

Addition of Nitromethane to a Disilene and a Digermene: Comparison to Surface Reactivity and the Facile Formation of 1,3,2-Dioxazolidines**

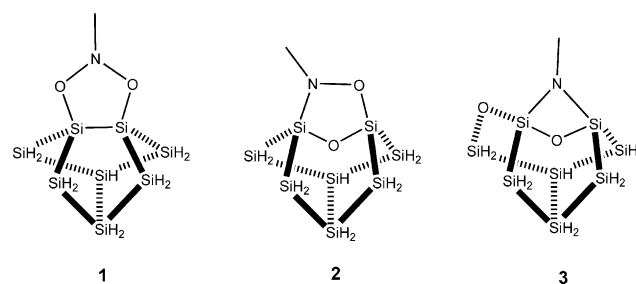
Nada Y. Tashkandi, Frederick Parsons, Jiacheng Guo, and Kim M. Baines*

Abstract: The addition of nitromethane to tetramesityldisilene and tetramesityldigermene leads to the formation of the novel 1,3,2,4,5-dioxazadisil- and digermolidine ring systems, respectively. The 1,3,2,4,5-dioxazadisilolidine isomerizes to the 1,4,2,3,5-dioxazadisilolidine ring system, whereas the 1,3,2,4,5-dioxazadigermolidine undergoes ring opening to the isomeric oxime. The preferential formation of the 1,3,2,4,5-dioxazadisilolidine, and its rearrangement to a 1,4,2,3,5-dioxazadisilolidine, provides support for the suggested reaction pathway between nitromethane and the Si(100) 2 × 1 reconstructed surface.

By attaching complex organic molecules to Group 14 semiconductors, hybrid devices having a semiconductor substrate and an organic surface are possible, with a range of potential applications designed to take advantage of the chemical function of the organic layer. With this objective in mind, the organic functionalization of silicon and germanium surfaces has been widely studied.^[1] Of particular interest to us is the functionalization of Si(100) and Ge(100) 2 × 1 reconstructed surfaces, which are composed of rows of surface dimers isolated by trenches.^[1e] An effective molecular model for the dimers on the Si(100) and Ge(100) reconstructed surfaces can provide valuable insight into the chemistry at the surface, including the structure of surface adducts. Such insight will be critical if a complex functional molecule is to be attached to the surface through a primary layer. Based on our previous work,^[2] we have proposed that tetramesityldisilene^[3] (Mes₂Si=SiMes₂, Mes = 2,4,6-Me₃C₆H₂) and tetramesityldigermene^[4] (Mes₂Ge=GeMes₂) can serve as effective molecular models for the corresponding Si(100) or Ge(100) 2 × 1 reconstructed surfaces, respectively. The main differences between the molecular and surface species are the geometry about the double bond (planar in the case of the disilene^[5] and *trans*-bent in the case of the digermene^[2c] versus *cis* bent on the surface) and the nature of the substituents (aryl versus silyl/germyl). Despite these differences we have shown that

the reactivity of surface disilenes and digermenes are comparable to their molecular counterparts.^[2]

The addition of nitromethane to the Si(100) 2 × 1 surface has been recently studied.^[6] Three different binding energy features were identified by N 1s X-ray photoelectron spectroscopy and assigned to three different types of adducts with the aid of DFT calculations: 1) cycloadduct **1**, with two NO bonds, present as a minor product; 2) adduct(s) **2** where one oxygen of the nitro group inserted into the silicon lattice; and 3) adduct(s) **3** where the two oxygen atoms of the nitro group have inserted into the silicon lattice (major product). The authors proposed that adduct **1** is metastable and rapidly undergoes rearrangement creating Si–O bonds at the expense of N–O bonds (Scheme 1).



Scheme 1. Selected products from the reaction of nitromethane with the Si(100) 2 × 1 surface. Several isomers are possible for **2** and **3**.^[6]

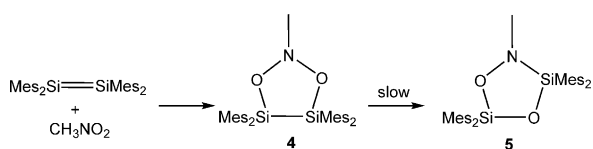
The formation of adduct **1** suggests a rather unusual and interesting reaction pathway for nitroalkanes: 1,3-dipolar cycloaddition through the nitro functional group. Thus, given our use of tetramesityldisilene as a model for the Si(100) reconstructed surface, we have investigated the reaction of nitromethane with tetramesityldisilene and compared our results to those on the surface. For comparison purposes, we have also examined the addition of nitromethane to tetramesityldigermene (see the Supporting Information for experimental details).

