ABSTRACT: In order to estimate the reactivity of disilylated
germylene phosphine adducts, a cyclic version of this
compound class was reacted with a number of different
reagents. Reactions with the chalcogens sulfur, selenium, and
tellurium led to dimers of the heavy ketone analogues.
Reactions with water and ethyl bromide proceeded to give the
respective oxidized germanol and germyl bromide. Two
different reactions with alkynes were observed which led
either to a germacyclopropene, by addition of tolane to the
germlyne, or to a silagermacyclobutene, likely formed by
addition of the alkyne across a silagermene. Reaction via the
silagermene was also observed in the reaction with
benzophenone. Reaction of a germylene phosphine adduct
with GeCl2·(dioxane) provided insertion of the silylated
germlyne into a Ge−Cl bond, leading to a germylated
chlorogermylene
phosphine adduct.

INTRODUCTION

The chemistry of higher carbene analogues (tetrylenes) is a
very active field of research. Most of the studied compounds
bear amino substituents, which stabilize the coordinative
unsaturation of the divalent group 14 element by π-donation
of the nitrogen lone pairs into its empty p orbital. Compounds
with σ-donating alkyl or aryl substituents, which lack this
particular stabilization, are intrinsically more reactive and
require bulky substituents to prevent di- or oligomerization.

In the course of the last few years we have investigated the
chemistry of tetrylenes with even more σ-donating oligosilanyl
and germyl substituents.

RESULTS AND DISCUSSION

Recently, we have described the synthesis of a cyclic
germlyne by reaction of an oligosilanyl-1,3-diide with GeCl2·(dioxane). The formed
germlyne was found to be unstable and dimerizes
to an exocyclic digermene, which subsequently undergoes a
rearrangement to form an endocyclic digermene. While this
reaction was found to be remarkably clean, attempts to carry
out analogous reactions with oligosilanyl-1,4-diides 2a,b turned
to be rather messy (Scheme 1). The only compounds that
could be isolated from these reactions were 3a,b, which contain
extra trimethylsilyl groups in comparison to the starting
material. While the reason for this is unclear, it should be
mentioned that in the recent attempted synthesis of a related
disilylated silylene by reducing the respective dichlorosilane,
also a compound with an additional trimethylsilyl group was
obtained and it thus seems not unlikely that 5a,b were formed
in the course of the reactions but are likely too reactive to be
detected or isolated (Scheme 1).

This unfortunate situation was resolved carrying out the
reaction of 1,4-silanediide 1a with GeBr2·(dioxane) in the
presence of either PEt3 or PMe3. This way germlyne 5a is

Received: June 15, 2016
Published: August 3, 2016
trapped as a base adduct (4a,b) (Scheme 2) and cannot undergo a 1,2-silyl shift to yield a silagermene.25,26

Scheme 2. Synthesis of Phosphine Adducts 4a,b of the Five-Membered Cyclic Disilylated Germylene 5a

In order to study the principal reactivity of silylated germylene phosphine adducts, a number of addition reactions were carried out. Oxidation of divalent germanium compounds with elemental chalcogens formally causes the formation of heavy ketone analogues. However, due to the limited stability of double bonds between germanium and the heavier chalcogens, usually products of dimerization via head-to-tail [2 + 2] cycloadditions are observed. This was reported for cyclic16−20 and acyclic21−23 germylenes with sulfur,16−22,24 selenium16,17,21−23 and tellurium.16,21−23 For very bulky germylenes Tokito and co-workers have shown that stable thianones and selenones can be isolated.25,26

For the case of phosphine adduct 4b, in the reactions with 2 mol equiv of either sulfur or selenium and with 1 equiv of tellurium clean conversion was observed to yield compounds 7a−c, in addition to the respective oxidized phosphines SPEt3 and SePET3 for the S and Se cases (Scheme 3). The formation of the dimeric compounds clearly shows that the steric bulk exercised by the trimethylsilyl groups at the silicon atoms in a position α to the germylene is by no means sufficient to inhibit head-to-tail dimerization processes of the presumably initially formed heavy ketone analogues 6a−c (Scheme 3).

Also of interest were addition reactions of the germylene with polar reagents and unsaturated organic compounds. The first group of reagents is expected to test for nucleophilic reactivity, whereas the second group is more likely to indicate electrophilic reactivity of the tetraylne.

While reactions of germynes with water have received some theoretical attention,7 the number of actual examples of clean reactions is surprisingly small. A reason for this lack seems to be facile follow-up reactions. For instance, exposure of Lappert’s Ge[CH(SiMe3)2]2 to atmospheric conditions caused hydrolyses to give HGe[CH(SiMe3)2][CH(SiMe3)2(SiMe3O)].28 While Power and co-workers found that reactions of the divalent germylene Ge(ArMe6)2 (ArMe6 = C6H3-2,6-{C6H2-4,6-CH3}) with water gave the Ge(IV) insertion product (ArMe6)Ge(μ-OH)2, the analogous stannylene Sn(ArMe6)2 reacted to give the Sn(II) species {ArMe6Sn(μ-OH)}2 with elimination of ArMe6H.29 Related compounds containing the RGe(H)OH structural motif were obtained upon hydrolysis of Tamao’s spectacular germalone (Eind)2GeO (Eind = 1,1,3,3,5,5,7,7-octaethyl-1,3-dioxa-2-hydrindacen-4-yl)30 and presumably in the hydrolysis of a germolated germylene.31

In any case reaction of 4b with water was found to occur cleanly by insertion of the germylene into the O−H bond, yielding germanol 8 (Scheme 4).

The situation for reactions of germynes with alkyl halides is somewhat similar. Again only a few clear-cut examples have been reported. Baines and co-workers found that NHC adducts of several germynes with alkyl iodides led mainly to the alkylation of the germylene lone pair and upon further reaction with CDCl3 provided the oxidation product Mes2Ge(Cl)R.32 Conversely, reaction of Lappert’s Ge(CH2SiMe3)2 with methyl iodide gave Me(1)Ge(CH2SiMe3)2.33 It is likely that such reactions involve the transient formation of germyl radicals. Banaszak Holl and co-workers have been able to exploit this reactivity for facile C−H activation chemistry.34 In order to probe the reactivity of 4b against alkyl halides, a reaction with ethyl bromide was carried out, leading cleanly to the ethylated germyl bromide 9, which is the product of oxidative addition of 5a (Scheme 4).

