

Homogeneous Catalytic Reduction of CO₂ with Silicon-Hydrides, State of the Art

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Dedication ((optiona

Abstract: During the last recent years, the catalytic transformation of CO₂ using silicon-hydrides as reductants has emerged as a promising methodology that allows the selective reduction of CO₂ to the formate, formaldehyde, methoxide or methane level under mild reaction conditions. Moreover, some catalysts have been employed for the formylation and/or methylation of the N-H bonds of secondary and/or primary amines by their reaction with CO₂ and hydrosilanes. This work summarizes the different catalytic systems that have shown to be efficient for the above-mentioned reactions. Furthermore, a brief description of the reactions performance and the conditions employed in each case is included.

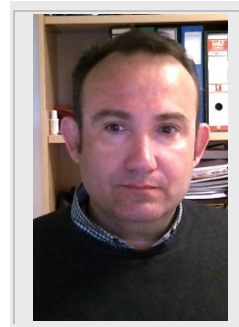
1. Introduction

The development of environmentally friendly methodologies that allow the utilization of carbon dioxide as a chemical feedstock remains a challenge.^[1] This is because the thermodynamic stability and kinetic inertness of CO₂ hinder its chemical transformation. The design of catalysts, which allows overtaking the kinetic barriers, has proven to be an effective tool to achieve the CO₂ conversion under mild reaction conditions. Indeed, in recent years there has been significant improvement in knowledge about the fundamental reaction mechanisms and principles that determine the catalytic transformation of CO₂ into value added chemicals.^[1,2] However, more research efforts are still needed in order to be able to effectively use CO₂ as raw material at industrial scale.

Among all the processes developed during the last years is the catalytic reduction of CO₂ with hydrosilanes, which presents the advantage of being thermodynamically favored.^[3] However, the poor atomic economy of these reactions and the high price of most hydroorganosilanes are important drawbacks inherent to this methodology. In this sense, it should be mentioned that to use commercially available hydrosiloxanes such as

polyhydromethylsiloxane (PHMS), tetramethyldisiloxane (TMDS) or heptamethyltrisiloxane (HTMTS) instead of hydroorganosilanes could be of great interest from the economic point of view since they are cheaper and produced in ton scale as residues from the silicone industry.^[4] In addition, they are easily to store and handle. Conversely, many research efforts are still needed in order to be able to use hydrosiloxanes as recyclable hydrogen sources for the catalytic transformation of CO₂. The reason is that these processes end in the formation of highly oxygenated siloxanes which are very stable and difficult to reduce.^[5] Therefore, the development of sustainable methodologies for the catalytic reduction of highly oxygenated siloxanes to hydrosiloxanes should be desirable for the industrial application of the catalytic reduction of CO₂ with hydrosiloxanes. The first examples of catalytic transformations of CO₂ using hydrosilanes as reducing agents were reported in the early 80s of the last century.^[6] However, it was during the year 2012 that the breakthrough of this chemistry took place, from then until today, the number of catalytic systems effective for the reduction of CO₂ with hydrosilanes has considerably grown-up.^[3b] Herein, a brief description of the state of the art emphasizing the recent contributions, together with a review of the different typologies of catalytic systems used for the reduction of CO₂ with silicon-hydrides is included.

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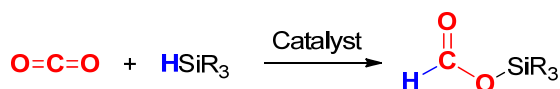
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Luis A. Oro obtained his Ph. D. from the University of Zaragoza in 1970. His post-doctoral studies were undertaken at Cambridge University under the supervision of Professor the Lord Lewis. It was during this time that he became interested in organometallic chemistry. He has served on the faculties of the Universities of Zaragoza, Madrid Complutense, and Santander. He became full professor of Inorganic Chemistry in Zaragoza in 1982 and served as head and founder of the Homogeneous Catalysis Institute (2004-2013). He has (co)authored well over 600 scientific papers, several reviews and some books on synthesis, reaction mechanisms and homogeneous catalysis of platinum group metal complexes. He has received numerous awards and honors, and is member of several international scientific academies. He has been President of the European Association for Chemistry and Molecular Sciences (EuCheMS) (2008-11).



2. Catalytic Reaction of Carbon Dioxide with Silicon Hydrides

The catalytic hydrosilylation of CO₂ could be considered as the simplest methodology for the preparation of silylformates (Scheme 1). While these processes are favored from the thermodynamic point of view, they are kinetically hindered. However, the kinetic barriers associated with the Si-H and C=O bonds activation could be easily overtaken by different metal based and metal-free catalysts.^[3]



Scheme 1. Catalytic hydrosilylation of CO₂.

Silylformates are moisture sensitive and react easily with water to afford formic acid and the corresponding siloxane and/or silanol.^[3] They have been proposed as intermediates in the synthesis of formamides, bis(silyl)acetals, methoxysilanes, methanol and methane by catalytic reduction of CO₂ with hydrosilanes and/or hydrosiloxanes.^[3] Furthermore, silylformates have also been used as hydrosilane surrogates in transfer hydrosilylation and silylation processes.^[7]

One of the challenges of the catalytic hydrosilylation of CO₂ is the selectivity. This is because under the catalytic reaction conditions, excess of silicon-hydride containing species, some CO₂ hydrosilylation catalysts are also able to catalyze the subsequent hydrosilylation of the carboxylic group of the silylformates to afford bis(silyl)acetals, which could further react with silanes to give the corresponding methoxysilane and siloxane, and even methoxysilanes, in presence of some catalysts, could be transformed into methane and siloxane. Therefore, the development of selective catalysts remains a

challenge for the reduction of CO₂ with silicon-hydride containing species

2.1. Metal-based catalysts for the hydrosilylation of CO₂ to silylformate

During the last recent years various examples of catalysts based on metal complexes have found to be active for the selective reduction of CO₂ with hydrosilanes (or hydrosiloxanes) to the silylformate level. The effectiveness of these catalytic systems depends on the nature of the catalyst and of the silicon compound employed as reductant as well as on the solvent (Table 1).

The first reports of selective catalysts effective for the hydrosilylation of CO₂ to silylformates were based on acetonitrile solutions of RuCl₃ species.^[8] These studies allowed to conclude that using the complex *mer*-[RuCl₃(NCMe)₃] (**1**) as catalyst precursor is possible to achieve the complete conversion of HSiMe₂Ph into the corresponding silylformate in a few minutes (TOF = 3700 h⁻¹) (Table 1).^[8a] This methodology requires the activation of the catalyst, by heating the solution during 15 min at 358 K, previously to the pressurization with CO₂ (40 bar). Indeed, when the reaction was carried out without induction period a decrease of the reaction rate (TOF = 390 h⁻¹) was observed.^[8a]

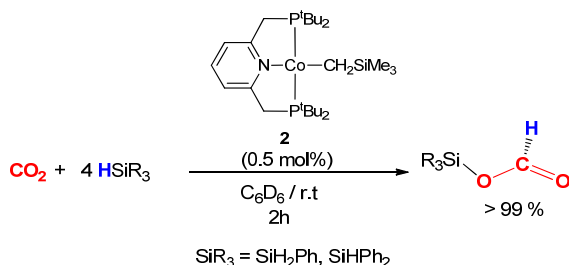
Table 1. Selection of active catalysts for the selective hydrosilylation of CO₂ to silylformate.

Catalyst ^[ref] / loading	CO ₂ (bar)	Yield (%)	Time (h) / TOF (h ⁻¹)	Si-H / Solvent
1 ^[8] / 0.2 mol%	40	86	0.1 / 3700	HSiMe ₂ Ph / MeCN
2 ^[9] / 0.5 mol%	2.8	>99	2 / 400	PhSiH ₃ / C ₆ D ₆
3 ^[10] / 0.5 mol% ^[a]	1	90	2 / 400	HSiMe ₂ Ph / MeCN ^[a]
4 ^[11] / 1.0 mol%	8	100	1 / 100	HSiMe(OSiMe ₃) ₂ and HSiMe ₂ Ph / solvent-free
8 ^[14] / 0.1 mol%	1	92	1 / 19300	HSiMe ₂ Ph / DMF
9 ^[16] / 0.5 mol%	5	100	0.28 / 714	H ₃ SiBu / CH ₂ Cl ₂
12 ^[20] / 0.5 mol%	1	81	6 / 1350	PHMS ^[b] / Dioxane
13 ^[22] / 0.01 mol%	1	71 ^[c]	6 / 1248	HSi(OEt) ₃ / solvent-free

[a] The addition of 0.5 mol% of K₂CO₃ is required; [b] PHMS = polyhydromethylsiloxane; [c] isolated yield.

