

Reversible Uptake of CO₂ by Pincer Ligand Supported Dimetallynes

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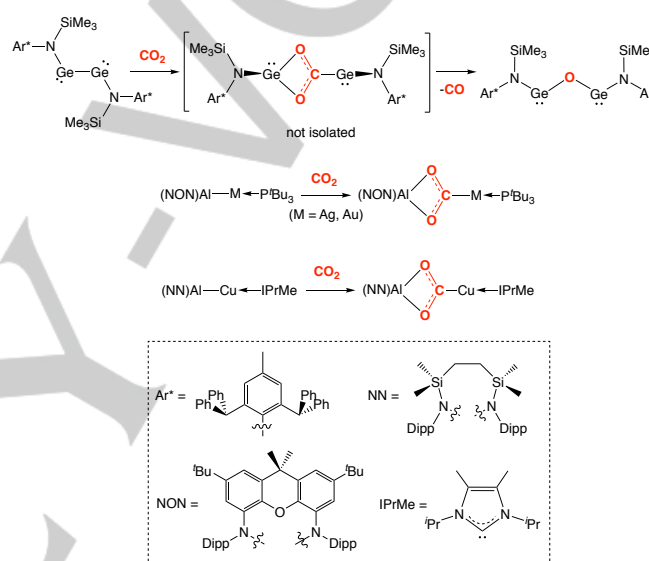
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Abstract: We report on the reversible uptake of carbon dioxide by dimetallynes featuring ancillary hemi-labile pincer ligands. Insertion into the Ge–Ge/Sn–Sn bonds yields species containing an E(CO₂)E unit, with the mode of ligation of the CO₂ fragment determined crystallographically being found to be dependent on the identity of the group 14 element. The thermodynamics of CO₂ uptake/loss can be established through VT-NMR ($\Delta H^\circ = +24.6(2.3)$ kJ mol⁻¹, $\Delta S^\circ = +64.9(3.8)$ J mol⁻¹ K⁻¹, $\Delta G^\circ_{298} = +5.3(1.9)$ kJ mol⁻¹ for the loss of CO₂ in the Ge case), and the chemical consequences of reversibility demonstrated by thermodynamically-controlled exchange reactions.

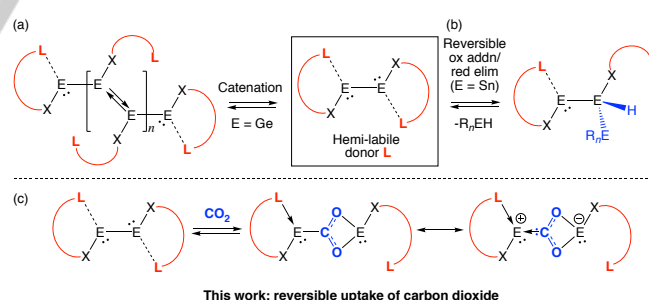
The advent of dimetallynes - the heavier group 14 analogues of alkynes - contributed to a reappraisal of the chemical capabilities of Main Group elements,^[1-3] both in defining multiple bonding among compounds of the heavier p-block elements,^[4] and by establishing patterns of electronic structure suitable for the activation of small molecules in 'Transition Metal like' fashion.^[3,5] The activation of dihydrogen by a terphenyl-ligated digermene represented the first example of such a process mediated by a main group molecule at room temperature,^[6a] and subsequent studies of these and related systems^[6] have also led to the activation of other small molecules including iso(nitriles),^[7,8] alkenes^[6f,9] and alkynes^[10] (in some cases reversibly).^[11]

In addition to these substrates, the chemistry of carbon dioxide has also been targeted, reflecting the desirability of CO₂ as a C₁ feedstock, and the possibility of exploiting the reductive capabilities of E(I) compounds of the group 14 elements in the conversion of CO₂ to CO.^[6f,8] The abstraction of oxygen from CO₂ by a diamidogermene to give a Ge–O–Ge unit has been proposed by Jones and Frenking to proceed via initial insertion of CO₂ into the Ge–Ge bond (Scheme 1) - although in this case the putative intermediate is stable only at temperatures below -40°C.^[8] Isolable compounds featuring a M(CO)₂M' motif formed directly from CO₂ have emerged more recently via insertion into more polarized M–M' bonds (e.g. M–Al, M = Cu, Ag, Au).^[12]