Although we are not aware of reactions of germynes with α-diketones, it was reported that (Bu3MeSi)2GeGe(SiMe2Bu3)2 reacts with 3,5-di-tert-butyl-1,2-benzoquinone as a masked germylene.35,36 Related reactions with transient silylenes were studied by Ando et al. and were found to lead to 1,3-dioxa-2-silacyclopent-4-enes.37 An analogous product was obtained in the reaction of 4b with diacetyl (2,3-butanedione), which led to the respective 4,5-dimethyl-1,3-dioxa-2-germacyclopent-4-ene 10 (Scheme 4).

Addition of an alkyne to disilylated germynes was achieved by Sekiguchi and co-workers, who reacted disilylated dichlorogermeranes with molten potassium, in the presence of bis(trimethylsilyl)acetylene without a solvent, to obtain the corresponding germacycloprenes after 19 h at reflux.38 The related reaction of 4b with tolane occurred under less drastic conditions and provided germacyclopene 11 in a yield of 86% (Scheme 4). As the reaction of 4b with tolane can be considered to be analogous to the addition of bis-(trimethylsilyl)acetylene to titanocene59 or zirconocene,60 we wondered whether the reaction of 4b with 1,4-bis-(trimethylsilyl)butadiyne would also mimic the respective reaction with titanocene.61 However, instead of addition to the germylene to give either a cumulene or an alkynyl-substituted germacyclopene, the diyne underwent [2 + 2] cycloaddition to the silagermene isomer of 5a,10 yielding a mixture of the two regioisomers 12a,b (Scheme 4).

Addition of phenylacetylene across silagermenes was observed previously in a similar way by Baines42 and Sekiguchi.43,44 Scheschkewitz’s [2 + 2] cycloaddition of phenylacetylene to a NH2-stabilized silagermenyldiene constitutes another related precedent.45

The formation of 12a,b seems to indicate that in solution 4b is in equilibrium with 5a (Scheme 1) and its silagermene isomer. Although we have found that the silagermene can...
undergo dimerization via a head-to-tail [2 + 2] cycloaddition,\(^\text{10}\) the addition of an alkyne to the Ge–Si double bond seems to be energetically much more facile. The presence of a silagermene isomer was further substantiated by the reaction of 4b with benzophenone.\(^\text{46}\) Again, addition across the Si–Ge double bond was observed in a regioselective manner to form Si–O and Ge–C bonds in compound 13 (Scheme 4). This behavior is consistent with earlier studies by Baines and co-workers.\(^\text{47−49}\)

Reaction of 4b with GeCl\(_2\)·(dioxane) provides another interesting insertion reaction where the silylated germylene inserts into a Ge–Cl bond. In this way the germylated chlorogermylene adduct 15 forms. The dioxane which served as the Lewis base in GeCl\(_2\)·(dioxane) is replaced by PEt\(_3\). The reaction is not completely selective, and in addition to compound 15 also a similar amount of dichlorogermylene 14 forms (Scheme 4). Repeating the reaction at different

Table 1. Selected NMR Spectroscopic Data (Chemical Shifts in ppm) of Germylene Derivatives 4a,b, 7a–c, 8–11, 14, and 15, Sharing the 1-Germa-2,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilane Backbone

| compd | \(^1\text{H}\) | \(^{13}\text{C}\) | \(^{29}\text{Si}\) | \(^{28}\text{Si}\) | other |
|-------|---------------|---------------|---------------|---------------|-------|
| 3a    | 0.41          | 0.44          | −1.1 to −1.6  | −10.5         |       |
| 4a    | 0.32          | 0.51          | 3.8           | 1.2           |       |
| 4b*   | 0.43          | 0.51          | 3.8           | −1.2          |       |
| 7a    | 0.54          | 0.41          | 5.0           | −1.2          |       |
| 7b    | 0.55          | 0.39          | 4.4           | −1.8          |       |
| 7c    | 0.57          | 0.35          | 4.1           | −2.2          |       |
| 8b    | 0.34          | 0.39          | 3.0           | −2.1          |       |
| 9     | 0.27          | 0.28          | 2.1           | −7.3          |       |
| 10    | 0.25          | 0.35          | 3.5           | −2.2          |       |
| 11    | 0.32          | 0.50          | 3.6           | −1.8          |       |
| 14    | 0.38          | 0.40          | 2.9           | −2.3          |       |
| 15    | 0.32          | 0.50          | 3.6           | −1.8          |       |

*Values taken from ref 10.

DOI: 10.1021/acs.organomet.6b00482
Organometalics 2016, 35, 2728−2737
temperatures and concentrations did not have an influence on the amount of formation of 14.

Recently, there have been reports of reactions of carbenes and other low-valent main-group compounds with hydrogen and carbon monoxide. We have therefore attempted reactions of these two small molecules with 4b, but no reaction was observed. This lack of reactivity may be explained by the fact that despite it being very electrophilic, germylene is not nucleophilic enough to participate in carbylation or hydrogenation reactions.

**NMR Spectroscopy.** The NMR spectroscopic characterization of the magnesium germanide 2b is not as straightforward as it is for 2a, where the typical upfield-shifted resonances of metalated silicon atoms around −170 ppm are very characteristic. The 29Si NMR spectrum of 2b displays only the SiMe3 and SiMe2 signals at −3.4 and −23.7 ppm, respectively, which are slightly shifted toward low field; this is common for germanium-connected silyl groups. The same is observed in the 29Si NMR spectrum of 3a, where the trimethylsilyl group attached to germanium is found at 0.6 ppm. The other 29Si signals of 3a are two SiMe3 resonances for the two different ring sides at −3.4 and −7.8 ppm and the SiMe2 (−24.3 ppm) and Si(SiMe3) (−105.2 ppm) resonances with rather ordinary chemical shifts.