Examples of group 9 transition metal based catalysts which allow the selective hydrosilylation of CO₂ are also known. So, ¹H NMR studies of the reaction of ¹³CO₂ (2.8 bar, 298 K) with

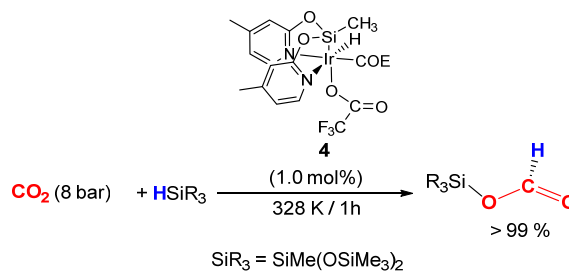
H₃SiPh or H₂SiPh₂ in presence of the cobalt complex [Co(CH₂SiMe₃)(^tBuPNP)] (**2**) (0.5 mol%) (^tBuPNP = 2,6-bis(di-tert-butylphosphinomethyl)pyridine) evidenced the quantitative formation of the corresponding silylformate after 2 hours of reaction (Scheme 2, Table 1).^[9]



Scheme 2. Cobalt-catalyzed CO₂-hydrosilylation with H₃SiPh and H₂SiPh₂.

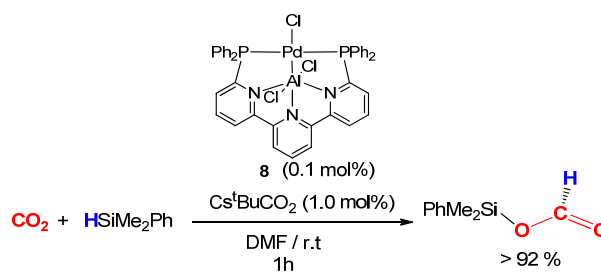
The catalytic system formed by the commercially available rhodium complex [Rh₂(AcO)₄] (**3**) and K₂CO₃ has found to be an active catalyst for the selective hydrosilylation of CO₂ with HSiMe₂(*p*-C₆H₄X) (X = H, OMe, Cl, CF₃), HSiMePh₂, HSiPh₃ and HSiEt₃.^[10] These reactions were performed at around 1 bar of CO₂ and at room temperature. It is noteworthy that the reactions did not take place in absence of base. The catalytic activity of the system **3** (0.25 mol%) / K₂CO₃ (0.5 mol%) depends on the nature of the silane and on the solvent. Thus, in the series of HSiMe₂(*p*-C₆H₄X) derivatives the activity increased in the order of X = OMe < H < Cl. In addition, the hydrosilylation with relatively bulky hydrosilanes such as HSiPr₃ is hindered and no reaction was observed after 24 h.^[10] The best reaction performance was achieved using MeCN as solvent. Other solvents such as acetone, 1,4-dioxane, THF, 1,2-dichloroethane or hexane produces a dramatic decrease of the activity.^[10]

The catalytic system based on the iridium complex [Ir(H)(CF₃CO₂)(NSiN)(coe)] (**4**) (NSiN = *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl), developed by us, has proven to be an efficient catalyst precursor for the solvent-free hydrosilylation of CO₂ with HSiMe(OSiMe₃)₂ in gram scale (Scheme 3, Table 1).^[11] The best reaction performance was achieved using **4** (1.0 mol%), 8 bar of CO₂ and 328 K. This catalyst is also active with HSiMe₂Ph, HSiMePh₂, HSiEt₃ or HSi(OSiMe₃)₃ as reducing agents. However, the higher activity was obtained with HSiMe(OSiMe₃)₂.^[12] It should be mentioned that the activity of **4** is higher than that obtained using the previously reported catalysts [Ir(H)(CF₃SO₃)(NSiN)(L)] (NSiN* = *fac*-bis-(pyridine-2-yloxy)methylsilyl); L = NCMe, **5**; coe, **6**), which contains a triflate instead of a trifluoroacetate ligand and a non-methylated NSiN ligand,^[13] and the iridium-triflate derivative [Ir(H)(CF₃SO₃)(NSiN)(coe)] (**7**) which bears the same NSiN ligand than **4**.^[11] The reason behind the higher activity of **4** in comparison with these related iridium species could be that the reaction takes place via a different reaction mechanism. Indeed, while theoretical calculations support an inner-sphere mechanism for the catalytic system based on **4**,^[12] an outer-sphere mechanism has been proposed for the system based on the iridium-triflate derivatives **5** and **6**.^[13]



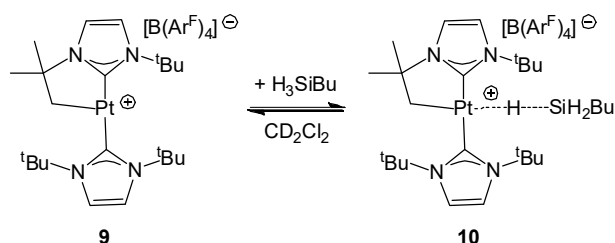
Scheme 3. Iridium-catalyzed solvent-free CO₂-hydrosilylation with HSiMe(OSiMe₃)₂.

The catalyst based on the palladium complex **8**, which contains an aluminum-metalloligand has shown the highest activity in CO₂-hydrosilylation reported so far (Scheme 4).^[14] The reactions were performed in DMF at 298 K. This catalytic system requires a low catalyst loading (0.1 mol%) however the addition of Cs^tBuCO₂ (1.0 mol%) is needed to achieved the selective hydrosilylation of CO₂ with HSiMe₂Ph to yield the corresponding silylformate, which was obtained in 92% (TOF = 19300 h⁻¹).^[14]



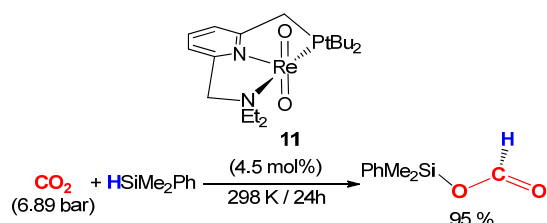
Scheme 4. Palladium-catalyzed CO₂-hydrosilylation with HSiMe₂Ph.

The species [Pt(ItBu')(ItBu)][BAR^F] (**9**)^[15] (0.5 mol%) (BAR^F = tetrakis(3,5-trifluoromethyl)phenyl)borate) has demonstrated to be an effective catalyst for the hydrosilylation of CO₂ (5 bar) with H₃SiBu in CH₂Cl₂ at r.t. to afford the corresponding silylformate H₂SiBu(OCOH) in 15 min (TOF = 714 h⁻¹).^[16] The activity of this catalytic system depends on the silane. Thus, using H₂SiEt₂ the hydrosilylation reactions are slower than with H₃SiBu. ¹H NMR studies of the reactions of complex **9** with H₃SiBu evidenced the formation of the σ-Si-H adduct [Pt(ItBu')(ItBu){η¹-(H₃SiBu)}][BAR^F] (**10**), whose structure was proposed based on ¹H and ²⁹Si NMR spectroscopy in solution at 223 K (Scheme 5).^[16] In this regard, it is remarkable that Conejero and collaborators have recently reported the characterization by X-ray diffraction methods of a cation platinum σ-silane species, related to **10**, bearing the silane HSiEt₃ (or HSiPh₃) in η¹-(Si-H) coordination mode.^[17] These results suggest that cation platinum σ-silane species, analogous to **10**, could be considered as reaction intermediates of the **9**-catalyzed CO₂ hydrosilylation processes.



