

**<sup>2</sup>((Catch Phrase))**

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# Reversible CO<sub>2</sub> Addition to Si=O Bond and Synthesis of a Persistent SiO<sub>2</sub>-CO<sub>2</sub>-Cycloadduct Stabilized by a Lewis Donor-Acceptor Ligand

Ricardo Rodriguez, Isabel Alvarado-Beltran, Jérémy Saouli, Nathalie Saffon-Merceron, Antoine Baceiredo, Vicenç Branchadell, Tsuyoshi Kato\*

**Abstract:** The donor-stabilized sila-β-lactone **1** reacts with CO<sub>2</sub> via a remarkable reversible [2+2]-cycloaddition reaction to form the spiro-cyclic silicon carbonate derivative **2**. Furthermore, photolysis of **2** under pressure of CO<sub>2</sub> affords the first persistent SiO<sub>2</sub>-CO<sub>2</sub>-cycloadduct **3**, presenting a Si<sub>2</sub>O<sub>4</sub>-like structure, which is stabilized by a Lewis donor-acceptor type ligand. As predicted by theoretical calculations, in marked contrast to the thermodynamically stable SiO<sub>2</sub>-dimer, the SiO<sub>2</sub>-CO<sub>2</sub> mixed cycloadduct **3** is labile and readily releases CO<sub>2</sub>.

Although carbon dioxide (CO<sub>2</sub>) and silicon dioxide (SiO<sub>2</sub>) are two archetypal group-14 oxides with great basic and applied significance in chemistry, their physical and chemical properties are completely different. CO<sub>2</sub> is a thermodynamically stable molecule held together by C=O double bonds, which exists in the gas phase under ambient conditions. The activation of this highly stable molecule, in order to use it as renewable carbon source,<sup>[1,2]</sup> as well as its capture and its storage<sup>[3]</sup> are particularly important issues in current chemistry. In marked contrast, monomeric SiO<sub>2</sub> is a very unstable molecule and forms extremely stable 3D-network structures constituted only by Si-O σ-bonds. Found in nature in many different forms, such as sand or quartz, silica (SiO<sub>2</sub>)<sub>n</sub> is the

most abundant component in the earth's crust. The dimerization processes of CO<sub>2</sub> and SiO<sub>2</sub> clearly highlight their differences. Indeed, in contrast to the strongly exothermic dimerization of SiO<sub>2</sub> (ΔE = -81.6 kcal/mol) leading to [2+2] cycloadduct Si<sub>2</sub>O<sub>4</sub> **I**, the dimerization of CO<sub>2</sub> to give **II** is not a favored process (ΔE = +42.7 kcal/mol).<sup>[4]</sup> Instead, CO<sub>2</sub> forms a weak dimer **III** in which two molecules are held together by van der Waals-type interactions,<sup>[5]</sup> and the formation of carbon-SiO<sub>2</sub>-like network structures requires extremely high pressure conditions (> 40 GPa).<sup>[6,7]</sup>

What about the reaction between these two oxides to form [2+2] cycloadduct **IV**? Such a fundamental reaction has been poorly studied to date in spite of the great potential of the mixed SiO<sub>2</sub>-CO<sub>2</sub>-related network polymers. Moreover, theoretical calculations predicted a moderately exothermic SiO<sub>2</sub>-CO<sub>2</sub> [2+2] cycloaddition process (ΔE = -9.9 kcal/mol), indicating that the reaction is thermodynamically feasible.<sup>[8]</sup> Recently, it was described that the reaction of CO<sub>2</sub> with porous silica needs very high pressures (18 - 26 GPa), and the resulting silicon carbonate phases were characterized by IR.<sup>[9]</sup> Furthermore, the expected SiCO<sub>4</sub> molecule, generated *in situ* as a highly reactive species, via laser ablation of silicon in a O<sub>2</sub>/CO<sub>2</sub>/Ar gas mixture, was only detected by IR spectroscopy at 11 K.<sup>[8]</sup>

