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The Facile Reduction of Carbon Dioxide to Carbon Monoxide with an Amido-Digermyne**

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The steady increase in the atmospheric concentration of the greenhouse gas, CO_2, since the industrial revolution is thought to be the main cause of recent increases in global temperatures.[1] The future implications of this phenomenon are driving significant current efforts to develop efficient methods for the sequestration of CO_2,[2] and for its use as a C_1 feedstock in the formation of useful chemicals.[3] With regard to the latter, the reduction of CO_2 to CO is of particular interest as carbon monoxide can be used as a fuel or as a chemical feedstock in its own right. However, CO_2 reduction is problematic because of the considerable strength of its O=C(O) bond (532 $kJ\,mol^{-1}$),[4] and for kinetic reasons.[3] With that said, CO_2 reduction has been achieved, either stoichiometrically or catalytically, in nature (e.g. with CO dehydrogenase/acetyl-coenzyme A synthase)[5] and in the laboratory by use of photolytic,[6] electrochemical,[7] or metal-based oxygen abstraction protocols.[8]

While the vast majority of methodologies for the reduction of CO_2 to CO require d- or f-block metal-containing materials to proceed, a handful of low oxidation state p-block compounds have recently been shown to effect CO_2 reductions at room temperature. These include three-coordinate, intramolecularly donor-stabilized (D→) silylenes (R_2(D→)Si:),[9,10] a disilyne (R(D→)SiSi(←D)R),[10] and *N*-heterocyclic carbenes.[11] Moreover, a small number of normal oxidation state p-block systems, for example, Al/P-based "frustrated Lewis pairs", have been reported to reduce CO_2 to CO.[12] The reduction reactions involving these compounds exemplify the rapidly emerging interest in the "transition-metal-like" reactivity of main group compounds.[13] We have become involved in this area with, for example, the preparation of the bulky amido-substituted two-coordinate digermyne, [LGe-GeL] **1** (L = N(Ar*)($SiMe_3$), Ar* = $C_6H_2\{C(H)Ph_2\}_2$Me-2,6,4).[14] Unlike all previously reported bulky aryl-substituted digermynes which have Ge–Ge multiple bonds,[15,16] compound **1** has an extremely long (2.7093(7) Å) Ge–Ge single bond, which is thought to be the basis of its very narrow HOMO–LUMO energy gap (0.62 eV, calculated using RI-BP86/def2-SVP; HOMO/LUMO = highest occupied/lowest unoccupied molecular orbital). The resultant high reactivity of **1** has been demonstrated by the fact that it quantitatively and rapidly activates dihydrogen, to give [LGeGe$(H)_2$L], at temperatures as low as −10 °C, both in solution and the solid state. It seemed reasonable to us that **1** could participate in other small molecule activations that have not been previously achieved with germanium compounds, and which are normally thought to be the realm of transition-metal systems. In this respect, here, we show that the digermyne facilely and quantitatively reduces CO_2 to CO at temperatures as low as −40 °C. The mechanism of this reduction has been explored using spectroscopic and computational techniques, and the reductions of the CO_2 analogs, CS_2 and *t*BuNCO, are also described.

A toluene solution of **1** was exposed to an excess of dry CO_2 at −70 °C, and the reaction vessel was sealed. Upon warming, the solution slowly lost the deep purple color of the digermyne at about −60 °C and became orange-brown. From about −40 to −30 °C the color of the solution changed to pale yellow, and remained that color when warmed to room temperature. At that point, an IR spectroscopic analysis of the head space gas of the reaction vessel confirmed the presence of CO ($\tilde{\nu}$ = 2143 cm^{-1}). Subsequent removal of volatiles from the mixture afforded an essentially quantitative yield of the novel bis(germylene) oxide **2** (Scheme 1). To ascertain the yield of generated CO, the method of Baceiredo