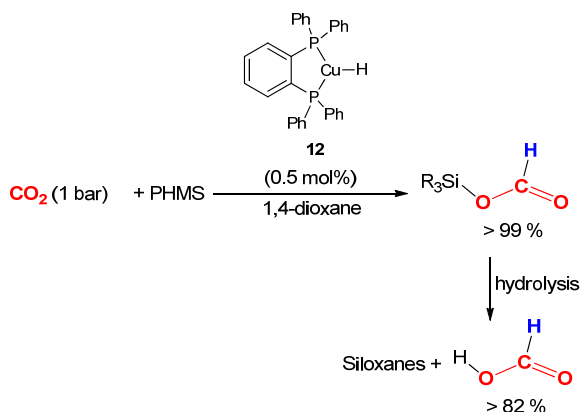
Scheme 5. Formation of the species **10** by interaction of **9** with H_3SiBu .^[16]

Abu-Omar et al. have reported that the rhenium complex $[\text{Re}(\text{O})_2(\text{PNN})][\text{TfO}]$ (**11**) (PNN = 1-(6-((di-tert-butylphosphino)methyl)pyridin-2-yl)-N,N-diethylmethanamine) catalyzed the reaction of CO_2 (6.89 bar) with HSiMe_2Ph at 298 K in dichloromethane to give the corresponding silylformate (95 % after 24 h (Scheme 6)).^[18]



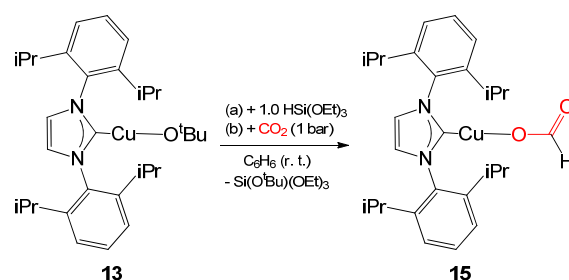
Scheme 6. Rhenium-catalyzed CO_2 -hydrosilylation with HSiMe_2Ph in CD_2Cl_2 .

Baba et al. showed that the copper complex **12**, which was previously reported by Lipshutz et al.,^[19] catalyzed the hydrosilylation of CO_2 with polyhydromethylsiloxane (PHMS) to yield the corresponding silylformate, which after hydrolysis affords formic acid (Scheme 7).^[20] This catalytic system operates at a relatively high reaction rate ($\text{TOF} = 1350 \text{ h}^{-1}$). ^1H and ^{13}C NMR studies of the **12**-catalyzed reaction of CO_2 with PHMS in C_6D_6 evidenced the presence of copper-formate intermediates during the catalytic process.^[20] It is worth mentioning that PHMS is a cheap and easy to handle reducing agent produced as a byproduct of the silicone industry.^[21]



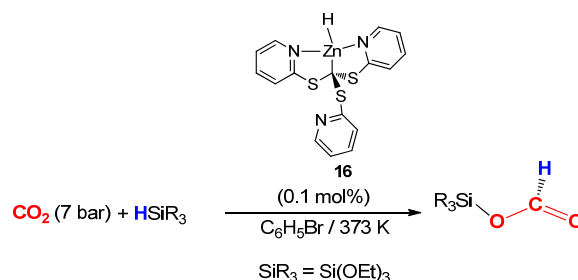
Scheme 7. Copper-catalyzed hydrosilylation of CO_2 with polyhydromethylsiloxane (PHMS) and subsequent hydrolysis to afford formic acid.

Copper(I)-NHC (NHC = N-heterocyclic carbene) complexes have also been proposed as catalyst precursors for CO_2 -hydrosilylation processes.^[22] The catalytic system based on the species $[\text{Cu}(\text{O}^t\text{Bu})(\text{IPr})]$ (**13**) (Scheme 8) is able to promote the reduction of CO_2 with $\text{HSi}(\text{OEt})_3$ ^[23] under solvent-free conditions to yield the corresponding silylformate, which was isolated in 70%. The copper-hydride $[\text{Cu}(\text{H})(\text{IPr})]$ (**14**), which could be prepared in situ by treatment of **13** with $\text{HSi}(\text{OEt})_3$, reacts with CO_2 (1.0 bar) to afford $[\text{Cu}(\text{OC}(\text{O})\text{H})(\text{IPr})]$ (**15**), which has been isolated and fully characterized (Scheme 8). As expected complex **14** is also a highly active catalyst for the CO_2 hydrosilylation with $\text{HSi}(\text{OEt})_3$. Therefore, based on these findings the authors proposed that complexes **14** and **15** are intermediates of the catalytic process.^[22]



Scheme 8. Two steps reaction of species **13** with $\text{HSi}(\text{OEt})_3$ and CO_2 (1 bar) in C_6H_6 at r.t. to yield the copper-formate complex **15**.

Examples of zinc-catalyzed CO_2 hydrosilylation processes have also been reported.^[24,25] Thus, the hydride complex $[\text{Zn}(\text{H})(\kappa^3\text{-Tptm})]$ (**16**) (Tptm = tris(2-pyridylthio)methyl) (0.1 mol%) catalyzes the reaction of CO_2 (7.0 bar) with $\text{HSi}(\text{EtO})_3$ ^[23] at 373 K, to selectively afford $\text{HCO}_2\text{Si}(\text{OEt})_3$ on a 20 g scale ($\text{TOF} = 2.9 \text{ h}^{-1}$) (Scheme 9).^[24]



Scheme 9. Example of zinc-catalyzed solvent-free CO_2 -hydrosilylation with $\text{HSi}(\text{OEt})_3$.

Others, examples of zinc species such cationic zinc-bis-NHC complexes of the type $[\text{Zn}(\text{X})(\text{IDipp})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) ($\text{X} = \text{Me}$, **17a**; CH_3CO_2 , **17b**)^[25] have also found to be active for the hydrosilylation of CO_2 (1.5 bar) with $\text{HSi}(\text{OEt})_3$ ^[23] using bromobenzene as solvent at 363 K, to give the corresponding silylformate, which was isolated in 76 %.^[25] However, this catalytic system requires long reaction time (60 h) and a catalyst loading of 6-7 mol%.^[25] In this context, Mösch-Zanetti and collaborators have recently reported that the complex $[\text{Zn}(\text{H})(\text{Tntm})]$ (**18**) (Tntm = tris(6-tert-butyl-3-

thiopyridazinyl)methanide) catalyzes the hydrosilylation of CO₂ (1 bar) with HSi(OMe)₃^[223] in C₆D₆ under mild reaction conditions to afford the corresponding silylformate in 99% yield in 4.5 (298 K) or 2 h (318K).^[226]

2.2. Metal-free catalysts for the hydrosilylation of CO₂ to silylformate level

Some examples of metal-free catalytic systems active in CO₂ hydrosilylation to formate level processes including inorganic salts and organocatalysts have also been reported. The first example of organocatalytic reduction of CO₂ with hydrosilanes was reported in 2009 by Ying et al., they showed that using N-heterocyclic carbene based catalytic systems was possible to reduce CO₂ to methoxysilanes using H₂SiPh₂ as reducing agent.^[27]

1,3,2-Diazaphospholene (5.0 mol%) has also been used as catalyst for the reduction of CO₂ (1.0 bar) with H₂SiPh₂ in acetonitrile at 298 K. This reaction allows the formation of bis(formate)diphenylsilane (95%) in one hour (TOF = 19 h⁻¹).^[28] Phosphazenes have also been employed as catalysts for the hydrosilylation of CO₂ to silylformates. Thus, phosphazene based catalysts (1.25 mol%) promoted the selective reduction of CO₂ (5 bar) with H₂SiPh₂ to the silylformate HC(O)OSiHPh₂ (97%) using DMF as solvent. When using others Si-H containing species such as HSiEt₃ or HSi(OEt)₃ as reducing agents no reaction or poor conversion were observed, respectively.^[29] Interestingly, the authors reported that the reaction solvent, DMF, shows catalytic activity in absence of the phosphacene catalyst. So, the catalyst-free reaction of CO₂ (1.0 bar) with H₂SiPh₂ in DMF allows the conversion of the 82% of the starting hydrosilane after 24 h to give a mixture of HC(O)OSiHPh₂ (68%), CH₂(OSiHPh₂)₂ (29%) and CH₃OSiHPh₂ (3%).^[29] In this context, Baba et al. have shown that simple fluoride and carbonate salts catalyzed the hydrosilylation of CO₂ (1.0 bar) with HSiMe₂Ph in DMSO at 333 K to afford HC(O)OSiMe₂Ph and formic acid (Table 2).^[30]

Table 2. Selection of data reported for the fluoride and carbonate salts (0.1 mol) catalyzed hydrosilylation of CO₂ (1.0 bar) with HSiMe₂Ph (2.9 mmol) in DMSO at 333 K after 24 h of reaction.^[30]

Catalyst	Conversion (%)	TOF (h ⁻¹)	Yield (%) ^[a]
CsF	90	0.94	87
TBAF·3H ₂ O	96	1	87
KHF ₂	87	0.73	69
KF	86	0.64	62
Cs ₂ CO ₃	96	0.83	72
Cs ₂ CO ₃ ^[b]	83	1.6	80
K ₂ CO ₃	84	0.84	83

Na₂CO₃

43

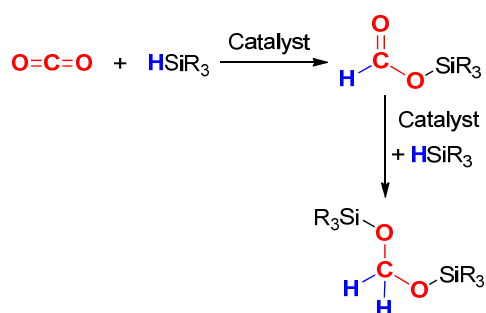
0.18

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[a] Yield of formate (silylformate + formic acid) based on ¹H NMR using mesitylene as internal standard.^[30] [b] reaction time close to 13 hours.

