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Hypervalent and binuclear silicon and germanium derivatives from bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide

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Abstract

The reactions of bis-(3,5-di-*tert*-butyl-2-phenol)oxamide (**1**) with Cl_2SiR_2 (Me or Ph) or Cl_2GeR_2 (Me, *n*Bu or Ph) in THF provided binuclear pentacoordinated silicon and germanium compounds: bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-dimethylsilane (**2**), bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-diphenylsilane (**3**), bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-dimethylgermane (**4**), bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-di-*n*-butylgermane (**5**) and bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-diphenylgermane (**6**). The mono-nuclear tetracoordinated silicon compounds *N*-acetyl-bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-amide-bis-(dimethylsilane) (**8**) and *N*-acetyl-bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-amide-bis-(diphenylsilane) (**9**) were synthesized from *N-(3,5-di-tert-butyl-2-phenol)acetamide* (**7**) and Cl_2SiR_2 (R = Me and Ph). Comparison of the ^{29}Si NMR chemical shifts of the penta- (**2 and 3**) and tetracoordinated (**8 and 9**) silicon compounds provided information about the intramolecular coordination of the carbonyl group to the silicon atom. Compounds **3** and **6** were characterized by single-crystal X-ray analyses. They have planar hexacyclic structures where the central atoms present distorted tbp geometries with one nitrogen and two carbon atoms in equatorial positions and two oxygen atoms in apical positions.

Keywords: Organosilane; Organogermane; X-ray structures; ^{29}Si NMR; Aromatic hexacycles

1. Introduction

The group 14 elements show a versatile chemistry due to their diverse electronegativities and metallic characters and to their ability to show hypervalent coordination numbers [1]. Even though pentacoordinated silicon atoms were first described in the beginning of XIX century by Gay-Lussac [2] and Davy [3], it is only in the last three decades that silicon and germanium compounds with high coordination numbers have been widely studied, due to their structural interest and applications in synthesis [4–6]. On the other hand, oxamides are well known as excellent ligands with transition metals and have been the subject of several reviews [7,8]; however less attention has been paid to oxamide coordination compounds with main group elements. Indeed there are scarce reports of solid state analyses of these kinds of crystalline structures [9–14]. Additionally, oxamides have been described as inhibitors of HIV [15,16] and responsible of hypoglycemic activity [17].

We recently reported the synthesis and characterization of pentacoordinated tin compounds derived from the symmetric bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide (**1**) [18,19] as well as optically active oxamides [20] (Scheme 1).

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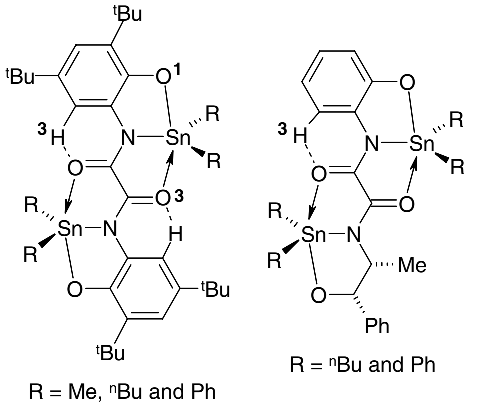


Scheme 1. Tin compounds derived from ligand **1** [18,19] and from (1*S*,2*R*)-(−)-[*N*-(2-hydroxy-1-methyl-2-phenyl-ethyl)-N′-(2-hydroxy- phenyl)-oxalamide [20]. The distance of the C–H3 proton to the C=O is ≈2.2–2.4 Å.

Continuing with this research based on coordination compounds of main group elements, we decided to prepare the corresponding organosilicon and organogermanium binuclear compounds derived from ligand **1**, in order to establish a comparative study of their structures and spectroscopic properties with those of the tin compounds, already reported. It was important to determine if silicon or germanium atoms could become hypervalent. Furthermore, in order to evaluate the coordination bond in the silicon compounds by ^{29}Si NMR, we have prepared two tetracoordinated silicon derivatives from *N*-(3,5-di-*tert*-butyl-2-phenol)-acetamide (**7**) to be used as models of tetracoordinated silicon compounds.

