DALTON
FULL PAPER

Siloles and germoles modified by partial hypercoordination through aminoxy substituents

Udo Losehand and Norbert W. Mitzel *

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany. E-mail: N.Mitzel@lrz.tum.de

Received 3rd December 1999, Accepted 8th February 2000

1-Dimethylaminoxy-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**), 1,2-bis(dimethylaminoxy)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**2**) and 1,2-bis(dimethylaminoxy)-2,3,4,5-tetraphenyl-1-germacyclopentadiene (**3**) have been prepared by the reactions of the corresponding chloro-2,3,4,5-tetraphenyl-1-(sila/germa)cyclopentadienes with $LiONMe_2$. They are yellow crystalline materials, which have been identified by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si), mass spectrometry and elemental analysis. The UV–VIS spectra of **1**, **2** and **3** show the absorption bands of the silole/germole to be only slightly affected by the Si · · · N interaction, which indicates that orbital interactions of the type lp(N)→σ*(SiC) do not play a significant role and thus the Si · · · N attraction is better interpreted as a dipole interaction. The crystal structures of **2** and **3** reveal planar C_4Si and C_4Ge rings, with a propeller-like arrangement of the phenyl groups. The SiON and GeON groups contain short Si · · · N distances [2.473(3) and 2.503(3) Å in **2**, and 2.535(7) to 2.608(7) Å in **3**]. **2** adopts a *gauche-gauche* conformation for the NOSiON backbone, while in **3**, two independent molecules are found in the asymmetric unit, one with an *anti-gauche* conformation and one with a *gauche-gauche* conformation.

Introduction

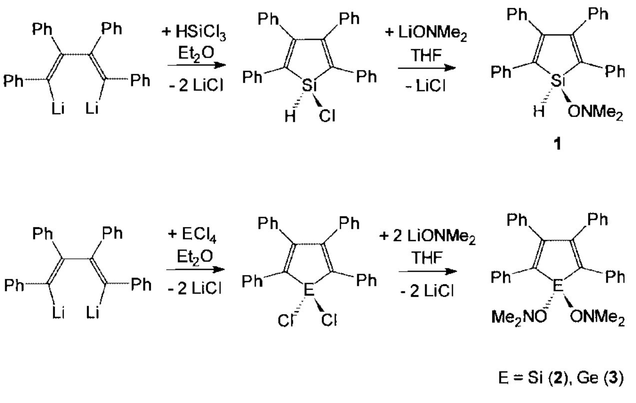
Silacyclopentadienes, also known as siloles, are the subject of recent intensive investigations due to their interesting electronic properties, which make them applicable for organic light-emitting devices. The first prototypes of such devices, *e.g.* illuminated displays, have already been successfully demonstrated to function.[1] At the moment, a number of groups are involved in the development of π-conjugated silole polymers because unique material properties can be expected, including small band gaps, electroluminescent, non-linear optic and thermochromic behaviour.[2,3] The advantage of siloles as compared to conventional π-conjugated polymers based on pyrrole, furan, thiophene and pyridine units is their large electron affinity caused by the energetically low-lying LUMO.[4] The colour (in general yellow to orange) of the siloles is a result of this small HOMO–LUMO gap. The low energy level of the LUMO has been attributed to the interaction between the butadiene π*-orbital and the exocyclic σ*-orbitals of the silicon centre.[2]

We intended to modify the electronic properties of siloles and germoles by binding ONR_2 substituents to their group 14 atoms, E = Si and Ge, as compounds with SiON[5] and GeON[6] (and SnON)[7] linkages are known to show attractive interactions between the E and N centres. This has been demonstrated for a series of compounds, whereby the strength of this interaction (characterised by the Si · · · N distances and Si–O–N angles) ranges from predictably weak interactions in $Me_3SiONMe_2$ [gas; 2.566(8) Å, 107.9(6)°],[6] $H_3SiONMe_2$ [2.453(1) Å, 102.6(1)°][6] and $Cl_3SiONMe_2$ [2.437(av.) Å, 103.0(av.)°][8] through medium strength interactions in $H_2Si(ONMe_2)_2$ [2.138(av.) Å, 95.2(av.)°][9] to very strong ones in $ClH_2SiONMe_2$ [*anti* conformer in the solid state; 2.028(1) Å, 79.7(1)°].[9] Models to rationalise these experimental facts include anomeric interactions of the type lp(N)→σ*(Si–X), which promise to give an observable effect on the electronic properties of siloles and germoles if ONR_2 substituents are bound to the Si and Ge atoms. Alternative explanations for the Si · · · N and Ge · · · N attractions are based on intermolecular dipole interactions,[10] which should then lead to less pronounced changes in the electronics of the silole and germole rings. The HOMO–LUMO gaps in the siloles and germoles give rise to absorptions in the visible region of the spectrum, which makes UV–VIS spectroscopy a valuable tool to evaluate the effect of this substitution and obtain more detailed information about the nature of the E · · · N secondary interactions. It should be mentioned that the synthesis of a partially hypercoordinate silole containing an 8-dimethylaminonaphthyl substituent has already been reported by Tamao and co-workers.[11]

