Different reactivity of the heavier group 14 element alkyne analogues Ar′MMAr′ (M = Ge, Sn; Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) with R_2NO†

Geoffrey H. Spikes, Yang Peng, James C. Fettinger, Jochen Steiner and Philip P. Power*

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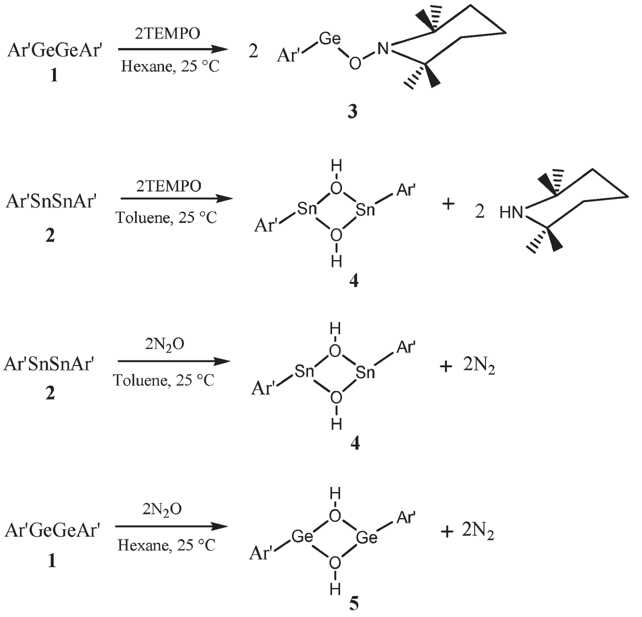
The reactions of the digermanium and ditin alkyne analogues Ar′MMAr′ (M = Ge or Sn) with R_2NO, (R_2NO = $Me_2C(CH_2)_3CMe_2NO$ or N_2O), result in complete MM bond cleavage to afford the germylene :Ge(Ar′)ONR_2 or the germanium(II) or tin(II) hydroxides {M(Ar′)(μ–OH)}$_2$.

Stable heavier group 14 alkyne congeners RMMR are now known for all the heavier elements.[1] Their reactivity has been little explored but preliminary results suggest that the germanium derivative Ar′GeGeAr′ (**1**) is considerably more reactive than its tin counterpart Ar′SnSnAr′ (**2**).[2] This is counterintuitive on the basis of the bond energies, bond polarities and steric effects. It has been proposed that the main reason for this difference is the greater diradical character of Ar′GeGeAr′.[3] In this paper we show that the germanium compound, **1**, is not only more reactive towards TEMPO (tetramethylpiperidineoxide) than its tin analogue, **2**, but that different types of products are obtained. A similar difference in the reactivity of **1** and **2** is observed upon treatment with N_2O but in this case congeneric products are obtained.

Upon the addition of 2 equiv. of TEMPO to a stirred solution of **1** in hexane at *ca.* 25 °C, a rapid color change from dark red to pale yellow was observed. Reduction of the solution volume and subsequent recrystallization at *ca.* −18 °C led to to the isolation of pale yellow crystals of the germylene :Ge(Ar′)TEMPO, **3**, in high yield. For the corresponding reaction of **2** with 2 equiv. of TEMPO in toluene at *ca.* 25 °C the dark green solution slowly faded to a pale red color overnight. Recrystallization from a minimum volume of toluene at *ca.* −18 °C gave the tin(II) hydroxide {Sn(Ar′)(μ–OH)}$_2$, **4**, as colorless crystals in high yield. When the reaction was repeated, and the solvent removed after overnight stirring, analysis by ^1H NMR spectroscopy revealed the presence of **4** and 2,2,6,6-tetramethylpiperidine.

The addition of 2 equiv. of N_2O to a stirred solution of **1** at *ca.* 25 °C led to a rapid fading (*ca.* 1 min) of the red color to colorless with concomitant evolution of N_2. Upon workup the hydroxide, {Ge(Ar′)(μ–OH)}$_2$, **5**, was isolated in high yield as pale yellow crystals by recrystallisation from a minimum volume of toluene at *ca.* −18 °C (Scheme 1). The corresponding reaction with **2** resulted in slow evolution of N_2 and bleaching of the color over a period of several hours to yield the analogous tin(II) hydroxide{Sn(Ar′)(μ–OH)}$_2$, **4**.



