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Efficient Fluoride-Catalyzed Conversion of CO_2 to CO at Room Temperature

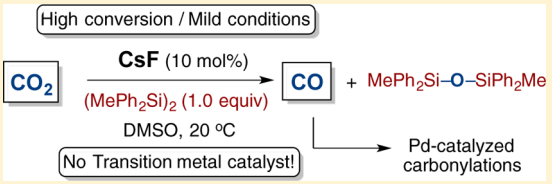
Camille Lescot,[†] Dennis U. Nielsen,[†] Ilya S. Makarov,[†] Anders T. Lindhardt,*[,‡] Kim Daasbjerg,[†] and Troels Skrydstrup*[,†]

[†]The Center for Insoluble Protein Structures (inSPIN), the Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus, Denmark

[‡]The Interdisciplinary Nanoscience Center (iNANO), Biological and Chemical Engineering, Department of Engineering, Aarhus University, Finlandsgade 22, 8200 Aarhus N, Denmark

Supporting Information

ABSTRACT: A protocol for the efficient and selective reduction of carbon dioxide to carbon monoxide has been developed. Remarkably, this oxygen abstraction step can be performed with only the presence of catalytic cesium fluoride and a stoichiometric amount of a disilane in DMSO at room temperature. Rapid reduction of CO_2 to CO could be achieved in only 2 h, which was observed by pressure measurements. To quantify the amount of CO produced, the reduction was coupled to an aminocarbonylation reaction using the two-chamber system, COware. The reduction was not limited to a specific disilane, since $(Ph_2MeSi)_2$ as well as $(PhMe_2Si)_2$ and $(Me_3Si)_3SiH$ exhibited similar reactivity. Moreover, at a slightly elevated temperature, other fluoride salts were able to efficiently catalyze the CO_2 to CO reduction. Employing a nonhygroscopic fluoride source, KHF_2, omitted the need for an inert atmosphere. Substituting the disilane with silylborane, (pinacolato)$BSiMe_2Ph$, maintained the high activity of the system, whereas the structurally related bis(pinacolato)diboron could not be activated with this fluoride methodology. Furthermore, this chemistry could be adapted to ^{13}C-isotope labeling of six pharmaceutically relevant compounds starting from $Ba^{13}CO_3$ in a newly developed three-chamber system.



Carbon monoxide (CO) is an industrially important gas for the production of aldehydes, carboxylic acids, alcohols, and hydrocarbons.[1] This diatomic molecule also serves as a useful C1-building block in numerous transition-metal-catalyzed transformations for the construction of relevant compounds of pharmaceutical and agrochemical interest.[2] Nevertheless, its high toxicity remains a significant disadvantage requiring specialized facilities for its handling. On the other hand, if CO could be generated from a safe and inexpensive precursor, this would considerably enhance the utility of this gas. Carbon dioxide could represent a valuable CO source being abundant, nonflammable, and nontoxic in low concentrations.[3] Furthermore, there is an increasing interest in identifying useful applications of this greenhouse gas as a source for chemical production.[4,5] A significant hurdle, though, for the transformation of CO_2 to CO is the need to cleave a strong C═O bond (bond energy = 804 kJ/mol).[6] Although considerable advances have been made applying photo- and electrocatalytic processes, such systems are complex and their optimization can be difficult.[7]

We recently demonstrated the usefulness of a two-chamber reactor for performing a number of Pd-catalyzed carbonylation reactions.[8] In this setup, the chemically controlled release of the diatomic gas from a carbon monoxide precursor is spatially separated from the CO consuming reaction (carbonylation reaction) being connected by a bridge, thus simplifying workup and allowing carbonylation reactions to be run with just stoichiometric amounts of CO. As the carbon monoxide precursors were prepared from CO_2, we speculated whether we could replace these precursors by CO_2 and thereby identify suitable conditions for the reduction of CO_2 to CO in this two-chamber system. Furthermore, this deoxygenation step should be sufficiently rapid in order to be useful for a Pd-catalyzed carbonylation reaction.

In this paper, we report the successful identification of a simple, efficient, and stoichiometric conversion of CO_2 to CO performed at room temperature with catalytic cesium fluoride in the presence of a disilane. In particular, the process can be coupled up to Pd-catalyzed amino- and alkoxycarbonylations with aryl bromides and iodides, thereby allowing for the synthesis of a range of known pharmaceuticals directly from this greenhouse gas.