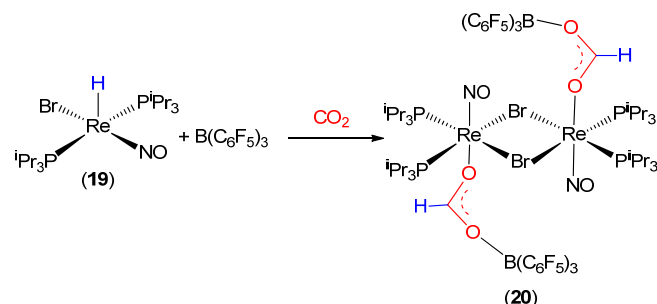
2.3. Catalytic reduction of CO₂ with silicon-hydrides to the bis(silyl)acetal level

Some catalysts promote the selective transformation of CO₂ into bis(silyl)acetals by its reaction with silicon-hydrides. The formation of the corresponding bis(silyl)acetal is consequence of the hydrosilylation of the silylformates previously obtained by the catalytic hydrosilylation of CO₂ (Scheme 10).



Scheme 10. Catalytic reduction of CO₂ to the bis(silyl)acetal level.

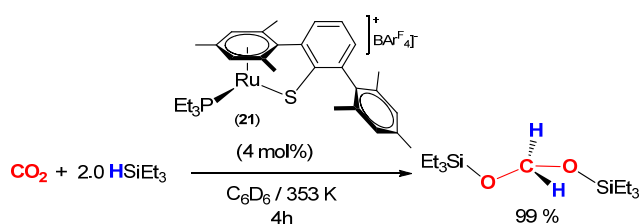
One of the earliest examples of selective reduction of CO₂ with hydrosilanes to the bis(silyl)acetal level was reported by Berke and coworkers in 2013. They found that the reaction of CO₂ (1 bar) with HSiEt₃ carried out in C₆D₆ at 353 K in presence of catalytic amounts of [Re(H)(Br)(NO)(PⁱPr₃)₂] (**19**) and B(C₆F₅)₃ (1.0 mol%) allows the conversion of CO₂ into CH₂(OSiEt₃)₂, which was obtained in 35% after 4 h.^[31] In order to clarify the reaction mechanism they performed the stoichiometric reaction of **19** with B(C₆F₅)₃ and CO₂. This reaction affords complex [Re(μ-Br)(NO){κ¹-O-(OCH=O-B(C₆F₅)₃)}(PⁱPr₃)₂]₂ (**20**) (Scheme 11). When complex **20** (1.0 mol%) was used as catalyst precursor for the reduction of CO₂ (5.0 bar) with HSiEt₃ the formation of CH₂(OSiEt₃)₂ (87%) together with traces of CH₃OSiEt₃ and O(OSiEt₃)₂ was observed.^[31]



Scheme 11. Reactivity of complex **19** with B(C₆F₅)₃ and CO₂.

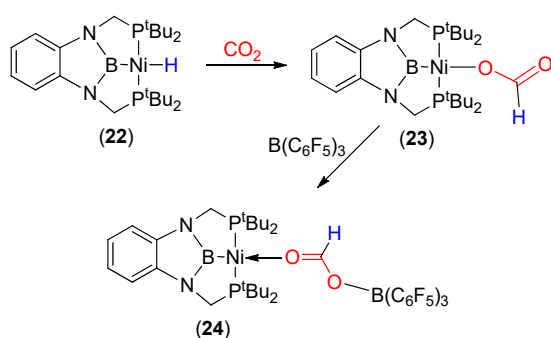
Oestreich and Metsänen have reported that the tethered complex [Ru(PEt₃)₃{η⁶-mesityl:κ¹-S-(SDmp)}][BAR₄^F] (**21**) (SDmp = 2,6-dimesitylphenyl thiolate; BAR₄^F = 3,5-bis(trifluoromethyl)phenylborate), previously reported by Ohki,

Tatsumi et al.,^[32] catalyzed the selective reduction of CO₂ (5.0 bar) with HSiEt₃, HSiMe₂Et, HSiMePh₂ and HSiMe₂Ph in C₆D₆ at 353 K to afford the corresponding bis(silyl)acetal.^[33] The best results were achieved using a catalyst loading of 4.0 mol%. In all the cases the corresponding bis(silyl)acetal was obtained in > 92% yield. HSiEt₃ has proven to be the most efficient reducing agent under the above mentioned reaction conditions, allowing the selective transformation of CO₂ into the corresponding bis(silyl)acetal (99%) after four hours (Scheme 12).^[33] The Ru-S catalyst **21** promotes the heterolytic cleavage of the Si-H bond of hydrosilanes in a cooperative fashion via a ruthenium metal hydride-sulfur-stabilized silicon cation intermediate.^[34]



Scheme 12. Complex Ru-S (**21**)-catalyzed CO₂-reduction with HSiEt₃ to the bis(silyl)acetal level.

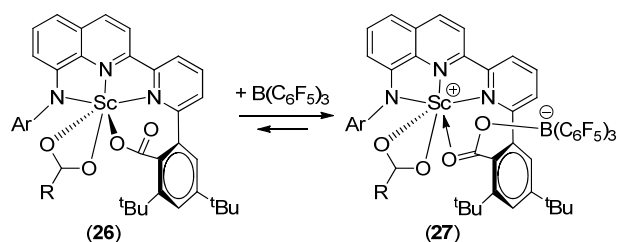
The nickel-hydride species [Ni(PBP)(H)] (**22**) with a bis(di-tert-butylphosphano) ligand reacts with CO₂ to afford complex [Ni(PBP){OC(O)H}] (**23**), which interacts with B(C₆F₅)₃ to give the complex [Ni(PBP)(OCH(O)-B(C₆F₅)₃)] (**24**) (Scheme 13). Complex **24** has proven to be a highly active and selective catalyst for the reduction of CO₂ with HSiEt₃, HSiMePh₂ and HSiMe₂Ph, to yield the corresponding bis(silyl)acetal.^[35] Theoretical calculations at the DFT level supports that the ion pair [Ni(PBP)][HB(C₆F₅)₃] (**25**) is a key intermediate in the catalytic process and promotes the activation of the CO₂ molecule to give **22**.^[35b]



Scheme 13. [Ni(PBP)]-catalyzed CO₂-reduction with hydrosilanes to the bis(silyl)acetal level.

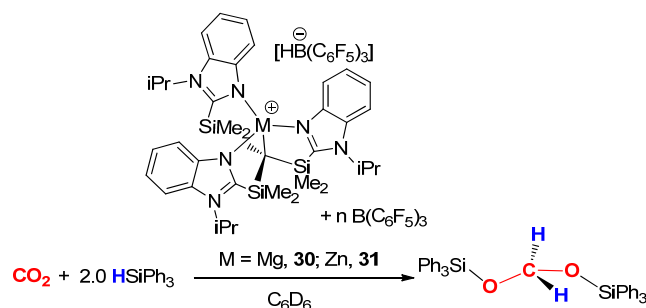
Examples of selective catalysts efficient for the CO₂ reduction to bis(silyl)acetals based on non-precious metals have also been reported. Thus, the scandium species [Sc(RCO₂)(AbP^tBu₂)] (**26**) (R = CH₂SiMe₂Ph) (Scheme 14), where AbP^tBu₂ is an anilido bipyridyl ligand with two 3,5-ditertbutylphenyl groups, catalyzes the reaction of CO₂ (5.0 bar) with HSiEt₃ under neat conditions to selectively give the bis(silyl)acetal CH₂(OSiEt₃)₂ (94%) after 96 hours of reaction at 338 K (TON = 940; TOF = 9.8 h⁻¹).^[36] In

presence of B(C₆F₅)₃ complex **26** is in equilibrium with the adduct **27** (Scheme 14).^[36]



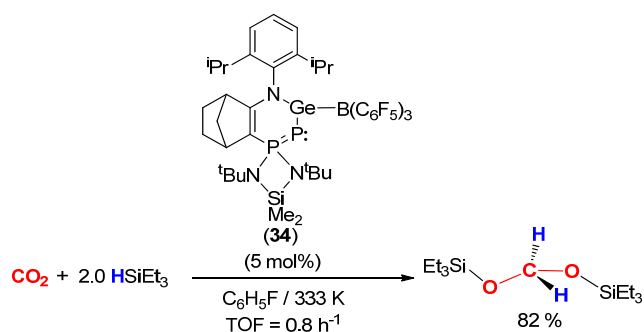
Scheme 14. Reaction of [Sc(RCO₂)(AbP^tBu₂)] (**26**) with B(C₆F₅)₃. Ar = 3,5-ditert-butylphenyl, R = CH₂SiMe₂Ph.