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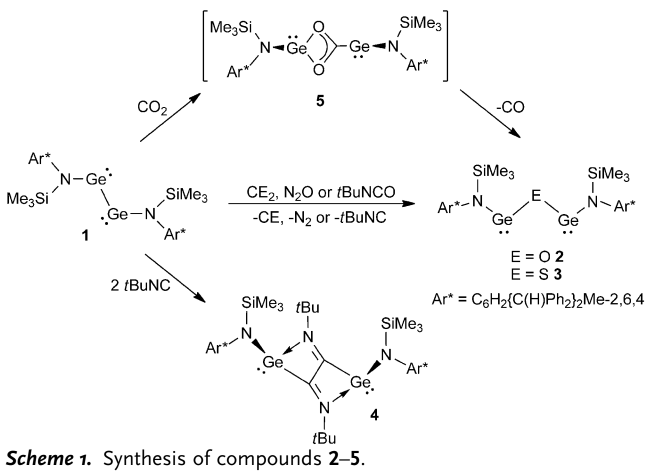
Supporting information for this article, including full synthetic and spectroscopic details for compounds **2–5**, crystallographic data for **2–4**, and full details and references for the DFT calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.201203607.



Scheme 1. Synthesis of compounds **2–5**.

and co-workers was employed.[10] That is, the reaction was repeated in a vessel that was connected through a gas bridge to another vessel containing half an equivalent of [RhCl(COD)(IPrMe)] (COD = cycloocta-1,5-diene; IPrMe = :C{N(iPr)C(Me)}$_2$) in a [D$_6$]benzene solution. The sealed two-component vessel was allowed to stand for 48 h at 20 °C, after which time an ^{1}H NMR spectroscopic analysis of the [D$_6$]benzene solution revealed the quantitative conversion of [RhCl(COD)(IPrMe)] to [RhCl(CO)$_2$(IPrMe)] and free COD (see the Supporting Information for further details). Accordingly, the reduction of CO_2 to CO by **1** was confirmed to be essentially quantitative.[17]

A series of related reactions were subsequently investigated for the purpose of comparison (Scheme 1). First, compound **2** was found to be alternatively accessible in high yield by treatment of **1** with excess N_2O. Interestingly, the germanium(II) centers of **2** are not further oxidized by N_2O. This outcome contrasts with the reaction of Power's multiply bonded digermyne, Ar′GeGeAr′ (Ar′ = $C_6H_3(C_6H_3i Pr_2\text{-}2,6)_2$-2,6), with N_2O, which yields a cyclic germanium(IV) peroxo-species.[18] The reaction of **1** with an excess of CS_2 proceeded rapidly at −70 °C and afforded a high yield of the pale yellow bis(germylene) sulfide **3** after subsequent warming to ambient temperature. Treatment of **1** with the isocyanate, tBuNCO, gave a mixture of products which included significant quantities of **2**, but no observable tBuNC. It was thought that if tBuNC was generated in this reaction it could compete with tBuNCO for reaction with **1**. This proposal was assessed by reacting **1** directly with tBuNC, which gave a good yield of the green reductively coupled product **4**. Compound **4** was subsequently found to be a component of the tBuNCO/digermyne reaction mixture (as determined by NMR spectroscopy). Therefore, it seems likely that tBuNC is generated in that reaction, but is rapidly consumed by reduction with **1**. While reductive coupling reactions of isonitriles with low oxidation state main group complexes are not uncommon,[19] the reaction of tBuNC with Power's digermyne, Ar′GeGeAr′, yielded only the 1:1 adduct, [Ar′GeGe(Ar′)(CNtBu)].[18] This could indicate that **1** is both more electrophilic and more reducing towards isonitriles than Ar′GeGeAr′.

The spectroscopic data for **2**–**4** are fully consistent with their solid-state structures (see the Supporting Information for details). Compounds **2** and **3** represent the first crystallographically characterized examples of two-coordinate, amido-substituted bis(germylene) chalcogenides (Figure 1), though two related three-coordinate examples, [{(amid′)Ge}$_2$E] (E = O or S, amid′ = {($C_6H_3i Pr_2$-2,6)N}$_2$CtBu), and a two-coordinate aryl-substituted complex, [Ar′GeOGeAr′], have been reported.[20] The two compounds in the current study are broadly isostructural, though it is noteworthy that they exhibit markedly different Ge-E-Ge angles (E = O: 122.30(9)°; S: 98.21(3)°), in line with the lesser propensity of sulfur, relative to oxygen, to undergo hybridization. The Ge–E distances in both compounds are in the normal range for single-bond interactions,[21] while their Ge–N distances are close to those in **1** (1.872(2) Å). It is interesting that the germanium lone pairs in **2** and **3** adopt a *cis* disposition relative to each other, and therefore the compounds have the potential to act as chelating Ge-donor ligands (compare the three-coordinate bis(silylene) oxide complex, [(COD)Ni{Si(amid)}$_2$O], amid = (tBuN)$_2$CPh).[22] The molecular structure of **4** (Figure 2) reveals the compound to be a dimeric digermabicycle with pyramidal germanium(II) centers, the lone pairs of which are