Our inspiration for the development of the catalytic transformation of CO_2 to CO came from the work of Sadighi[9] and Kleeberg,[10] demonstrating the possibility of the copper(I) complex, (IPr)Cu−O*t*Bu (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidene), to catalyze this oxygen abstraction process in the presence of excess bis(pinacolato)diboron or (pinacolato)$BSiMe_2Ph$ (Scheme 1). In the proposed catalytic cycles, the copper(I) complexes (IPr)Cu−Bpin and (IPr)Cu−$SiMe_2Ph$ formed from a σ-bond metathesis pathway represent

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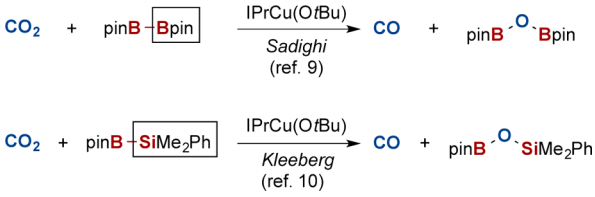
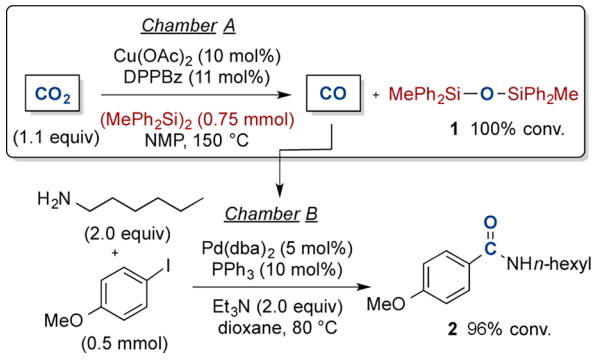
Scheme 1. Selected Approaches for the Reduction of CO_2 to CO



key intermediates followed by CO_2 insertion to generate (IPr)Cu–O_2CBpin and (IPr)Cu–O_2CSiMe$_2$Ph, respectively.

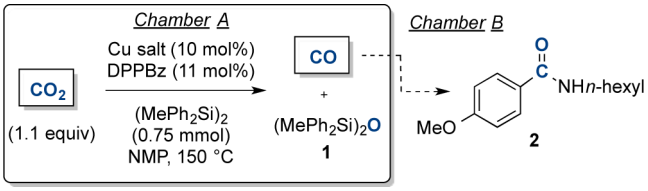
Initial efforts were set out to explore this reduction chemistry applying the two-chamber reactor for trapping the synthesized CO in a Pd-catalyzed aminocarbonylation. Furthermore, another goal was to simplify the catalytic protocol for this reduction step. After considerable experimentation, we discovered that the combination of a catalyst derived from $Cu(OAc)_2$ and the bidentate ligand, DPPBz,[11] with stoichiometric amounts of dimethyltetraphenyldisilane in *N*-methylpyrrolidinone (NMP) at 150 °C, efficiently reduced CO_2 to carbon monoxide as measured by the formation of the corresponding disiloxane **1**. Coupling of this process in a two-chamber system with the Pd-catalyzed carbonylative coupling of *p*-iodoanisole and *n*-hexylamine at 80 °C for 18 h provided the amide **2** in a 96% yield, as depicted in Scheme 2.[12]

Scheme 2. Initial Experiment on the CO_2 Reduction and Application in a Pd-Catalyzed Aminocarbonylation



In our efforts to optimize these new reduction conditions for the transformation of CO_2 to CO with disilane, we decided to investigate the effect of the copper source (Table 1). The two copper(I) salts that were examined were ineffective as shown in entries 1 and 2. $Cu(acac)_2$ furnished disiloxane **1** from the disilane with a conversion of 67% (entry 3), while $Cu(OCOCF_3)_2$ in entry 4 proved to be almost as efficient as $Cu(OAc)_2$ (94% conversion). On the other hand, $Cu(OTf)_2$ did not lead to any conversion at all (entry 5). Due to the large influence of the different counterions of the Cu(II) salts, we speculated whether they would exhibit catalytic activity in the absence of copper. Hence, a similar set of experiments were performed as illustrated in Scheme 2, though with the exception that the $Cu(OAc)_2$/DPPBz combination was replaced with KOAc.[13] To our delight, complete conversion to the disiloxane **1** and amide **2** was observed (Table 2, entry 1) with only 10 mol % of added potassium acetate suggesting that indeed CO_2 reduction to CO could be catalyzed by this simple salt. Lowering the reaction temperature to 80 °C led to a substantial drop in the conversion, whereas, at 20 °C, no