The addition of excess nitromethane to a bright yellow solution of tetramesityldisilene in hexanes or C₆D₆ at room temperature gave a pale yellow solution. Removal of the solvent yielded a pale yellow solid, which revealed the presence of compound **4** along with minor amounts of at least two additional products (**5** and **6**) in a 10:1:1 ratio, respectively, by ¹H NMR spectroscopy (Scheme 2). The high-resolution mass spectral data of **4** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the molecular formula Si₂C₃₇H₄₇NO₂, a 1:1 adduct between

[*] N. Y. Tashkandi, F. Parsons, J. Guo, Prof. K. M. Baines
Department of Chemistry, The University of Western Ontario
London, Ontario, N6A 5B7 (Canada)
E-mail: kbaines2@uwo.ca

[**] We thank the NSERC (Canada) and the University of Western Ontario for financial support and the King Abdul Aziz University (Saudi Arabia) for a scholarship to N.Y.T. We also thank Paul Boyle for assistance in the X-ray structure determination of **4** and Margaret A. Hanson for assistance in the computational work.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201409707>.



Scheme 2. Addition of nitromethane to tetramesityldisilene.

tetramesityldisilene and nitromethane. The ^1H NMR spectrum of **4** revealed the presence of two sets of signals assigned to two non-equivalent mesityl groups and a singlet at 3.10 ppm that integrated to 3H, indicating that a methyl group, most likely attached to nitrogen, was present. Only one signal, at 1 ppm, in the ^{29}Si dimension of the ^{29}Si - ^1H gHMBC spectrum of **4** correlated to the signal at 3.10 ppm in the ^1H dimension. The structure of **4** was unambiguously identified as 4,4,5,5-tetramesityl-1,3,2,4,5-dioxazadisilolidine by single-crystal X-ray diffraction (Figure 1).^[19] All bond lengths and angles in **4** are within normal ranges; the structural metrics of the ONO linkage are similar to those of a carbon analogue.^[8]

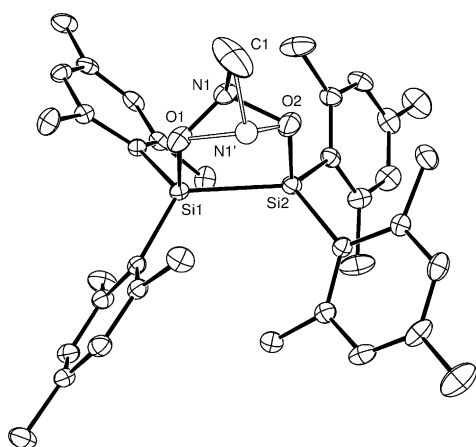
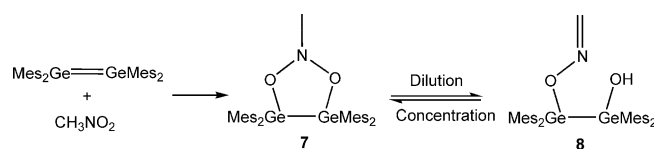


Figure 1. Structure of **4** (ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity) showing the disorder located at the nitrogen atom. Selected bond lengths [Å] and angles [°]: Si1–O1 1.701(17), Si1–Si2 2.41(9), Si2–O2 1.699(18), O1–N1 1.36(3), O2–N1 1.47(3); O1–Si1–Si2 88.47(6), O2–Si2–Si1 87.81(6), N1–O1–Si1 110.72(15), N1–O2–Si2 114.22(15), O1–N1–O2 109.7(2).^[19]