2. Results and discussion

The bis-(2-phenol)-oxamide is a planar molecule with two strong bifurcated N–H hydrogen bonds. It is interesting to note that the C3–H forms a short hydrogen bond with the carbonyl oxygen (2.22 Å). Furthermore, the planar conformation forces the C3–H proton to approach the carbonyl group shifting the ^{1}H signal to higher frequencies [21], Fig. 1a. The substituted oxamide molecule bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide has a different conformation where the OH group is not on the same side as the N–H. A view of its solid state structure is shown in Fig. 1b. The ^{1}H NMR spectra confirm that the same conformation was found in solution, as was deduced from the C3–H signal, $\delta = 7.31$ ppm. This fact could be explained by this different conformation where the O–H proton can avoid the steric effect produced by the *tert*-butyl group [19].

However, in spite of the preferred non-planar structure of ligand **1**, the tin derivatives acquire a planar conformation in order to form bimetallic fused hexacycles. The ligand acts as a clamp, due to the high acidity of the OH and NH protons. The metal atom which takes their place becomes a very acidic center. This atom has the effect of imposing a rigid and planar structure on the ligand, which in turn forces the C=O so close to the metal that it cannot avoid coordination with it, giving strongly bonded penta-

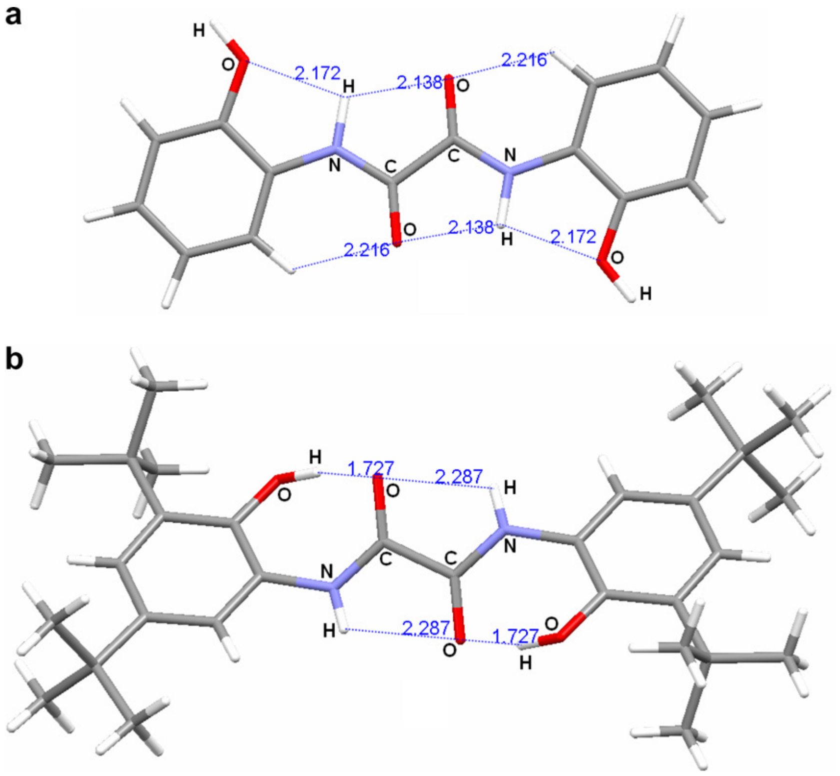


Fig. 1. (a) Solid state structures for *bis*-(2-phenol)oxamide [21], and (b) bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide [19].

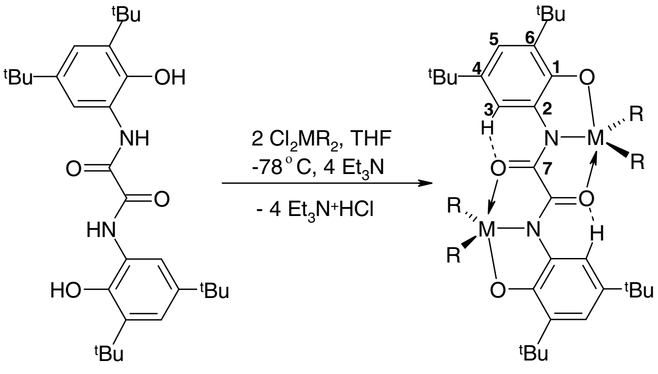
coordinated tin atoms [19], (C=O → Sn coordination bond length is 2.22 Å, while the covalent bond O–Sn is 2.06 Å), Scheme 1. As a consequence of these findings, we decided to prepare the corresponding hypervalent silicon and germanium compounds and to explore, if in spite of the fact that these elements have less metallic character than tin, the structure of the ligand could force the formation of isostructural pentacoordinated compounds, especially in the case of silicon which has a weaker metallic character.