Table 1. Copper Source Screening for the Reduction of CO_2 to CO with Disilane[a]



entry	copper source	$R_3SiOSiR_3$ **1** % conv[b,c]	amide **2** % conv[b]
1	CuI	0	0
2	CuCN	0	0
3	$Cu(acac)_2$	67	100
4	$Cu(OCOCF_3)_2$	94	100
5	$Cu(OTf)_2$	0	0

[a]Conditions: Chamber A was loaded with $(MePh_2Si)_2$ (0.75 mmol), copper salt (0.075 mmol), DPPBz (0.083 mmol), NMP (3.0 mL), and last CO_2 (21 mL, 0.85 mmol) by injection through the septum. Chamber B was loaded with *p*-iodoanisole (0.50 mmol), *n*-hexylamine (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.050 mmol), Et_3N (1.0 mmol), and dioxane (3.0 mL). The reaction mixture in Chamber B was stirred at 80 °C for 18 h and in Chamber A at 150 °C for 18 h. [b]Conversions were measured by analysis of the ^{1}H NMR spectra of the crude product mixtures in the individual chambers (see Supporting Information). [c]Since 1.5 equiv of the disilane was used, only 67% conversion is needed for the full conversion to the amide **2**.

conversion was observed at all in both chambers (entries 2 and 3).

An increase in reactivity was nevertheless noted when potassium acetate was replaced with 10 mol % potassium fluoride. Hence, at 80 °C and even at 40 °C, the conversions to **1** and **2** were high (entries 4 and 5) implying that the CO_2 reduction step was indeed effective at these temperatures. On the other hand, negligible reactivity was again observed at 20 °C (entry 6). A screening of various solvents (entries 7–13) proved rewarding and revealed that the use of DMSO permitted the effective transformation of CO_2 to CO at 20 °C (entry 13). Finally, after examining other fluoride sources including TBAF, LiF, NaF, and CsF (entries 14–17), the latter was found to exhibit the highest reactivity leading to complete conversion in both chambers. Hence, cesium fluoride proved to be an excellent catalyst for the room temperature and stoichiometric reduction of CO_2 to carbon monoxide with the disilane, $(MePh_2Si)_2$.

Furthermore, the catalyst loading could be reduced down to 5 mol% without lowering the conversions in both chambers (entry 18). Less reactive substrates for the aminocarbonylation reaction generally need a slight excess of CO.[8] To meet this requirement a slight excess of CO was indirectly applied by increasing the amount of disilane. With these conditions, a 99% isolated yield of amide **2** could be secured (entry 19).[14]

After optimizing the parameters for the catalytic activation of diphenylmethyldisilane for the reduction of CO_2, it was decided to screen other disilanes (Table 3). Having only methyl or phenyl groups present on the disilane proved detrimental for the reaction (entries 1 and 2). However, it is worth noting that hexaphenyldisilane was insoluble in DMSO, which could explain its lack of reactivity. Substituting two of the phenyl substituents with methyl groups provided the high activity of the system (entry 3). The presence of *o*-methoxy substituents on the aromatic rings completely shuts down the reaction, which could possibly be explained by coordination between the

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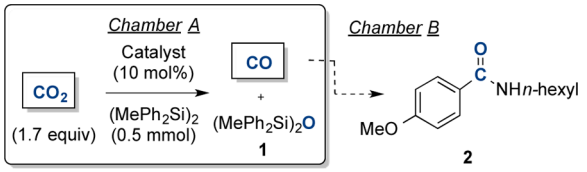
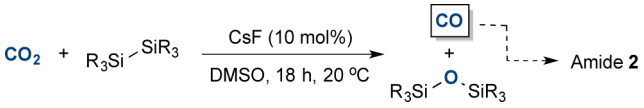
Table 2. Optimization of the Reduction of CO_2 to CO with Disilane Catalyzed by Simple Salts[a]