The reactions of 4b can be conveniently monitored using 29Si NMR spectroscopy. The chemical shifts of the 1H (and to some extent also the 13C) resonances of the formed products are very similar and do not cover a vast spectral region. Thus, these signals are not very indicative. Nevertheless, the number and intensity of observed 1H and 13C resonances provide straightforward insight into the molecular symmetry. Compounds 4a,b (Table 1) are interesting compounds, as the 1H, 13C, and 29Si spectra taken at ambient temperature show different rates for the inversion of the coordination sphere around the low-valent germanium center. For 4a two different signals for the trimethylsilyl groups were observed in the 1H, 13C, and 29Si spectra (Table 1). Although this means that the inversion process at germanium is slow on the NMR time scale, the observed signals are broad, indicating that the coalescence temperature is close to ambient temperature. JSi−P and JSi−P couplings to the germylated silicon atom and the SiMe2 unit can be observed with values of 16 and 10 Hz, respectively. For 4b the slightly diminished degree of interaction between the germylene and the phosphine leads to an increased rate of inversion of germanium. The signals for the trimethylsilyl groups at the two different sides of the ring therefore coalesce at room temperature and are only visible as broad singlets. The signals for the Si(SiMe3)2 (−127.1 ppm) and SiMe2 (−22.7 ppm) atoms are not affected by the inversion process and appear as sharp doublets due to the coupling to 31P with JSi−P and JSi−P coupling constants very similar to those observed for 4a.

The reactions of 4b with elemental chalcogens to give the structurally related compounds 7a−c result, as expected, in rather similar 29Si spectra. The signals of the trimethylsilyl groups and of the germylated silicon atoms resonate at unusually low field at −5.4, −90.8 (7a), −4.7, −92.6 (7b), and −3.2, −99.4 (7c) ppm (Table 1). As the resonances of the SiMe3 groups around −30 ppm are rather conventional, the downfield shift can likely be assigned to the proximity of the chalcogen atoms. In this context it should be noted that both selenium and tellurium possess spin 1/2 nuclei with abundances of 7.58% for 7Se and 6.99% for 125Te. Despite the fact that JP−Si coupling was clearly visible for 4b, no satellite signals were observed for JSi−P or JSi−P coupling in 7b or 7c, respectively. The structure of the dichlorogermane 14 is actually rather similar to those of 7a−c, and accordingly the 29Si NMR spectrum of 14 is similar to the signals of the SiMe3 groups and of the germylated silicon atoms at −4.3 and −96.7 ppm (Table 1).

While the spectra of germirene are remarkable, compound 15 is more interesting. As observed for 7a−c and 14, the attachment of heavy atoms to germinium causes the aforementioned downfield shift of the SiMe3 and SiGe resonances to −3.9/−4.3 and −102.5 ppm for 15 (Table 1). The presence of the PEt3 is visible by a JSi−P coupling of 6.0 Hz to the germylated silicon atoms. The spectroscopic appearance of compound 15 suggests C2v symmetry. This leads to the conclusion that the germylene atom cannot be configuratively stable and at ambient temperature the inversion process must be fast on the NMR time scale. The 31P resonance at 10.5 ppm indicates a diminished degree of interaction in comparison to that in 4b, where the 31P resonance of PEt3 was observed at 14.8 ppm. The 29Si NMR spectra of compound 10 are similar to those of 14 without the strong deshielding effect on the SiMe3 and SiGe groups. Spectra of compounds 8 and 9 are similar to those of 15, indicating side differentiation of the five-membered ring. 29Si NMR chemical shifts of 8 and 9 are comparable and completely lie within the range of expected values (Table 1). Like compound 14, 10 also has C2v symmetry, giving similar spectra. However, the two oxygen atoms attached to germinium in 10 do not cause the same downfield shift behavior as observed for 7a−c, 14, and 15 (Table 1). The C2v symmetric silagermene addition products 12a,b and 13 are more interesting with respect to their 29Si NMR spectra.

Isomeric compounds 12a,b were formed in a 1:1 ratio and could not be separated. Therefore, a 29Si NMR spectrum with each silicon atom giving rise to two signals was observed. Nevertheless, a tentative assignment of resonances is possible. The trimethylsilyl groups at germanium appear around −3.5 ppm, and four trimethylsilyl resonances were found between −7.4 and −12.6 ppm which can be assigned to the three silyl-substituted and the vinyalted SiMe3 groups. Two signals between −22.1 and −28.4 ppm can be associated with SiMe2 units, and that around −37 ppm corresponds to the silicon atom which is part of the silagermanbutene ring with a strong downfield shift, as expected for four-membered rings. The signal at −112.5 ppm is in the typical region for tetrasilylated silicon atoms. The 29Si NMR spectrum of 13 is much like that of 12a,b but is less complicated. The oxygenate silicon incorporated into the four-membered ring resonates at 40.3 ppm. Again the trimethylsilyl group at germanium is shifted downfield (−2.1 ppm), and the other SiMe3 groups are found at −7.9, −8.5, and −14.0 ppm. The signals for the two SiMe2 groups at −25.3 and −37.2 (SiMe3) and the tetrasilylated silicon atom at −104.7 ppm complete the spectrum.

