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Facile Metathetical Exchange between Carbon Dioxide and the Divalent Group 14 Bisamides $M[N(SiMe_3)_2]_2$ (M = Ge and Sn)

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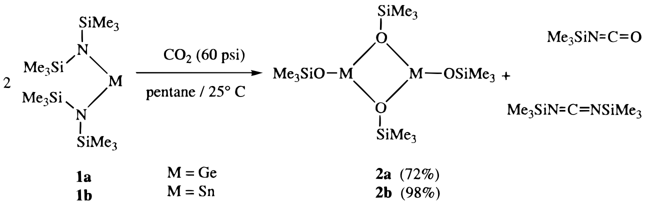
Ligand metathesis reactions, processes through which component parts of different molecules are exchanged to produce new structures, lie at the heart of many fundamental metal-mediated industrial and biological transformations. Of these, metathetical exchanges involving oxo- and nitrene-transfer from small molecules, such as carbon monoxide, carbon dioxide, dioxygen, and dinitrogen, are perhaps the most important in that they provide essential pathways for the production of feedstock materials through the "fixation" of these readily available gaseous reactants.[1] For this reason, there remains considerable current interest in the identification/development of additional metal-mediated transformations that fall into this category.[2] Herein, we describe a new class of oxo-transfer reaction that involves the unprecedented metathetical exchange between carbon dioxide and the divalent group 14 bisamides $M[N(SiMe_3)_2]_2$ (**1a** and **1b**) (M = Ge and Sn, respectively).[3−5] This process is noteworthy in that, along with the production of trimethylsilyl isocyanate and 1,3-bis(trimethylsilyl)carbodiimide (BTSCD), it generates, in high yield, the respective dimeric divalent group 14 bisalkoxide complexes $[M(OSiMe_3)_2]_2$ (**2a** and **2b**), according to Scheme 1. Although previously mentioned in the literature, **2a** and **2b** have not, until now, been obtained in pure form, nor was the latter compound readily accessible by the published route.[6] A convenient source of large quantities of **2b** is important since it has recently been shown that this compound can be converted, in nearly a quantitative yield, to the structurally and chemically intriguing polynuclear cluster $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OSiMe_3)_4$.[7]

As an illustrative example of the metathesis reaction shown in Scheme 1, a solution of 23.3 g (53 mmol) of **1b** in 100 mL of pentane was transferred to two pressure reaction vessels[8] in equal portions, and these were then pressurized to 60 psi with research grade carbon dioxide (99.99%). Within 10 min, the deep orange-red reaction mixture lightened to a pale yellow color, and after 1 h, it was nearly colorless. At this time, low-boiling volatile material was removed (and collected) from the combined portions by vacuum transfer at room temperature to leave behind a light yellow material that was then fractionally distilled under vacuum to yield 12.3 g of a colorless oil (bp 85 °C at 0.05 mmHg), shown to be pure **2b** on the basis of detailed chemical and spectroscopic analyses (98% yield).[9] Analysis of the low-boiling material by gas chromatography (GC) and ^1H NMR spectroscopy revealed that it consisted of a mixture of pentane, Me_3SiNCO, and BTSCD, and pure samples of the latter two were then obtained by fractional distillation at atmospheric pressure. Following the reaction by ^1H NMR spectroscopy (toluene-d_8, $c = 0.34$ M, 60 psi) established that the metathesis process proceeds virtually quantitatively, and on this scale (i.e., 105 mg of **1b**), the ratio of Me_3SiNCO to BTSCD formed is *ca* 4:1. However, on a preparative scale, this ratio was shown by GC and ^1H NMR analyses to be sensitive to temperature, concentration, and the amount of starting material, thereby indicating that the isocyanate product might be able to competitively react with **1b** to produce the carbodiimide. Indeed, in a separate study, the reaction between **1b** and 2 equiv of pure Me_3SiNCO was also found to occur rapidly at room temperature to produce both **2b** and BTSCD in high yield. Finally, it was determined that **2a** (bp 66 °C at 0.025 mmHg) could be prepared in a similar manner in a 72% yield by starting with **1a**; although in this case, a reaction time of 12 h was utilized, since the metathesis process visually appeared to proceed much more slowly.[10]