Parkin et collaborators have published examples of zinc and magnesium complexes with the *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl (Tism^{iPrBenz}) ligand, [Mg(H)(Tism^{iPrBenz})] (**28**)^[37] and [Zn(H)(Tism^{iPrBenz})] (**29**),^[38] which in combination with B(C₆F₅)₃ have been used as catalysts for the selective reduction of CO₂ with HSiPh₃ to the bis(silyl)acetal level.^[38] The catalytic system based on the magnesium derivative **28** (TOF = 178 h⁻¹) is more active than the catalytic system based on the zinc species **29** (TOF = 0.1 h⁻¹). The initial steps of the proposed catalytic cycle involves the reaction of the hydride species **28** and **29** to give the corresponding ion pair [M(Tism^{iPrBenz})]⁺[HB(C₆F₅)₃]⁻ (M = Mg, **30**; Zn, **31**) (Scheme 15), which reacts with CO₂ to afford the resultant formatoborate species [M(Tism^{iPrBenz})(OCHOB(C₆F₅)₃)] (M = Mg, **32**; Zn, **33**).^[38]



Scheme 15. CO₂-reduction with HSiPh₃ to the bis(silyl)acetal level catalyzed by ion pairs **30** (0.5 mol% + 2.0 mol% of B(C₆F₅)₃) and **31** (2.0 mol% + 8.0 mol% of B(C₆F₅)₃).

It should be mentioned that not only metal complexes but also the N,P-heterocyclic germylene-B(C₆F₅)₃ adduct (**34**) has been employed as catalyst for the selective reduction of CO₂ with HSiEt₃ to the bis(silyl)acetal level (Scheme 16).^[39]



Scheme 16. CO₂-reduction with HSiEt₃ to the bis(silyl)acetal level catalyzed by the N,P-heterocyclic germylene-B(C₆F₅)₃ adduct (**34**).

2.4. Catalytic reduction of CO₂ with silicon-hydrides to the methoxysilane level

The first examples of CO₂ reduction to the methoxide level using hydrosilanes as reducing agents was reported in 1989 by Eisenschmid and Eisenberg.^[40] They found that in presence of catalytic amounts of [Ir(CN)(CO)(dppe)] (**35**) (dppe = 1,2-bis(diphenylphosphano)ethane) CO₂ reacts slowly with HSiMe₃ at 313 K in C₆D₆ to quantitatively give CH₃OSiMe₃ after two weeks of reaction. ¹³C NMR spectra of these reactions, when using ¹³CO₂ instead of CO₂, allowed the observation of ¹³CH(O)OSiMe₃ and ¹³CH₂(OSiMe₃)₂ as intermediates of the reduction process.^[40]

The examples of catalytic systems effective for the reduction of CO₂ to the methoxysilane level reported since then are scarce. This could be explained by the fact that further reduction from the bis(silyl)acetal level usually requires forcing reaction conditions and long reaction times. For example, using the above mentioned ruthenium complex **21** as catalyst precursor, it has been possible to achieve the conversion of CH₂(OSiMe₂Et)₂, in situ generated by **21**-catalyzed reaction of CO₂ with HSiMe₂Et, into CH₃OSiMe₂Et (77%) after 7 days of reaction at 423 K.^[33]

In this context, it is noteworthy that the anion complex [N(hexyl)₄][ReO₄] (**36**)^[41] and the cation species [Zn(C₆F₅)(IPr)][B(C₆F₅)₄] (**37**)^[42] have promoted the reduction of CO₂ with hydrosilanes to the corresponding methanol silylated species after few hours of reaction. The activity of the rhenium derivative **36** depends on the solvent, thus while using acetonitrile-d₃ it has been possible to reduce CO₂ (1.0 bar) with H₃SiPh and H₂SiPh₂ to the corresponding methoxysilane in 98% and 93% yield respectively after 16 h at 353 K, in C₆D₆ mixtures containing the corresponding silylformate as major reaction product were obtained.^[41] It should be mentioned that using **35** as catalyst precursor under the same reaction conditions no reaction of CO₂ (1.0 bar) with HSiEt₃ was observed. On the other hand the zinc based catalyst **37** promoted the selective reduction of CO₂ (1.5 bar) with HSiEt₃ in C₆D₅Br at 363 K to quantitatively afford CH₃OSiEt₃ after 12 h of reaction.^[42]

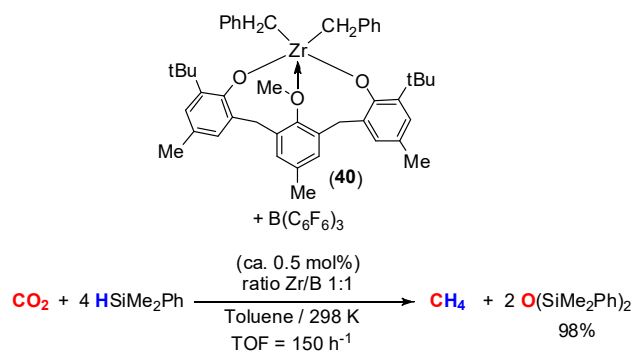
The Gallium species [Ga(2,6-ⁱPr₂C₆H₃)Et₂] (**38**) reacts with the silylium derivative [SiEt₃][CHB₁₁Cl₁₁] to afford the ion pair [Ga(2,6-ⁱPr₂C₆H₃)Et][CHB₁₁Cl₁₁] (**39**), which has found to be active catalyst for the reduction of CO₂ (1.3 bar) with HSiEt₃ in C₆D₆ at 353 K to give the corresponding methoxysilane and methane.^[43]

Metal-free catalytic systems based on N-heterocyclic carbenes with bulky substituents are also efficient catalysts for the

reduction of CO₂ to the methoxide level. Thus, the reaction of CO₂ with H₂SiPh₂ in presence of 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IMes) gives a mixture of (MeO)₂SiPh₂ and (MeOSiPh₂O)_n, which after treatment with NaOH/H₂O affords methanol in 90% yield (based on initial H₂SiPh₂).^[27] This reaction needs polar aprotic solvents such as THF, DMF or acetonitrile. The best reaction performances have been achieved in DMF.^[27]

2.5. Catalytic reduction of CO₂ with silicon-hydrides to methane

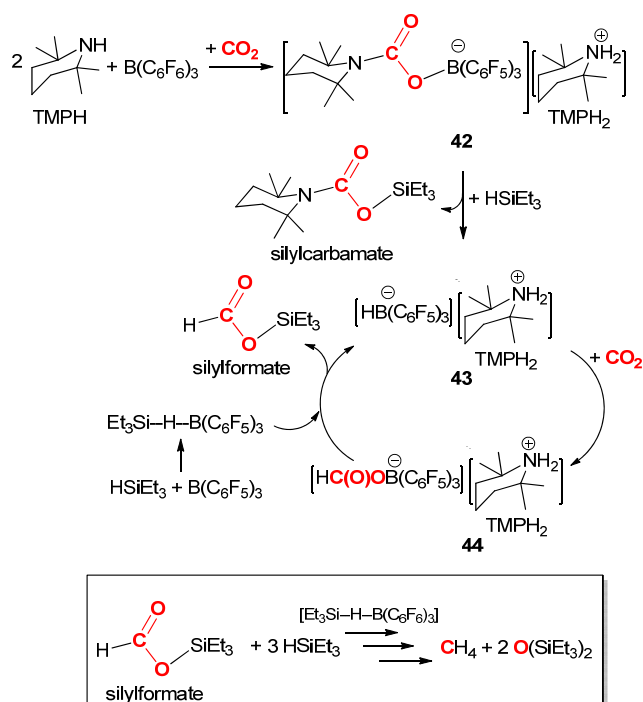
One of the first examples of catalytic reduction of CO₂ with hydrosilanes to methane was reported in 2006 by Matsuo and Kawaguchi.^[44] The most efficient catalyst of those included in that work was based in a zirconium(IV)benzyl cation complex in situ generated by reaction of complex [Zr(CH₂Ph)₂(κ³-BisPhen)] (**40**) (BisPhen = {(2-methoxy-5-methyl-1,3-phenylene)bis(methylene))bis(2-(tert-butyl)-4-methylphenolate)}) with one equivalent of B(C₆F₅)₃ (Scheme 17). This catalytic system allowed the reduction of CO₂ with various hydrosilanes, however its activity depends on the steric hindrance around the Si-H of the silanes. Thus, HSiEt₃ react more slowly than HSiMe₂Ph. The highest activity (TOF = 225 h⁻¹) was achieved using a catalyst loading of around 0.5 mol%, a Zr/B ratio ~ 1, HSiMe₂Ph as reducing agent and toluene at 298 K as reaction solvent. The authors proposed that the Lewis acid B(C₆F₅)₃ plays a double role, i) reacts with complex **40** to generate the cationic active species [Zr(CH₂Ph)(κ³-BisPhen)][B(C₆F₅)₃(CH₂Ph)] (**41**) by abstraction of a benzyl ligand from the metal and, ii) forms a R₃Si-H-B(C₆F₅)₃ adduct which facilitates the Si-H bond activation along the reduction process.^[44]