In recent work we have begun to probe the applications of low-valent main group complexes featuring hemi-labile ancillary donors. Within group 14 chemistry, such ligands offer a means of manipulating access to the reactive metal centres found in two-coordinate metallylenes.^[13,14] This approach can be exploited (i) to generate extended chains of Ge(I) centres akin to oligo-acetylenes through the formation of Lappert-type double bonds between 'decomplexed' metal centres (Scheme 2a);^[13,15] and (ii) to facilitate reversible bond activation via oxidative addition/reductive elimination at Sn(I) (Scheme 2b).^[14]



Scheme 1. Selected examples of the insertion of CO₂ into metal-metal bonds.



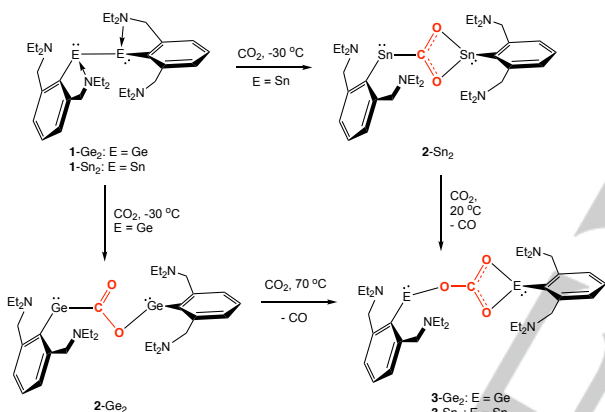
Scheme 2. Exploiting hemi-lability in dimetallynes to control access to two-coordinate group 14 metal centres: applications in (a) catenation;^[13] (b) reversible E–H bond activation;^[14] and (c) reversible CO₂ capture (this work).

We also perceived that the versatile coordination capabilities afforded by hemi-labile donors would allow dimetallynes of this sort to participate in reaction chemistry generating metal centres with appreciably different electronic requirements (Scheme 2c). In particular, we hypothesized that this might allow for the isolation of molecular species (containing E–C and E–O bonds) resulting from direct insertion of CO₂ into the E–E bond. Here we show that this approach is not only feasible, but can also allow for the *reversible* uptake of CO₂, and

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for thermodynamically-driven exchange of the inserted CO₂ moiety between dimetallynes in a manner consistent with the structural differences between germanium and tin analogues.

The reactions of the pincer-ligand supported dimetallynes (Ar^{NEt2}E)₂ (**1-Ge₂** (E = Ge);^[13] **1-Sn₂** (E = Sn, see ESI); where Ar^{NEt2} = C₆H₃(CH₂NEt₂)_{2,6}) with CO₂ proceed rapidly at -30 °C, leading to the loss of the distinctive colour associated with the starting material (orange/red, respectively). The pale yellow (E = Ge) or colourless (E = Sn) products are characterized by an additional low-field ¹³C NMR resonance (at δ_C = 206.0 and 220.6 ppm, respectively),^[8,12] and, in the case of the tin system, by the appearance of two new ¹¹⁹Sn resonances at δ_{Sn} = 80.9 and 90.4 ppm (cf. 639.6 for **1-Sn₂**). The identity of the product in each case (**2-Ge₂** and **2-Sn₂**; Scheme 3) can be confirmed by X-ray crystallography to result from insertion of the CO₂ molecule into the E–E bond of the respective dimetallene (Figure 1). While compounds of this type have been postulated as intermediates in the transformation of CO₂ by low-valent group 14 systems,^[8] these systems (to our knowledge) represent the first time that examples have been isolated and structurally characterized.



Scheme 3. Reactions of dimetallynes **1-Ge₂** and **1-Sn₂** with CO₂, leading to insertion of CO₂ and ultimately to the formation of binuclear carbonate derivatives (plus CO).