[\*] Dr. R. Rodriguez, Dr. I. Alvarado-Beltran, J. Saouli, Dr. A. Baceiredo, Dr. T. Kato  
Université de Toulouse, UPS, and CNRS, LHFA UMR  
5069, F-31062 Toulouse, France.  
Fax: (+33) 5-6155-8204  
E-mail: kato@chimie.ups-tlse.fr  
Homepage: <http://hfa.ups-tlse.fr>

Prof. V. Branchadell  
Departament de Química  
Universitat Autònoma de Barcelona  
08193 Bellaterra (Spain)

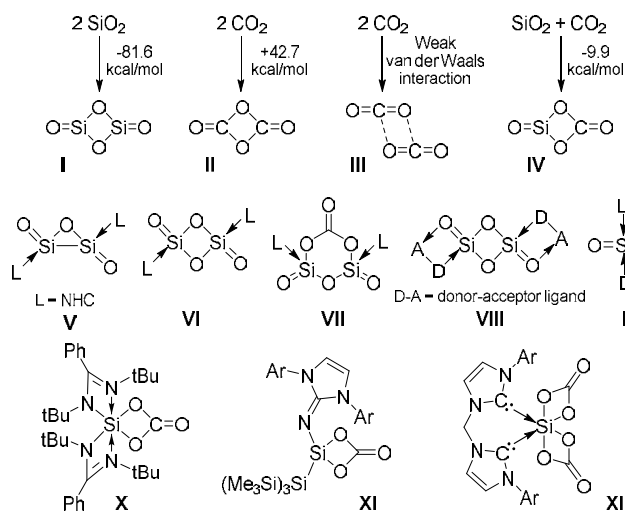
Dr. R. Rodriguez  
Departamento de Química Inorgánica  
ISQCH-Universidad de Zaragoza  
50009 Zaragoza (Spain)

Dr. N. Saffon-Merceron  
Université de Toulouse, UPS, and CNRS, ICT FR2599, 118  
route de Narbonne, F-31062 Toulouse, France

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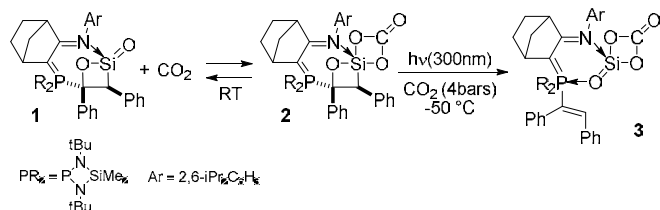
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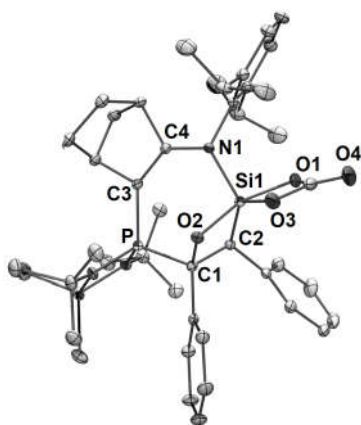
Recently, Robinson et al. have isolated the three-membered cyclic silicon oxide **V** and the SiO<sub>2</sub>-dimer **VI** which are well stabilized by strongly electron donating and bulky *N*-heterocyclic carbene (NHC) ligands.<sup>[10]</sup> The same research group also reported the synthesis of cyclic six-membered mixed silicon and carbon oxide **VII** by reaction of **V** with CO<sub>2</sub>.<sup>[11]</sup> However, they have mentioned that the SiO<sub>2</sub>-dimer **VI** is not stable in the presence of CO<sub>2</sub>, preventing the formation of the corresponding mixed SiO<sub>2</sub>-CO<sub>2</sub> cycloadduct. In the same vein we have recently reported the synthesis of SiO<sub>2</sub>-dimer **VIII** stabilized by an iminophosphorane

