

Copper-Mediated Reduction of CO₂ with pinB-SiMe₂Ph via CO₂ Insertion into a Copper–Silicon BondChristian Kleeberg,^{*,†} Man Sing Cheung,[‡] Zhenyang Lin,[‡] and Todd B. Marder[§][†]Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina zu Braunschweig, Hagenring 30, 38106 Braunschweig, Germany[‡]Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (China)[§]Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.

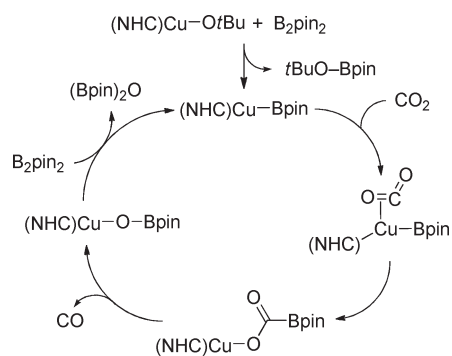
S Supporting Information

ABSTRACT: Reaction of [(IPr)Cu-OtBu] (1) with pinB-SiMe₂Ph (2) leads to the Cu-silyl complex [(IPr)Cu-SiMe₂Ph] (3). Insertion of CO₂ into the Cu–Si bond of 3 is followed by transformation of the resulting silanecarboxy complex [(IPr)Cu-O₂CSiMe₂Ph] (4) to the silanolate complex [(IPr)Cu-OSiMe₂Ph] (5) via extrusion of CO. As 5 reacts readily with 2 to regenerate 3, a catalytic CO₂ reduction to CO is feasible. The individual steps were studied by *in situ* ¹³C NMR spectroscopy of a series of stoichiometric reactions. Complexes 3, 4, and 5 were isolated and fully characterized, including single-crystal X-ray diffraction studies. Interestingly, the catalytic reduction of CO₂ using silylborane 2 as a stoichiometric reducing agent leads not only to CO and pinB-O-SiMe₂Ph but also to PhMe₂Si-CO₂-SiMe₂Ph as an additional reduction product.

Copper-catalyzed silylation reactions employing silylboranes as silyl sources have recently attracted considerable attention.¹ It has been proposed that in these reactions an electrophilic substrate (e.g., α,β -unsaturated carbonyl compound, imine, allyl chloride) reacts with a nucleophilic copper silyl species to form a copper γ -silylalcoholato, α -silylaminato, or halo complex. From this complex the copper silyl species is regenerated by a transmetalation reaction with a silylborane. This is believed to proceed either directly, in the case of copper γ -silylalcoholato complexes, or after formation of a copper alcoholato complex, in the case of α -silylaminato and halo complexes.^{1,2} A recently published synthetic and mechanistic study on the 1, 2-silylboration of aldehydes supports this general mechanism. However, for kinetic reasons the transmetalation step itself, hence the regeneration of the copper silyl species, could not be studied in the particular system used.² In this study, we examined the reaction of a (IPr)Cu silyl complex with CO₂ as an exemplary electrophile.

The reaction of copper complexes of the type [(NHC)Cu-E] (NHC = *N*-heterocyclic carbene) with CO₂ has been studied for E = B((OC(CH₃)₂)₂) = Bpin, SnPh₃, CH₃, 4-(CH₃O)C₆H₄,³ but for E = SiPh₃, the reaction has only been noted briefly to give [(IPr)CuOSiPh₃] (IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene).^{3b} In agreement with this report is a recently published DFT study suggesting that the initially formed complex [(IPr)-Cu-O₂C-SiPh₃] releases CO to give [(IPr)CuOSiPh₃].⁴

Scheme 1. Simplified Mechanism of the Copper-Catalyzed Reduction of CO₂ to CO with B₂pin₂ According to DFT Calculations⁵



The corresponding reaction for E = Bpin has been studied in detail both experimentally^{3a} and by DFT calculations (Scheme 1).⁵ For E = Bpin the formation of [(NHC)Cu-OBpin] along with the reduction of CO₂ to CO is observed.^{3a} This complex reacts with B₂pin₂, regenerating the boryl complex and producing (pinB)₂O. Hence, the overall process is the Cu-catalyzed reduction of CO₂ to CO by B₂pin₂. The thermodynamically crucial step in CO₂ reduction to CO is the cleavage of the very stable O=C double bond (532 kJ mol⁻¹).⁶ The aforementioned Cu-catalyzed process overcomes this by forming B–O bonds (806 kJ mol⁻¹),⁶ providing the thermodynamic driving force for the process.