**X-ray Crystallography.** Compounds 2b (Figure 1), 3b (Figure S1 in the Supporting Information), 4a (Figure 2), 7a (Figure 3), 7b (Figure S2 in the Supporting Information), 7c (Figure S3 in the Supporting Information), 8 (Figure 4), 9 (Figure 5), 10 (Figure S4 in the Supporting Information), 11 (Figure S5 in the Supporting Information), 12a (Figure 6), 13 (Figure 7), 14 (Figure S6 in the Supporting Information), and 15 (Figure 8) reported in this study were subjected to single-crystal X-ray diffraction analysis (Table 2 and Tables S1−S3 in the Supporting Information). The cyclic 1,4-digermymagne...
The PMe₃ coordinates in an orthogonal fashion to the
1.8182(16), Si(1) −92.0(2), O(1) −Si(4) 2.3919(18), Ge(2)
−109.37(7), Si(5) 2.637(2), Mg(1) −Si(1A) 2.2888(17), Ge(1)−Si(1) 2.2906(17), Ge(1)−Si(1) 2.4448(19), Ge(1)−Si(4) 2.4798(19), S(1)−Ge(1A) 2.2889(17), Si(1)−Si(2) 2.348(2), Si(2)−C(1) 1.887(7); S(1A)−Ge(1)−Si(1) 92.42(6), S−Ge(1)−Si(110.44(7), S(1)−Si(1) 111.15(6), S(1A)−Ge(1A)−Si(4) 120.61(6), S(1)−Ge(1)−Si(4) 114.66(6), Si(1)−Ge(1A)−Si(4) 107.00(7), Ge(1A)−S(1)−Ge(1) 87.58(6).

Figure 1. Molecular structure of 2b (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) 2.041(5), Mg(1)−O(2) 2.052(5), Mg(1)−Ge(1) 2.636(2), Mg(1)−Ge(2) 2.637(2), Ge(1)−Si(5) 2.373(2), Ge(1)−Si(6) 2.3770(19), Ge(1)−Si(4) 2.3919(18), Ge(2)−Si(1) 2.371(2), Ge(2)−Si(2) 2.374(2), Ge(2)−Si(3) 2.3970(19), Si(3)−Si(4) 2.337(3); O(1)−Mg(1)−O(2) 92.0(2), O(1)−Mg(1)−Ge(1) 114.62(15), Ge(1)−Mg(1)−Ge(2) 109.37(7), Si(5)−Ge(1)−Si(6) 104.34(8), Si(5)−Ge(1)−Si(4) 106.44(7).

Figure 2. Molecular structure of 4a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−P(1) 2.3484(6), Ge(1)−Si(1) 2.4533(6), Ge(1)−Si(4) 2.4589(5), P(1)−C(17) 1.8182(16), Si(1)−Si(2) 2.3504(6), Si(2)−C(1) 1.8914(15); P(1)−Ge(1)−Si(1) 102.163(19), P(1)−Ge(1)−Si(4) 105.239(18), Si(1)−Ge(1)−Si(4) 102.70(2).

Figure 3. Molecular structure of 7a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1A) 2.2888(17), Ge(1)−S(1) 2.2906(17), Ge(1)−Si(1) 2.4448(19), Ge(1)−Si(4) 2.4798(19), S(1)−Ge(1A) 2.2889(17), Si(1)−Si(2) 2.348(2), Si(2)−C(1) 1.887(7); S(1A)−Ge(1)−Si(1) 92.42(6), S−Ge(1)−Si(110.44(7), S(1)−Si(1) 111.15(6), S(1A)−Ge(1A)−Si(4) 120.61(6), S(1)−Ge(1)−Si(4) 114.66(6), Si(1)−Ge(1A)−Si(4) 107.00(7), Ge(1A)−S(1)−Ge(1) 87.58(6).

Figure 4. Molecular structure of 8 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−O(1) 1.788(4), Ge(1)−H(90) 1.3807(2), Ge(1)−Si(1) 2.3929(7), Si(1)−Si(2) 2.3563(6), Si(2)−C(1) 1.8814(16); O(1)−Ge(1)−Si(1) 113.46(12), Si(1A)−Ge(1)−Si(1) 110.55(3).

Organometallics 2016, 35, 2728–2737
DOI: 10.1021/acs.organomet.6b00482

While the structural features of 2a,b are essentially the same, it is interesting to note that the Ge−Mg distances of 2.637(2) Å in 2b are slightly shorter than the analogous interactions in 2a.55 The structure of 2-bromo-1,2,3-trigerma-1,1,2,3,3-pentakis(trimethylsilyl)tetracyclopentasilane 3b (Figure S1), which crystallizes in the triclinic space group P1̅, is somewhat unusual. The five-membered ring exhibits a rather flat envelope conformation with the trimethylsilyl group attached to germanium in an equatorial position with the bromine atom in the sterically less demanding axial position. Ge−Ge (2.453(1)/2.4623(9) Å), Ge−Si (2.389(1)/2.402(1) Å), and Ge−Br (2.4080(8) Å) distances of 3b are within the expected ranges.

The solid-state structure of germylene phosphine adduct 4a (Figure 2) is quite similar to those of 4b and a related digermylated PEt₃ adduct.10 The ring exhibits an envelope conformation with one of the Si(SiMe₃)₂ units out of plane. The PMe₃ coordinates in an orthogonal fashion to the germanium atom (d₃−Si = 2.3484(6) Å) with the angle between the SiGeSi plane and the phosphine of 112.3° similar to the 113.6° of 4b. As found for other disilylated germylene base adducts, the Si−Ge distances of 4a are elongated to 2.4589(5) and 2.4533(6) Å. Si−Ge distances of compounds with an analogous ring skeleton but tetravalent germanium atoms are typically close to 2.40 Å (see below).

Compounds 7a (Figure 3), 7b (Figure S2 in the Supporting Information), and 7c (Figure S3 in the Supporting Information) are structurally much alike, and it was therefore expected that these compounds would exhibit similar structures in the solid state. However, 7a was found to crystallize in the monoclinic space group C2/c together with a disordered pentane molecule, whereas 7b,c crystallize in the triclinic space group P1. Nevertheless, the molecular structures of 7a−c in the crystal form are analogous. In all molecules planar Ge−E−Ge−E (E = S, Se, Te) units are found.

The 1-germa-2,2,5,5-tetrasilyl-tetracyclopentasilane units of 7a−c, which over the SiGeSi plane and the phosphine of 112.3° similar to the 113.6° of 4b. As found for other disilylated germylene base adducts, the Si−Ge distances of 4a are elongated to 2.4589(5) and 2.4533(6) Å. Si−Ge distances of compounds with an analogous ring skeleton but tetravalent germanium atoms are typically close to 2.40 Å (see below).