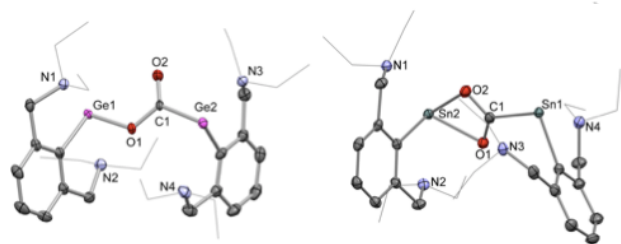


Figure 1. Molecular structures of (Ar^{NEt2}Ge)₂(μ-κ¹(C)-κ¹(O)-CO₂) (**2-Ge₂**; left) and (Ar^{NEt2}Sn)₂(μ-κ¹(C)-κ²(O,O')-CO₂) (**2-Sn₂**; right) in the solid state as determined by X-ray crystallography. Second disorder component (for **2-Ge₂**) and H atoms omitted, and Et groups shown in wireframe format for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°): (for **2-Ge₂**) Ge1–N 2.553(4), 2.372(4), Ge1–O2 1.957(7), C1–O1 1.204(10), C1–O2 1.339(11), Ge2–C1 2.074(8), Ge2–N 2.337(3), 2.678(3), O–C–O 121.6(8); (for **2-Sn₂**) Sn1–N 2.662(3), 2.542(3), Sn1–C1 2.247(4), C1–O 1.268(6), 1.288(4), Sn2–O 2.288(3), 2.344(3), Sn2–N 2.650(4), 2.648(4), O–C–O 116.6(3).

While **2-Ge₂** and **2-Sn₂** both feature E–C and E–O bonds formed by insertion of the carbon dioxide molecule, the structure of the bridging unit revealed crystallographically is dependent on

the identity of the group 14 element. Thus, (Ar^{NEt2}Ge)₂(μ-κ¹(C)-κ¹(O)-CO₂) (**2-Ge₂**) contains a (formal) [CO₂]²⁻ ligand which features distinct C–O single and C=O double bonds (1.339(11) and 1.204(10) Å), and can also be thought of as a κ¹-germa-carboxylate complex of Ge1. By contrast, the C–O distances in (Ar^{NEt2}Sn)₂(μ-κ¹(C)-κ²(O,O')-CO₂) (**2-Sn₂**) are identical within error (1.268(6) and 1.288(4) Å), consistent with a κ² mode of coordination of the corresponding stanna-carboxylate fragment. The associated Sn–O distances (2.288(3), 2.344(3) Å) are also consistent with such a model, with the structural differences compared to **2-Ge₂** (both in terms of bond length and mode of coordination) presumably reflecting the greater size of tin over germanium.^[16]

Under more forcing conditions, in the presence of excess CO₂, both **2-Ge₂** and **2-Sn₂** can be shown to be converted into the corresponding carbonate compounds (**3-Ge₂** and **3-Sn₂**; Scheme 3), with accompanying generation of CO. For the germanium system, onward conversion to **3-Ge₂** requires elevated temperatures (70 °C for 22 h), while the corresponding tin chemistry is more facile, going to completion at room temperature. Both **3-Ge₂** and **3-Sn₂** give rise a ¹³C NMR resonance in the region characteristic of the [CO₃]²⁻ ligand (δ_C = 163.5 and 168.2 ppm, respectively, cf. 167.5 ppm for the related N/Pr₂-ligated system (Ar^{iPr2}Sn)₂(μ-κ¹(O)-κ²(O',O'')-CO₃),^[14] and in the case of the tin compound, structural authentication was possible by X-ray crystallography (Figure 2). The net conversion of two equivalents of CO₂ in this fashion to CO and a bridging carbonate ligand has previously been reported for only one distannyne system,^[14,17] while a small number of digermynes have been reported to convert CO₂ into CO with accompanying formation of the corresponding bridging oxide.^[6f,8]