Results

Preparation

The first synthesis of silycyclopentadiene[12,13] was described in 1959. We have adapted the preparation methods developed by Jutzi and Karl[14] to generate our starting materials, 1-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (chlorosilole), 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (dichlorosilole) and -germacyclopentadiene (dichlorogermole), which were subsequently reacted with $LiONMe_2$ to give the desired substituted siloles and germoles **1**, **2** and **3** (Scheme 1). These



Scheme 1

DOI: 10.1039/a909547k

Table 1 UV–VIS Absorption maxima of pentane solutions of $Ph_4C_4SiH(ONMe_2)$ (**1**), $Ph_4C_4Si(ONMe_2)_2$ (**2**), $Ph_4C_4Ge(ONMe_2)_2$ (**3**) and $Ph_4C_4SiCl_2$

	Absorption maxima/nm	
	λ_1	λ_2
$Ph_4C_4SiH(ONMe_2)$ **1**	375	244
$Ph_4C_4Si(ONMe_2)_2$ **2**	372	244
$Ph_4C_4Ge(ONMe_2)_2$ **3**	367	234
$Ph_4C_4SiCl_2$	378	231

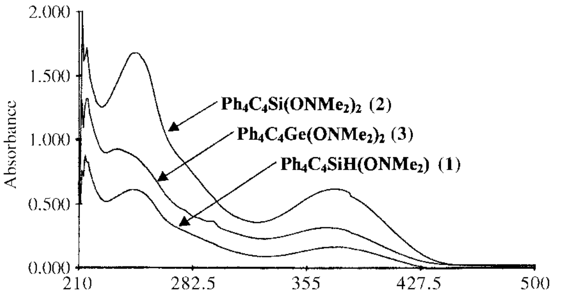


Fig. 1 UV–VIS Spectra of pentane solutions of $Ph_4C_4SiH(ONMe_2)$ (**1**), $Ph_4C_4Si(ONMe_2)_2$ (**2**) and $Ph_4C_4Ge(ONMe_2)_2$ (**3**).

compounds are obtained as bright yellow crystalline powders, which can be purified by recrystallisation from benzene–hexane mixtures.

NMR spectroscopy

The identity of the compounds **1**, **2** and **3** was proven by ^1H, ^{13}C, ^{15}N, ^{17}O and ^{29}Si NMR spectroscopy, mass spectroscopy and elemental analyses. The proton NMR spectra show multiplets for the phenyl protons and singlets for the methyl protons of the Me_2NO groups. A further singlet for the Si–H proton is observed in the spectrum of **1**. The signals in the aromatic region of the ^{13}C NMR spectra are similar to those of the corresponding starting materials, with an additional signal for the methyl groups of the Me_2NO substituents appearing at about 50 ppm. The ^{29}Si NMR spectrum of **1** shows a doublet at -15.9 ppm, while **2** gives rise to a singlet at -22.7 ppm. The ^{17}O NMR signal of **2** appears at 19 ppm, which is 122 ppm to low frequency relative to $H_2Si(ONMe_2)_2$ (141 ppm) and possibly indicates a dissimilar electronic situation at oxygen in these two molecules. Despite repeated experiments under a variety of conditions, we could not observe ^{17}O NMR signals for **1** and **3**. The ^{15}N NMR chemical shifts of both siloles **1** and **2** are found at -242.0 ppm, which is in the established range found for other aminoxysilanes. The resonance of **3** occurs at -256.8 ppm, which is between that of $Cl_2Ge(ONMe_2)_2$ (-231.8 ppm) and $Me_3GeONMe_2$ (-250.6 ppm).