Compounds 7a (Figure 3), 7b (Figure S2 in the Supporting Information), and 7c (Figure S3 in the Supporting Information) are structurally much alike, and it was therefore expected that these compounds would exhibit similar structures in the solid state. However, 7a was found to crystallize in the monoclinic space group C2/c together with a disordered pentane molecule, whereas 7b,c crystallize in the triclinic space group P1. Nevertheless, the molecular structures of 7a−c in the crystal form are analogous. In all molecules planar Ge−E−Ge−E (E = S, Se, Te) units are found.

The 1-germa-2,2,5,5-tetrasilyl-tetracyclopentasilane units of 7a−c, which over the germanium atoms have a spirocyclic connection to the Ge−E−Ge−E rings, all show the five-membered rings in envelope
conformations with one of the a SiMe₂ units serving as the flap extending about 0.9–1.0 Å from the (SiGeSiSi) ring plane.

All Si–Si distances and angles of these five-membered rings are rather similar (Table 2). The two rings of the spirocyclic arrangement are situated almost orthogonally to each other (angles between planes between 87.8 and 89.5°). The arguably most unusual structural property of compounds 7a–c is the Ge–Si distance. In previous studies we have noticed that this particular bond is sensitive to the germanium oxidation state. The Si–Ge distances of PR₃ adducts of disilylated germylene are typically around 2.47 Å, whereas Si–Ge distances of tetravalent germanes are close to 2.40 Å. The respective distances in 7a–c are between 2.44 and 2.48 Å (Table 2), indicating at least some degree of unsaturation at germanium. The number of dimeric structures of higher germanones which have been subjected to structural analysis in the solid state is small.

The CCDC database lists 26 examples comparable to compound 7a featuring four-membered rings with alternating Ge and S atoms. The Ge–S distances are in a narrow range between 2.209 and 2.258 Å with a mean value of 2.235 Å. The corresponding Ge–S distance in compound 7a is 2.291(1) Å and thus is considerably longer. This is most likely caused by a combination of the bulky silanylene substituents of the germylene unit and its stronger electron-donating character. CCDC examples of four-membered rings with alternating Ge and Se atoms comparable to 7b exhibit Ge–Se distances in a range between 2.350 and 2.433 Å, with most compounds exhibiting Ge–Se distances at the lower limit. The compound with the longest distance (TtBMesGeSe)₂ features very large substituents at germanium and a folded asymmetric ring. All other compounds contain perfectly planar SeGeSeGe rings with two equivalent Ge–Se distances. Due to its lower...
molecular symmetry, compound 7b exhibits several Ge–Se distances which lie between 2.412(2) and 2.423(2) Å. Despite these values being on the longer side of those for known compounds, the SeGeSeGe rings of 7b are planar.

The CCDC database lists only five examples of Ge–Te comparable to 7c. These compounds again feature planar four-membered GeTeGeTe rings and Ge–Te distances between 2.56 and 2.60 Å. For compound 7c with a planar ring the Ge–Te distances were found to be 2.632(1) Å. Much like 7a–c, also compounds 11 (Figure S5 in the Supporting Information) and 10 (Figure 5) feature spirocyclic structures. The germacyclopentasilane rings of the latter also engage in envelope conformations which, however, are substantially flatter than those of 7a–c.

In addition, the Ge–Si distances of 11 (2.38 Å) and 10 (2.40 Å) (Table 2) are shorter and are more in the expected range for fully saturated compounds. The germacyclopentasilane ring units of the structures of compounds 14 (Figure S6 in the Supporting Information), 8 (Figure 4), and 9 (Figure S4 in the Supporting Information) are similar to those of 11 and 10 in the sense that they all exhibit envelope conformations with the flap being one of the SiMe3 units.

The Si–Si bond lengths are within the expected ranges, and the Si–Ge distances remain below or at least very close to 2.40 Å. Although the number of structurally characterized germacycloprene14,38,58–61 is rather small, the range of Ge–C bond lengths is surprisingly broad, ranging from 1.915(6) to 2.005 Å. The value found for compound 11 is 1.958(2) Å, which is a rather typical Ge–C distance and is comparable to that of the related bis[tris(trimethylsilyl)]germirene reported recently.15

The Ge–Cl distance of dichlorogermane 14 (2.1961(9) Å), the Ge–OH distance of germolin 8 (1.788(4) Å), the Ge–OC distance of 10 (1.834(4) Å), and the Ge–Br distance of 9 (2.3672(9) Å) are all somewhat shorter than the values typically found but are still completely within the ranges of what is expected.

The germylene adduct 15 (Figure 8), however, exhibits a rather long Ge–Ge distance of 2.5290(9) Å, which is quite long but is likely a consequence of the fact that one of the two Ge atoms involved is in the divalent state. This is further reflected by the Ge–Cl distance in compound 15. The bond to the tetravalent Ge atom is, at 2.283(1) Å, shorter than the respective bond to the divalent Ge atom (2.319(2) Å). In addition to 7a–c compound 15 is also the only other structure displaying significantly elongated Si–Ge bond lengths (2.422(1) and 2.431(2) Å).