Scheme 1



Spectroscopic data presented here[9,10] support the previous conclusion[6a,c] that **2a** and **2b** retain their dimeric structure in solution, and in this regard, they resemble the corresponding *tert*-butoxy analogs $[M(OBu^t)_2]_2$ (**3a** and **3b**) (M = Ge and Sn, respectively).[11] Interestingly, it has been reported that **2b** cannot be prepared through the salt-elimination method that utilizes tin(II) dichloride and sodium trimethylsilanolate,[6c] and indeed, we find that only a low yield (35%) of **2b** can be obtained by this procedure. One possible problem with employing this standard synthetic methodology is that it has been determined that, in solution, **2b** reacts readily with sodium trimethylsilanolate to provide a crystalline complex possessing the empirical formula $Na(OSiMe_3)_3Sn$ but which is likely the dimer.[12,13] The alternative reported procedure for the synthesis of **2b** involves alcoholysis of dicyclopentadienyltin(II) (stannocene) with trimethylsilanol; however, this is not a practical method for the large-scale preparation of this particular compound.[6c] Thus, the carbon dioxide metathesis route shown in Scheme 1 is not only novel but also represents the best current method for the synthesis of **2b**.

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(1) (a) Guczi, L., Ed.; *New Trends in CO Activation. Studies in Surface Science and Catalysis*; Elsevier: New York, 1991; Vol. 64. (b) Ayers, W. M., Ed.; *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series 363; American Chemical Society: Washington, D.C., 1988. (c) Barton, D. H., Martell, A. F., Sawyer, D. T., Eds.; *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Plenum Press: New York, 1993. (d) Hardy, R. W. F., Bottomly, F., Burns, R. C., Eds.; *A Treatise on Dinitrogen Fixation*; Wiley-Interscience: New York, 1979.

(2) For the first demonstration of dinitrogen metathesis involving a well-defined transition metal complex, see: Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

(3) Commercially available **1a** and **1b** can be prepared from the corresponding metal dihalides via the salt elimination method, see: Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.

(4) For a review of the structures, properties, and chemical reactivities of **1a** and **1b**, see: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides. Syntheses, Structures, and Physical and Chemical Properties*; Ellis Horwood Limited: Chichester, 1980.

(5) An oxo-transfer reaction between carbon dioxide and decamethylsilicocene, $Cp^*{}_2Si$, ($Cp^* = C_5Me_5$), not involving metathetical exchange, has recently been reported, see: Jutzi, P.; Eikenberg, D.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 753.

(6) For **2a**, see: (a) du Mont, W.-W.; Grenz, M. *Chem. Ber.* **1981**, *114*, 1180. For **2b**, see: (b) Tatlock, W. S.; Rochow, E. G. *J. Org. Chem.* **1952**, *17*, 1555. (c) du Mont, W.-W.; Grenz, M. *Z. Naturforsch.* **1983**, *38B*, 113.

(7) Sita, L. R. Submitted.

(8) Messerle, L. In *Experimental Organometallic Chemistry. A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357, American Chemical Society: Washington, D.C., 1987; Chapter 7.

(9) Anal. Calcd for $C_6H_{18}O_2Si_2Sn$: C, 24.26; H, 6.11. Found: C, 24.37; H, 6.53. ^1H NMR (300 MHz, toluene-d_8) δ 0.40 (s) at 20 °C, 0.38 (s, 9 H), 0.18 (s, 9 H) at −70 °C. ^{119}Sn NMR (186 MHz, toluene-d_8) δ −220 at 20 °C, −218 [$^2J(^{119}Sn-^{117}Sn) = 234$ Hz] at −50 °C.

(10) Anal. Calcd for $C_6H_{18}O_2Si_2Ge$: C, 28.72; H, 7.23. Found: C, 28.21; H, 7.37. ^1H NMR (300 MHz, toluene-d_8) δ 0.26 (br s) at 20 °C, 0.21 (s, 9 H), 0.05 (s, 9 H) at −70 °C.