UV–VIS spectra

In order to explore the electronic changes in the silole core, UV–VIS spectra (Fig. 1) of the new compounds **1**, **2** and **3** were recorded in pentane solution. They all show absorption maxima in similar regions, with the germole **3** absorbing at the shortest wavelength. For comparison, a spectrum of the starting material $Ph_4C_4SiCl_2$ was recorded under the same conditions.

The absorption maxima (Table 1) of the two siloles **1** and **2** at 375 and 372 nm are assigned to the HOMO–LUMO transition (π–π^*) and appear at longer wavelengths than those of the less electronegatively substituted compounds 1,1-dimethyltetraphenylsilole ($\lambda_1 = 351$ nm)[15] and hexaphenylsilole ($\lambda_1 = 365$ nm[13] or 360 nm[15]). This red-shift is also observed for the germole **3** (Table 1) with $\lambda_1 = 367$ nm [λ_1(1,1-dimethyltetraphenylgermole) = 348 nm, λ_1(hexaphenylgermole) = 354 nm]. This is in variance with the small decrease in the π–π^*-transition energy with increasing substituent electronegativity, as has been found in the siloles $Me_2(Me_3Si)_2C_4SiX_2$ with $\lambda_1(X = F)$ being 13 nm longer than $\lambda_1(X = H)$. It has thus proven difficult to gauge the influence of the *N*-donor atom in a β-position relative to the Si and Ge centres. For comparison, Tamao's partially hypercoordinate silole with an 8-dimethylaminonaphthyl group bound to a Ph_4C_4SiMe silole silicon atom[11] does not show any difference in the position of the absorption maximum from the corresponding purely four-coordinate naphthyl compound without the dimethylamino substituent. Partial hypercoordination at silicon thus seems not to exert an observable effect on the π-system of siloles. This can also be understood as an argument against the interpretation of the Si · · · N attraction in SiON compounds as a remote type of negative hyperconjugation of the type $lp(N) \rightarrow \Sigma\sigma^*(SiX)$, as this should lead to a change in the energetics of the silole π-system. However, care should be taken to not over-interpret these findings.

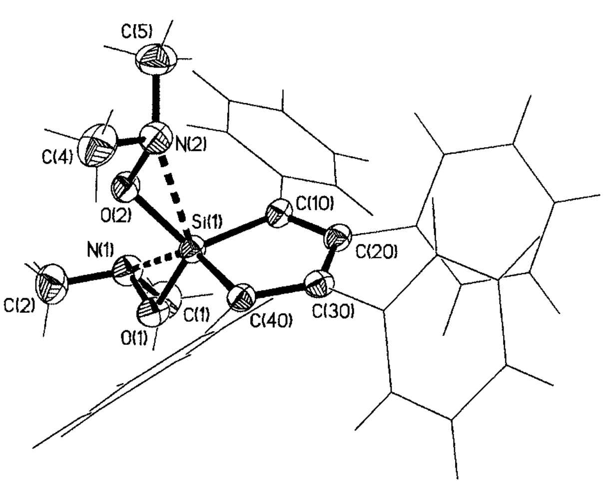


Fig. 2 Crystal structure of $Ph_4C_4Si(ONMe_2)_2$ (**2**). The phenyl rings are shown as wire models for clarity.

Crystal structures of $Ph_4C_4Si(ONMe_2)_2$ (2) and $Ph_4C_4Ge(ONMe_2)_2$ (3)