type donor-acceptor (D/A) ligand as well as the first SiO<sub>2</sub> molecule **IX** stabilized by a mixed (donor) L- and (donor-acceptor) D/A-ligand system.<sup>[12]</sup> The stability of these molecules is mainly due to the peculiar effect of the D/A-ligand which efficiently binds the silanone (>Si=O) moiety.<sup>[12,13]</sup> Here, we report a unique RT reversible [2+2] cycloaddition between a silanone function and CO<sub>2</sub>, leading to the first persistent SiO<sub>2</sub>-CO<sub>2</sub>-cycloadduct of type **IV** stabilized by a D/A-ligand. To the best of our knowledge, this is the first report describing the reversible addition of CO<sub>2</sub> on stable silanones.<sup>[14,15]</sup> Nonetheless, a few examples of stable sila-carbonates (**X** and **XI**)<sup>[16]</sup> and sila-dicarbonate **XII**,<sup>[17]</sup> synthesized by the reactions of transient silanones or SiO<sub>2</sub>-complexes with CO<sub>2</sub>, have recently been characterized.

A CDCl<sub>3</sub> solution of base-stabilized sila- $\beta$ -lactone **1**<sup>[13]</sup> readily reacts with CO<sub>2</sub> (4 bars), in a J-Young NMR tube at -50 °C, affording the [2+2] cycloadduct **2** (Scheme 1). The reaction is stereospecific leading to the formation of two diastereomers of **2** in the same proportions as those of sila- $\beta$ -lactone **1** as indicated by <sup>31</sup>P-NMR spectroscopy [ $\delta$  = 54.3 ppm (92 %), and  $\delta$  = 50.9 ppm (8 %)]. In the <sup>29</sup>Si-NMR spectrum, a doublet was observed at  $\delta$  = -98.3 ppm ( $J_{\text{SiP}}$  = 16.2 Hz) for the spiro-silicon atom, at considerably higher field compared with that of **1** ( $\delta$  = -52.7 ppm), which is in agreement with the formation of a pentacoordinate silicon center.<sup>[18]</sup> The carbonyl carbon atom appears in the <sup>13</sup>C-NMR spectrum as a singlet signal at  $\delta$  = 154.8 ppm.



**Scheme 1.** Reversible reaction of **1** with CO<sub>2</sub>.

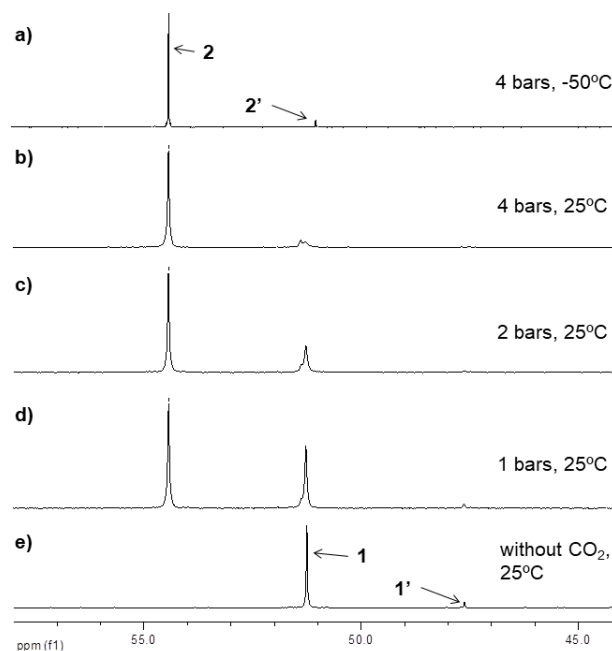


**Figure 1.** Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-O1 1.804(2), Si1-O2 1.716(2), Si1-O3 1.726(2), Si1-C2 1.899(2), O2-C1 1.443(3), C1-C2 1.567(3), O1-C5 1.321(4), C5-O4 1.205(3), C5-O3 1.359(3), C1-P1 1.866(2), N1-Si1 1.775(2), O1-Si1-O2 160.69(8), Si1-O2-C1 96.22(12), O2-C1-C2 99.59(16), C1-C2-Si1 85.20(12), C2-Si1-O2 78.82(8), O3-Si1-O1 73.63(9).