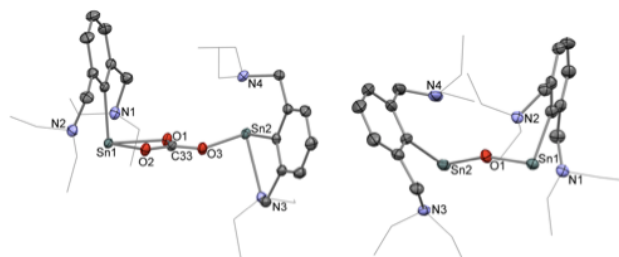
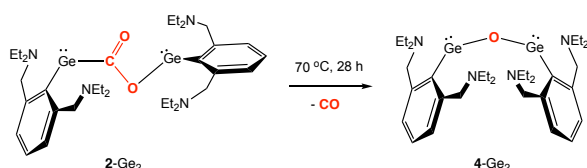


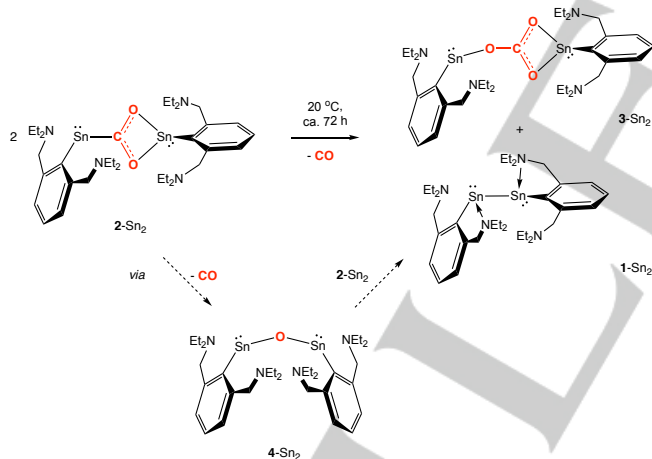
Figure 2. Molecular structures of (Ar^{NEt2}Sn)₂(μ-κ¹(O)-κ²(O',O'')-CO₃) (**3-Sn₂**; left) and (Ar^{NEt2}Sn)₂(μ-O) (**4-Sn₂**; right) in the solid state as determined by X-ray crystallography. Second component of asymmetric unit (for **3-Sn₂**) and most H atoms omitted, and Et groups shown in wireframe format for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°): (for **3-Sn₂**) Sn1–N 2.647(3), 2.670(3), Sn1–O 2.262(2), 2.696(2), C–O 1.275(4), 1.281(4), 1.300(4), Sn2–O 2.121(2), Sn2–N 2.568(3), 2.591(3); (for **4-Sn₂**) Sn1–N 2.596(6), 2.683(4), Sn1–O 1.983(3), Sn2–O 1.957(3), Sn2–N 2.590(4), 2.719(6).

In light of differing propensities of **2-Ge₂**/**2-Sn₂** to react with further CO₂, and the mechanisms proposed for the formation of bimetallic carbonate systems via the intermediacy of a bridging oxide,^[8] we examined the thermal stabilities of the isolated CO₂ insertion compounds in the *absence* of additional carbon dioxide. Accordingly, **2-Ge₂** extrudes CO to give the corresponding oxide species **4-Ge₂** over a period of 28 h at 70 °C (Scheme 4), i.e. under conditions consistent with the hypothesis that the oxide is an intermediate in the conversion of **2-Ge₂** to **3-Ge₂** (in the presence of additional CO₂).



Scheme 4. Thermal loss of CO from **2-Ge₂** to generate the bridging oxide species **4-Ge₂**.