Molecules of $Ph_4C_4Si(ONMe_2)_2$ (**2**) (Fig. 2) crystallise as monomers together with half a formula unit of benzene in the asymmetric unit. Selected bond lengths and angles for **2** are listed in Table 2. They adopt an *anti-gauche* conformation for their NOSiON skeletons. This conformation is somewhat distorted with respect to an ideal *anti-gauche* conformation, as one Me_2NO group is positioned with an O–Si–O–N torsional angle of 61.1(1)°, whereas the other adopts a torsion angle of 164.8(2)°, which is clearly distinct from the ideal value of 180°. This deformation can be explained by the steric requirements of the tetraphenylbutadiene part of the molecule, as one H atom of the *anti*-Me_2NO group is separated by only 2.415 Å from an H atom of the neighbouring phenyl ring (Σ van der Waals radii 2.40 Å), which prevents a further closing up of these groups, as would be required to adopt an O–Si–O–N torsional angle of 180°. The related bis(*N*,*N*-dimethylaminoxy)silanes $X_2Si(ONMe_2)_2$ (X = F, Cl) without sterically demanding ligands do not show a corresponding distortion. Despite the different conformations of the Me_2NOSi groups, the Si–O–N angles are remarkably similar. By contrast, in $ClH_2Si–O–NMe_2$ a small Si–O–N angle in the *anti* [87.1(9)°] and a larger Si–O–N angle in the *gauche* conformer [104.7(11)°] was observed in the gas phase.[9] The partial hypercoordination at silicon in **2** is not as pronounced as in $Cl_2Si(ONMe_2)_2$ [Si–O–N 102.8(1) and 103.7(1)°],[16] but stronger than in $Me_3SiONMe_2$ [107.9(6)°].[7]

Table 2 Selected geometry parameter values, as determined by low-temperature X-ray diffraction of $Ph_4C_4Si(ONMe_2)_2$ (**2**) and $Ph_4C_4Ge(ONMe_2)_2$ (**3**) single crystals. The values are listed in different columns to represent the different $ONMe_2$ groups

Bond lengths (Å) and angles (°)	$Ph_4C_4Si(ONMe_2)_2$ (**2**)		$Ph_4C_4Ge(ONMe_2)_2$ (**3**)			
			Molecule 1 (*gauche-gauche*)		Molecule 2 (*anti-gauche*)	
	$O(1)N(1)Me_2$	$O(2)N(2)Me_2$	$O(1)N(1)Me_2$	$O(2)N(2)Me_2$	$O(1)N(1)Me_2$	$O(2)N(2)Me_2$
E–O	1.651(2)	1.654(2)	1.802(5)	1.776(5)	1.785(5)	1.789(5)
E···N	2.473(3)	2.503(3)	2.568(7)	2.596(7)	2.535(7)	2.608(7)
O–N	1.478(3)	1.481(2)	1.460(8)	1.472(7)	1.480(7)	1.468(8)
N–C1	1.457(3)	1.452(4)	1.448(11)	1.437(10)	1.455(8)	1.444(10)
N–C(2)	1.445(4)	1.452(4)	1.449(12)	1.475(10)	1.457(9)	1.457(9)
EON	104.3(1)	105.8(1)	103.4(4)	105.8(4)	101.5(4)	105.5(4)
O–N–C(1)	105.2(1)	104.8(1)	106.7(7)	104.9(6)	105.5(5)	105.1(6)
O–N–C(2)	105.4(1)	105.8(1)	105.0(7)	104.1(6)	103.7(5)	103.9(7)
O–E–C(40)	109.1(1)	115.0(1)	116.9(3)	110.7(3)	117.8(2)	108.9(2)
O–E–C(10)	113.6(1)	118.5(1)	114.5(3)	115.0(2)	115.2(2)	120.4(2)
τO–E–O–N	61.1(1)	164.8(2)	78.8(7)	71.4(7)	172.5(7)	57.6(7)
E–C(40)	1.853(2)		1.928(7)		1.921(7)	
E–C(10)	1.858(3)		1.932(7)		1.926(7)	
C(10)–C(20)	1.362(3)		1.360(9)		1.353(10)	
C(20)–C(30)	1.512(4)		1.543(8)		1.518(9)	
C(30)–C(40)	1.358(3)		1.330(9)		1.355(9)	
O(1)–E–O(2)	106.3(1)		107.6(2)		102.7(2)	
C(40)–E–C(10)	94.0(1)		91.8(3)		92.4(3)	

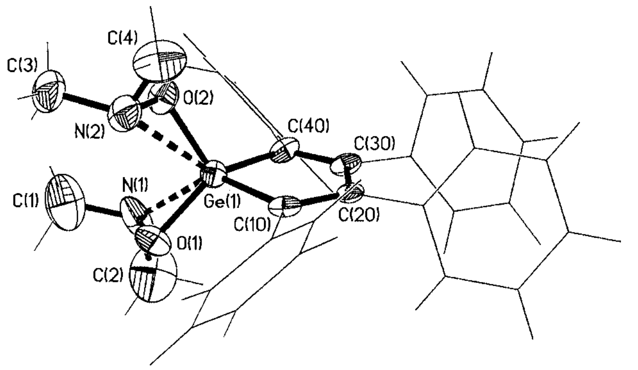


Fig. 3 Crystal structure of one molecule of $Ph_4C_4Ge(ONMe_2)_2$ (**3**) in the asymmetric unit. The phenyl rings are shown as wire models for clarity.