Scheme 1 Reactions of **1** and **2** with TEMPO and N_2O to give **3**–**5**.

Compounds **3**, **4** and **5** were characterized by ^1H and ^{13}C NMR, IR and UV spectroscopy as well as by X-ray crystallography.‡ The electronic spectrum of **3** demonstrated a strong absorption at 374 nm. No O–H or N–H absorptions were observed in the IR spectrum. At room temperature in C_6D_6 the ^1H NMR spectrum showed the expected pattern for the Ar′ ligand as well as three broad resonances at 0.41, 0.90 and 1.31 ppm due to the bound TEMPO. A variable temperature ^1H NMR study demonstrated a sharpening of these resonances at elevated temperature indicating restricted rotation around the N–O bond. The X-ray crystal structure (Fig. 1) showed that the Ge–Ge bond has been completely cleaved by the addition of a TEMPO to each Ge center to afford two monomeric :Ge(Ar′)TEMPO germylene units. The coordination at Ge is V-shaped with an interligand angle of 100.15(6)°. The Ge–O bond, 1.804(2) Å, in **1** is similar to the 1.802(8) and 1.812(7) Å in the aryloxide Ge $(OAr)_2$ (Ar = C_6H_2-2,6-Bu^t-4-Me)[4a] and is slightly shorter than those in Ge$(OCBu^t_3)_2$ (1.896(6) and 1.832(11)Å).[4b] The long N–O bond, 1.476(2)Å, and pyramidal geometry of the nitrogen atom (Σ°N = 334.0(3)°) indicates that the TEMPO ligand is fully reduced and is comparable to the only previously reported example of a germanium TEMPO derivative, the germanium(IV) species

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Department of Chemistry, University of California Davis, One Shields Ave., Davis, CA 95616, USA. E-mail: pppower@ucdavis.edu; Fax: 001 530 752 8995; Tel: 001 530 752 6913
† Dedicated to the memory of Ian Rothwell

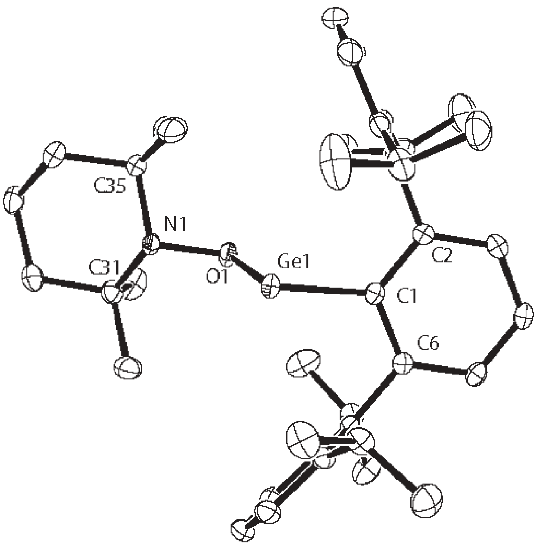


Fig. 1 Thermal ellipsoid (50%) drawing of **3**, H atoms are not shown. Selected bond lengths (Å) and angles (°): Ge1–O1 1.804(2), Ge1–C1 2.033(2), O1–N1 1.476(2), O1–Ge1–C1 100.15(6), N1–O1–Ge1 106.57(9), O1–N1–C35 107.52(12), O1–N1–C31 107.0(1), C35–N1–C31 119.4(1).