As the Si–O bond is thermodynamically comparable (799 kJ mol⁻¹),⁶ an analogous reaction mechanism involving a silyl copper complex can be envisaged. The copper alcoholato complex [(IPr)CuOtBu] (1) is known to undergo transmetalation with B₂pin₂ and with (OCH₂CMe₂CH₂O)B-(4-MeOC₆H₄) via a σ -bond metathesis pathway to form the corresponding boryl or aryl complex, respectively.^{3a,d,5,7} The related reaction with pinB-SiMe₂Ph is suggested to occur in the recently reported, Cu-catalyzed silyl(bor)ation reactions.¹ Indeed, [(IPr)CuSiMe₂Ph] (3) is formed quantitatively (NMR)⁸ via reaction of 1 with pinB-SiMe₂Ph (2) under mild conditions and can be isolated in 89% yield. The selectivity of this reaction, hence, formation of the Cu silyl

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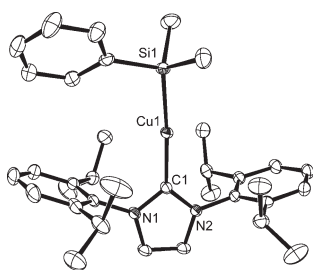


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Cu1–C1 1.933(1), Cu1–Si1 2.2784(4), C1–Cu1–Si1 170.53(4).⁸

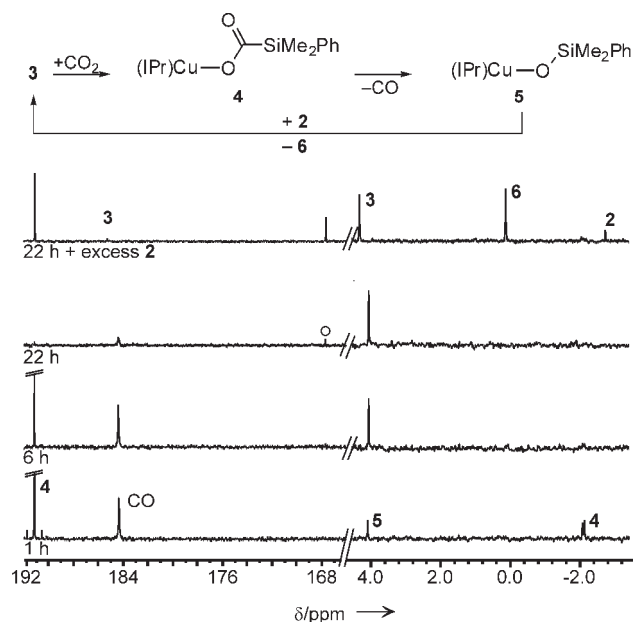


Figure 2. Time-dependent *in situ* $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the reaction of **3** with $^{13}\text{CO}_2$ in C_6D_6 at ambient temperature (O = unidentified signal).

rather than boryl complex, can be rationalized by the ease of quaternization of the Bpin moiety compared to the more difficult increase in coordination number from four to five at the silicon atom.⁹

Linear complex **3** was fully characterized, including a single-crystal X-ray structure determination (Figure 1).⁸ The silyl group in **3** has, in agreement with computational data, a *trans*-influence similar to that of the Bpin moiety and significantly stronger than that of anionic tin and carbon ligands.^{3f}