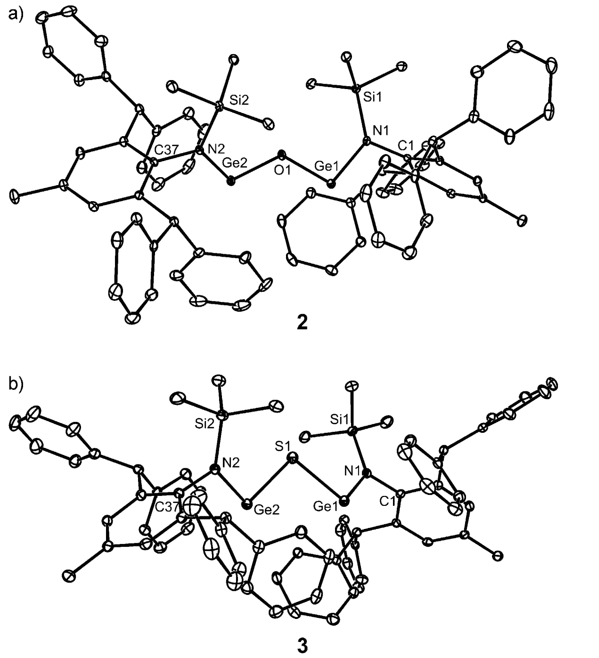


Figure 1. Molecular structures of compounds a) **2** and b) **3** (25% ellipsoids; hydrogen atoms are omitted). Relevant bond lengths (Å) and angles (°). **2**: Ge(1)-O(1) 1.8088(16), Ge(1)-N(1) 1.8784(19), Ge(2)-O(1) 1.8154(15), Ge(2)-N(2) 1.8749(19), O(1)-Ge(1)-N(1) 100.95(8), O(1)-Ge(2)-N(2) 97.50(8), Ge(1)-O(1)-Ge(2) 122.30(9). **3**: Ge(1)-N(1) 1.868(2), Ge(1)-S(1) 2.2854(8), Ge(2)-N(2) 1.877(2), Ge(2)-S(1) 2.2869(8), N(1)-Ge(1)-S(1) 99.41(7), N(2)-Ge(2)-S(1) 99.73(7), Ge(1)-S(1)-Ge(2) 98.21(3).