Cycloadduct **2** was isolated as colorless crystals from a cold (-50 °C) CH<sub>2</sub>Cl<sub>2</sub> solution under CO<sub>2</sub> pressure (4 bars). The X-ray diffraction analysis reveals a spiro cyclic structure at the Si1 atom,

with two four-membered silicon carbonate- and 1,2-oxasilatane rings (Figure 1).<sup>[19]</sup> The structure also shows a strongly distorted trigonal pyramidal geometry around the penta-coordinate Si1 atom with O1 and O2 atoms in the axial positions (O1-Si1-O2: 160.69°), and two quite different Si-O bond lengths. Indeed the Si-O1 distance (1.804 Å) in the carbonate fragment is similar to those observed for other pentacoordinate Si compounds,<sup>[20]</sup> while the Si-O2 distance (1.716 Å) is slightly longer than that of **1** (Si-O: 1.691 Å). The C-O bond lengths (C5-O1: 1.321 Å, C5-O3: 1.359 Å, C5-O4: 1.205 Å) are very similar to those observed for the previously reported cyclic sila-carbonate **X**.<sup>[16]</sup>

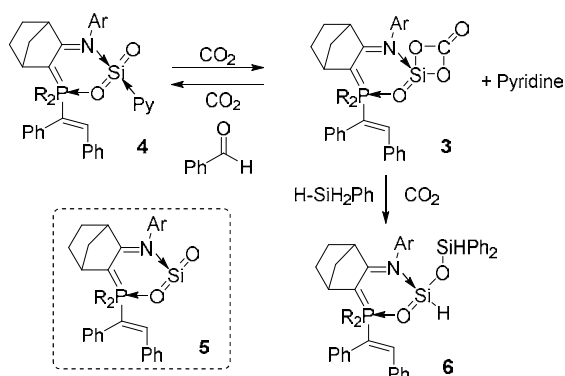
Of particular interest, the formation of cycloadduct **2** is a reversible process as indicated by the temperature and CO<sub>2</sub>-pressure dependence of the relative proportions of both species **1** and **2** in solution. Indeed, the <sup>31</sup>P-NMR spectroscopy indicates that **2** is the only detectable species at -50 °C, while a mixture of **1** and **2** (1:10) is observed at 25 °C (Figure 2a). Furthermore, the gradual reduction of the CO<sub>2</sub> pressure (4 bars → 1 bar) increases the proportion of **1** (10 % → 50 %) and the CO<sub>2</sub> replacement by an argon atmosphere leads to a clean regeneration of the starting sila- $\beta$ -lactone **1** (Figure 2b-d). This CO<sub>2</sub>-release also takes place in the solid state, since colorless crystals of **2** gradually become yellow at room temperature under argon, and the clean regeneration of **1**, in the solid state, was confirmed by <sup>31</sup>P-NMR spectroscopy. In good agreement with these experimental observations, the calculated Gibbs free energy of the reaction is quite small ( $\Delta G$  = -2.5 kcal/mol).



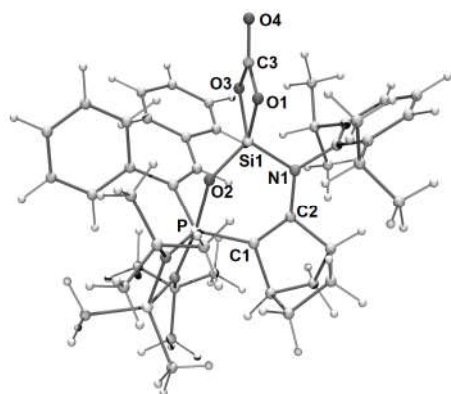
**Figure 2.** Monitoring the reaction of **1** with CO<sub>2</sub> at different CO<sub>2</sub> pressures (bars) at room temperature and -50 °C by <sup>31</sup>P-NMR. **1'** and **2'** are the corresponding minor diastereomers of compounds **1** and **2**.