The reaction of **3** with excess $^{13}\text{CO}_2$ was monitored by ^1H and ^{13}C NMR spectroscopy (Figure 2).⁸ After 1 h the complete consumption of **3** (signal of the SiMe_2 moiety at 4.3 ppm, carbene C signal at 185.7 ppm) and the exclusive formation of two new species were observed. A signal at 191.1 ppm with Si satellites ($J_{\text{CSi}} = 91$ Hz, ^{13}C -enriched) indicates a carbonyl C atom next to a Si atom. This signal is assigned, together with a doublet at -2.2 ppm ($^2J_{\text{CC}} = 4$ Hz, SiMe_2), to compound **4**. Additionally, a singlet at 4.0 ppm (SiMe_2), indicative for **5**, and a signal indicative for free CO at 184.4 ppm are observed. After 6 h, the signals at 191.1 and -2.2 ppm have nearly vanished while the signal at 4.0 ppm has increased; after 22 h, only the signal at 4.0 ppm is observed. Hence, the ^{13}C NMR data suggest the fast initial formation of **4** from **3** and CO_2 followed by a slow but

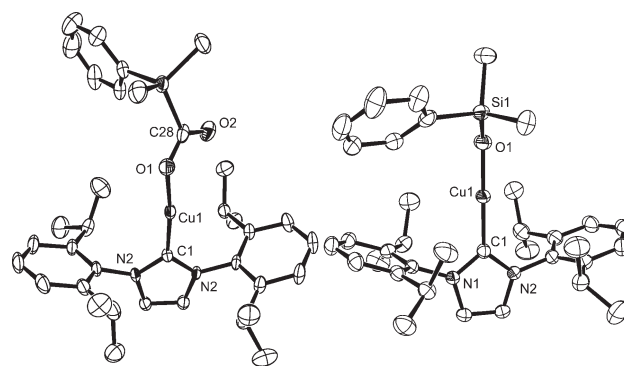


Figure 3. Molecular structures of **4** and **5**. Selected bond lengths [Å] and angles [°]: for **4** (left), Cu1–C1 1.861(2), Cu1–O1 1.844(2), O1–C28 1.282(3), O2–C28 1.237(3), C1–Cu1–O1 173.6(1); for **5** (right), Cu1–C1 1.854(2), Cu1–O1 1.797(2), O1–Si1 1.602(2), C1–Cu1–O1 179.41(8).⁸

clean conversion to **5** with release of CO.⁸ The fast insertion of CO_2 into the Cu–Si bond is in agreement with the calculated barriers for this process of 27.0 and 22.3 kcal mol^{−1}, respectively, for two different model systems.^{4,8} The formation of the silane-carboxylate complex **4** instead of the isomeric complex [(IPr)Cu–C=O(OSiMe₂Ph)] is attributed to the high kinetic nucleophilicity of the silyl moiety in **3**, in contrast to its high thermodynamic oxophilicity.^{5,10} The insertion product **4** releases CO with formation of the silanolate complex **5**. The formation of **5** as the final product is in agreement with the report by Sadighi et al. and the related Cu-boryl system.^{3a,b,5} Computational data on this step support a higher barrier of activation than for the initial insertion step of 24.6 (SiPh₃) and 31.3 kcal mol^{−1} (SiMe₂Ph), respectively, rendering this step rate-determining in the overall reaction.^{4,8} The calculated barrier for the related Cu-boryl system is lower (22.0 kcal mol^{−1}), rationalizing the fact that no intermediate carboxyl complex was observed for this system.^{3a,5}

The above results and close similarities to the CO_2 -reducing Cu-boryl system of Sadighi et al. suggest that **3** should catalyze the reduction of CO_2 to CO using **2** as a stoichiometric reducing agent.^{3a} The only additional reaction necessary in a proposed catalytic cycle analogous to Scheme 1, but with **2** instead of B₂pin₂, is the regeneration of **3** from the silanolate complex **5** and **2**. This reaction is related to the formation of **3** from **2** and [(IPr)Cu–OtBu] and to the reported formation of [(IPr)Cu–Bpin] from [(IPr)Cu–OBpin] and B₂pin₂.^{3a} Monitoring the reaction of **5** with pinB–SiMe₂Ph revealed that, indeed, **3** is formed cleanly along with pinB–O–SiMe₂Ph (**6**) (Figure 2, top).⁸ The reaction was performed with **5** prepared *in situ* after exchanging the $^{13}\text{CO}_2$ atmosphere for dinitrogen. The presence of residual dissolved $^{13}\text{CO}_2$ gives rise to the formation of traces of **4**, illustrating the viability of the proposed catalytic reduction. DFT calculations predicted an activation barrier of 22.0 kcal mol^{−1} for this transmetalation step, significantly higher than that for the related step in the Cu-boryl system (14.3 kcal mol^{−1}).^{5,8}