After a long period of time (months), adduct **4** was found to isomerize to **5**. The ^1H NMR spectrum of **5** is similar to that of **4**, with two sets of mesityl groups and a singlet at 3.20 ppm. The signal at 3.20 ppm, assigned to the NCH_3 group, and the signals at 2.36 and 6.64 ppm, assigned to one mesityl group, in the ^1H dimension of the ^{29}Si - ^1H gHMBC spectrum of **5** correlated to the signal at –21 ppm in the ^{29}Si dimension and the signals at 2.55 and 6.64 ppm, assigned to a second mesityl group, correlated to the signal at –18 ppm in the ^{29}Si dimension. Based on the similarity of the ^{29}Si chemical shifts of **5** to those of the closely related N-phenyl analogue,^[9] **5** was identified as 3,3,5,5-tetramesityl-1,4,2,3,5-dioxazadisilolidine.

The addition of excess nitromethane to a bright yellow solution of tetramesityldigermene in THF or hexanes at room



Scheme 3. Addition of nitromethane to tetramesityldigermene.

temperature gave a clear, colorless solution. Evaporation of the solvent yielded a clear, pale yellow oil and analysis of the product by ^1H NMR spectroscopy revealed the formation of compound **7**, which cleanly isomerizes to **8** when the concentration of the solution is lowered (Scheme 3).

Adduct **7** was isolated by recrystallization from a saturated hexanes solution at low temperature. The ^1H NMR spectrum of a concentrated sample of **7** (ca. 0.02 M) is similar to that of **4**, with two sets of signals assigned to non-equivalent mesityl groups. The spectrum also revealed a singlet at 3.18 ppm assigned to a methyl group attached to nitrogen. Single-crystal X-ray diffraction data unequivocally provided the structure of **7** (Figure 2), 4,4,5,5-tetramesityl-1,3,2,4,5-diox-

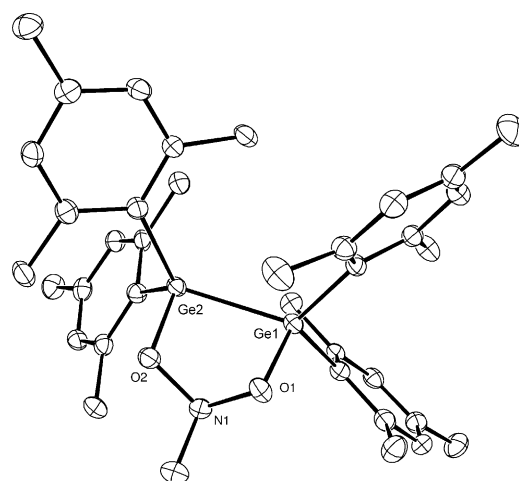


Figure 2. Structure of **7** (ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–O1 1.835(2), Ge2–O2 1.838(2), Ge1–Ge2 2.4963(7), O1–N1 1.447(3), O2–N1 1.454(3), N1–C1 1.461(4); O1–Ge1–Ge2 87.27(6); O2–Ge2–Ge1 86.74(6), N1–O2–Ge2 103.37(15), N1–O1–Ge1 100.68(15), O1–N1–O2 105.41(19).^[19]

zadigermolidine.^[19] All bond lengths and angles are within normal ranges. The identity of the compound in solution was found to be dependent on the concentration of the solution. At higher concentration (ca. 0.02 M), adduct **7** predominates, whereas at lower concentrations (ca. 6×10^{-3} M), **7** tautomerizes to **8**.

The ^1H and ^{13}C NMR spectra of **8** revealed the presence of two non-equivalent mesityl groups. Two doublets were also present in the ^1H NMR spectrum of **8**, at 5.87 and 6.68 ppm, with a coupling constant of 9 Hz. The chemical shifts of the two doublets suggest the presence of vinylic hydrogen atoms. The magnitude of the geminal coupling constant is consistent with that observed between the vinylic hydrogens in the

structurally-related oxime, $(\text{HO}(\text{CH}_2)_2\text{ON}=\text{CH}_2, J = 8 \text{ Hz})$,^[10] After an extended period of time (months), compound **8** predominates in solution; concentrating the solution did not result in the isomerization of **8** back to **7**. Monitoring the conversion of **7** to **8** over two weeks by ^1H NMR spectroscopy revealed direct conversion with no evidence of any intermediate.