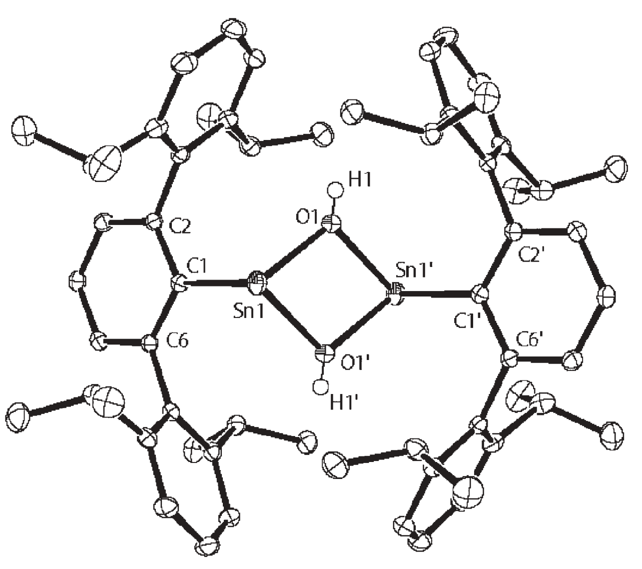
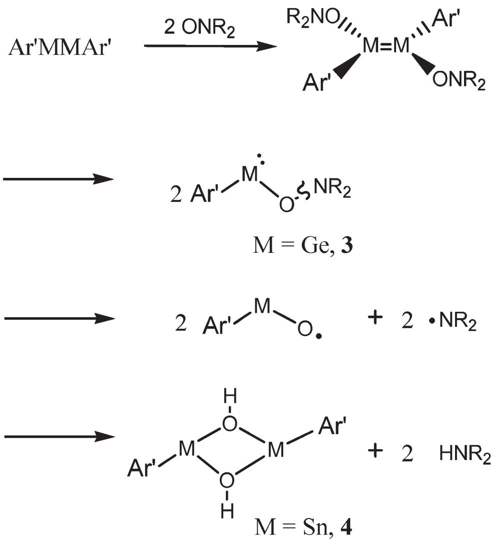


Fig. 2 Thermal ellipsoid (50%) drawing of **4**, H atoms (except OH) are not shown. Selected bond lengths (Å) and angles (°): Sn1–O1 2.145(2), Sn1–O1′ 2.149(1), Sn1–C1 2.227(2), O1–Sn1–O1′ 72.27(6), O1–Sn1–C1 95.33(6), O1′–Sn1–C1 94.60(6), Sn1–O1–Sn1′ 107.73(6).

$GeC\{(SiMe_3)_2(CH_2)_2C(SiMe_3)_2\}(TEMPO)_2$ (average Ge–O = 1.825(2)Å; average N–O = 1.482(4)Å) which was synthesised by the reaction of TEMPO with the germylene $:GeC(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$.[5]

The X-ray crystal structure of the tin derivative **4** shows that the Sn–Sn bond in the precursor **2** has been cleaved. However the product does not have a structure like that of **3**. Instead a hydroxy-bridged dimer is obtained. It represents the first example of a structurally characterised molecular tin(II) hydroxide. A number of tin(II) hydroxide salts have been isolated in which tin has a high coordination number[6] but there are relatively few examples of structurally characterized molecular species possessing Sn(II)–O bonds. The Sn–O distances in **4** (average Sn–O = 2.143(3)Å) are similar to those observed in bridged tin(II) alkoxides (average Sn–O = 2.147 Å).[4,7] The Sn_2O_2 core is planar with an acute angle, 72.27(6)°, at Sn and a wider angle, 107.73(6)°, at O (Fig. 2). The electronic spectrum of **4** exhibited a strong absorption at 319 nm while the IR spectrum displayed an absorption at 3480 cm^{-1} corresponding to the O–H stretching mode. The ^1H NMR spectrum showed the expected pattern for the Ar′ ligand as well as a resonance at −0.86 ppm that was assigned to the hydroxide hydrogens. A ^{119}Sn NMR signal was found at 216.4 ppm which is similar to that previously observed for $Sn(N(SiMe_3)_2)(OAr)$, 227 ppm, and downfield from that observed for $Sn(OAr)_2$, −193 ppm, (Ar = C_6H_2-2,6-Bu^t-4-Me).[7a] The germanium(II) hydroxide **5** is precedented only by the recently reported monomeric LGeOH (L = {N(Ar)C(Me)CHC(Me)N(Ar)}; Ar = C_6H_3-2,6-$Pr^i{}_2$).[8] Its structure is very similar to that of its tin analogue **4** and has significantly longer Ge–O distances (average Ge–O = 1.975(2) Å) than that reported for LGeOH, 1.828(1)Å, as a result of the bridging nature of the bonding.[9] It is similar to the average Ge–O distance, 1.988Å, found previously for bridged germanium(II) alkoxides.[7c,7f–g,10] The Ge_2O_2 core is planar although it is less rhomboid (internal angles 75.34(6)°, at Ge and, 104.66(6)°, at O) than that in **4**. The electronic spectrum of **5** gave strong absorptions at 290 and 316 nm while the IR spectrum displayed an absorption at 3540 cm^{-1} corresponding to the O–H stretching mode. The ^1H NMR spectrum showed the expected pattern for the Ar′ ligand as well as a resonance at 0.91 ppm that was assigned to the hydroxide protons.