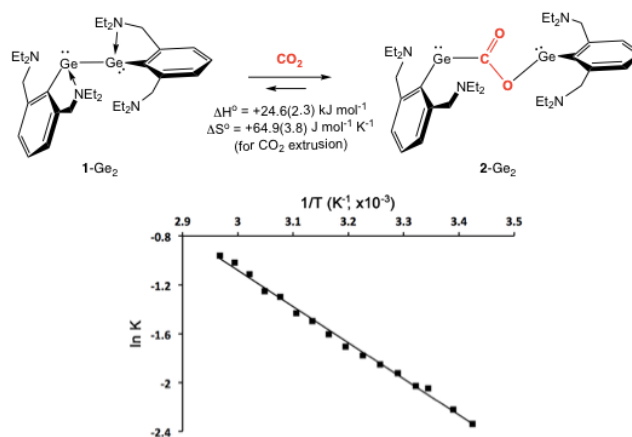
In contrast to **2-Ge₂**, **2-Sn₂** is more thermally fragile, being transformed at 20 °C over a period of several days, somewhat surprisingly, into a 1:1 mixture of carbonate species **3-Sn₂** and the starting distannylene **1-Sn₂** (Scheme 5). We hypothesized that the formation of **3-Sn₂** arises from initial extrusion of CO from **2-Sn₂** to give the bridging oxide species **4-Sn₂** (analogous to the final product in the germanium system), and that this oxide then sequesters CO₂ from a second equivalent of **2-Sn₂**, thereby generating the carbonate product **3-Sn₂**, along with one equivalent of the starting distannylene. The last step inherent in this mechanistic proposal implies that there is chemical reversibility in the uptake of CO₂ by distannylene **1-Sn₂**. In order to verify this hypothesized reaction pathway, the tin oxide species, (Ar^{NEt₂}Sn)₂(μ-O) (**4-Sn₂**) was independently synthesized via the reaction of **1-Sn₂** with pyridine-N-oxide (Scheme 5 and Figure 2). Subsequent reaction of isolated samples of **4-Sn₂** with one equivalent of the CO₂ insertion compound **2-Sn₂** can then be shown to generate the same 1:1 mixture of carbonate **3-Sn₂** and distannylene **1-Sn₂** (Scheme 5).



Scheme 5. Thermal decomposition of **2-Sn₂**, to generate a 1:1 mixture of carbonate complex **3-Sn₂** and distannylene **1-Sn₂**, via tin oxide **4-Sn₂**.

The chemically reversible uptake of CO₂ by **1-Sn₂** prompted us to investigate more broadly the thermodynamics/ kinetics of carbon dioxide sequestration. In this part of the study we focussed on the germanium systems **1-Ge₂/2-Ge₂**, since the latter has much greater thermal stability than its tin counterpart, allowing for investigation of CO₂ uptake/release over a wider temperature range. Initially we examined the exchange reaction between **2-Ge₂** and isotopically labelled ¹³CO₂. The kinetics of this process (at room temperature and ca. 1 atm pressure ¹³CO₂) are such that complete exchange of the label into the Ge(μ-κ¹(C)-κ¹(O)-CO₂)Ge position occurs in the time taken for acquisition of

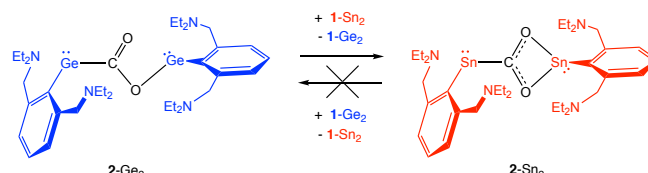
a ¹³C NMR spectrum (ca. 15 min). From a thermodynamic perspective, the release of CO₂ from **2-Ge₂** to regenerate **1-Ge₂** can be monitored by variable temperature ¹H NMR in benzene-d₆ solution in the temperature range 19 – 64 °C (292 – 337 K). The derived van't Hoff plot (Scheme 6) allows the thermodynamic parameters ΔH° = +24.6(2.3) kJ mol⁻¹, ΔS° = +64.9(3.8) J mol⁻¹ K⁻¹ and ΔG°₂₉₈ = +5.3(1.9) kJ mol⁻¹ to be determined for the loss of CO₂ from **2-Ge₂**, consistent with the



Scheme 6. Reversible CO₂ uptake/extrusion by **1-Ge₂/2-Ge₂**; van't Hoff plot derived from variable temperature ¹H NMR measurements ($R^2 = 0.995$ for linear best fit).

release of carbon dioxide at/just above room temperature. The reversible uptake of CO₂ in this manner via insertion into the E–E bond of a dimetallene is to our knowledge unprecedented.