Table 2. Compilation of Structural Data of Germylene Derivatives 4a, 7a–c, 8–11, 14, and 15, sharing the 1-Germa-2,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilane Backbone

| compd | d_{Ge–C} (Å) | d_{Ge–Si} (Å) | d_{Si–Si} (Å) | d_{Si–SiMe3} (Å) | d_{Si–Ge} (Å) | ∠SiGeSi (deg) |
|-------|--------------|--------------|--------------|------------------|--------------|--------------|
| 4a    | 2.3484(6) (E = P) | 2.4589(5), 2.4533(6) | 2.3493(6)–2.3598(6) | 2.3605(7), 2.3504(6) | 102.70(1) |
| 7a    | 2.291(2) (E = S) | 2.456(2), 2.450(2) | 2.361(4)–2.392(5) | 2.349(4)–2.374(4) | 106.3(1), 106.4(1) |
| 7b    | 2.412(2)–2.423(2) (E = Se) | 2.361(4)–2.483(3) | 2.346(4)–2.367(3) | 107.00(6) |
| 7c    | 2.632(1) (E = Te) | 2.452(4), 2.453(4) | 2.342(1), 2.343(9) | 113.88(4) |
| 8     | 1.788(4) (E = O) | 2.392(7) | 2.347(2), 2.357(2) | 114.37(7) |
| 9     | 2.3672(9) (E = Br), 1.973(12) (E = C) | 2.411(1), 2.408(1) | 2.346(4)–2.356(3), 2.364(3), 2.343(3) | 114.37(7) |
| 10    | 1.834(4), 1.839(5) (E = O) | 2.396(2), 2.400(2) | 2.346(1), 2.338(1) | 2.34(1) |
| 11    | 1.958(2) (E = C) | 2.3861(8) | 2.338(1), 2.344(1) | 2.358(1) |
| 14    | 2.1961(9) (E = Cl) | 2.3874(8) | 2.338(1), 2.344(1) | 2.358(1) |
| 15    | 2.5290(9) (E = Ge), 2.283(1) (E = Cl) | 2.431(2), 2.422(1) | 2.351(2)−2.370(2) | 107.57(5) |

CONCLUSION

Recently reports of small-molecule activation of carbenes and other low-valent main-group compounds have attracted considerable attention. The main reasons these compounds exhibit such interesting reactivity are the coordinative unsaturation, small singlet–triplet gaps, and fitting orbital energies. In order to investigate the question of whether the recently introduced class of silylated germylene phosphine adducts is also capable of small-molecule activation, we studied the reactions of a cyclic disilylated germylene phosphine adduct with a number of small molecules including elemental chalcogens, water, alkyl halides, alkenes, ketones, and α-diketones. All these reagents reacted in a defined way with the germylene or its silagermene isomer in a manner that can be considered as oxidation of the germylene or the silagermene isomer. Further attempted reactions with carbon monoxide and hydrogen, however, did not proceed.

It has been pointed out conclusively that the range of the small singlet–triplet gap energy (ΔE_{ST}) of a low-valent main-group compound can be considered as an inverse measure of its electrophilicity and further that the orbital energy of the HOMO (lone pair) is proportional to its nucleophilicity.55 A qualitative comparison of the values for ΔE_{ST} and HOMO of 5a12 reveals a small ΔE_{ST} of 86 kJ/mol,12 consistent with it having highly electrophilic behavior, whereas the HOMO energy of ~6.46 eV14,62 indicating low basicity, explains the lacking nucleophilic properties. This picture is fully consistent with the facile addition chemistry and the reactions with polar reagents, and it also clarifies the reluctant behavior in the attempted hydrogenation and carbynylation reactions.

EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents were dried using a column-based solvent purification system.63 Chemicals were
obtained from different suppliers and used without further purification. Compounds 1a, 1b, 2b, 2a, 4b, GeBr2(dioxane), and MgBr2E t-O were prepared by following reported procedures.

\(^1\)H (300 MHz), \(^13\)C (75.4 MHz), \(^29\)Si (59.3 MHz), and \(^31\)P (121.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer and are referenced to Me_4Si (\(^1\)H, \(^13\)C, \(^29\)Si) and 85% H_2PO_4 (\(^31\)P) if not noted otherwise. The solvent of the samples was C_6D_6. To compensate for the low isotopic abundance of \(^29\)Si, the mass spectrometry (ESI-MS) spectra were recorded on a Thermo Fisher Scientific Orbitrap LTQ XL mass spectrometer and the raw data were analyzed using the Excalibur computer program.

**X-ray Structure Determination.** For X-ray structure analyses the crystals were mounted onto the tip of glass fibers. Data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation (0.71073 Å). The data were reduced to F_2 and corrected for absorption effects with SADABS (25, 26) respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97). If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as CCDC supplementary publication nos. 1473871 (C), 1473863 (C), and 1473864 (C). For X-ray structure analyses the solvent was evaporated and the product was extracted with pentane (3 × 5 mL). The solution was concentrated to give an inseparable mixture of yellow crystals of 7a and white crystals of SPEI._

**Reactions of Germene Adduct 4b. Reaction with Sulfur (7a).** A mixture of 4b (33 mg, 0.05 mmol) and S (3 mg, 0.013 mmol) was stirred in THF (1 mL) at 80°C for 3 h at room temperature. The solvent was removed under reduced pressure, and the product was extracted with pentane (3 × 5 mL). The solution was concentrated to give an inseparable mixture of yellow crystals of 7b and white crystals of SPEI. NMR (δ in ppm): \(^1\)H: 0.45 (s, 12H, SiMe_2), 0.39 (s, 24H, MeSi), 1.1C (SiMe_3), -1.2 (SiMe_3), -30.5 (SiMe_3) -92.6 (Si(SiMe_3)). HR ESI-MS: calcd for C_{11}H_{20}GeSi_6O: m/z = 617.02; found, m/z = 617.04.

**Reaction with Tellurium (7c).** A mixture of Te (26 mg, 0.20 mmol) and 4b (131 mg, 0.20 mmol) was stirred in THF (2 mL) at room temperature for 18 h. The same workup procedure as for 7a gave a mixture of yellow crystals of 7c and white crystals of SPEI. NMR (δ in ppm): \(^1\)H: 0.55 (s, 72H, Me_3Si), 0.41 (s, 18H, SiMe_3), 1.0C (SiMe_3), -3.2 (SiMe_3), -30.4 (SiMe_3) -99.4 (Si(SiMe_3)).