The reaction of Ar′GeGeAr′, **1**, with TEMPO can be postulated as a two step oxidation of the 'digermyne' unit *via* an interaction of the SOMO of TEMPO with the LUMO of **1** (which is the n_+ combination).[11] Steric crowding, and the introduction of an electronegative ligand, favours the dissociation of the dimer into two monomeric germylene molecules[12] which can be isolated as the stable species **3**. The corresponding reaction of TEMPO with Ar′SnSnAr′, **2**, proceeds more slowly than that of its germanium counterpart. A tin analogue of **3** could not be isolated from this reaction mixture. The isolation of the hydroxide **4** may be



Scheme 2 Possible mechanism for the formation of **3** and **4**.

accounted for in terms of N–O bond cleavage in the putative :Sn(Ar′)TEMPO intermediate where the N–O bond is weakened by the more electropositive tin. The Ar′SnO· and $\cdot NR_2$ fragments may then abstract hydrogen from the solvent to afford **4** and HNR_2.[5,13–16] In contrast, upon reaction with N_2O, both **1** and **2** afford the hydroxide products (**4** and **5**). It may be assumed that the coordination of N_2O to the metal centers in **1** and **2** affords unstable species that contain the Ar′M–O–N_2 moiety which eliminates N_2 rapidly to give the radical Ar′MO·. Hydrogen abstraction then yields the hydroxide product. The examination of reactions of **1** and **2** with other oxygen transfer agents is in hand.§

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Notes and references

‡ Crystallographic data for: **3** CCDC 284211. **4**·2PhMe CCDC 284212. **5**·2PhMe CCDC 284213. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513189h