The reversible uptake/extrusion of CO₂ by **1-E₂/2-E₂** (E = Ge, Sn) also implies that it should be possible to transfer carbon dioxide between the germanium and tin systems. Accordingly, we set out to investigate the reaction of **2-Ge₂** with distannylene **1-Sn₂**, and the reverse reaction of **2-Sn₂** with digermene **1-Ge₂**. Interestingly, while the transfer of CO₂ from **2-Ge₂** to **1-Sn₂** to generate **2-Sn₂** appears to be quantitative in benzene-d₆ solution at room temperature, the reverse reaction i.e. transfer of carbon dioxide from the tin system to **1-Ge₂** does not occur (Scheme 7). Given that CO₂ extrusion from both **2-Ge₂** and **2-Sn₂** is facile under such conditions (see below), we hypothesize that the origins of this differential reactivity are thermodynamic, driven by the stronger E–E bond in the digermene, allied to the different (chelating) binding mode adopted by the metalla-carboxylate group in tin compound **2-Sn₂**.

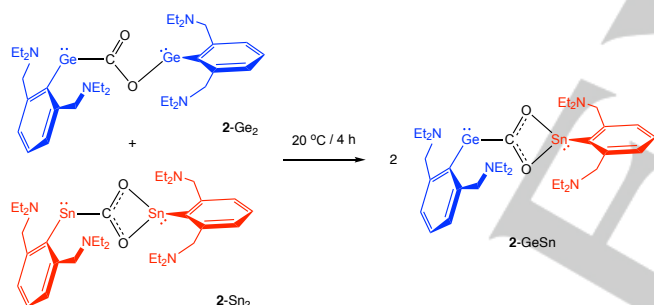


Scheme 7. Exchange of CO₂ from **2-Ge₂** to **1-Sn₂** (i.e. from digermene to distannylene); non-exchange in the reverse sense.

Further evidence that these systems operate under thermodynamic control comes from the exchange reaction that occurs between **2-Ge₂** and **2-Sn₂**. An equimolar mixture of the two CO₂ insertion compounds can be shown by *in situ* NMR

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monitoring to be converted into a single product over a 4 h period at 20 °C. A combination of multinuclear NMR and X-ray crystallography reveals that the product is $(\text{Ar}^{\text{NEt}_2}\text{Ge})(\mu\text{-}\kappa^1(\text{C})\text{-}\kappa^2(\text{O},\text{O}')\text{-CO}_2)(\text{SnAr}^{\text{NEt}_2})$ (**2-GeSn**; Scheme 8 and Figure 3) which features the bridging CO_2 ligand bound in κ^1 fashion via the carbon atom at Ge1 and in $\kappa^2(\text{O},\text{O}')$ fashion at Sn1. The binding of the oxygen atoms of the $[\text{CO}_2]^{2-}$ ligand at tin in this manner is consistent with the greater thermodynamic stability associated with the chelating mode of attachment (as noted above), while the preferential formation of the Ge–C bond (over Sn–C) presumably reflects established trends in σ -bond strengths for p-block elements. Moreover, the formation of **2-GeSn** from **2-Ge₂** and **2-Sn₂** in this manner implies kinetic lability for both E–C and E–O bonds, and we hypothesize that a viable mechanistic pathway involves loss of CO_2 from both insertion compounds to generate the dimetallynes **1-Ge₂** and **1-Sn₂**; E–E bond scrambling then generates a mixture which includes the 'crossover' Ge–Sn bonded system, **1-GeSn**. Re-insertion of CO_2 would then generate a mixture of **2-Ge₂**, **2-Sn₂** and **2-GeSn**, with the latter being driven to be the sole product under thermodynamic control (at the limits of NMR detection) for the reasons outlined above. Consistent with this hypothesis, mixing of equimolar solutions of **1-Ge₂** and **1-Sn₂** in benzene- d_6 rapidly gives rise to a mixture which contains a third (unsymmetrical) species, postulated to be **1-GeSn**. While the mechanism for this exchange process is not yet clear, both radical and metathesis pathways have some literature precedent.^[19]



Scheme 8. Scrambling between **2-Ge₂** and **2-Sn₂** in solution at 20 °C to generate a single product, **2-GeSn**.