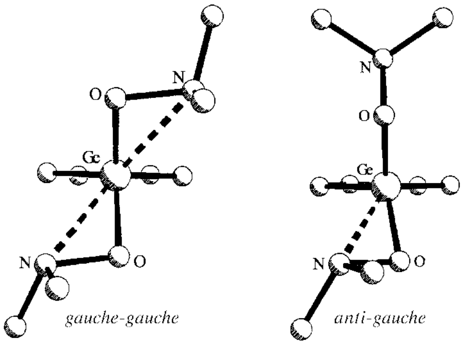


Fig. 4 The $C_4Ge(ONC_2)_2$ skeletons of the two independent molecules in the asymmetric unit of the $Ph_4C_4Ge(ONMe_2)_2$ (**3**) crystal. The view is along the local C_2 axis of the germole ring.

The geometry of the silole ring is very similar to that of Tamao's hypercoordinate silole[11] and the bis-methylated silole $Ph_4C_4SiMe_2$.[17] All these compounds show a propeller-like arrangement of the phenyl groups.

$Ph_4C_4Ge(ONMe_2)_2$ (**3**) (Fig. 3) crystallises from hexane with two independent molecules in the asymmetric unit. The geometry of the germole ring and the orientation of the phenyl groups is similar in both molecules, but the conformations of the $Ge(ONMe_2)_2$ units are completely different (Fig. 4). One molecule adopts an *anti-gauche* conformation, similar to that of the silole **2**, whereas the other features an almost C_2 symmetric *gauche-gauche* conformation. The distortion of the *anti-gauche* conformer by repulsive H···H contacts is less pronounced than in the silole **2**. Selected bond lengths and angles for **3** are listed in Table 2. The GeON angle of the *anti*-Me_2NOGe unit in the germole **3** [*anti-gauche* conformer, 101.5(4)°] is smaller than the respective Si–O–N angle in silole **2**. All the other E–O–N angles fall over a range of about 3°. The Ge–O–N angles in **3** are similar to those in the compound $Cl_2Ge(ONMe_2)_2$ [Ge–O–N 102.0(1), 102.0(1)°],[16] but slightly smaller than in $Me_3GeONMe_2$ [108.9(7)°].[6] The Si···N and Ge···N distances in both compounds **2** and **3** are smaller than the sum of the Bartell's one-angle-radii[18,19] for Si/Ge and N (2.69 and 2.72 Å), which justifies the classification of these compounds as (4 + 2) coordinate.

On the basis of the presented results and earlier investigations on hypercoordinate siloles we conclude that (partial) hypercoordination of the Si and Ge atoms in siloles and germoles does not affect the electronic structure of the silole or germole rings significantly.

Experimental

General

The syntheses were carried out using a standard Schlenk line under a purified nitrogen gas atmosphere. All NMR spectra were recorded at 21 °C on a Jeol JNM-LA400 spectrometer in C_6D_6 solvent dried over K–Na alloy. 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene,[20] 1-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene and 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene were prepared according to or by adapting literature procedures.[14]

1-(*N*,*N*-Dimethylaminoxy)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1)

n-Butyllithium (0.2 g, 2.5 mmol, 1.7 M solution in hexane) was added dropwise to a solution of *N*,*N*-dimethylhydroxylamine (0.5 ml, 7 mmol) in pentane (25 ml) at −20 °C. The reaction mixture was allowed to warm to ambient temperature and was