Adducts **4** and **7** appear to be derived from a formal [3+2] cycloaddition of nitromethane to the dimetallene to give the unusual 1,3,2-dioxazolidine ring system. The two different mesityl groups observed by ^1H NMR spectroscopy for **4** and **7** leads to the conclusion that the nitrogen does not undergo the rapid inversion typically observed in amines. DFT calculations performed at the TPSS/6-31G(d) level of theory show that the barrier for inversion at the nitrogen in the model compound $\text{MeN}(\text{OGeH}_3)_2$ is 112 kJ mol^{-1} , which is in reasonable agreement with the estimated inversion barrier for the nitrogen in the parent 2H-1,3,2-dioxazolidine (111 kJ mol^{-1})^[12] and sufficiently high for the nitrogen to be configurationally stable.^[13] As a consequence, the mesityl groups exhibit two sets of signals by NMR spectroscopy.

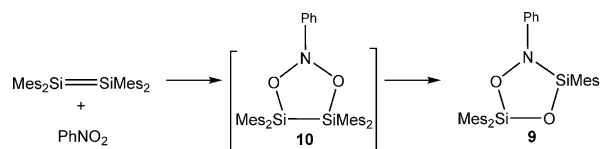
Compounds **4** and **7** are new heterocyclic ring systems containing the O-N-O moiety and are formed easily and in high yield. It is interesting to compare the chemistry of the disilene and digermene with nitromethane to that of an alkene. The reaction of alkenes with nitroalkanes generally proceeds through the nitronate isomer and not by cycloaddition through only the nitro group.^[14] The 1,3,2-dioxazolidine ring system can be generated by a limited number of methods;^[15] however, the synthesis of these ring systems by cycloaddition of a nitro group to an alkene only occurs under special circumstances. Thermally, the reaction proceeds only between highly strained alkenes and aromatic nitro compounds.^[16] The photochemical 1,3-addition of a nitro group to an alkene forming a 1,3,2-dioxazolidine is also known.^[8,17] Thus, the reactivity of nitromethane towards tetramesityldisilene and tetramesityldigermene in terms of both kinetics and reaction pathway was somewhat surprising. The addition reactions are undoubtedly facilitated by weakness of the $\text{M}=\text{M}$ bond and the strength of $\text{M}-\text{O}$ bond.

Although both the silicon and the germanium analogues of the 1,3,2-dioxazolidine ring systems are somewhat stable in solution at room temperature, both are prone to rearrangement albeit by two different pathways. In the case of silicon, the formation of two isomeric products in minor yield was evident in the crude product mixture (namely, **5** and **6**) and **5** grew in over time at the expense of **4**. Isomer **5** is derived from the cleavage of an N-O bond in favor of the formation of a Si-O bond to give the 1,4,2-dioxazolidine ring system, that is, the oxygen inserted into the former Si-Si bond. The 1,4,2,3,5-dioxazadisilolidine ring system was found to be more stable than the 1,3,2 isomer by 342 kJ mol^{-1} as determined by DFT calculations (M06/6-31G(d)). In comparison, the addition of nitromethane to the Si(100) reconstructed surface produces an adduct(s) where both oxygen atoms have inserted into the underlying silicon matrix as the major product. With mesityl groups as the substituents in the molecular system, insertion of oxygen into the Si-C bond of the substituent is less thermodynamically stable in compar-

ison to insertion into a Si-Si bond, and thus does not occur; the substituents of the molecular disilene have a major influence on the products formed. In comparison, the analogous adduct where one oxygen has inserted between the silicon atoms of a surface dimer (**2**, Scheme 1) is only 82 kJ mol^{-1} more stable than adduct **1** because of the constrained geometry of the subsurface silicon substituents, and thus is not formed in appreciable quantities.^[6b] Notably, neither the molecular nor the surface reactions were carried to equilibrium, and thus, the relative ratios of the products is kinetically and not thermodynamically controlled.

In the case of germanium, the 1,3,2-dioxazolidine ring system opens to give oxime **8** which is stabilized by 236 kJ mol^{-1} compared to the 1,3,2-dioxazolidine ring system and by 40 kJ mol^{-1} compared to the 1,4,2-dioxazolidine isomer, as determined by DFT calculations (M06/6-31G(d)). The weaker Ge-O bond apparently does not provide a sufficient driving force for rearrangement to the 1,4,2-dioxazolidine ring system and suggests that the addition of nitromethane to the Ge(100) 2×1 reconstructed surface may be simpler in comparison to the multiple products formed on the silicon surface.