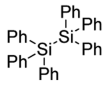
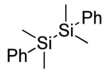
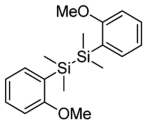
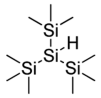


entry	cat.	solvent	T [°C]	$R_3SiOSiR_3$ **1** % conv[b]	amide **2** % conv[b]
1	KOAc	NMP	150	100	100
2	KOAc	NMP	80	50	50
3	KOAc	NMP	20	0	0
4	KF	NMP	80	100	99
5	KF	NMP	40	95	95
6	KF	NMP	20	4	4
7	KF	THF	20	0	0
8	KF	dioxane	20	0	0
9	KF	MeCN	20	0	0
10	KF	toluene	20	0	0
11	KF	DCE	20	0	0
12	KF	DMF	20	75	75
13	KF	DMSO	20	90	90
14	TBAF	DMSO	20	0	0
15	LiF	DMSO	20	0	0
16	NaF	DMSO	20	0	0
17	CsF	DMSO	20	100	100
18	CsF[c]	DMSO	20	100	100
19[d]	CsF	DMSO	20	100	100[99][e]

[a]Conditions: Chamber A was loaded with $(MePh_2Si)_2$ (0.50 mmol), activator (0.050 mmol), solvent (3.0 mL), and last CO_2 (21 mL, 0.85 mmol) by injection through the septum. Chamber B was loaded with *p*-iodoanisole (0.50 mmol), *n*-hexylamine (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.050 mmol), Et_3N (1.0 mmol), and dioxane (3.0 mL). The reaction mixture in Chamber B was stirred at 80 °C for 18 h. [b]Conversions were measured by analysis of the ^1H NMR spectra of the crude product mixtures in the individual chambers (see Supporting Information). [c]Loading of CsF was reduced to 0.025 mmol. [d]Loading of disilane was increased to 0.75 mmol. [e]Isolated yield (%) of amide **2**.

Table 3. Screening of Disilanes for the Reduction of CO_2 at Room Temperature[a]



Entry	Disilane	Amide **2** % Conv. (% yield)[b]
1		7
2		0
3		100 (90%)
4		0
5[c]		90 (78%)

[a]Conditions: Chamber A was loaded with disilane (0.50 mmol), CsF (0.050 mmol), DMSO (3.0 mL), and last CO_2 (21 mL, 0.85 mmol) by injection through the septum. Chamber B was loaded with *p*-iodoanisole (0.50 mmol), *n*-hexylamine (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.050 mmol), Et_3N (1.0 mmol), and dioxane (3.0 mL). The reaction mixture in Chamber B was stirred at 80 °C for 18 h and in Chamber A at 20 °C for 18 h. [b]Based on ^1H NMR conversion. [c]Disilane (0.17 mmol).

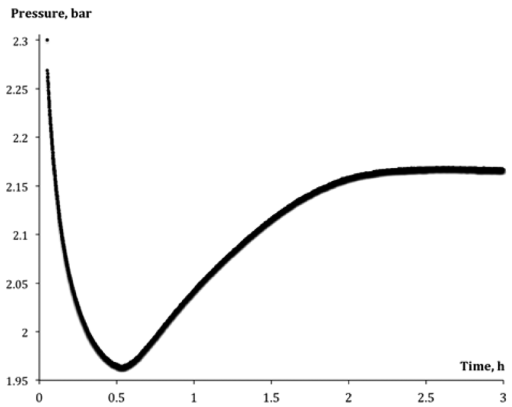


Figure 1. Profile of the pressure measurement experiment. Conditions: $(PhMe_2Si)_2$ (0.50 mmol), CsF (0.050 mmol), DMSO (3.0 mL), CO_2 (0.85 mmol) injected through a septum. The reaction mixture was stirred at 20 °C.

silicon and oxygen. Interestingly, as opposed to hexamethyldisilane (entry 1), tris(trimethylsilyl)silane proved to be very efficient even with a loading approximately 3 times less than that for the other disilanes, which is undoubtedly due to the presence of multiple Si–Si bonds in this structure (entry 5). Surprisingly, it does not appear that the Si–H bond is involved in this reduction step, as neither the silyl formate nor the methoxysilane could be observed in the crude NMR.[11,15]

To further quantify the reactivity of the system, we followed the reduction of CO_2 to CO by measuring the pressure of the system over time without the CO-consuming reaction (Figure 1). After the injection, carbon dioxide rapidly goes into solution, causing a quick pressure decay. As the reaction proceeds, the less soluble carbon monoxide is produced and after 30 min the pressure commences to increase, achieving a constant value after approximately 2 h when the reduction is complete.

