, J.F. Britten, M. Onyszchuk, Main Group Met. Chem. 15 (1992) 141.

[13] M. Dahrouch, M. Rivière-Baudet, H. Gornitzka, G. Bertrand, J. Organomet. Chem. 562 (1998) 191.

[14] J. Pfeiffer, W. Maringgele, M. Notlemeyer, A. Meller, Chem. Ber. 122 (1989) 245.

[15] J.B. Hall, D. Britton, Acta Crystallogr. Sect. B 28 (1972) 2133.

[16] G. Ferguson, J.F. Gallagher, D. Murphy, T.R. Spalding, C. Glidewell, H.D. Holden, Acta Crystallogr. Sect. C 48 (1992) 1228.

[17] A. Treinin, in: S. Patai (Ed.), The Chemistry of the Azide Group, Wiley–Interscience, New York, 1972, pp. 1–52.

[18] E.F.V. Scriven, Azides and Nitrenes: Reactivity and Utility, Academic Press, New York, 1984.

[19] M. Kaftory, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Halides, Pseudohalides, and Azides, Wiley, New York, 1983, pp. 1254–1258.

[20] S.S. Zigler, K.J. Haller, R. West, M.S. Gordon, Organometallics 8 (1989) 1656.

[21] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, 4th edition, Harper Collins, New York, 1993, p. 877. A.L. Allred, E.G. Rochow, J. Inorg. Nucl. Chem. 5 (1958) 269.

[22] T.N. Tarkhova, L.E. Nikolaeva, E.V. Chuprinov, M.A. Simonov, N.V. Belov, Sov.-Phys. Crystallogr. 21 (1976) 216.

[23] G.M. Sheldrick, R. Taylor, J. Organomet. Chem. 87 (1975) 145.

[24] J.D. Andose, K. Mislow, J. Am. Chem. Soc. 96 (1974) 2168.

[25] J.F. Blunt, K. Mislow, Tetrahedron Lett. (1974) 909.

[26] H. Preut, F. Huber, Acta Crystallogr. Sect. B 35 (1979) 83.

[27] H. Puff, K. Braun, H. Reuter, J. Organomet. Chem. 409 (1991) 119.

[28] M. Dräger, J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, Organometallics 7 (1988) 1010.

[29] M. Lazraq, C. Couret, J.P. Declercq, A. Dubourg, J. Escudié, M. Rivière-Baudet, Organometallics 9 (1990) 845.

[30] M. Lazraq, J. Escudié., C. Couret, J. Satgé, M. Drager, R. Dammel, Angew Chem. Int. Ed. Engl. 27 (1988) 828.

[31] M. Dahrouch, M. Rivière, J. Satgé, M. Mauzac, C.J. Cardin, J.H. Thorpe, Organometallics 17 (1998) 623.

[32] T. Tsumuraya, S. Sato, W. Ando, Organometallics 7 (1988) 2015.

[33] J. Konnert, D. Britton, Y.M. Chow, Acta Crystallogr. Sect. B 28 (1972) 180.

[34] O. Schlemper, D. Britton, Inorg. Chem. 5 (1966) 511.

[35] P. Rivière, M. Rivière-Baudet, Organomet. Syn. 4 (1988) 542.

[36] T. Tsumaraya, W. Ando, Chem. Lett. (1989) 1043.

[37] E.J. Gabe, Y. Le Page, J.P. Charland, F.C. Lee, P.S. White, J. Appl. Crystallogr. 22 (1989) 384.