Scheme 17. Zr/B-catalyzed reduction of CO₂ with HSiMe₂Ph to the methane.

Some years later in 2010 Piers et al. published that the ion pair [TMPH₂][TMP-C(O)OB(C₆F₅)₃] (**42**), formed by reaction of two equivalents of 2,2,6,6-tetramethylpiperidine (TMPH) and B(C₆F₅)₃ with CO₂ catalyzed the reduction of CO₂ with HSiEt₃ in C₆D₅Br at 329 K to give CH₄ (Scheme 18).^[45] It should be mentioned that the treatment of **42** with stoichiometric HSiEt₃ yields the corresponding silylcarbamate and the previously reported ion pair [TMPH₂][HB(C₆F₅)₃] (**43**),^[46] which reacts with CO₂ to afford the formatoborate [TMPH₂][B(C₆F₅)₃(OC(O)H)] (**44**).^[47] Moreover, the reaction of **44** with one equivalent of HSiEt₃ affords the corresponding silylformate and regenerates **43** (Scheme 18). These studies show that the presence of one

additional equivalent of $B(C_6F_5)_3$ is required to have a good catalytic performance for the CO_2 reduction process. Thus, the authors proposed that analogously to the above described Zr/B catalytic system $B(C_6F_5)_3$ also promotes the Si-H bond activation of the $HSiEt_3$ to give the $R_3Si-H-B(C_6F_5)_3$ adduct which reacts with **44** to afford the corresponding silylformate and to regenerate **43** (Scheme 18).^[45] The formation of methane is assumed to take place via $B(C_6F_5)_3$ -catalyzed sequential reduction of silylformate with $HSiEt_3$ to CH_4 (Scheme 18).^[44] This assumption is based on the previously reported activity of $B(C_6F_5)_3$ as catalyst for the reductive hydrosilylation of carbonyl compounds^[48] and on 1H NMR studies of the catalytic process, which evidenced the presence of HCO_2SiEt_3 , $CH_2(OSiEt_3)_2$, CH_3OSiEt_3 and $O(SiEt_3)_2$ throughout the reaction. In this context, it should be mentioned that no examples of $B(C_6F_5)_3$ -catalyzed CO_2 hydrosilylation have reported so far. Conversely, Okuda et al. have published that the weaker Lewis acid BPh_3 (10 mol%) promoted the selective reduction of CO_2 to the corresponding silylformate by its reaction with $H_2SiMePh$ or H_3SiPh in acetonitrile at 313 K.^[49]

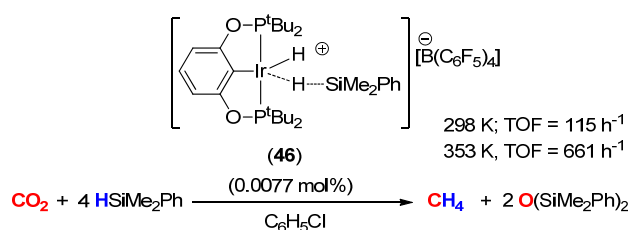


Scheme 18. Mechanism proposed for the reduction of CO_2 with $HSiEt_3$ to give methane in presence of $TMPH$ and $B(C_6F_5)_3$.

Therefore, according with the above described examples it seems that ion pairs containing as electrophilic cation partnered the borate anion $[HB(C_6F_5)_3]^-$ allows the reduction of CO_2 with hydrosilanes to give silylformates, which are easily reduced to methane by the catalytic system $HSiR_3 / B(C_6F_5)_3$. Accordingly with that assumption, the ion pair $[ScCp^*_2][HB(C_6F_5)_3]$ (**45**) (Cp^* = pentamethylcyclopentadienyl) with a highly Lewis acidic cationic moiety, $[ScCp^*_2]^+$, has found to be a very active catalyst for the reduction of CO_2 with $HSiEt_3$ to give methane.^[50] The previously mentioned species $[M(Tism^{iPr^{Benz}})][HB(C_6F_5)_3]$ ($M = Mg$, **30**; Zn , **31**) (Scheme 15),^[38] which have proven to be active catalysts for the reduction of CO_2 with H_3SiPh to afford methane

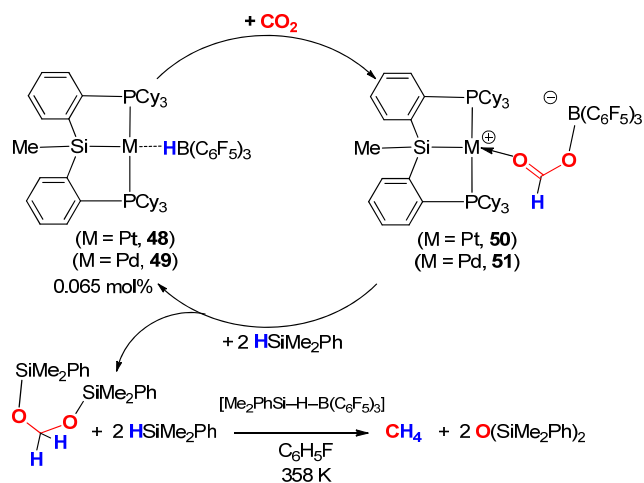
could also be included in the family of catalysts based on ion pairs containing the anion $[HB(C_6F_5)_3]^-$.

In 2012, two groups reported independently examples of ion pairs based on late transition metal cationic species and borate anions,^[51,52] which were used as effective catalysts for the reduction of CO_2 to methane using hydrosilanes as reducing agents. Brookhart et al reported that the iridium-hydride cationic species $[Ir(H)(\eta^1-HSiR_3)(POCOP)][B(C_6F_5)_4]$ (**46**) ($POCOP = 2,6$ -bis((di-tert-butylphosphanyl)oxy)benzen-1-yl), generated in situ by reaction of $[Ir(H)(Me_2CO)(POCOP)][B(C_6F_5)_4]$ (**47**) with the corresponding silane $HSiR_3$, catalyzed the reduction of CO_2 (1.0 bar) with various silanes to yield mixtures of reduction products.^[51] The selectivity of this catalytic system depends on the nature of the hydrosilane. Thus, using $HSiMe_2Ph$ as reductant and a catalyst loading of 0.0077 mol% the full reduction of CO_2 to CH_4 was achieved after 72 h of reaction. It should be mentioned that increasing the temperature to 353 K the reaction could be complete in 3h (Scheme 19).^[51]



Scheme 19. Ir-POCOP-catalyzed reduction of CO_2 with $HSiMe_2Ph$ to methane.