Treatment of quinone **1** with Cl_2SiR_2 (R = Me or Ph) or Cl_2GeR_2 (R = Me, ^{n}Bu or Ph) in THF and NEt_3 at low temperature resulted in the pentacoordinated silicon and germanium binuclear derivatives in good yield (Scheme 2), Both compounds are isostructural with the tin compounds previously reported [19].

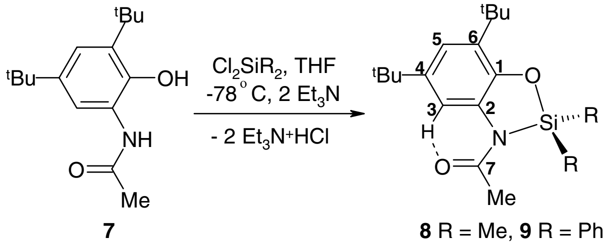
Under the same conditions, the reaction of the phenolamide **7** with Cl_2SiR_2 (R = Me or Ph) afforded the tetracoordinated organosilicon compounds **8** and **9** (Scheme 3).

The silicon derivatives **2**, **3**, **8** and **9** are unstable in the presence of air and moisture whereas the germanium compounds **4**–**6** are very stable. All compounds were characterized by NMR in solution and the molecular structures of **3** and **6** were determined in the solid state by X-ray crystallography.

The mass analyses show the molecular ions of compounds **2** [M^+] 608, **3** [M^+] 856, **4** [M^+] 698, **5** [M^+] 867, and **6** [M^+] 946. In all cases, the first loss observed corresponds to the organyl groups bonded to the central atom, indicating that the hexacyclic framework is very stable.



Scheme 2. Heterobinuclear compounds derived from oxamides.



Scheme 3. Synthesis of tetracoordinated silicon compounds.

Comparison of the IR stretching vibrations of the C=O groups in **2** (1664 cm^{-1}) and **3** (1666 cm^{-1}) and the free ligand (1662 cm^{-1}), does not clearly indicate the presence of an intramolecular coordination of the oxygen towards the silicon atoms. This may be due to the fact that the free ligand shows a strong intramolecular coordination of the N–H proton.

2.1. NMR studies

An important probe for the coordination to silicon or germanium in solution, is the shift to higher frequencies of the ^{1}H NMR signals for H-3 [**2** (8.12), **3** (8.22), **4** (8.32), **5** (8.24), **6** (8.52 ppm)], with respect to the signal in ligand **1** (7.31 ppm). This shift could be due to the proximity of the carbonyl group to H3, when the molecules **2**–**6** adopt a planar conformation. This intramolecular interaction is confirmed in the solid state of **3** and **6** by X-ray diffraction, which showed a short distance C3–H···O=C (2.45 Å in **3** and 2.30 Å in **6**).

The ^{29}Si NMR spectra of the organosilicon compounds **2** and **3** shows a singlet at δ ^{29}Si = −21.6 and −60.9 ppm, respectively, which correspond to pentacoordinated silicon atoms [22]. The ^{29}Si chemical shift difference between **2** and **3** is due to the electronic properties of the Si–Me and Si–Ph groups. In order to confirm the pentacoordinated structure of the silicon compounds **2** and **3**; model compounds without the carbonyl group were prepared. The synthesis of tetracoordinated organosilicon compounds was carried out as described in Scheme 3. The ^{29}Si spectra of compounds **8** and **9** exhibit resonances (at −10.1 and −11. 8 ppm, respectively) which correspond to tetracoordinated silicon atoms. Comparison of ^{29}Si data of compounds **2**, **3**, **8** and **9**, clearly indicates the pentacoordination of **2** and **3**, and confirms the same molecular structures in solution and in solid state (*vide infra*).

2.2. X-ray diffraction analyses

Structures of compounds **3** and **6** are similar. Compound **3** is shown in Fig. 2. Both compounds have two silicon or two germanium atoms in hexacyclic planar arrays. Based on the bond angles analyses, it is deduced that the central atoms present a tbp geometry with a distortion due to rings tension. One nitrogen and two carbon atoms are in equatorial positions and two oxygen atoms are in apical positions (Fig. 1). Selected bonds and angles are presented in Table 1 and compared with data of the analogue tin compound [19].

