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An Unsymmetric Oxo/Imido-Bridged Germanium-Centered Singlet Diradicaloid

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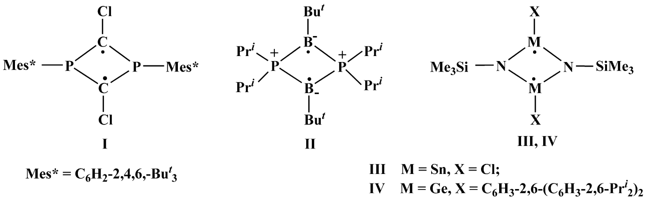
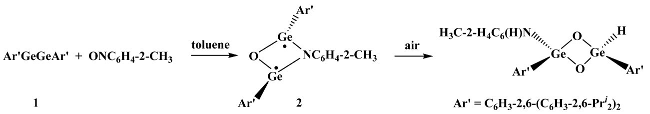
The isolation and characterization of stable singlet diradicaloid derivatives of the main-group elements are of high current interest, and several different classes of diradicaloids are now known.[1] Among the most prominent are those featuring four-membered-ring skeletons, as shown in Scheme 1.[2] These rings incorporate N or P atoms as well as B or a group-14 element. Elegant experimental and theoretical work by Bertrand and Scholler[3a,b] and theoretical studies by various groups[3] showed that the singlet diradical character of the B−P species (**II** in Scheme 1) can be regulated by altering the substitutents on the B or P atoms. In addition, calculations suggested that changing the atoms within the rings could also have a considerable effect on the molecular energy levels and hence the extent of diradical character. This has not been supported by experiments, however.[3a,c] We showed earlier that the reaction of Ar′GeGeAr′ [**1**; Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$] with N_3SiMe_3 afforded the purple diradicaloid Ar′Ge(μ-$NSiMe_3$)$_2$GeAr′ in good yield with N_2 elimination.[2d] The structural data suggested that the bulky aryl ligand Ar′ would be sufficiently large to stabilize rings in which the imido substituents are replaced by smaller atoms or groups. We now report that treatment of **1** with ONC_6H_4-2-CH_3 affords an unsymmetric singlet diradicaloid, the oxo/imido-bridged species Ar′Ge(μ-O)(μ-NC_6H_4-2-CH_3)GeAr′ (**2**), which was characterized by spectroscopy, X-ray crystallography, and density functional theory (DFT) computations. The synthesis of Ar′Ge(μ-O)$_2$GeAr′ was also investigated.

Scheme 1



Dropwise addition of a toluene solution of ONC_6H_4-2-CH_3 to 1 equiv of **1** in toluene at ~0 °C yielded, after workup, purple-black crystals of compound **2** (Scheme 2) in 68% yield. The UV−vis spectrum of **2** in *n*-hexane shows a strong absorption maximum at $\lambda_{max} = 554$ nm ($\varepsilon = 2600\ M^{-1}\ cm^{-1}$). The deep-purple color of **2** disappeared when the compound was heated to 186 °C in a sealed capillary tube.

Scheme 2



The structure of **2** has a planar GeNGeO core arrangement (Figure 1a). The coordination geometry at Ge is pyramidal (sum of interligand angles = 318.6°) and that at N is trigonal-planar (sum of interligand angles = 359.7°). The two Ar′ rings are disposed in a trans fashion across the four-membered GeNGeO ring. The Ge−N bond lengths [1.866(8) and 1.888(8) Å] are within the range found in dimeric Ge(IV) imides (1.70−1.88 Å),[4] while the Ge−O bond lengths [1.786(7) and 1.817(7) Å] are shorter than that in 1,3-cyclodigermoxane [$R_2Ge(\mu$-O)]$_2$ [Ge−O = 1.857(3) Å, R = 2,6-diethylphenyl][5] but similar to the average Ge−O bond length [1.805(9) Å] found in the compound [{($Me_3Si)_2N$}$_2$Ge(μ-O)]$_2$.[5] The long N···O distance (2.466 Å) clearly demonstrates a N═O double-bond cleavage of the nitrosoarene. The Ge···Ge separation [2.7280(16) Å] is ~0.3 Å longer than a normal Ge−Ge single bond (average 2.44 Å),[6] indicating essentially no Ge−Ge bonding. The long Ge···Ge separation is consistent with the singlet diradical character of **2**. Its normal ^1H and ^{13}C NMR signals indicate that it has a singlet ground state. Compound **2** is extremely air- and moisture-sensitive and, when exposed to the atmosphere, rapidly changes to a white powder that was shown to be a bisoxo-bridged germanium amide hydride (Scheme 2; for structural details, see the Supporting Information).