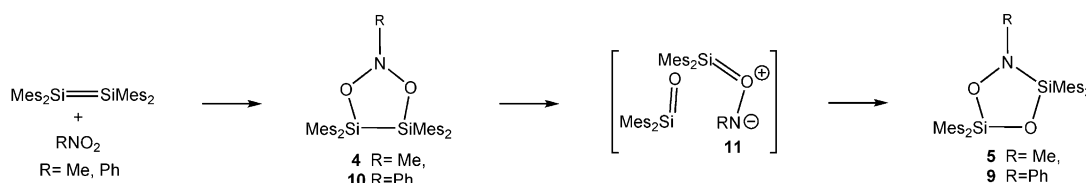
It is also interesting to compare the results of the addition of nitromethane to tetramesityldisilene to that of nitrobenzene performed by West and co-workers.^[9] The addition of nitrobenzene to $\text{Mes}_2\text{Si}=\text{SiMes}_2$ produces 1,4,2,3,5-dioxazadisilolidine **9** as the only product in comparison to the formation of **4**. The mechanism for the formation of **9** was postulated by West to proceed through one of two pathways: [3+2] cycloaddition to give **10** followed by rearrangement to form **9** (Scheme 4) or [2+2] cycloaddition to give a 1,2,3,4-



Scheme 4. Addition of nitrobenzene to tetramesityldisilene.

oxazadisilolidine-*N*-oxide, followed by rearrangement to give **9**. Evidence for the former pathway was provided by monitoring the reaction at low temperature by ^{29}Si NMR spectroscopy. The formation of an intermediate with only one ^{29}Si NMR signal, at 0.64 ppm, was observed suggesting the formation of **10**. More recently, a DFT computational study of the relative stability of the adducts of nitromethane to a model of the Si(100) reconstructed surface suggests that the 1,2,3,4-oxazadisilolidine-*N*-oxide ring system is unstable relative to the 1,4,2,3,5-dioxazadisilolidine ring system.^[6b] Notably, the ^{29}Si chemical shift of **10** is similar to that of **4**, and thus our results provide additional support for the [3+2] dipolar cycloaddition route as proposed by West. In contrast to **4**, **10** undergoes an apparently facile rearrangement to **9** compared to the slow conversion of **4** to the 1,4,2,3,5-dioxazadisilolidine ring system **5** which occurs over an extended period of time in solution at room temperature.

We propose that the formation of **5** (and **9**) follows a mechanism similar to the well-known Criegee mechanism



Scheme 5. Proposed mechanism for the rearrangement of the 1,3,2,4,5-dioxazadisilolidine to the 1,4,2,3,5-dioxazadisilolidine ring system.

for the formation of ozonides (Scheme 5).^[18] Ring cleavage of **4** (or **10**) takes place initially to give dimesitylsilanone and the zwitterionic species **11**. Recombination of these two species gives **5/9**. The rate of this rearrangement appears to depend on the stability of species **11**. With a substituent which can stabilize the negative charge at nitrogen, such as a phenyl substituent, rearrangement is rapid; however, with an alkyl substituent at nitrogen (such as methyl), rearrangement is slow (Scheme 5).

In summary, we have presented a facile way to synthesize the unusual 1,3,2,4,5-dioxazadisilolidine and 1,3,2,4,5-digermolidine ring systems and provided some insight into their rearrangement chemistry. Our work allows for a coherent picture of the chemistry between nitro compounds and molecular and surface disilenes (and digermenes) to emerge. We continue to investigate the scope of the reaction between nitro compounds and Group 14 dimetallenes.