The five bond lengths around the central atom are slightly longer than covalent bonds indicating delocalized structures with some anionic character at the silicon or germanium atom and a delocalized positive charge in the ligand. N1–C1 and C1–O1 bonds of the oxamide group have double bond character, whereas the central C1–C1 bond lengths correspond to single bonds. It is quite interesting that N–C=O angles are wide (127.8–132.5°), Table

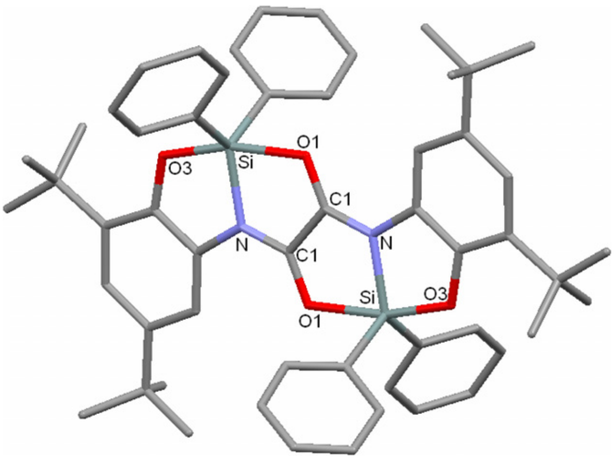


Fig. 2. Single crystal X-ray diffraction of compound **3**. Hydrogen bonds are omitted for clarity.

1. As expected, the central atom bond lengths increase in the order Si < Ge < Sn, and the less distorted bpt geometry is that of the silicon, due to a longer N–Si bond and the smaller size of the silicon atom.

Compound **3** shows, in the unit cell, three $CHCl_3$ molecules. One of them is disordered over two positions. Compound **6** shows two molecules in the unit cell with one disordered molecule of THF.

3. Summary

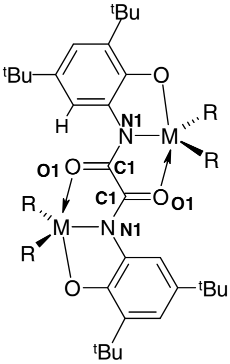
Reactions of bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide (**1**) with diorganyldichlorosilicon and germanium reagents gave selectively bimetallic hexacyclic symmetric heterocycles bearing pentacoordinated silicon or germanium compounds. The silicon atoms are strongly coordinated by the carbonyl group, in solution, as was deduced from the ^{29}Si NMR, and in solid state, as was determined by X-ray diffraction. It was confirmed that the structure of ligand **1** allows a strong coordination to silicon atoms, comparable to that of germanium and tin atoms.

4. Experimental

4.1. General comments

All manipulations were carried out in a vacuum line. THF was dried by distillation from sodium–benzophenone. NEt_3 was dried by distillation from KOH and then from CaH_2. The organosilicon and organogermanium compounds were purchased from Aldrich and used without further purification. The bis-(3,5-di-*tert*-butyl-2-phenol)-oxamide was prepared according to the literature [19]. The melting points were obtained on a Mel-Temp II apparatus and are uncorrected. IR spectra were recorded on an FT-IR 1600 Perkin–Elmer spectrophotometer using KBr pellets in the 4000–400 cm^{-1} range. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett–Packard HP 5989 spectrometer. Fast atom bombardment mass spectrometry (FAB+) was performed on a Jeol SX102A instrument of inverted geometry, in a matrix of 3-nitrobenzyl alcohol and in the 0–2200 *m*/*z* range. Elemental analyses were performed on Eager 300 equipment. NMR spectra

Table 1
Selected bond lengths and angles for **3**, **6** and their tin analogue [19]



Bonds	Sn^{19}	Ge	Si	Angles	
M–O1	2.22(1)	2.204(3)	2.026(5)	O1–Si–O3	166.9(2)
M–O3	2.07(1)	1.864(3)	1.739(5)	O1–Ge–O3	161.84(12)
M–N	2.15(1)	1.937(4)	1.852(5)	O1–Sn–O3	151.4(3)
M–C	2.12(1)	1.936(5)	1.869(8)	C–Si–C	119.3(3)
M–C	2.14(1)	1.937(5)	1.856(6)	C–Ge–C	120.3(2)
C2–N1	1.41(1)	1.427(5)	1.410(9)	C–Sn–C	129.7(4)
C1–N1	1.30(1)	1.311(5)	1.301(9)	(Si) N1–C1–O1	132.5(6)
C1–C1	1.52(2)	1.511(5)	1.489(9)	(Ge) N1–C1–O1	129.3(4)
O1–C1	1.28(1)	1.257(5)	1.273(8)	(Sn) N1–C1–O1	127.8(4)

were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Advance 300 MHz.