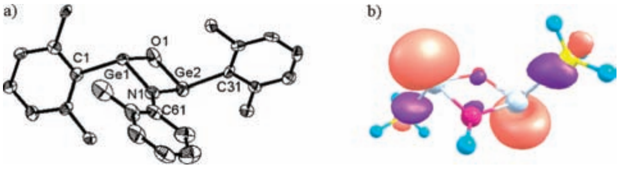


Figure 1. (a) Thermal ellipsoid (50%) plot of **2**. H atoms and flanking rings are not shown. Selected bond distances (Å) and angles (deg) for **2**: Ge1−N1, 1.888(8); Ge1−O1, 1.817(7); Ge1−C1, 2.032(9); Ge1···Ge2, 2.7280(16); N1−C61, 1.410(11); N1−Ge1−O1, 83.4(3); Ge1−N1−Ge2, 93.2(3); Ge1−O1−Ge2, 98.4(3); N1−Ge1−C1, 118.3(3); O1−Ge1−C1, 111.0(3). (b) Representation of the HOMO of MeGe(μ-O,μ-NH)GeMe from DFT calculations. Color code for atoms: gray, Ge; red, N; purple, O; yellow, C; blue, H.

To further understand **2**, we performed DFT calculations[7] at the UB3LYP/6-31G* level on the model compound MeGe(μ-NH)-(μ-O)GeMe (**2′**), in which Ar′ was replaced by a smaller methyl group and C_6H_4-2-CH_3 by H (for details, see the Supporting Information). **2′** was found to be an energy minimum whose geometrical parameters compare well to those found in the X-ray structure of **2**. Inspection of the frontier Kohn−Sham orbitals (Figure 1b) shows that the HOMO corresponds mainly to a nonbonding combination centered on the Ge atoms with a minor component at the N centers. This HOMO orbital also has a weak Ge−C component. The calculated HOMO−LUMO gap (55.3 kcal/mol) for **2′** is close to the energy difference of 51.60 kcal/mol suggested by the experimental UV−vis absorption of **2**.

A proposed reaction pathway for the formation of **2** is presented in Scheme 3. The initial step is the interaction between the frontier orbitals of the digermyne **1** and ONC_6H_4-2-CH_3, which gives an

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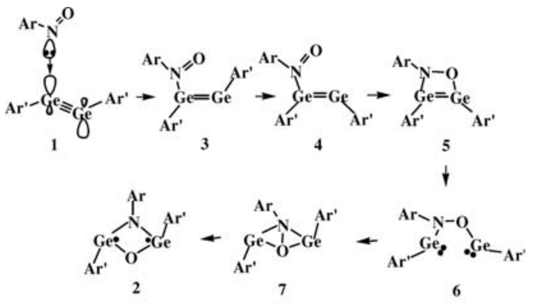
intermediate **3** in which ONC_6H_4-2-CH_3 is σ-bonded through N to one Ge atom in the C(ipso)GeGeC(ipso) plane.[8] The intramolecular donor−acceptor interaction leads to the [2 + 2] cycloaddition species **5**, which transforms to **6** because of weakening of the Ge═Ge double bond by the electronegative substituents.[8] The structure of **6** is related to that of Ar′Ge(Ph)NN(Ph)GeAr′, which is formed from the reaction of **1** with PhN═NPh and also has no Ge−Ge bond.[9] This allows rotation around the N−O bond to give intermediate **7**, in which each Ge atom weakly coordinates both to N and O atoms.[8] Cleavage of the N−O bond affords the singlet diradicaloid **2**.