The photolysis of **2** ( $\lambda$  = 300 nm) under CO<sub>2</sub> pressure (4 bars) at -50 °C leads to the formation of the mixed SiO<sub>2</sub>-CO<sub>2</sub> cycloadduct **3** stabilized by an iminophosphorane D/A-ligand (Scheme 1). Similarly to the previously reported SiO<sub>2</sub>-dimer **VIII**,<sup>[12]</sup> in **3**, the silanone moiety is well stabilized by the push-pull system of the iminophosphorane ligand. Indeed, in the <sup>29</sup>Si NMR spectrum, the signal corresponding to the sila-carbonyl function appears as a doublet at  $\delta$  = -69.1 ppm ( $J_{\text{SiP}}$  = 14.9 Hz) in the same range as that

of **VIII** (-74.0 ppm).<sup>[12]</sup> Moreover, the strong interaction between the oxygen of silanone fragment and phosphorus (acceptor part of the iminophosphorane ligand) in **3**, is clearly indicated by the high-field chemical shift at  $\delta = -40.9$  ppm, in the  $^{31}\text{P}$ -NMR spectrum, which is in good agreement with the presence of penta-coordinate phosphorus atom. The photolytic ring-opening reaction of 1,2-oxasiletane fragment of cycloadduct **2** led to the formation of the phospho-vinyl function in **3** which shows two typical doublets in the  $^{13}\text{C}$ -NMR spectrum ( $\delta = 149.0$  ppm,  $^1J_{\text{PC}} = 164.6$  Hz and  $\delta = 122.3$  ppm,  $^2J_{\text{PC}} = 20.6$  Hz). All the NMR data of  $\text{SiO}_2\text{-CO}_2$  cycloadduct **3** are almost identical to those  $\text{SiO}_2$ -dimer **VIII** except the carbonyl signal in the  $^{13}\text{C}$ -NMR spectrum (149.6 ppm). DFT calculations indicate that the isomerization of **2** to **3** is slightly exergonic ( $\Delta G_{3,2} = 2.6$  kcal/mol). Of particular interest, the same  $\text{SiO}_2\text{-CO}_2$  cycloadduct **3** can be readily obtained by addition of  $\text{CO}_2$  (5 bars) on the stable  $\text{SiO}_2$ -complex **4** featuring an iminophosphorane and pyridine ligands, after releasing free pyridine (Scheme 2). Up to now, the fragility and the high solubility of **3** did not allow any characterization in the solid state by X-ray diffraction analysis. Calculated geometry of **3** by DFT calculations at the M06-2X/6-31G(d) level is similar to that observed for  $\text{SiO}_2$ -dimer **VIII** (Figure 3).<sup>[12]</sup>



**Scheme 2.** Synthesis and reactivity of  $\text{SiO}_2\text{-CO}_2$  cycloadduct **3**.



**Figure 3.** Calculated structure of  $\text{SiO}_2\text{-CO}_2$  cycloadduct **3** (M06-2X/6-31G(d) level). Selected bond lengths [Å] and angles [°]: Si1-O1 1.707, Si1-O2 1.577, O2-P 1.878, N-Si1 1.716, O1-C3 1.373, C3-O3 1.185, O1-Si-O3 78.73, Si-O1-C389.02, O1-C3-O3 103.52, N1-Si1-O2 107.58.

Although DFT calculations predict that the dissociation of  $\text{CO}_2$  from  $\text{SiCO}_4$  complex **3** ( $\Delta G_{3 \rightarrow 5} = 17.2$  kcal/mol) is more endergonic than that from free  $\text{SiCO}_4$  **IV** ( $9.9^{[8]}-11.4$  kcal/mol), **3** is still labile.