Table 3 Crystallographic data for compounds **2** and **3**

Compound	**2**	**3**
Formula	$C_{32}H_{32}N_2O_2Si\cdot0.5C_6H_6$	$C_{32}H_{32}N_2O_2Ge$
Molecular mass	543.74	549.19
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	12.547(2)	12.399(4)
b/Å	9.905(2)	12.543(3)
c/Å	24.461(4)	19.955(3)
$\alpha, \beta, \gamma/°$	90, 96.91(1), 90	81.16(2), 84.37(2), 66.05(2)
V/Å^3	3017.9(9)	2780.2(12)
Z	4	4
μ(Mo-Kα)/mm^{-1}	0.71073	1.133
Temperature/K	158(2)	143(2)
Measured reflections	6509	10945
Independent reflections	6509	10945
R_1/wR_2	0.0500, 0.1389	0.0659, 0.1825

stirred for 1 h. The solvents were removed under reduced pressure. The $LiONMe_2$ formed was suspended in THF (20 ml) and cooled to −196 °C. 1-Chloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1.2 g, 2.4 mmol) dissolved in THF (30 ml) was added and the mixture allowed to warm to −96 °C (toluene–liquid N_2 slush). The mixture was stirred for 1 h and then slowly warmed to ambient temperature. The THF was removed under reduced pressure from the resulting yellow solution. The residue was extracted with benzene and the solution filtered. The benzene was removed by evaporation and a yellow powder remained, which was further purified by recrystallisation from benzene to yield 0.94 g (1.9 mmol, 78%) of **1**. ^{1}H NMR: δ 7.5–6.5 (m, Ph-H), 5.78 (s, SiH) 2.48 (s, H_3C). $^{13}C\{^1H\}$ NMR: δ 155.0, 139.2, 138.9, 132.7, 130.1, 129.9, 127.8, 127.7, 127.5, 126.5 (Ph-C/1-silacyclopentadiene-C), 50.7 (CH_3). $^{15}N\{^1H\}$ NMR: δ −242 (s). $^{29}Si\{^1H\}$ NMR: δ −15.9 (d, $^1J_{SiH} = 226.4$ Hz). MS(CI): $m/z = 445$ [M$^+$].

1,1-Bis(*N*,*N*-dimethylaminoxy)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (2)

n-Butyllithium (0.9 g, 14 mmol, 1.7 M in hexane) was added dropwise to a solution of *N*,*N*-dimethylhydroxylamine (1.0 ml, 14 mmol, 0.86 g) in pentane (25 ml) at −20 °C. The mixture was warmed to ambient temperature, stirred for 1 h and the solvents were removed under reduced pressure to yield $LiONMe_2$. This solid was suspended in THF (20 ml) and cooled to −196 °C. 1,1-Dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (3.16 g, 6.9 mmol) dissolved in THF (50 ml) was added, the resulting mixture stirred for 1 h at −96 °C (toluene–liquid N_2 slush) and the THF removed under vacuum. The product was extracted with benzene, the resulting yellow solution filtered and the benzene removed *in vacuo* to yield microcrystalline **2**, which was further purified by recrystallisation from benzene–hexane (50:50) to yield 2.9 g of pure **2**$\cdot0.5C_6H_6$ (5.7 mmol, 83%) as bright yellow, hexagonally-shaped crystals. ^{1}H NMR: δ 7.5–6.5 (m, Ph-H), 2.48 (s, H_3C). $^{13}C\{^1H\}$ NMR: δ 155.0, 139.2, 138.9, 132.7, 130.1, 129.9, 127.8, 127.7, 127.5, 126.5 (Ph-C/1-silacyclopentadiene-C), 50.7 (CH_3). $^{15}N\{^1H\}$ NMR: δ −242.0 (s). ^{17}O NMR: δ 19 (s). $^{29}Si\{^1H\}$ NMR: δ −22.7. MS(CI): $m/z = 504$ [M$^+$], 461 [M$^+$ − NMe_2], 444 [M$^+$ − $ONMe_2$], 418 [M$^+$ − $2NMe_2$], 356 [$C_4Ph_4^+$], 266 [$C_3Ph_3^+$], 178 [$C_2Ph_2^+$]. Analysis for $C_{32}H_{32}O_2N_2Si\cdot0.5C_6H_6$ (M = 543.74): calcd. C 77.31, H 6.49, N 5.15: found C 75.57, H 6.58, N 4.55%.