Cesium fluoride is hygroscopic, and hence an inert atmosphere should be applied when working with this salt. This is also the case with the previously reported systems for the CO_2 to CO reduction by Sadighi[9] and Kleeberg,[10] when utilizing the air- and moisture-sensitive copper(I) complex, (IPr)Cu–O*t*Bu. Therefore, the substitution of CsF with a nonhygroscopic fluoride source should allow these transformations to be carried out without the need for an inert atmosphere. Gratifyingly, the reaction setup in air with KHF_2 as a catalyst (10 mol %) under the otherwise optimal conditions (Scheme 3) provided 63% conversion of *p*-iodoanisole into the amide **2** after 18 h. The conversion is incomplete due to the lower reactivity of potassium hydrogen fluoride; however, it can

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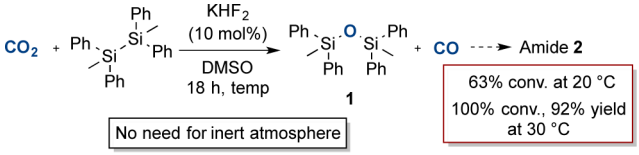
Scheme 3. Reduction of CO_2 in the Presence of Air[a]

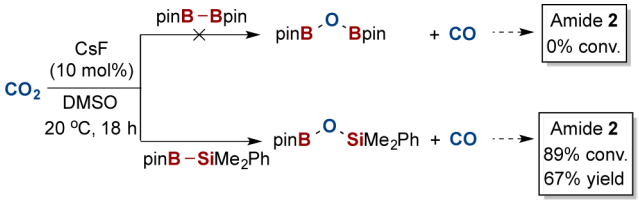


[a]Conditions: Chamber A was loaded with $(Ph_2MeSi)_2$ (0.50 mmol), KHF_2 (0.050 mmol), DMSO (3.0 mL), and last CO_2 (21 mL, 0.85 mmol) by injection through the septum. Chamber B was loaded with *p*-iodoanisole (0.50 mmol), *n*-hexylamine (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.050 mmol), Et_3N (1.0 mmol), and dioxane (3.0 mL). The reaction mixture in Chamber B was stirred at 80 °C for 18 h and in Chamber A at specified temperature for 18 h.

be increased to 100% by performing the CO_2 reduction in chamber A at 30 °C.

It was also interesting to compare the reactivity of the disilanes with the two related reductants used in the copper(I)-catalyzed variants of the transformations of carbon dioxide to carbon monoxide.[9,10] Similar experiments were therefore carried out as in the case for the disilanes applying a two-chamber system whereby chamber A was instead loaded with either bis(pinacolato)diboron or (pinacolato)$BSiMe_2Ph$ (Scheme 4). The reduction of CO_2 with $pinBSiMe_2Ph$ led to

Scheme 4. CsF-Catalyzed Reduction of CO_2 with B_2pin_2 and $pinBSiMe_2Ph$[a]

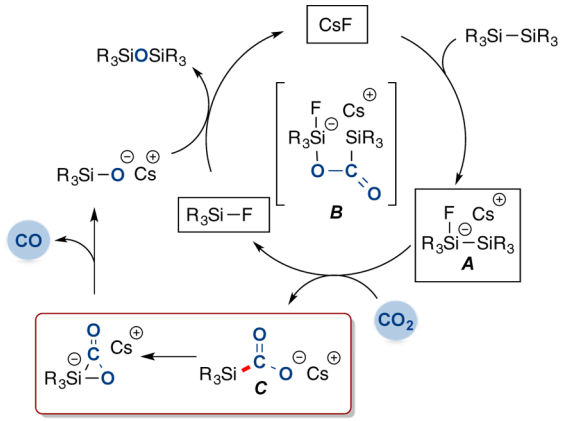


[a]Conditions: Chamber A was loaded with $pinBSiMe_2Ph$ (0.50 mmol) or B_2pin_2 (0.50 mmol), CsF (0.050 mmol), DMSO (3.0 mL), and last CO_2 (21 mL, 0.85 mmol) by injection through the septum. Chamber B was loaded with *p*-iodoanisole (0.50 mmol), *n*-hexylamine (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.050 mmol), Et_3N (1.0 mmol), and dioxane (3.0 mL). The reaction mixture in Chamber B was stirred at 80 °C for 18 h and in Chamber A at 20 °C for 18 h.