Complex **4** was initially obtained as several single crystals from a solution of **3** in the presence of traces of CO_2 . More reproducible and suited for the preparation of larger quantities is the reaction of **3** with a 1:1 mixture of CO and CO_2 and crystallization of **4** under a CO atmosphere (29% yield). It may be that a CO adduct of **4** inhibits its decomposition to **5**. The dependence of the stability of **4** on the presence of CO is a subject of ongoing computational and kinetic studies. Complex **5**

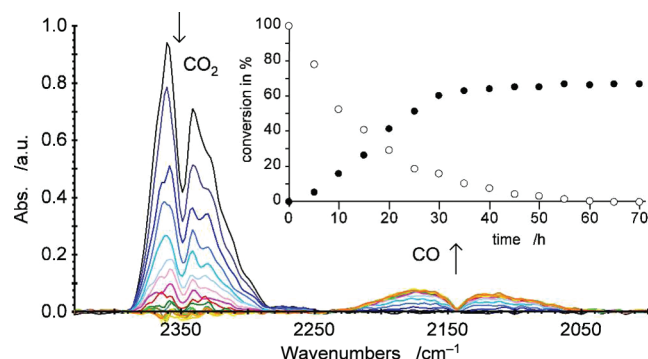


Figure 4. Detail of time-dependent IR spectra during the reduction of CO₂ to CO with **2** in the presence of catalytic amounts of **3**. Inset: Conversion of CO₂ to CO (○, amount of CO₂; ●, amount of CO).⁸

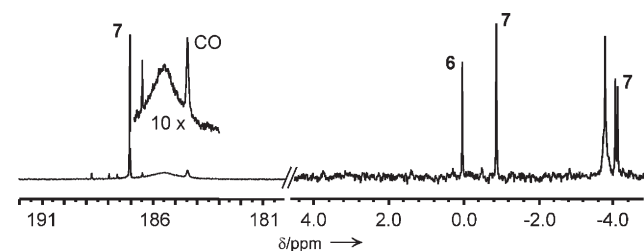


Figure 5. *In situ* ¹³C{¹H} NMR spectrum of the reduction of ¹³CO₂ with **2** in the presence of a catalytic amount of **3** after complete consumption of **2** (79 h).

was readily isolated in 79% yield by crystallization from the reaction mixture of **3** and excess CO₂ (Figure 3).⁸

The reaction of excess **2** (220 μmol) with CO₂ (98 μmol) in the presence of a catalytic amount of **3** (19 μmol, 20 mol %)⁸ was monitored *in situ* by IR spectroscopy of the gas phase above the reaction mixture,⁸ which showed that CO₂ is converted slowly, but catalytically, to CO (Figure 4). However, complete consumption of the CO₂ results in only 70% conversion to CO in the gas phase (Figure 4).

Reaction of **2** with a ca. 35% excess of ¹³CO₂ in the presence of 10 mol % of **3** was monitored by *in situ* ¹³C NMR spectroscopy. Complete consumption of **2** requires 79 h at ambient temperature and pressure (Figure 5).^{8,11} The expected products CO and pinB-O-SiMe₂Ph (**6**) were identified by their distinctive ¹³C NMR signals (CO, 184.4 ppm; **6**, 0.1 ppm (SiMe₂)). However, additional signals at 187.1 (s), −4.1 (d, ²J_{CC} = 4.8 Hz), and −0.9 ppm (s) were assigned to Me₂PhSiCO₂-SiMe₂Ph (**7**) by comparison with an authentic sample. Additionally, the presence of (Bpin)₂O was detected.⁸ Signals at ca. −3.8 (two signals, one broadened) and 185 ppm (broadened) have not yet been assigned but arise from species containing a carbonyl and a SiMe₂ moiety.⁸ During the catalysis, a single set of signals characteristic for *i*Pr moieties is present, suggesting that there is one Cu complex present in detectable amounts and that it is not **3**, **4**, or **5**.⁸ This indicates that the catalytic process is more complicated than expected from the stoichiometric reactions. In accord with this, crystals grown at low temperature from the catalytic reaction before completion proved to be Cu complex **8** (Figure 6), which was also characterized by NMR spectroscopy.⁸