§ All manipulations were conducted under strict exclusion of air and moisture in an atmosphere of dry argon or *in vacuo* using Schlenk line and glovebox techniques. **:Ge(Ar′)(TEMPO), 3:** To a solution of Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (0.30 g, 0.32 mmol) in hexane (20 mL) was added a solution of TEMPO (0.10 g, 0.64 mmol) in hexane (20 mL) dropwise. The red solution faded to pale yellow over 2 min. Reduction of the solvent *in vacuo* to incipient crystallisation and storage at −18 °C yielded **3** as pale yellow crystals in high yield 0.26 g, 0.24 mmol, 74%). Mp: 198–200 °C. ^1H NMR (C_6D_6, 300.08 MHz): δ 0.41 (br, s, 12H), 0.90 (br, s, 2H), 1.11 (d, 12H, J = 6.9 Hz, CH*Me*$_2$), 1.31 (br, s, 4H), 1.42 (d, 12H, J = 6.9 Hz, CH*Me*$_2$), 3.17 (sept, 4H, J = 6.6 Hz, C*H*Me$_2$), 7.14 (m, 3H, Ar–H), 7.24 (m, 6H, Ar–H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 17.7 (C*Me*$_2$), 23.3 (CH*Me*$_2$), 25.7 (CH*Me*$_2$), 31.3 (*C*HMe$_2$), 40.6 (*C*Me$_2$), 58.1 (*C*H$_2$–*C*H$_2$–*C*H$_2$), 114.7, 123.8, 124.7, 129.0, 129.1, 132.1, 143.7, 147.1 (unsaturated carbon). IR (KBr, Nujol): 870 (w), 760 (s), 750 (s), 460 (m), 390 (m) cm^{-1}. UV-Vis (*n*-hexane): 374 nm (ε = 2300). **{Sn(Ar′)(μ–OH)}$_2$, 4, Method A:** To a solution of Ar′SnSnAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (0.20 g, 0.19 mmol) in toluene (20 mL) was added a solution of TEMPO (0.06 g, 0.38 mmol) in toluene (20 mL) dropwise. The dark green solution faded to pale red over 24 h. Reduction of the solvent *in vacuo* to incipient crystallisation and storage at −18 °C yielded **4** as colorless crystals in high yield (0.16 g, 0.13 mmol, 68%). Mp: 190 °C (dec). ^1H NMR (C_6D_6, 300.08 MHz): δ −0.86 (s, 2H), 1.03 (d, 24H, J = 6.9 Hz, CH*Me*$_2$), 1.11 (d, 24H, J = 6.9 Hz, CH*Me*$_2$), 3.00 (sept, 8H, J = 6.6 Hz, C*H*Me$_2$), 7.05 (m, 6H, Ar–H), 7.12 (m, 8H, Ar–H) 7.21 (m, 4H, Ar–H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 23.5 (CH*Me*$_2$), 26.5 (CH*Me*$_2$), 31.0 (*C*HMe$_2$), 119.0, 123.6, 128.9, 129.8, 139.6, 145.5, 147.1, 175.2 (unsaturated carbon). ^{119}Sn NMR (C_6D_6, 149.00 MHz): δ 216.4. IR (KBr, Nujol): 3480 (w, O–H), 760 (s), 730 (s), 450 (m), 380 (w) cm^{-1}. UV-Vis (*n*-hexane): 319 nm (ε = 2300). The remaining solvent was removed *in vacuo* and the residue was identified as a mixture of **4** and 2,2,6,6-tetramethylpiperidine by ^1H NMR spectroscopy. **Method B:** To a solution of Ar′SnSnAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (0.20 g, 0.19 mmol) in toluene (20 mL) was added N_2O (8.5 mL, 0.38 mmol). The dark green solution faded to pale yellow over 4 h. The solvent was removed *in vacuo* and the residue identified as **4** by ^1H NMR spectroscopy. **{Ge(Ar′)(μ–OH)}$_2$, 5, Method A:** To a solution of Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (0.30 g, 0.32 mmol) in hexane (20 mL) was added N_2O (14.3 mL, 0.64 mmol). The red solution faded to pale yellow over 30 s. Reduction of the solvent *in vacuo* to incipient crystallisation and storage at −18 °C yielded **5** as pale yellow crystals in high yield 0.26 g, 0.27 mmol, 84%). Mp: 157–158 °C. ^1H NMR (C_6D_6, 300.08 MHz): δ 0.91 (s, 2H), 1.02 (d, 24H, J = 6.9 Hz, CH*Me*$_2$), 1.04 (d, 24H, J = 6.9 Hz, CH*Me*$_2$), 3.00 (sept,. 8H, J = 6.6 Hz, C*H*Me$_2$), 7.00 (m, 6H, Ar–H), 7.12 (m, 8H, Ar–H) 7.23 (t, 4H, Ar–H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 23.5 (CH*Me*$_2$), 26.2 (CH*Me*$_2$), 31.1 (*C*HMe$_2$), 111.0, 118.3, 124.1, 126.9, 129.0, 129.8, 146.7 (unsaturated carbon). IR (KBr, Nujol): 3540 (w, O–H), 940 (w), 750 (s), 720 (s), 460 (m), 390 (w) cm^{-1}. UV-Vis (*n*-hexane): 316 nm (ε = 2400), 290 (ε = 2400). Crystal data for **3**, **4** and **5** at 90(2) K with MoK_α (λ = 0.71073 Å). **3**: $C_{39}H_{55}GeNO$, M = 626.43, triclinic, space group $P\bar{1}$, Z = 2, μ = 0.887 mm^{-1}, a = 10.693(1) Å, b = 11.120(1) Å, c = 16.042(1) Å, α = 100.976(1)°, β = 91.353(1)° γ = 108.140(1)°, V = 1785(1) Å^3, $R1$ = 0.0375 for 10297 ($I > 2\sigma(I)$) reflections, $wR2$ = 0.0942 (all data). **4**·2PhMe: $C_{44}H_{54}OSn$, M = 717.56, triclinic, space group $P\bar{1}$, Z = 2, μ = 0.711 mm^{-1}, a = 11.965(5) Å, b = 13.328(5) Å, c = 13.730(9) Å, α = 111.010(8)°, β = 102.783(8)° γ = 102.983(6)°, V = 1879.0(16) Å, $R1$ = 0.0309 for 11343 ($I > 2\sigma(I)$) reflections, $wR2$ = 0.0695 (all data). **5**·2PhMe: $C_{39}H_{55}GeO$, M = 671.46, triclinic, space group $P\bar{1}$, a = 11.990(1) Å, b = 13.109(1) Å, c = 13.771(1) Å, α = 110.633 (1)°, β = 103.258(1)° γ = 102.685(1)°, V = 1864.4(2), $R1$ = 0.0383 for 10680 ($I > 2\sigma(I)$) reflections, $wR2$ = 0.1015 (all data).

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