an 89% conversion of *p*-iodoanisole into the amide **2** and full consumption of the silylborane after 18 h at room temperature. The incomplete conversion of CO_2 into CO is most likely due to some unidentified side reactions.[10] This experiment demonstrates that cesium fluoride is a more active catalyst for deoxygenating CO_2 with $pinBSiMe_2Ph$ than (IPr)Cu–O*t*Bu used by Kleeberg. Indeed, with 20 mol % of this copper species, 1 equiv of carbon dioxide is completely consumed after 79 h giving approximately 70% of CO,[10] whereas with CsF (10 mol %) the same consumption is achieved after only 18 h and the yield of carbon monoxide is higher. Unlike the disilanes and silylborane, B_2pin_2 was unreactive under our optimized conditions. These results suggest that the presence of a silicon atom is necessary for the fluoride to be an active catalyst for the CO_2 to CO reduction.

A possible catalytic cycle for the fluoride promoted reduction of CO_2 to carbon monoxide with disilane is depicted in Scheme 5. Hiyama and co-workers have earlier demonstrated the ability to generate metal-free silyl anions from the treatment of disilanes with tetrabutylammonium fluoride in HMPA.[16]

Scheme 5. Proposed Mechanism for CO_2 Reduction with CsF and Disilane



Whether CO_2 reacts with a free silyl anion under our reaction conditions or a hypervalent species ***A*** by fluoride coordination to one of the two silyl atoms is at the moment not clear. Nevertheless, subsequent CO_2 insertion into ***A*** would generate the *O*-silylated silacarboxylic acid ***B***. Liberation of the silacarboxylate generates the corresponding cesium salt ***C***, which possibly undergoes a Brook rearrangement to liberate CO and a silyloxide, in analogy to similar observations on the fluoride and hydroxide promoted generation of CO from silacarboxylic acids.[8b,17] Subsequent generation of the disiloxane from attack of the siloxide with the silyl fluoride regenerates the cesium fluoride.

With this surprisingly simple catalytic protocol in hand for the efficient conversion of CO_2 into CO without the need of a transition metal catalyst, we proceeded to investigate its usefulness for the preparation of a number of pharmaceutically relevant molecules as depicted in Scheme 6. As with the optimization studies, all reactions were run in a two-chamber system and, for best coupling yields, 1.5 equiv of CO were applied. Gratifyingly, all the amino- and alkoxycarbonylations proved to be highly efficient, indicating again that the CO_2 reduction step to CO performed exceptionally well.

Further studies were also undertaken to validate this protocol for selective ^{13}C-carbon isotope labeling of the same bioactive compounds. As a convenient source of $^{13}CO_2$, we chose commercially available ^{13}C-labeled $Ba^{13}CO_3$. This required a closed three-chamber system, whereby CO_2 is liberated in one of the three chambers by the treatment of the barium carbonate with camphorsulfonic acid.[18] As shown in the results in Scheme 6, the addition of a third reaction in an additional chamber did not have a detrimental effect on the efficiency of the carbon dioxide reduction step or the Pd-catalyzed transformation, and hence, all ^{13}C-isotopically labeled pharmaceutical compounds were prepared in good yields.

In conclusion, a simple and mild protocol for the conversion of CO_2 to CO has been developed, which does not require a transition metal catalyst. Notably, this transformation is promoted by catalytic cesium fluoride in the presence of a disilane and at room temperature. This is the first example utilizing a disilane for the reduction of CO_2 to CO.[19] Furthermore, the process can be coupled to Pd-catalyzed amino- and alkoxycarbonylations in a two-chamber system providing excellent coupling yields of a range of pharmaceutically relevant compounds. Finally, with a three-chamber system, ^{13}C-isotope labeling of the same compounds with $Ba^{13}CO_3$