**Addition of Water (8).** Degasified H_2O (1.0 μL, 0.1 mmol) was added to a stirred solution of 4b (65 mg, 0.10 mmol) in THF (1 mL) for 18 h at room temperature. The solvent was removed under reduced pressure, and from the residue the product was extracted with pentane (3 × 5 mL). The solvents was removed and the residual was dissolved in a minimum amount of toluene to give yellowish crystals of 8 (50 mg, 90%). Mp: 123-125°C. NMR (δ in ppm): \(^1\)H: 6.38 (J_{H-H} = 1.6 Hz, 1H, GeH), 0.39 (s, 6H, SiMe_3), 0.34 (s, 18H, SiMe_3), 0.28 (s, 6H, SiMe_3), 0.27 (s, 18H, SiMe_3), 0.24 (d, J_{H-H} = 1.1 Hz, 3H, OH), 1.1C (SiMe_3), 0.34 (d, J_{H-H} = 1.1 Hz, 3H, OH), 1.1C (SiMe_3), 0.19 (s, 18H, SiMe_3), -4.7 (SiMe_3), -7.3 (SiMe_3), -25.5 (SiMe_3), -113.9 (Si(SiMe_3)).

**Addition of Ethyl Bromide (9).** Ethyl bromide (5 mg, 0.05 mmol) and 4b (33 mg, 0.05 mmol) were stirred in THF (2 mL) for 2 h at room temperature. The same workup procedure as for 7a gave colorless crystals of 9 (29 mg, 91%). Mp: 136-138°C. NMR (δ in ppm): \(^1\)H: 0.25 (s, 18H, SiMe_3), 0.35 (s, 6H, SiMe_3), 0.44 (s, 6H, SiMe_3), 0.48 (s, 18H, SiMe_3), 1.46 (t, J_{H-H} = 3H, CH_3), 1.60 (m, 2H, GeCH_2CH_3), 1.1C (SiMe_3), -2.2 (SiMe_3), -1.8 (SiMe_3), 3.5 (SiMe_3), 3.6 (SiMe_3), 12.5 (CH_3), 19.4 (GeCH_2CH_3), -8.1 (SiMe_3), -25.9 (SiMe_3), -111.5 (Si(SiMe_3)).

**Addition of Diacetyl (10).** A mixture of diacetyl (5 mg, 0.05 mmol) and 4b (33 mg, 0.05 mmol) was stirred in THF (2 mL) for 24 h at room temperature. The same workup procedure as for 7a gave yellow crystals of 10 (31 mg, 98%). Mp: 153-155°C. NMR (δ in ppm): \(^1\)H: 1.96 (s, 6H, CMe_3), 0.40 (s, 12H, SiMe_3), 0.38 (s, 36H, SiMe_3), 1.1C (CO), 14.9 (CMe_3), 2.9 (SiMe_3), -2.3 (SiMe_3), -25.9 (SiMe_3), -117.0 (Si(SiMe_3)).

**Addition of Tolane (11).** A mixture of tolane (18 mg, 0.1 mmol) and 4b (65 mg, 0.15 mmol) was stirred in THF (2 mL) for 24 h at room temperature. The same workup procedure as for 8 gave colorless crystals of 11 (62 mg, 86%) at 65°C. Mp: 167-169°C. NMR (δ in ppm): \(^1\)H: 7.86 (m, 4H), 7.23 (m, 4H), 7.04 (m, 4H), 0.50 (s, 12H, SiMe_3), 0.32 (s, 36H, SiMe_3), 1.1C (CO), 148.1, 135.7, 131.9, 129.2, 128.6, 3.6 (SiMe_3), -1.8 (SiMe_3), -25.9 (SiMe_3), -97.3 (SiMe_3), -30.3 (SiMe_3), -120.1 (Si(SiMe_3)).
Addition of 1,4-Bis(trimethylsilyl)-1,3-butadiyne (12a, b). 1,4-Bis(trimethylsilyl)-1,3-butadiyne (8 mg, 0.05 mmol) was added to a stirred solution of 4b (35 mg, 0.05 mmol) in THF (1 mL). The same workup procedure as for 4 gave an inseparable mixture of colorless crystals of 12a and 12b. NMR (δ in ppm, D2O capillary): 29Si, −3.9, −3.9 (15, SiMe3), −4.3 (15, SiMe3), −7.6 (14, SiMe3), −22.8 and −24.6 (both SiMe3), −96.7 (14, Si(SiMe3)), −102.5 (15, d, Si(SiMe3)), −141 (7JSi−P = 6 Hz). 31P (in THF with D2O cap.), +0.5.

Notes

* In this work, a financial interest.

**Funding information**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Support for this study was provided by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF) via the projects P-22679 (C.M.) and P-25124 (J.B.).