4.2. Syntheses

*4.2.1. Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(dimethylsilane) (**2**)*

General procedure for compounds **2**–**6** and **8**–**9**.

To a solution of 0.1 g (0.2 mmol) of oxamide **1** in THF (15 mL) at 0 °C was added dropwise *via* syringe NEt_3 (0.1 mL, 0.083 mmol). After 1 h $SiMe_2Cl_2$ (0.05 mL, 2 mmol) was added dropwise at −78 °C. The reaction mixture was warmed to rt and stirred for 18 h. The solvent was evaporated *in vacuum* and the residue washed twice with cold THF (5 mL) to yield an orange solid of **2** (112 mg, 92%). Mp: 284–286 °C. NMR ($CDCl_3$): ^1H δ 0.62 (CH_3, Me_2Si), 1.37 (s, *t*-Bu-4, 18 H), 1.42 (s, *t*-Bu-6, 18H), 7.18 [d, H5, ^4J(H,H) 2.2 Hz, 2H], 8.12 [d, H3, ^4J(H,H) 2.2 Hz, 2H]. ^{13}C: δ 2.28 (CH_3, Me_2Si), 29.3 [(CH_3) *t*-Bu–C6], 31.8 [(CH_3) *t*-Bu–C4, 34.8 (*t*-Bu–C6)], 35.6 (*t*-Bu–C4), 112.6 (C3), 121.7 (C5), 127.9 (C2), 134.8 (C6), 140.5 (C4), 148.6 (C1), 157.6 (C7). ^{29}Si: δ −21.6 ppm. MS (EI, 20 eV) *m*/*z*: [M^+] 608. IR (KBr) v (cm^{-1}): 1664 (C=O), 1483, 1433, 1361, 1261. Anal. Calc. for $C_{34}H_{52}N_2O_4Si_2$ THF: C, 67.06; H, 8.61; N, 4.60. Found: C, 67.41; H, 8.33; N, 4.14%.

*4.2.2. Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(diphenylsilane) (**3**)*

Compound **3** is an orange solid (320 mg, 95%). Mp: 296–298 °C. NMR $CDCl_3$ ^1H, δ 1.42 (s, *t*-Bu-4, 18H), 1.50 (s, *t*-Bu-6, 18H), 7.29 [d, H5, ^4J(H,H) 2.2 Hz, 2H], 8.21 [d, H3, ^4J(H,H) 2.2 Hz, 2H], 7.32 [m, *m*,*p*-H, Ph_2Si, 12H], 8.00 [d, *o*-H, Ph_2Si, ^3J(H,Sn) 69 Hz, 8H]. ^{13}C: δ 29.8 [(CH_3) *t*-Bu–C6], 31.7 [(CH_3) *t*-Bu–C4], 31.3 (*t*-Bu–C6), 34.8 [(C) *t*-Bu–C4], 113.0 (C3), 122.9 (C5), 127.1 (C2), 134.0 (C6), 141.6 (C4), 149.1 (C1), 157.6 (C7), 134.9 (C-*i*, Ph_2Si), 136.4 (C-*o*, Ph_2Si), 128.6 (C-*m*, Ph_2Si), 130.9 (C-*p*, Ph_2Si). ^{29}Si: δ −60.9 ppm. MS (EI, 20 eV): [M^+] 856 *m*/*z*. IR (KBr) v (cm^{-1}): 1666 (C=O), 1480, 1434, 1387, 1303, 1262. Anal. Calc. for $C_{54}H_{60}N_2O_4Si_2$ $CHCl_3$: C, 67.06; H, 6.29; N, 2.86. Found: C, 67.14; H, 6.15; N, 2.69%.