Received: October 2, 2014

Revised: November 8, 2014

Published online: December 8, 2014

Keywords: cycloaddition · digermene · dioxazadisilolidines · disilene · nitromethane

- [1] a) J. S. Kachian, K. T. Wong, S. F. Bent, *Acc. Chem. Res.* **2010**, *43*, 346; b) R. J. Hamers, *Annu. Rev. Anal. Chem.* **2008**, *1*, 707; c) P. W. Loscutoff, S. F. Bent, *Annu. Rev. Phys. Chem.* **2006**, *57*, 467; d) A. Bilić, J. R. Reimers, N. S. Hush in *Properties of Single Organic Molecules on Crystal Surfaces* (Eds.: P. Grütter, W. Hofer, F. Rosei), Imperial College Press, London, **2006**, p. 333; e) J. M. Buriak, *Chem. Rev.* **2002**, *102*, 1271.
- [2] a) J. A. Hardwick, L. C. Pavelka, K. M. Baines, *Dalton Trans.* **2012**, *41*, 609; b) K. L. Hurni, K. M. Baines, *Chem. Commun.* **2011**, *47*, 8382; c) K. L. Hurni, P. A. Rupar, N. C. Payne, K. M. Baines, *Organometallics* **2007**, *26*, 5569; d) S. E. Gottschling, K. K. Milnes, M. C. Jennings, K. M. Baines, *Organometallics* **2005**, *24*, 3811; e) S. E. Gottschling, M. C. Jennings, K. M. Baines, *Can. J. Chem.* **2005**, *83*, 1568; f) M. S. Samuel, K. M. Baines, *J. Am. Chem. Soc.* **2003**, *125*, 12702; g) M. S. Samuel,

- H. A. Jenkins, D. W. Hughes, K. M. Baines, *Organometallics* **2003**, *22*, 1603.
- [3] For a Review of disilene chemistry, see: M. Kira, T. Iwamoto, *Adv. Organomet. Chem.* **2006**, *54*, 73.
- [4] For a Review of digermene chemistry, see: N. Tokitoh, R. Okazaki in *Chemistry of Organic Germanium, Tin, and Lead Compounds* (Ed.: Z. Rappoport), Wiley, New York, **2002**, pp. 843–901.
- [5] M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, J. Michl, *J. Chem. Soc. Chem. Commun.* **1983**, 1010.
- [6] a) J. Eng, Jr., I. A. Hubner, J. Barriocanal, R. L. Opila, D. J. Doren, *J. Appl. Phys.* **2004**, *95*, 1963; b) J. Barriocanal, D. J. Doren, *J. Phys. Chem. B* **2000**, *104*, 12269.
- [7] See the Supporting Information for more details about **6**.
- [8] K. Okada, Y. Saito, M. Oda, *J. Chem. Soc. Chem. Commun.* **1992**, 1731.
- [9] G. R. Gillette, J. Maxka, R. West, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 54.
- [10] D. W. Dixon, R. H. Weiss, *J. Org. Chem.* **1984**, *49*, 4487.
- [11] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.
- [12] I. I. Chervin, V. S. Nosova, V. F. Rudchenko, V. I. Shevchenko, R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.* **1988**, *24*, 396.
- [13] F. A. Davis, R. H. Jenkins Jr., in *Asymmetric Synthesis* (Eds.: J. D. Morrison, J. W. Scott), Vol. 4, Academic Press, New York, **1984**, pp. 313–353.
- [14] N. Ono in *The Nitro Group in Organic Synthesis*, Wiley, Hoboken, **2002**, pp. 231–301.
- [15] a) V. F. Rudchenko, V. I. Shevchenko, R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.* **1989**, *3*, 393; b) V. F. Rudchenko, V. I. Shevchenko, R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR Ser. Khim.* **1985**, 1685; c) V. F. Rudchenko, V. G. Shtamburg, Sh. S. Nasibov, I. I. Chervin, R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR Ser. Khim.* **1980**, 2181.
- [16] J. Leitich, *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 372; *Angew. Chem.* **1976**, *88*, 416.
- [17] a) J. L. Charlton, P. de Mayo, *Can. J. Chem.* **1968**, *46*, 1041; b) J. L. Charlton, C. C. Liao, P. de Mayo, *J. Am. Chem. Soc.* **1971**, *93*, 2463; c) G. Buchi, D. E. Ayer, *J. Am. Chem. Soc.* **1956**, *78*, 689.
- [18] R. L. Kuczkowski, *Chem. Soc. Rev.* **1992**, *21*, 79.
- [19] CCDC 1025988 (**4**) and 1025989 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.