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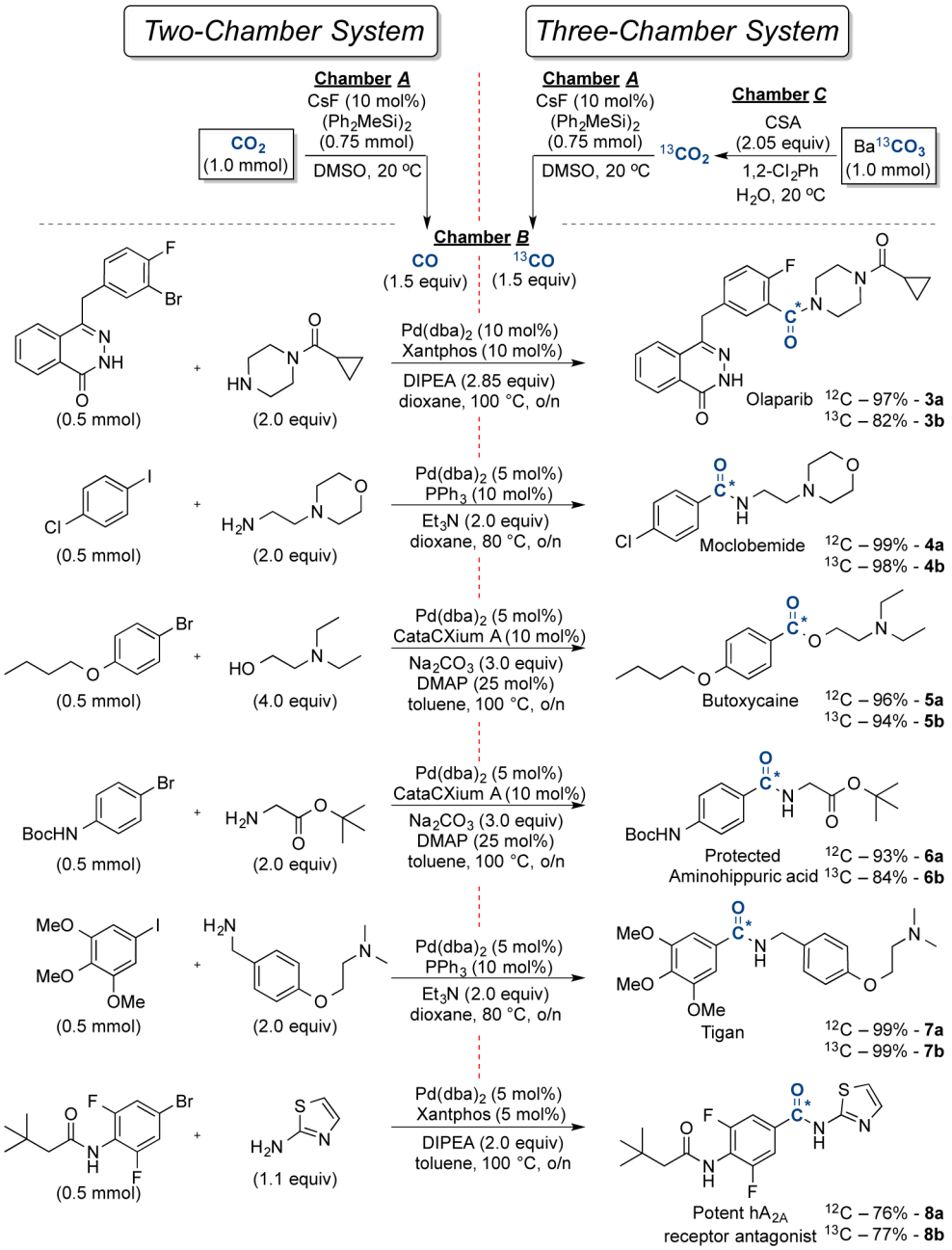
Scheme 6. Combining the CO_2 to CO Reduction Protocol with the Pd-Catalyzed Amino- and Alkoxycarbonylation



could be achieved. Further work is currently in progress to provide a more detailed understanding of this intriguing oxygen abstraction step from CO_2. This work will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR, ^{13}C and ^{19}F NMR spectra for all the coupling products, and details on experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

lindhardt@eng.au.dk
ts@chem.au.dk

Notes

The authors declare no competing financial interest.

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