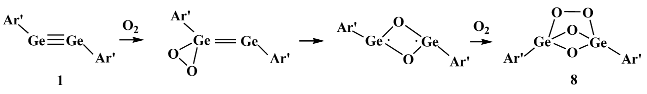
Scheme 3



Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$, Ar = ONC_6H_4-2-CH_3

DFT calculations[7] on simple models predicted that successive replacement of NH with isoelectronic O decreases the HOMO−LOMO gap by 8.1 kcal/mol and affords a shorter Ge···Ge separation (Table S1 in the Supporting Information). This increases the diradicaloid character and the isolation difficulty.[10] Nontheless, we investigated the synthesis of the oxo-bridged diradicaloid Ar′Ge(μ-O)$_2$GeAr′ by the reaction of **1** with O_2.

Scheme 4



Exposure of **1** in toluene to O_2 at room temperature provided a unique species {Ar′Ge(μ-O)$_2$(η^1,η^1:μ_2-O_2)GeAr′} (**8**), in which 2 equiv of O_2 was included. The single-crystal X-ray structure of **8** (Figure 2) clearly shows that the two Ge atoms are connected by two μ_2-oxo groups and an η^1,η^1:μ_2 O1−O2-coordinated peroxo bridge. Two terphenyl ligands complete the distorted tetrahedral environment at each Ge. The Ge1···Ge2 distance [2.4127(10) Å] is quite short, although there is no Ge−Ge bond. The four-membered Ge_2O_2 ring is folded (GeOGeO dihedral angle = 148.6°), in contrast to the related Ge(IV) {R_2Ge(μ-O)}$_2$ complexes that contain planar Ge_2O_2 rings.[5] The structure is in agreement with that calculated by DFT methods (see the Supporting Information). Heavier chalcogenide derivatives RM(μ-Ch)$_2$(η^1,η^1:μ_2-Ch_2)MR [R = C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$, M = Sn, Ch = Se; R = $(Me_3Si)_3C$, M = Si, Ch = S or Se) with related geometries have been reported.[11] It is possible that this reaction proceeds via the sequence shown in Scheme 4, during which cleavage of the O−O bond to give the singlet diradicaloid Ar′Ge(μ-O)$_2$GeAr′ and cycloaddition of 1 equiv of triplet diradical O_2 occur.

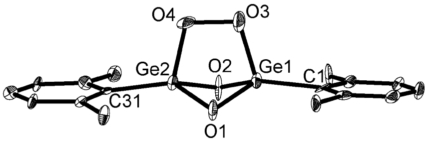


Figure 2. Thermal ellipsoid (50%) plot of **8**. H atoms and flanking rings are not shown. Selected bond distances (Å) and angles (deg): Ge1−O1, 1.792(5); Ge2−O2, 1.812 (5); Ge1−O3, 1.811(6); Ge2−O4, 1.825(5); O3−O4, 1.528(7); Ge1−C1, 1.911(6); O1−Ge1−O2, 87.1(2); Ge1−O1−Ge2, 84.2(2).

In summary, we have described the first example of a reaction of a nitrosoarene with a multiple bonded heavier main-group compound to give a rare example of a singlet diradicaloid incorporating oxygen. The reaction demonstrates an unexpected N═O double-bond cleavage and sharply differs from the reaction of alkynes with nitrosoarenes, which usually affords hydroxyindoles or methoxyindoles.[12] The UV−vis absorption for **2** is ∼3.3 kcal/mol less than that of the bisimido-bridged analogue **IV** (Scheme 1), which is in agreement with theoretically predicted 3.6 kcal/mol.[7,13] Future work will involve reactivity studies of **2** and reactions of **1** with other nitrosoarenes.

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Supporting Information Available: Crystallographic data for **2** and **8** (CIF), experimental details, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Molecular orbital calculations show that the HOMO−LUMO gaps for the model compounds MeGe(μ-$NSiH_3$)(μ-O)GeMe (53.2 kcal/mol) and MeGe(μ-NC_6H_5)(μ-O)GeMe (53.1 kcal/mol) are similar, indicating similar effects of the substituents $SiMe_3$ and C_6H_4-2-CH_3 on the diradical character. For details, see the Supporting Information.

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