Indeed, in the absence of  $\text{CO}_2$  atmosphere, it readily decomposes at room temperature leading to unidentified products. Furthermore, **3** immediately reacts with ambiphilic reagents such as phenylsilane at room temperature, releasing  $\text{CO}_2$ , to afford the corresponding 1,2-adduct **6** (Scheme 2). In marked contrast, the addition of nucleophiles such as pyridine or  $N,N$ -dimethylaminopyridine to **3** results in non-selective reactions and no regeneration of  $\text{SiO}_2$ -complex **4** was observed even in the presence of an excess amount of pyridine (20 eq.). This result is in disagreement with calculations which indicate a considerably small free-energy of the reaction ( $\Delta G_{3 \rightarrow 4} = -4.3$  kcal/mol) implying a possible reversibility of the process. This could be explained by the kinetically favored attack of the nucleophile on the carbon centre of  $\text{SiCO}_4$  fragment in **3** rather than on the sterically well-shielded silicon which triggers the retro-[2+2] cycloaddition leading to the extremely reactive  $\text{SiO}_2$ -complex **5** (Scheme 2) and ending up with non-selective reactions (Figure 3). Indeed, a smaller and weak nucleophile such as benzaldehyde ( $\text{PhCHO}$ ), which is probably able to reach to the silicon centre, catalyzes the reverse reaction to cleanly give back the corresponding  $\text{SiO}_2$  complex **4** with a pyridine ligand releasing a  $\text{CO}_2$  (Scheme 2). The regeneration of benzaldehyde and the release of  $\text{CO}_2$  after the reaction were confirmed by NMR analysis of the reaction mixture, demonstrating its catalytic behavior. As expected, in the case of even less nucleophilic and bulkier ketone such as 2,2,2-trifluoroacetophenone, the  $\text{SiCO}_4$  species **3** remains intact. The reaction probably starts with the retro-[2+2]-cycloaddition of **3** triggered by the coordination of  $\text{PhCHO}$  at the silicon centre to form a transient  $\text{PhCHO} \rightarrow \text{SiO}_2$  adduct **7**, which readily undergoes a ligand exchange reaction with more nucleophilic pyridine to afford **4**. This was supported by the DFT calculations indicating a decreased Gibbs activation energy for the  $\text{CO}_2$  dissociation to 22.1 kcal/mol ( $\Delta G_{3 \rightarrow 7}^\ddagger$ ) from 32.0 kcal/mol ( $\Delta G_{3 \rightarrow 5}^\ddagger$ ) by the interaction of benzaldehyde with **3** as well as the exergonic nature of the ligand exchange reaction from the  $\text{PhCHO}$  to the pyridine to afford the  $\text{SiO}_2$ -complex **4** ( $\Delta G_{7 \rightarrow 4} = -10.8$  kcal/mol).

In conclusion, we have successfully demonstrated that the donor stabilized sila- $\beta$ -lactone **1** reversibly reacts with  $\text{CO}_2$  at room temperature affording spiro-cyclic silicon carbonate **2**. Interestingly a photoinitiated retro-[2+2] cycloaddition of the oxasiletane fragment of **2**, has enabled the generation of the first persistent  $\text{SiO}_2\text{-CO}_2$  cycloadduct **3** stabilized by a D/A-ligand. Complex **3** is thermally labile and easily releases  $\text{CO}_2$  to generate the corresponding transient  $\text{SiO}_2$  complex. More detailed study on its properties and possible applications are under active investigation.

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- [1] T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365.
- [2] D. J. Darensbourg, *Inorg. Chem.* **2010**, *49*, 10765.
- [3] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724.
- [4] a) G. Frapper, J.-Y. Saillard, *J. Am. Chem. Soc.* **2000**, *122*, 5367; b) B. I. Dunlap, I. V. Schweigert, A. P. Purdy, A. W. Snow, A. Hu, *J. Chem. Phys.* **2013**, *138*, 134304.
- [5] S. Tsuzuki, T. Uchamaru, M. Mikami, K. Tanabe, *J. Chem. Phys.* **1998**, *109*, 2169.
- [6] V. Iota, C. S. Yoo, H. Cynn, *Science* **1999**, *283*, 1510.
- [7] M. Santoro, F. A. Gorelli, R. Bini, G. Ruocco, S. Scandolo, W. A. Crichton, *Nature* **2006**, *44*, 857.
- [8] J. Dong, L. Miao, M. Zhou, *Chem. Phys. Lett.* **2000**, *355*, 31.