The same year, Turculet and Mitton published that the in situ generated $[M\{HB(C_6F_5)_3\}(PSiP)]$ ($M = Pt$, **48**; Pd , **49**; $PSiP = bis\{2-(dicyclohexylphosphino)phenyl\}methylsilyl$) complexes catalyzed the reduction of CO_2 with $HSiMe_2Ph$ to methane.^[52] In order to shed light on the reaction mechanism, the authors studied stoichiometric reactions. Thus, treatment of freshly prepared benzene solutions of **48** (or **49**) with CO_2 affords the formatoborate adducts $[M\{HC(O)OB(C_6F_5)_3\}(PSiP)]$ ($M = Pt$, **50**; Pd , **51**) (Scheme 20), which were characterized in solution by means of NMR spectroscopy. The species of **50** (or **51**) reacts with one equivalent of $HSiMe_2Ph$ or $HSiEt_3$ to give the corresponding bis(silyl)acetal in 50% yield. The metal influences the activity of the catalytic system, thus the platinum catalyst **48** has shown to be more active than the related palladium species **49**. It should be noted that using the less Lewis acidic borane BPh_3 , instead of $B(C_6F_5)_3$, the formation of methane was not observed. This observation supports that the adduct $[Me_2PhSi-H-B(C_6F_5)_3]$ plays a relevant role in the reduction of the bis(silyl)acetal to methane (Scheme 20).^[52]



Scheme 20. M-(PSiP)-catalyzed (M = Pt, Pd) reduction of CO₂ with HSiMe₂Ph to methane.

Wehmschulte et al. have shown that C₆D₆ solutions of ion pairs based on carborane and strong Lewis acidic aluminium cations such as [AlEt₂][CH₆B₁₁I₆] (**52**)^[53], [Al(2,6-Mes₂C₆H₃O)₂][CHB₁₁Cl₁₁] (**53**)^[54] and [Al(2,6-ⁱPr₂C₆H₃)Et][CHB₁₁Cl₁₁] (**54**)^[43] (Figure 2) are active for deoxygenative reduction of CO₂ using silicon hydrides as reductants. Particularly, HSiEt₃ was found to be the most active of the employed hydrosilanes. These reactions afford not only CH₄ but also C₆D₅CH₃.^[43,53,54]

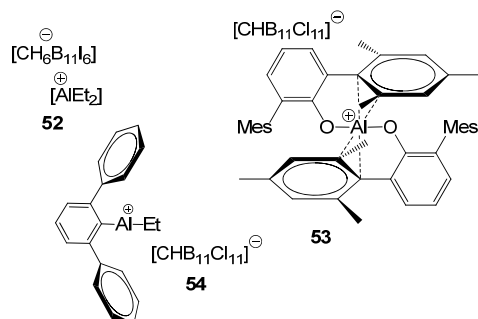


Figure 2. Examples of catalysts based on carborane anions and aluminium cations.

In this regard, Chen et al. have reported an interesting example of a catalytic system based on Al(C₆F₅)₃ and B(C₆F₅)₃ which has shown to be active for the catalytic reduction of CO₂ to methane using HSiEt₃ as reducing agent.^[55]

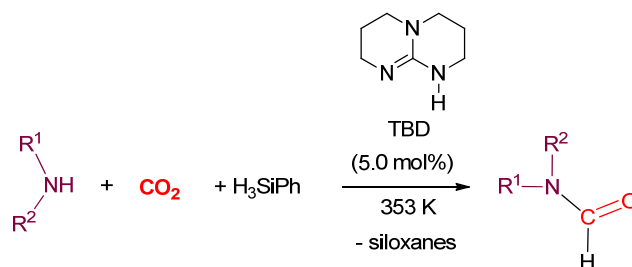
Finally it should be mentioned that García et al. have reported that in presence of [Ru₃(CO)₁₂] (1.0 mol%) and BEt₃ (10 mol%) carbon dioxide (6.89 bar) reacts with H₃SiPh in acetonitrile at 353K to afford methane (28% yield) after 48h.^[56]

3. Catalytic Reaction of Carbon Dioxide with Primary and Secondary Amines and Silicon Hydrides

The catalytic reduction of CO₂ with hydrosilanes in presence of secondary and primary amines has shown to be a promising methodology for the preparation of formamides, amins, methyl amines and silylcarbamates. A brief description of the most effective catalytic systems as well as the factors that determine their selectivity is included below.

3.1. Catalytic formylation of amines with CO₂ and hydrosilanes

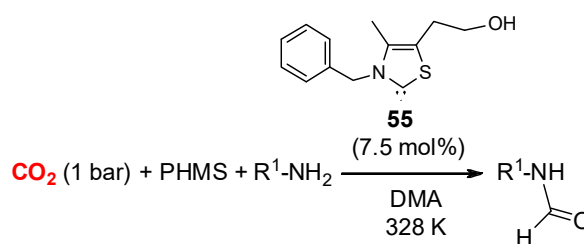
The first examples of catalytic systems effective for the formylation of amines with CO₂ using hydrosilanes as reducing agents were reported by Cantat and co-workers in 2012.^[57,58] They showed that in presence of catalytic amounts (5.0 mol%) of the Lewis base 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) it was possible to achieve the formylation of secondary aliphatic amines with CO₂ (3.0 bar) and H₃SiPh as reductant. The best conversions were obtained at 373 K and under solvent-free conditions (Scheme 21).^[57]



Scheme 21. Solvent-free TBD-catalyzed formylation of amines with CO₂ and H₃SiPh.

Shortly afterwards, this research group published that the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IPr) also catalyzed the formylation of a wide range of secondary aliphatic amines with CO₂ (1.0 bar) and H₃SiPh in THF at r.t. and using a catalyst loading of 5.0 mol%. Differently to TBD, IPr was also active for the formylation of primary amines, aniline derivatives and the N-H bond of some heterocycles.^[58] It should be noted that under the same reactions conditions IMes is less active catalyst than IPr for the formylation of amines with CO₂ and silicon compounds.^[58]

Thiazolium carbenes derived from vitamin B1, have also proven to be active catalyst for formylation of amines with CO₂ (1.0 bar) and polyhydromethylsiloxane (PHMS). The N-benzyl derivative **55** has found to be the most active catalyst of the thiazolium carbenes studied (Scheme 22).^[59]



Scheme 22. Thiazolium carbene **55**-catalyzed formylation of amines with CO₂ and PHMS.

Other examples of organocatalysts such as CO₂ adducts of phosphorus ylides^[60] and the phosphorus formate of 1,3,2-diazaphospholene^[28] have also been reported as catalysts for the formylation of amines.

Examples of transition metal based catalysts effective for the formylation of N-H bonds in amines have also been reported. In 2013 Mizuno et al. reported that the above described catalytic system formed by [Rh₂(AcO)₄] (**3**) and K₂CO₃ (0.5 mol%) is also an active catalyst for the selective formylation of secondary amines.^[10] The same year Baba and collaborators found that the Cu-diphosphano species **12**,^[20] in situ prepared by reaction of Cu(OAc)₂·H₂O with 1,2-bis(diphenylphosphano)benzene and PHMS in 1,4-dioxane, was found to be active homogeneous catalysts for formylation of various amines using CO₂ (1.0 bar) as C1 carbon source and PHMS as reductant. These Cu-catalyzed reactions were performed at 353 K and with a low catalyst loading (<0.1 %). This catalytic system has proven to be faster than the above mentioned rhodium, TBD and IPr catalysts, allowing the formylation of piperidine and morpholine with TOF values of 510 and 409 h⁻¹, respectively.^[61] Liu and Zhang showed that the catalytic system based on Cu(OAc)₂ and bis(diphenylphosphino)ethane (dppe) is a highly efficient catalyst, with only 0.1 mol% catalyst loading, for the formylation of amines at room temperature and low pressure of CO₂ (1.0 bar) in toluene. The authors proposed that the corresponding silylformates are intermediates of these formylation reactions.^[62] García et al. reported that the binuclear complex [(dippe)Ni(μ-H)]₂ (**56**), which was found to be poorly selective for the hydrosilylation of CO₂, is an efficient catalyst precursor for the formylation of primary amines with CO₂ (1.0 bar) using HSiEt₃ as hydrogen source to afford the corresponding formamide in around 80-85% yield.^[63] This nickel based catalytic system requires the addition of 10 mol% of BEt₃ as co-catalyst. The reactions were carried out in THF at 353 K and using a catalyst loading of 1.0 mol% under 1.0 bar of CO₂.^[63] Under the same reaction conditions secondary amines react with CO₂ and HSiEt₃ to afford mixtures containing the expected formamide and the corresponding silylcarbamate in around 50% and 30% yield, respectively.^[63]

In 2015 Cantat, Frogneoux and Jacquet described the first example of an iron based catalyst able to promote the formylation of various secondary and primary amines including some aniline derivatives by their reaction with CO₂ and H₃SiPh.^[64] This system showed low activity for the formylation of N-H bonds of indol and imidazole. The active species was obtained by reaction of Fe(acac)₂ with excess of tris[2-(diphenylphosphino)ethyl]phosphane (PP₃). The catalytic reactions were carried out in THF at r.t. during 18 h and using a catalyst loading of 5.0 mol%.^[64]