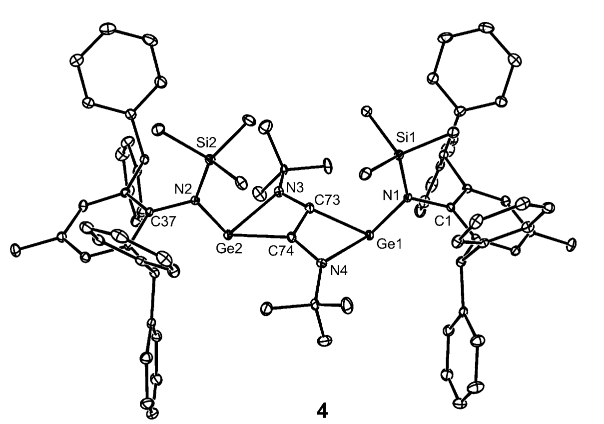


Figure 2. Molecular structure of compound **4** (25% ellipsoids; hydrogen atoms are omitted). Relevant bond lengths (Å) and angles (°). Ge(1)-N(1) 1.887(3), Ge(1)-C(73) 2.087(11), Ge(1)-N(4) 2.371(7), Ge(2)-N(2) 1.885(3), Ge(2)-C(74) 2.071(11), Ge(2)-N(3) 2.358(6), N(3)-C(73) 1.279(12), N(4)-C(74) 1.286(12), C(73)-C(74) 1.476(17), C(73)-Ge(1)-N(4) 60.1(4), N(1)-Ge(1)-N(4) 107.42(15), N(1)-Ge(1)-C(73) 105.3(3), C(74)-Ge(2)-N(3) 60.0(3), N(2)-Ge(2)-N(3) 108.34(15), N(2)-Ge(2)-C(74) 109.3(2), N(3)-C(73)-C(74) 107.6(12), N(4)-C(74)-C(73) 108.6(11).

in *cis* positions relative to each other, as in **2** and **3**. The geometry of the central coupled isonitrile unit is indicative of an essentially localized 1,4-diazabutadiene-2,3-diyl fragment, that is $(N=C\text{-})_2$, the N centers of which have markedly longer dative interactions with the Ge atoms than the exocyclic amide nitrogen atoms.

To shed light on the mechanism of the reduction of CO_2 by **1**, and the temperature-dependent color changes of the reaction mixture, the reaction was followed by ^{1}H and ^{13}C NMR spectroscopy ([D$_8$]toluene solution) from −70 to 30 °C (see the Supporting Information for NMR spectra). No reaction occurred at −70 °C, but upon warming to −60 °C signals for a new, unsymmetrical compound with chemically inequivalent amide ligands began to appear. After warming to −50 °C the conversion of **1** to this compound was largely complete. Although no signal was evident for free CO in the ^{13}C NMR spectrum of the mixture at this temperature, a low-field resonance ($\delta = 222.8$ ppm) had appeared. The unsymmetrical compound was stable until −40 °C, whereupon it began converting to symmetrical **2**. This conversion became more rapid at −30 °C, and was complete by −20 °C. There was essentially no further change in the NMR spectra up to 30 °C. At this temperature, the signal at $\delta = 222.8$ ppm in the ^{13}C NMR spectrum had vanished, and one for free CO ($\delta = 184.5$ ppm) had appeared. The results of this NMR experiment strongly suggest that the reduction of CO_2 proceeds through an unsymmetrical, metastable intermediate. Unfortunately, all attempts to isolate crystalline samples of this intermediate at low temperatures proved fruitless.

So as to elucidate the nature of this intermediate, the free-energy profile of the reaction of **1** with CO_2 was calculated using density functional theory with inclusion of dispersion interactions (BP86-D3/def2-TZVPP//BP86/SVP), and is depicted in Figure 3. We located two transition states, **TS1-2a** and **TS1-2b**, for the initial stage of the reaction, which involve a side-on approach of the CO_2 molecule to one or both Ge centers. While these transition states lead to the same intermediate, **IM2**, through the insertion of CO_2 into the Ge−Ge bond, the energetically lowest lying entrance channel (activation barrier of $\Delta G^{\neq} = 17.0$ kcal mol^{-1}) is through **TS1-2a**. Intermediate, **IM2**, then rearranges through a low-energy transition state (**TS2-3**, $\Delta G^{\neq} = 4.1$ kcal mol^{-1}) to give the *trans*-germacarboxylato germanium(II) amide complex, **IM3**, which is 5.0 kcal mol^{-1} lower in energy than **IM2**. The elimination of CO from this to give **2**, then proceeds with an energy barrier ($\Delta G^{\neq} = 16.3$ kcal mol^{-1}) similar to that for the entrance channel. The overall CO_2 reduction reaction is exergonic by only −17.7 kcal mol^{-1}. Because of the relatively low energy of intermediate **IM3**, and the calculated barrier to its elimination of CO, we conclude that the unsymmetrical, spectroscopically observed reaction intermediate resembles that compound (i.e. **5** in Scheme 1). Indeed, insertions of CO_2 into metal–metal bonds to give metalla-carboxylate complexes (compare **5**) are not uncommon,[3] and the low-field ^{13}C NMR resonance for **5** is in the expected region for such complexes. This conclusion is supported by calculation of the ^{13}C NMR chemical shift for a model compound of **5**, that is **IM4**, in which the amido groups (NMe_2) have methyl substituents. The calculated value at GIAO/MP2/TZVPP of $\delta = 216.3$ ppm is in good agreement with the experimental value of $\delta = 222.8$ ppm.