Complex **8** can be described as the Lewis acid/base adduct of **4** and pinB-O₂C-SiMe₂Ph (**9**). The formation of **9** suggests that

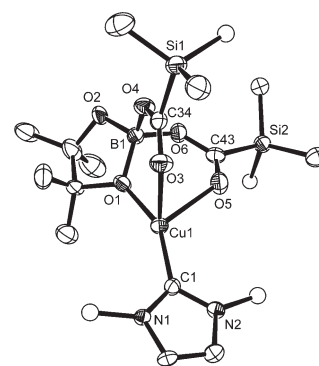


Figure 6. Molecular structure of **8**; the aromatic rings are represented by the *ipso*-carbon atom only (spheres). Selected bond lengths [Å] and angles [°]: Cu1–C1 1.869(7), Cu1–O1 1.988(4), Cu1–O3 2.248(4), Cu1–O5 2.315(5), C1–Cu1–O1 151.3(3), C1–Cu1–O3 116.3(2), C1–Cu1–O5 119.0(3).⁸

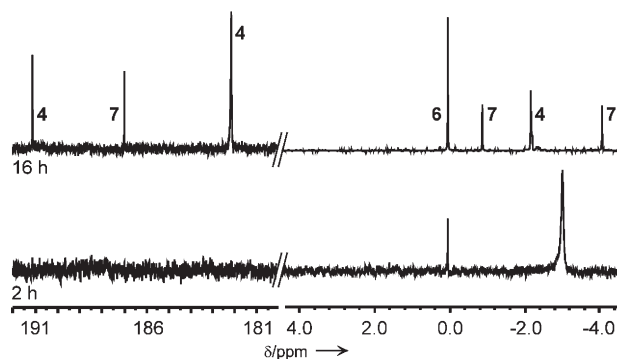
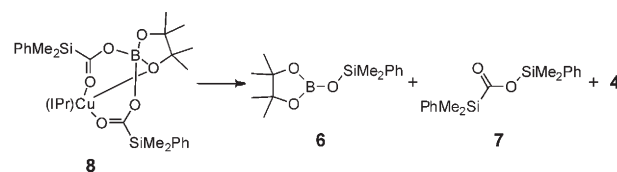
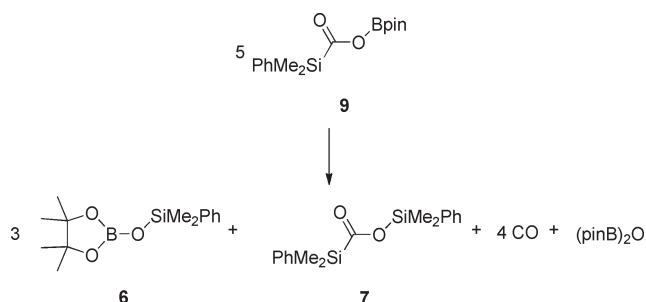
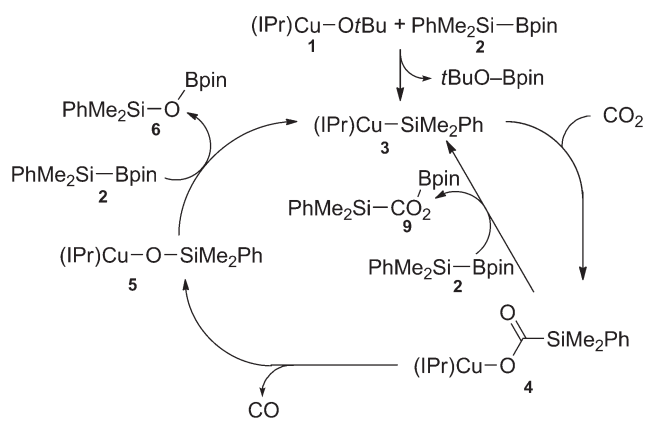