*4.2.3. Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(dimethylgermane) (**4**)*

Compound **4** is an orange microcrystalline solid (135 mg, 97%). Mp: 390 °C. NMR ($CDCl_3$), ^1H: δ 0.99 (CH_3, Me_2Ge), 1.36 (s, *t*-Bu-4, 18 H), 1.44 (s, *t*-Bu-6, 18H), 7.16 [d, H5, ^4J(H,H) 2.3 Hz, 2H], 8.42 [d, H3, ^4J(H,H) 2.3 Hz, 2H]. ^{13}C: δ 5.85 (CH_3, Me_2Ge), 29.3 [(CH_3) *t*-Bu–C6], 31.9 [(CH_3) *t*-Bu–C4], 34.7 (*t*-Bu–C6), 35.1, (*t*-Bu–C4], 113.7 (C3), 121.5 (C5), 127.6 (C2), 135.2 (C6), 139.0 (C4), 151.0 (C1), 158.5 (C7). MS (EI, 20 eV, DIP): [M^+] 698 *m*/*z*. IR (KBr) v (cm^{-1}): 1634 (C=O), 1478, 1424, 1360, 1260. Anal. Calc. for $C_{34}H_{52}N_2O_4Ge_2$: C, 58.51; H, 7.51; N, 4.01. Found: C, 58.94; H, 7.69; N, 3.95%.

*4.2.4. Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(di-n-butylgermane) (**5**)*

Compound **5** is an orange solid (330 mg, 95%), dec at 350 °C. NMR ($CDCl_3$), ^1H: δ 0.80 (t, CH_3-δ, *n*-Bu_2Ge, 12H), 1.42–1.72 [m, CH_2-α,β,γ, *n*-Bu_2Ge, 8 H], 1.27 (s, *t*-Bu-4, 18 H), 1.38 (s, *t*-Bu-6, 18H), 7.06 [d, H5, ^4J(H,H) 2.2 Hz, 2H], 8.25 [d, H3, ^4J(H,H) 2.2 Hz, 2H]. ^{13}C: 13.8 (CH_3-δ, *n*-Bu_2Ge), 22.6 [CH_2-α, *n*-Bu_2Ge), 25.7 [CH_2-γ, *n*-Bu_2Ge], 26.2 [CH_2-β, *n*-Bu_2Ge], 29.44 [(CH_3) *t*-Bu–C6], 31.9 [(CH_3) *t*-Bu–C4], 34.7 (*t*-Bu–C6), 35.1 (*t*-Bu–C4), 113.8 (C3), 121.3 (C5), 128.0 (C2), 135.1 (C6), 138.8 (C4), 151.4 (C1), 158.7 (C7). EM (FAB+): 867 *m*/*z*. IR (KBr) v (cm^{-1}): 1631 (C=O), 1477, 1422, 1359, 1263. Anal. Calc. for $C_{46}H_{76}N_2O_4Ge_2$: C, 63.78; H, 8.84; N, 3.23. Found: C, 63.45; H, 8.95; N, 2.89%.

*4.2.5. Bis-(3,5-di-tert-butyl-2-oxo-phenyl)-oxamido-bis-(diphenylgermane) (**6**)*

Compound **6** is an orange microcrystalline solid (340 mg, 89.5%). It was recrystallized in $CHCl_3/C_6H_6$ (2:8). Mp: 316 °C. NMR ($CDCl_3$), ^1H: δ 1.43 (s, *t*-Bu-4, 18 H), 1.64 (s, *t*-Bu-6, 18H), 7.33 [d, H5, ^4J(H,H) 6.9 Hz, 2H], 8.68 [d, H3, ^4J(H,H) 6.9 Hz, 2H], 7.40 (m, *m*,*p*-H, Ph_2Ge, 12H), 7.90 (d, *o*-H, Ph_2Ge, 8H). ^{13}C δ 29.9 [(CH_3) *t*-Bu–C6], 31.9 [(CH_3) *t*-Bu–C4], 35.0 (*t*-Bu–C6), 35.8 (*t*-Bu–C4), 115.9 (C3), 122.8 (C5), 128.3 (C2), 137.4 (C6), 138.5 (C4), 153.0 (C1), 158.1 (C7), 138.0 C-*i*, Ph_2Ge), 136.4 (C-*o*, Ph_2Ge), 128.6 (C-*m*, Ph_2Ge), 130.9 (C-*p*, Ph_2Ge). MS (FAB+) [M^+] 945 *m*/*z*. IR (KBr) v (cm^{-1}): 1633 (C=O), 1478, 1426, 1360, 1255. Anal. Calc. for $C_{54}H_{60}N_2O_4Ge_2$: C, 59.92; H, 5.79; N, 2.44. Found: C, 60.14; H, 5.83; N, 2.47%.