In summary, the quantitative reduction of CO_2 to CO by a digermyne at temperatures as low as −40 °C has been achieved. Moreover, strong evidence for the mechanism of the reaction has been gained from a combination of spectroscopic and computational studies. There is little precedent for

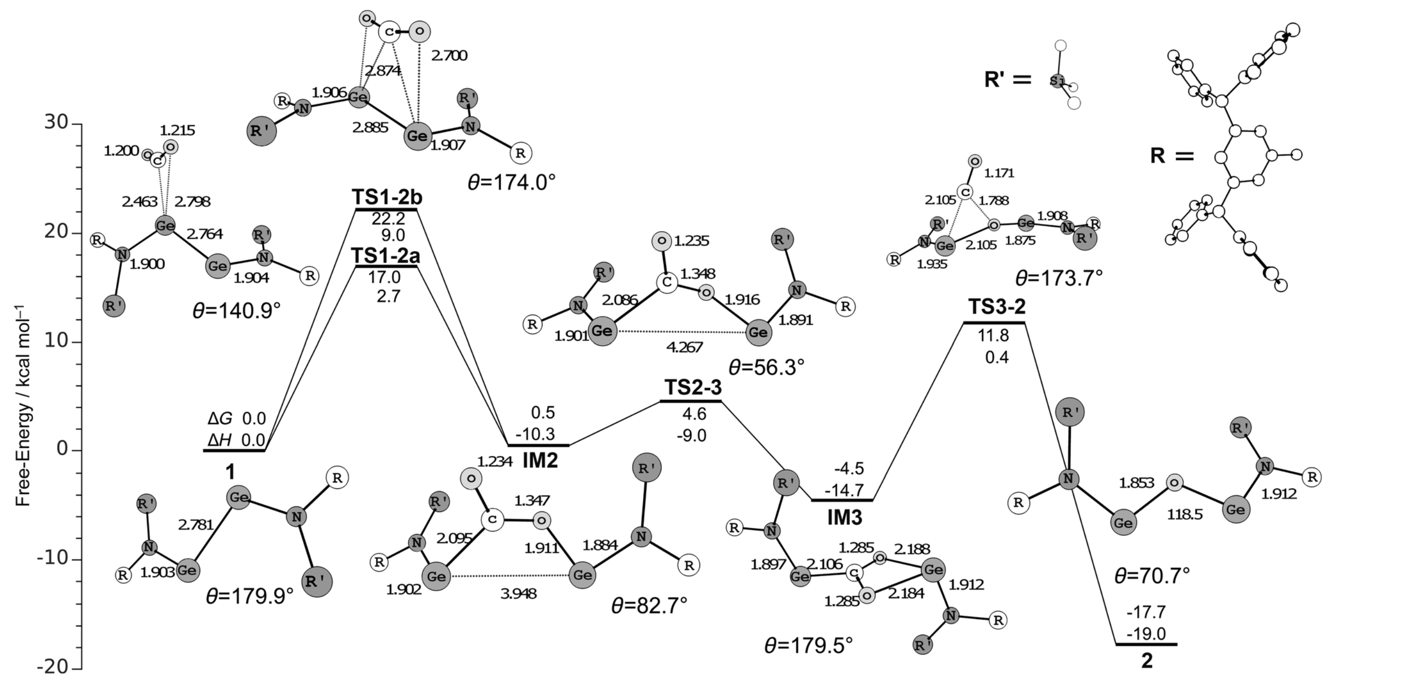


Figure 3. Free-energy profile of the reaction of **1** with CO_2 (BP86-D3/def2-TZVPP//BP86/def2-SVP). Selected interatomic distances (Å), bond angles (°), and NGeGeN torsion angles, θ (°), are given with the molecular structures.

the generation of CO from CO_2 using p-block compounds, and, as far as we are aware, none for germanium systems.[23] We are currently exploring the possibility of rendering the reduction reaction described above, catalytic; in addition to examining the activation of other small molecules using **1** and related compounds.

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