Figure 7. ¹³C{¹H} NMR spectra of **8** after 2 h (bottom) and after 16 h (top) at ambient temperature.

the transmetalation of a SiMe₂Ph moiety from **2** can occur not only by reaction of **5** with **2** to give **3** and **6**, but also by reaction of **4** with **2** to give **3** and **9**. However, neither **8** nor **9** was observed by NMR spectroscopy during the catalytic reduction. This may be explained by the low stability of **8** in solution (Figure 7).

¹H, ¹³C, and ¹¹B NMR spectra obtained from a freshly prepared solutions of **8** indicate the presence of essentially one species (Figure 7, bottom), consistent with the molecular structure of **8**. The broad SiMe₂ ¹H NMR signal (−3.0 ppm, Δ*w*_{1/2} = 11 Hz) suggests a dynamic process. Additionally, traces of **6** (0.1 ppm, Δ*w*_{1/2} = 2 Hz) indicate some decomposition of **8**. After 16 h, the ¹³C NMR spectrum dramatically changed; **4**, **6**, and **7** are unambiguously identified by the distinct ¹³C resonances (**4**, 191.1 (C=O), 182.2 (C–Cu), −2.2 ppm (Me₂Si); **6**, 0.05 ppm (Me₂Si); **7**, 187.1 (C=O), −0.9 (Me₂SiO), −4.1 ppm (Me₂SiCO₂)), and (pinB)₂O was detected.⁸ The formation of these species can be rationalized by fragmentation of **8** into **4** and **9** along with the decomposition of **9** into **6** and **7**. The formation of **7** and **6** from **9** along with the loss of CO is in agreement with the known reactivity of related silanecarboxylic acid derivatives.¹²

Scheme 2

Scheme 3. Proposed Catalytic Cycle for the Cu-Catalyzed Reduction of CO₂ to CO with 2

The stoichiometry of the decomposition of **9** can be rationalized by the equation given in Scheme 2. While the mechanism of this reactions is the subject of ongoing research, it may be related to the conversion of **4** to **5** and the well-known Brook rearrangement of α -silyl alcohols.¹²

It appears that the higher stability of the silanecarboxylic acid complex **4** compared to the related species in the Cu boryl system and its ability to undergo transmetalation with **2** forming **9** are crucial for the distinct reactivity observed here.^{3a,b,5} Plausible pathways relevant to the Cu-catalyzed reduction of CO₂ to CO with **2** are shown in Scheme 3.

In conclusion, the stoichiometric reduction of CO₂ to CO occurs via a two-step process. The insertion of CO₂ into a Cu–Si bond of complex **3** leads to formation of the isolable silanecarboxylato complex **4**, which slowly forms the silanolate complex **5**, releasing CO. However, *in situ* NMR spectroscopy during catalysis suggests a more complicated mechanism than postulated on the basis of the stoichiometric reactions, involving at least the reaction of **4** with **2**, forming **9** and, presumably, **3**. Detailed mechanistic and DFT studies are ongoing.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental procedures, analytical and crystallographic data, NMR spectra, and details of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) It was also verified that no reaction occurs between **2** and CO₂ in the absence of the copper complex as well as in the presence of CuCl under otherwise identical conditions. See SI for details.
- (12) The implied instability of **9** is also in agreement with the observation that the reaction of pinBH with Me₂PhSiCO₂H leads to **7** and not **9**. While the related reactions of pinBH with Me₂PhSiOH and of Me₂PhSiCl with Me₂PhSiCO₂H lead to **6** and **7**, respectively. See SI for details. For the stability of silanecarboxylic acid derivatives and related compounds, see: (a) Igawa, K.; Kokan, N.; Tomooka, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 728–731. (b) Brook, A. G. *J. Am. Chem. Soc.* **1955**, *77*, 4827–4829. (c) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84.