*4.2.6. N-(3,5-di-tert-Butyl-2-phenol)acetamide (**7**)*

A solution of 4,6-di-*tert*-butyl-2-aminophenol (2.0 g, 9.1 mmol) in acetic anhydride (25 mL) and in water (20 mL) was refluxed for 30 min, then the precipitate was filtered and washed with cold water. A white solid was obtained (2.3 g, 94%). Mp: 143–145 °C. NMR ($CDCl_3$), ^1H: δ 2.22 (t, CH_3, H-8, 3H), 1.23 (s, *t*-Bu-4, 9 H), 1.38 (s, *t*-Bu-6, 9H), 6.78 [d, H5, ^4J(H,H) = 2.1 Hz, 1H], 7.12 [d, H3, ^4J(H,H) = 2.1 Hz, 1H)], 7.28 (s, –OH, 1H), 8.41 (bs, –NH, 1H). ^{13}C: δ 23.67 (C8), 29.8 (*t*-Bu–C4), 31.7 (*t*-Bu–C6), 34.4 (*t*-Bu–C4), 35.6 (*t*-Bu–C6), 117.8 (C3), 122.4 (C5), 142.6 (C2), 140.2 (C6), 126.0 (C4), 146.5 (C1), 170.9 (C7). ^{15}N: δ −245 ppm, ^1J(^{15}N, ^1H) = 91 Hz. MS; (EI, 20 eV) *m*/*z* [M^+] 263. IR (KBr) v (cm^{-1}) O–H 3330, N–H 3275, C=O 1628, 1420, 1359, 1314, 1235, 951.

*4.2.7. N-Acetyl-bis-(3,5-di-tert-butyl-2-oxo-phenyl)-amide-bis-(dimethylsilane) (**8**)*

Compound **8** is an orange microcrystalline solid (105 mg, 90%). Mp: 226–228 °C. NMR ($CDCl_3$), ^1H: δ 0.15 (CH_3, Me_2Si), 1.27 (s, *t*-Bu-4, 18 H), 1.44 (s, *t*-Bu-6, 18H), 2.19 [s, Me–C(O)–], 6.82 [d, H5, ^4J(H,H) 2.2 Hz, 2H], 7.23 [d, H3, ^4J(H,H) 2.2 Hz, 2H]. ^{13}C: δ 0.52 (CH_3, Me_2Si), 29.9 (*t*-Bu–C6), 31.6 (*t*-Bu–C4), 34.4 (*t*-Bu–C6), 35.6 (*t*-Bu–C4), 117.9 (C3), 122.2 (C5), 126.2 (C2), 140.0 (C6), 142.4 (C4), 146.1 (C1), 171.1 (C7). ^{29}Si: δ −10.1 ppm.

4.2.8. N-Acetyl-bis-(3,5-di-tert-butyl-2-oxo-phenyl)-amide-bis-(diphenylsilane) (9)

Compound **9** is an orange microcrystalline solid (270 mg, 82%). Mp: 268–269 °C. NMR (CDCl$_3$), ^{1}H: δ 1.97 [s, MeC(O)–, 3H], 1.42 (s, *t*-Bu-4, 18 H), 1.50 (s, *t*-Bu-6, 18H), 7.29 [d, H5, ^4J(H,H) 2.2 Hz, 2H], 8.21 [d, H3, ^4J(H,H) 2.2 Hz, 2H], 7.32 (m, *m*,*p*-H, Ph$_2$Si, 12H), 8.00 (d, *o*-H, Ph$_2$Si, 8H). ^{13}C: δ 23.27 (CH$_3$CO), 29.8 (*t*-Bu–C6), 31.7 (*t*-Bu–C4), 31.3 (*t*-Bu–C6), 34.8 (*t*-Bu–C4), 113.0 (C3), 122.9 (C5), 127.1 (C2), 134.0 (C6), 141.6 (C4), 149.1 (C1), 157.6 (C7), 134.9 (C-*i*, Ph$_2$Si), 136.4 (C-*o*, Ph$_2$Si), 128.6 (C-*m*, Ph$_2$Si, 130.9 (C-*p*, Ph$_2$Si). ^{29}Si: δ −11.8 ppm.