1,1-Bis(*N*,*N*-dimethylaminoxy)-2,3,4,5-tetraphenyl-1-germacyclopentadiene (3)

The procedure is analogous to the preparation of **2**, with the following quantities of reagents employed: *n*-butyllithium (0.4 g, 6 mmol, 1.7 M in hexane), *N*,*N*-dimethylhydroxylamine (1.0 ml, 14 mmol) in 25 ml pentane, 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene (1.49 g, 3 mmol) dissolved in 30 ml THF. Yield 60% (1.98 g, 3.6 mmol), yellow, hexagonally-shaped crystals. ^{1}H NMR: δ 2.54 (s, H_3C), 6.84–7.58 (m, Ph-H). $^{13}C\{^1H\}$ NMR: δ 50.9 (CH_3), 152.0, 139.2, 138.9, 132.7, 130.1, 129.9, 127.8, 127.7, 127.5, 126.5 (Ph-C/1-germacyclopentadiene-C). $^{15}N\{^1H\}$ NMR: δ −256.8 (s). MS(CI): $m/z = 550$ [M$^+$], 490 [M$^+$ − $ONMe_2$], 356 [$C_4Ph_4^+$], 178 [$C_2Ph_2^+$]. Analysis for $C_{32}H_{32}O_2N_2Ge$ (M = 549.2): calcd. C 69.98, H 5.87, N 5.10, found C 66.82, H 6.40, N 4.66%.

Crystal structure determinations

Single crystals of **2** and **3** were mounted under inert perfluoropolyether on the goniometer of a CAD4 diffractometer. Details of the data collection and refinement are listed in Table 3. The structure solution was performed by direct methods, the refinement based on F^2 and carried out with the SHELXTL 5.01 program.[21]

CCDC reference number 186/1848.

See http://www.rsc.org/suppdata/dt/a9/a909547k/ for crystallographic files in .cif format.

Acknowledgements

This work was supported by the Bayerisches Staatsministerium für Wissenschaft, Forschung und Kunst (Bayerischer Habilitationsförderpreis 1996 for N. W. M.), the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Leonhard-Lorenz-Stiftung and by Bayer AG through a donation of *N*,*N*-dimethylhydroxylamine hydrochloride. We thank Dr G. Raudaschl-Sieber for measurement of the UV–VIS spectra. Generous support from Prof. H. Schmidbaur (Garching) is gratefully acknowledged.

References

1 K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa and S. Yamaguchi, *J. Am. Chem. Soc.*, 1996, **118**, 11974.

2 S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2327.

3 S. Yamaguchi, R.-Z. Jin and K. Tamao, *J. Organomet. Chem.*, 1998, **559**, 73.

4 S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, 1998, 3693.

5 N. W. Mitzel and U. Losehand, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2807; U. Losehand and N. W. Mitzel, *Inorg. Chem.*, 1998, **37**, 3175.

6 N. W. Mitzel, U. Losehand and A. Richardson, *Organometallics*, 1999, **18**, 2610.

7 N. W. Mitzel, U. Losehand and A. D. Richardson, *Inorg. Chem.*, 1999, **38**, 5323.

8 N. W. Mitzel, U. Losehand and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1999, 4291.

9 N. W. Mitzel and U. Losehand, *J. Am. Chem. Soc.*, 1998, **120**, 7320.

10 N. W. Mitzel, U. Losehand, A. Wu, D. Cremer and D. W. H. Rankin, *J. Am. Chem. Soc.*, in the press.

11 K. Tamao, M. Asahara and A. Kawachi, *J. Organomet. Chem.*, 1996, **521**, 325.

12 E. H. Braye and W. Hübel, *Chem. Ind.*, 1959, 1250.

13 E. H. Braye, W. Hübel and I. Chaplier, *J. Am. Chem. Soc.*, 1961, **83**, 4406.

14 P. Jutzi and A. Karl, *J. Organomet. Chem.*, 1981, **214**, 289.

15 J. Ferman, J. P. Kakareka, W. T. Kloster, J. L. Mullin, J. Quattrucci, J. S. Ricci, H. J. Tracy, W. J. Vining and S. Wallace, *Inorg. Chem.*, 1999, **38**, 2465.

16 N. W. Mitzel and U. Losehand, *Eur. J. Inorg. Chem.*, 1998, 2023.

17 L. Párkányi, *J. Organomet. Chem.*, 1981, **216**, 9.

18 L. S. Bartell, *J. Chem. Phys.*, 1960, **32**, 827.

19 C. Glidewell, *Inorg. Chim. Acta*, 1975, **12**, 219.

20 L. I. Smith and H. H. Hochni, *J. Am. Chem. Soc.*, 1941, **63**, 1184.

21 SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc., Madison, WI, 1995.

Paper a909547k