- [9] M. Santoro, F. Gorellia, J. Hainesc, O. Cambon, C. Levelut, G. Garbarino, *Proc. Natl. Acad. Sci.* **2011**, *106*, 7689.
- [10] Y. Wang, M. C. Y. Xie, P. Wei, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Nat. Chem.* **2015**, *7*, 509.
- [11] Y. Wang, M. Chen, Y. Xie, P. Wei, H. F. Schaefer, III, G. H. Robinson, *J. Am. Chem. Soc.* **2015**, *137*, 8396.
- [12] R. Rodriguez, D. Gau, J. Saouli, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 3935.
- [13] R. Rodriguez, D. Gau, T. Troadec, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, T. Kato, *Angew. Chem. Int. Ed.* **2013**, *52*, 8980.
- [14] X. Liu, X.-Q. Xiao, Z. Xu, X. Yang, Z. Li, Z. Dong, C. Yan, G. Lai, M. Kira, *Organometallics* **2014**, *33*, 5434.
- [15] P. Jutzi, D. Eikenberg, A. Möhrke, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 753.
- [16] K. Junold, M. Nutz, J. A. Baus, C. Burschka, C. F. Guerra, F. M. Bickelhaupt, R. Tacke, *Chem. Eur. J.* **2014**, *20*, 9319; b) D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 8134.
- [17] A. Burchert, S. Yao, R. Mglle, C. Schattenberg, Y. Xiong, M. Kaupp, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 1894.
- [18] R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927.
- [19] CCDC-1574750 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [20] K. C. K. Swamy, C. Sreelatha, J. Holmes, R. R. Holmes, *Inorg. Chem.* **1991**, *30*, 3126.

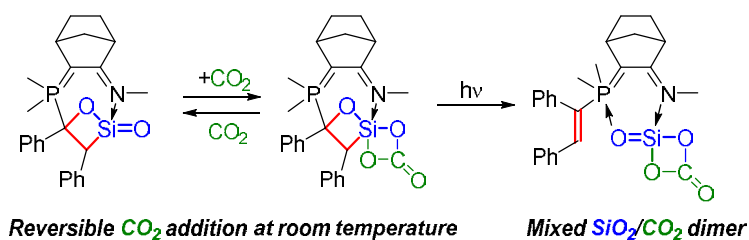
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R. Rodriguez, I. Alvarado-Beltran, J.  
Saouli, N. Saffon-Merceron, A.  
Baceiredo, V. Branchadell, T. Kato

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Reversible CO<sub>2</sub> Addition to Si=O Bond  
and Synthesis of a Persistent CO<sub>2</sub>-SiO<sub>2</sub>  
Dimer Stabilized by a Lewis Donor-  
Acceptor Ligand



The donor-stabilized sila-β-lactone reacts with CO<sub>2</sub> via a [2+2]-cycloaddition to form the spiro-cyclic silicon carbonate derivative **2**. Of particular interest, this process is reversible at room temperature. Furthermore, the photolysis of resulting CO<sub>2</sub> adduct affords the first persistent SiO<sub>2</sub>-CO<sub>2</sub> mixed dimer (SiCO<sub>4</sub>), presenting a Si<sub>2</sub>O<sub>4</sub>-like structure, which is stabilized by a Lewis donor-acceptor type ligand. As predicted by theoretical calculations, in marked contrast to Si<sub>2</sub>O<sub>4</sub>, the mixed dimer SiCO<sub>4</sub> is labile and readily releases CO<sub>2</sub>.

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