4.3. X-ray structural analysis of 3 and 6

Data were measured on a Nonius Kappa CCD instrument with area detector using graphite-monochromated Mo Kα radiation. Intensities were measured using $\varphi + \omega$ scans. Both structures were collected at rt. Compound **3** crystallized with three disordered CHCl$_3$ molecules in the unit cell. One of them is on an inversion center. All C–Cl bonds were restricted to have similar distances, the crystals of **3** are triclinic, space group $P\bar{1}$ [$a = 10.7886(6)$, $b = 11.8720(6)$, $c = 13.3859(8)$ Å; $\alpha = 111.1619(19)$, $\beta = 93.046(2)$, $\gamma = 99.783(2)$; $R_1 = 0.059$; $wR_2 = 0.0985$]. Compound **6** crystallized in the monoclinic space group $P2_1/c$, [$a = 16.8830(2)$, $b = 18.2799(3)$, $c = 20.1597(3)$ Å; $\beta = 106.5040(10)$; $R_1 = 0.066$; $wR_2 = 0.0668$] with one disordered THF and two water molecules in the asymmetric unit. The three solvent molecules have high thermal parameters. In both structures, all hydrogen atoms were geometrically placed, and were allowed to ride on their respective atoms. Structures were solved using direct methods with SHELX-97 [23] and the refinement for all structures (based on F^2 of all data) was performed by full matrix least-squares techniques with Crystals 12.84. All non-hydrogen atoms were refined anisotropically.

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Appendix A. Supplementary material

CCDC 654612 and 654611 contains the supplementary crystallographic data for **3** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.042.

References

[1] R.R. Holmes, Chem. Rev. 96 (1996) 927;
R.R. Holmes, Chem. Rev. 90 (1990) 17.

[2] J.L. Gay-Lussac, L.J. Thenard, Memoires de Physique et de Chimie de la Societe d' Arcueil 2 (1809) 317.

[3] J. Davy, Philos. Trans. Roy. Soc. London 102 (1812) 352.

[4] C. Chuit, R.J.P. Corriu, C. Reyé, in: K.-Y. Akiba (Ed.), Chemistry of Hypervalent Compounds, Wiley, New York, 1999, p. 81, Chapter 4.

[5] D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 1339, Chapter 23.

[6] E. Lukevics, L.M. Ignatovich, Appl. Organomet. Chem. 6 (1992) 113.

[7] H. Ojima, K. Nonoyama, Coord. Chem. Rev. 92 (1988) 85.

[8] R. Ruiz, J. Faus, F. Lloret, M. Julve, Y. Journaux, Coord. Chem. Rev. 193–195 (1999) 1069.

[9] U. Beckmann, E. Bill, T. Weyhermüller, K. Wieghardt, Eur. J. Inorg. Chem. (2003) 1768.

[10] F.J. Martínez-Martínez, J.L. Leon-Romo, I.I. Padilla-Martínez, M.J. Rosales-Hoz, R. Contreras, Phosphorous, Sulfur, Silicon Relat. Elements 115 (1996) 217.

[11] P.P.K. Claire, G.R. Willey, M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1987) 263.

[12] V.W. Klein, D. Krauss, H.P. Latscha, Z. Anorg. Allg. Chem. 401 (1973) 85.

[13] P. Fischer, R. Graf, J. Weidlein, J. Organomet. Chem. 144 (1978) 95.

[14] H.U. Schwering, J. Weidlein, P. Fischer, J. Organomet. Chem. 84 (1975) 17.

[15] M. Medou, G. Priem, G. Quélever, M. Camplo, J.L. Kraus, Tetrahedron Lett. 39 (1998) 4021.

[16] P.K. Hadhav, H.W. Man, Tetrahedron Lett. 37 (1996) 1153.

[17] J. Moronfolu, M. Ojo, Jpn. J. Pharmacol. 49 (1989) 135.

[18] R. Contreras, V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Rodríguez, B. Wrackmeyer, J. Organomet. Chem. 604 (2000) 229.

[19] V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, H. Nöth, R. Contreras, J. Organomet. Chem. 284 (2000) 614.

[20] V.M. Jiménez-Pérez, H. Nöth, A. Ariza-Castolo, A. Flores-Parra, R. Contreras, J. Organomet. Chem. 691 (2006) 1584.

[21] F.J. Martínez-Martínez, I.I. Padilla-Martínez, M.A. Brito, E.D. Geniz, R.C. Rojas, J.B.R. Saavedra, H. Höpfl, M. Tlahuextl, R. Contreras, J. Chem. Soc., Perkin Trans. 2 (1998) 401.

[22] (a) E.A. Williams, Ann. Rep. NMR Spectrosc. 15 (1983) 235;
(b) E.A. Williams, J.D. Cargioli, Ann. Rep NMR Spectrosc. 9 (1979) 221.

[23] SHELXS-96. G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.