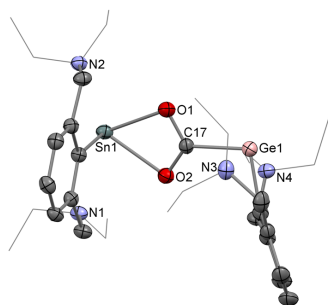


Figure 3. Molecular structure of $(\text{Ar}^{\text{NEt}_2}\text{Ge})(\mu\text{-}\kappa^1(\text{C})\text{-}\kappa^2(\text{O},\text{O}')\text{-CO}_2)(\text{SnAr}^{\text{NEt}_2})$ (**2-GeSn**) in the solid state as determined by X-ray crystallography. Most atoms omitted, and Et groups shown in wireframe format for clarity. Thermal ellipsoids set at the 40% probability level. Key bond lengths and angles (Å): Ge1–N 2.346(3), 2.618(3), Ge1–C17 2.050(4), C17–O 1.271(6), 1.283(6), Sn1–O 2.301(3), 2.336(3), Sn1–N 2.643(4), 2.667(4), O–C–O 117.2(4).

In conclusion, we show that the pincer ligand supported dimetallynes $(\text{Ar}^{\text{NEt}_2}\text{E})_2$ (E = Ge, Sn) take up CO_2 under mild conditions to generate insertion compounds of the type $\text{Ar}^{\text{NEt}_2}\text{E}(\text{CO})_2\text{EAr}^{\text{NEt}_2}$. The mode of ligation of the CO_2 fragment is dependent on the identity of the group 14 element, with the larger size of tin favouring a $\mu\text{-}\kappa^1(\text{C})\text{-}\kappa^2(\text{O},\text{O}')$ -binding mode (cf. $\mu\text{-}\kappa^1(\text{C})\text{-}\kappa^1(\text{O})$ in the germanium case). This uptake of carbon dioxide is uniquely reversible, as demonstrated spectroscopically by VT-NMR measurements and chemically through thermodynamically-controlled exchange reactions.^[18,20]

Acknowledgements

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Keywords: Carbon Dioxide • Digermynes • Distannynes • Dimetallynes • Pincer Ligands

The data that support the findings of this study are available in the supplementary material of this article.

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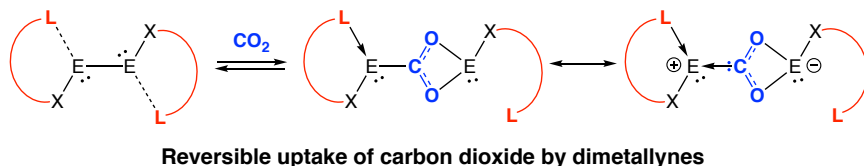
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- [18] Deposition Numbers 2129770-2129777 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
- [19] For a distannyne which undergoes reversible cleavage into arylSn(I) radicals in hydrocarbon solution, see (a) T. Y. Lai, L. Tao, R. D. Britt, P. P. Power, *J. Am. Chem. Soc.* **2019**, *141*, 12527-12530. For redistribution reactions in germanium-germanium bonded systems occurring via metathesis, see: (b) L. Klemmer, A. L. Thömmes, M. Zimmer, V. Huch, D. Morgenstern, D. Scheschke, *Nature Chem.* **2021**, *13*, 373-377.
- [20] During submission of this manuscript a related study of CO₂ uptake was reported by So and co-workers: J. Fan, S. Quek, M.-C. Yang, Z.-F. Zhang, M.-D. Su, C. W. So, *Chem. Commun.* **2022**, *58*, 1033-1036.

RESEARCH ARTICLE

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We report the reversible uptake of CO₂ by dimetallynes featuring ancillary hemi-labile pincer ligands. Insertion into the Ge–Ge/Sn–Sn bonds yields species containing an E(CO₂)E unit, with the mode of ligation of the CO₂ fragment being dependent on the group 14 element. The thermodynamics of CO₂ uptake can be established through VT-NMR, and the chemical consequences of reversibility demonstrated by thermodynamically-controlled exchange reactions.

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