## REFERENCES

1. Blom, B.; Driess, M. In Functional Molecular Silicon Compounds II; Scheschewitz, D., Ed.; Springer: Berlin, 2013; Vol. 156, pp 85-123.
2. Brown, Z. D.; Power, P. P. Inorg. Chem. 2013, 52, 6248-6259.
3. Kira, M.; Ishida, S.; Iwamoto, T. Chem. Rev. 2004, 4, 243-253.
4. Driess, M. Nat. Chem. 2012, 4, 525-526.
5. Mizuha, Y.; Sasaki, T.; Tokito, N. J. Chem. Soc. 2009, 109, 3479-3511.
6. Apel, H.; Baumgartner, J.; Marschner, C.; Müller, T. J. Am. Chem. Soc. 2011, 133, 5632-5635.
7. Apel, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. J. Am. Chem. Soc. 2012, 134, 6409-6415.
8. Apel, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. J. Am. Chem. Soc. 2012, 134, 10864-10875.
9. Apel, H.; Marschner, C.; Baumgartner, J.; Zark, P.; Müller, T. J. Am. Chem. Soc. 2013, 135, 7949-7959.
10. Hlina, J.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T. Organometallics 2013, 32, 3404-3410.
11. Hlina, J.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. Organometallics 2013, 32, 3300-3308.
12. Hlina, J.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T.; Jüokov, V. Chem. - Eur. J. 2014, 20, 9357-9366.
13. Hlina, J.; Apel, H.; Walewska, M.; Förcke, U.; Zanger, K.; Marschner, C.; Baumgartner, J. Organometallics 2014, 33, 7069-7077.
14. Walewska, M.; Baumgartner, J.; Marschner, C. Chem. Commun. 2015, 51, 276-278.
15. Xiao, X-Q.; Zhao, H.; Xu, Z.; Lai, G.; He, X.-L.; Li, Z. Chem. Commun. 2013, 49, 2706-2708.
16. Veith, M.; Noetzli, M.; Stahl, L.; Huch, V. Z. Anorg Allg. Chem. 1994, 620, 1264-1270.
17. Bazinet, P.; Yap, G. P. A.; Richeson, D. S. J. Am. Chem. Soc. 2001, 123, 11162-11167.
18. Al-Rafa', S. M. I.; Lumnis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. Inorg. Chem. 2010, 49, 9709-9717.
19. Huang, M.; Kireenko, M. M.; Zaitsev, K. V.; Oprunenko, Y. F.; Churakov, A. V.; Howard, J. A. K.; Lermontova, E. K.; Sorokin, D.; Linder, T.; Sundemeyer, J.; Karlov, S. S.; Zaitseva, G. S. Eur. J. Inorg. Chem. 2012, 2012, 3712-3724.
20. Liew, S. K.; Al-Rafa', S. M. I.; Goettel, J. T.; Lumnis, P. A.; McDonald, S. M.; Miedema, L. J.; Ferguson, M. J.; McDonald, R.; Rivard, E. Inorg. Chem. 2012, 51, 5471-5480.
21. Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Leung, W.-P.; Rai, A. K.; Taylor, R. E. Polyhedron 1991, 10, 1203-1213.
22. Wegner, G. L.; Jockisch, A.; Schier, A.; Schindlbaur, H. Z. Naturforsch, B: J. Chem. Sci. 2000, 55b, 347-351.
23. Weidenbruch, M.; Hagedorn, A.; Peters, K.; von Schnering, H. G. Chem. Ber. 1996, 129, 401-404.
24. Sasamaroi, T.; Sugiyama, Y.; Takeda, N.; Tokioto, N. Organometallics 2005, 24, 3309-3314.
25. Matsumoto, T.; Tokioto, N.; Okazaki, R. J. Am. Chem. Soc. 1999, 121, 8811-8812.
26. Tokioto, N.; Matsumoto, T.; Mannaru, K.; Okazaki, R. J. Am. Chem. Soc. 1993, 115, 8855-8856.
27. Wu, C.-S.; Su, M.-D. Dalton Trans. 2012, 41, 3253-3265.
28. Lappert, M. F. Pure Appl. Chem. 1978, 50, 703-708.
29. Erickson, J. D.; Vasko, P.; Riparetti, R. D.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. Organometallics 2015, 34, 5785-5791.
30. Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. Nat. Chem. 2012, 4, 361-365.
31. Li, L.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. J. Am. Chem. Soc. 2011, 133, 18622-18625.
32. Rupar, P. A.; Staroverov, V. N.; Baines, K. M. Organometallics 2010, 29, 4871-4881.
33. Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. J. Chem. Soc., Chem. Commun. 1984, 480-482.
34. Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. Am. Chem. Soc. 2003, 125, 8986-8987.
35. Lee, V. Y.; McNeice, K.; Ito, Y.; Sekiguchi, A. Chem. Commun. 2011, 47, 3272-3274.
36. Lee, V. Y.; McNiece, K.; Ito, Y.; Sekiguchi, A.; Geinik, N.; Becker, J. Y. Heterotax. Chem. 2014, 25, 313-319.
37. Ando, W.; Beno, M. J. Chem. Soc., Chem. Commun. 1979, 0, 655-656.
38. Sekiguchi, A.; Iizumi, R.; Ishii, S.; Ichinohe, M.; Lee, V. Y. Angew. Chem. Int. Ed. 2002, 41, 1598-1600.
39. Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Y. T.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Göhrs, J. J. Organomet. Chem. 1994, 476, 197-206.
16. Organometallics 1996, 105, 1228–1230.

17. Angew. Chem., Int. Ed. 1997, 36, 33–38.

18. Angew. Chem., Int. Ed. 2003, 42, 112–122.

19. Angew. Chem., Int. Ed. 2004, 43, 408–407.

20. Angew. Chem., Int. Ed. 2011, 50, 397–397.

21. Angew. Chem., Int. Ed. 2016, 55, 2737–2737.

22. Acta Crystallogr., Sect. A: Found. Crystallogr. 1995, 51, 33–38.

23. Acta Crystallogr., Sect. A: Found. Crystallogr. 2003, 59, 587–594.

24. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1996, 52, 3, 336–340.

25. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1997, 53, 3, 393–397.

26. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1998, 54, 1, 21–25.

27. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1999, 55, 1, 95–99.

28. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2000, 56, 5, 785–789.

29. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2001, 57, 4, 457–460.

30. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2002, 58, 2, 215–218.

31. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2003, 59, 2, 188–191.

32. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2004, 60, 4, 518–521.

33. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2005, 61, 3, 273–275.

34. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2006, 62, 2, 270–272.

35. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2007, 63, 2, 273–275.

36. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2008, 64, 2, 276–278.

37. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2009, 65, 1, 279–281.

38. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2010, 66, 1, 282–284.

39. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2011, 67, 2, 285–287.

40. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2012, 68, 4, 288–290.

41. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2013, 69, 2, 291–293.

42. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2014, 70, 1, 294–296.

43. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2015, 71, 2, 297–299.

44. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2016, 72, 2, 299–301.

45. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2017, 73, 2, 302–304.

46. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2018, 74, 2, 305–307.

47. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2019, 75, 2, 308–310.

48. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2020, 76, 2, 311–313.

49. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2021, 77, 2, 314–316.

50. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2022, 78, 2, 317–319.

51. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 2023, 79, 2, 320–322.