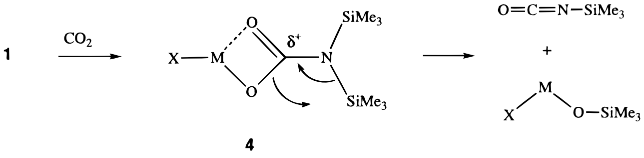
(11) Veith, M.; Weidner, S.; Kunze, K.; Käfer, D.; Hans, J.; Huch, V. *Coord. Chem. Rev.* **1994**, *137*, 297.

(12) Sita, L. R. Unpublished results.

(13) Compound **3b** reacts similarly with 1 equiv of $NaOBu^t$ to provide the dimer, $[Na(OBu^t)_3Sn]_2$.[11]

S0002-7863(96)02281-0 CCC: $12.00

Scheme 2



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X = N(SiMe$_3$)$_2$ or OCON(SiMe$_3$)$_2$

The mechanism by which the metathesis process occurs is important for several reasons. To begin, carbon dioxide is thermodynamically quite stable, and therefore, at first glance, the process shown in Scheme 1 might appear to be energetically unfavored. Consideration of relative M−N and M−O (M = Si, Ge, and Sn) bond energies, however, suggests that a strong driving force for this metathesis reaction is derived from the conversion of the former bond type into the more enthalpically favored latter.[4] Indeed, the same driving force is recognized as being responsible for the ready formation of a large variety of transition and main group metal carbamates (i.e., M−OCONR$_2$) from the insertion of carbon dioxide into the corresponding M−NR$_2$ bonds.[4] What remains unique about the present case, however, is that this is the first fully documented case where the initial carbon dioxide insertion process is apparently followed by a facile molecular rearrangement that involves elimination of an isocyanate fragment. Accordingly, an understanding of the factors that control this overall transformation may lead to the development of either new synthetic methods or new catalysts for the direct production of commercially important isocyanates via the metal-mediated carbonylation of amines. Given this, we put forth the mechanism shown in Scheme 2. As mentioned previously, there is substantial evidence obtained with other systems to support the insertion of carbon dioxide into the M−N bonds of **1** to form the carbamate complex **4**.[14] Here, however, an important point is made that, due to the subvalent nature of the group 14 metal center in **4**, we propose that the carbamate ligand binds in a bidentate fashion as shown. This particular mode of ligation might then facilitate the 1,3-shift of a trimethylsilyl group by the enhancement of its electrophilic character due to that of the carbonyl carbon. Support for this type of 1,3-molecular-shift rearrangement is scarce, but it does include the observation of the production of a small amount of Me$_3$SiNCO (5−10%) from the reaction of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Pr and Nd) with carbon dioxide.[15] In addition, in a somewhat related reaction, the production of methyl isothiocyanate (MeNCS) and methyl isocyanate (MeNCO) from the reaction of bis(trimethylstannyl)methylamine, (Me$_3$Sn)$_2$NMe, with carbon disulfide and carbonyl sulfide, respectively, has been observed to proceed with concomitant formation of bis(trimethyltin)sulfide.[16] With respect to this latter observation, it is important to note that the corresponding reaction of (Me$_3$Sn)$_2$NMe with carbon dioxide provides only *O*-trimethyltin-*N*-methyltrimethyltin carbamate, Me$_3$SnOCONMe(SnMe$_3$), with no evidence of MeNCO being produced.

In summary, a facile carbon dioxide metathesis reaction involving the subvalent group 14 bisamides **1a** and **1b** has been documented. Given that these starting materials are readily accessible from bis(trimethylsilyl)amine, this metathesis process can be viewed as providing the key oxo-transfer step in an overall carbonylation of an amine to produce an isocyanate through the fixation of carbon dioxide. The metathesis process also provides a practical route to the subvalent bis(trimethylsilanolato) complexes **2**, and we are currently exploring the extent to which similar transformations are accessible to other transition and main group metal complexes bearing the bis(trimethylsilyl)amido ligand.

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(14) No speculation is made as to whether a mono- or biscarbamate intermediate is initially formed.

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