In this context, it is worth noting that using a low loading (0.1 mol%) of the rhodium complex [Rh{bis(tzNHC)}(cod)][PF₆] (**57**) (tzNHC = (tz = 1,2,3- triazol-5-ylidene) it has been possible to obtain the reductive formylation of several amines with CO₂ and H₂SiPh₂ at room temperature in CH₂Cl₂, however high pressure CO₂ (25 bar) are required.^[65] The authors proposed that the activation of the CO₂ molecule occurs via Rh=SiPh₂ intermediates through outer-sphere mechanism to give Rh-silylformate adducts which react with amines to afford the corresponding formamide.^[65]

Zinc metal complexes have also been reported as catalysts for the formylation of amines in presence of tetrabutylammonium bromide (TBAB). Thus, using 0.5 mol% of the complex

[Zn(salen)] (**58**) in presence of 0.5 mol% of TBAB was possible to achieve the formylation of a number of amines with CO₂ (5.0 bar) and H₃SiPh at r.t. and under solvent-free conditions.^[66]

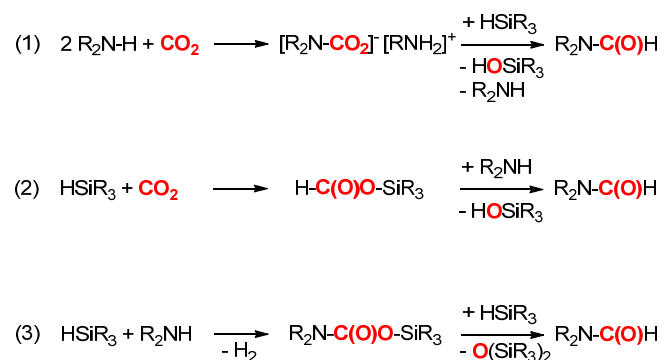
1-alkyl-3-methylimidazolium-based ionic liquids (ILs) have demonstrated to be effective catalysts for the synthesis of formamides under mild reaction conditions using low CO₂ pressure and H₃SiPh as hydrogen source. The authors found that the cations and anions of the ILs played synergistic role in the formylation reactions.^[67]

Lei and collaborators have reported that polar solvents such as DMSO or DMF promote the reaction of morpholine with CO₂ (1.0 bar) and H₃SiPh at r.t. to yield the corresponding formamide in >99% yield after 24h.^[68] The optimization of the reactions in DMSO has been allowed the formylation of a wide range of primary and secondary amines.^[68] In this regard, Song, Han et al. have reported that γ-valerolactone is an efficient solvent and catalyst for the formylation of various amines with CO₂ using H₃SiPh as reducing agent.^[69]

Alkali-metal carbonates have also shown catalytic activity for the selective formylation of amines with CO₂ and hydrosilanes. CsCO₃ has proven to be the most active of the metal carbonates used. Thus, in presence of CsCO₃ (1.0 mol%) has been possible the selective formylation of a wide range of amines with CO₂ (1.0 bar) and H₃SiPh at room temperature using acetonitrile as solvent.^[70]

Finally, it should be mentioned that examples of formylation of amines with CO₂ and hydrosilanes catalyzed by fluoride anions (TBAF) have also been reported.^[71,72] It has been proposed that in these processes the Si-H bond of the hydrosilane is activated by nucleophilic interaction with the fluoride anion to form hypervalent silicon species which finally transfer the hydride to the CO₂ molecule.^[72]

The examples described above illustrate that various catalytic systems, different in nature, effective for the formylation of the N-H bond of amines with CO₂ and hydrosilanes are known. However, there is a lack of knowledge about the reaction mechanism of these catalytic processes. The proposed reaction paths are summarized in Scheme 23.^[68, 73]



Scheme 23. Proposed reaction paths for explaining the catalytic formylation of N-H bonds with CO₂ and hydrosilanes.

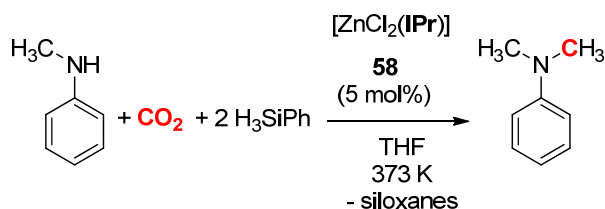
The first equation shown in Scheme 23 is based on the known reactivity of secondary and primary amines with CO₂ to give the corresponding ionic carbamate.^[74] This possibility was first proposed by Cantat et al., which reported that in situ generated carbamates react with hydrosilane to produce the corresponding formamide.^[67] In addition, it has been demonstrated that

silylformates obtained from the catalytic hydrosilylation of CO₂ react with amines to afford formamides and siloxanes (Equation 2 in Scheme 23). Theoretical investigations on the formylation of N-H bonds catalyzed by [ZnCl₂(IPr)] (**59**) showed that in this particular case path 2 is preferred to path 1.^[75] On the other hand, it has also been proposed that silylcarbamates generated by insertion of CO₂ into the Si-N bond of in situ formed silylamines could act as intermediates of the formylation process (Equation 3, in Scheme 23).^[68]

3.2. Catalytic methylation of amines with CO₂ and hydrosilanes

N-Methylated amines are chemicals reagents of great importance due to their multiple applications. Therefore, the development of sustainable methodologies for their preparation represents a challenge.^[76] In this regard, it is worth mentioning that some examples of catalytic reduction of amines with CO₂ and silicon-hydrides to produce the corresponding N-methylated amine have been reported.^[77]

The first catalytic systems effective for the methylation of N-H bonds using CO₂ as a C1 building block and hydrosilanes as reductants were based on zinc(II) complexes with N-heterocyclic carbene ligands.^[78] The activity of these systems depends on multiple factors such as the reducing agent, solvent, temperature and nature of the NHC ligand. Thus, the best catalytic performance was achieved in THF at 373 K using the species [ZnCl₂(IPr)] (**59**) (5.0 mol%) as catalyst precursor, CO₂ (1-5 bar) and H₃SiPh as reducing agent. Under these reaction conditions N,N-dimethylaniline was obtained in >99% from N-methylaniline (Scheme 24). The **59**-catalyzed methylation of other secondary and primary amines was also reported.^[78]



Scheme 24. Zn(II)-IPr catalyzed methylation of methylaniline with CO₂ (1-5 bar) and H₃SiPh in THF.

The same year, the group of Beller demonstrated that the catalytic system formed by [RuCl₂(DMSO)₄] (2.0 mol%) and the bulky phosphane ligand P(*n*Bu)(Ad)₂ (4.0 mol%) was able to promote the methylation of various secondary and primary amines using CO₂ as carbon source and H₃SiPh as reductant.^[79] These reactions were carried out in toluene at 373 K and required a high pressure of CO₂ (30 bar).^[79]

In this regard, it should be noted that the previously mentioned iron catalyst obtained by reaction of Fe(acac)₂ with tris[2-(diphenylphosphino)ethyl]phosphane (PP₃), which promotes the formylation of amines with CO₂ (1.0 bar) and H₃SiPh in THF at r.t., also catalyzes the methylation of aniline derivatives at 373K.^[64]

The above described formylation catalyst [(dippe)Ni(μ-H)]₂ (**55**) and the commercially available [Ni(COD)₂] / dcype (dcype = (1,2-bis-dicyclohexylphosphino)ethane) have also shown to be

effective for the catalytic N-methylation of primary and secondary aliphatic amines with CO₂ and H₃SiPh in toluene under mild reaction conditions (1.0 bar, 373 K) in moderate to good yields.^[80]

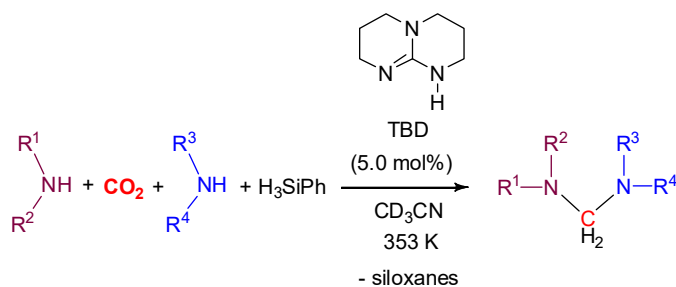
Cu-NHC complexes, particularly [Cu(IPr)(O^{*i*}Bu)] (**13**) have proven to be effective catalysts for the methylation of amines in toluene at 373 K with CO₂ and H₃SiPh. This methodology works very well for secondary amines, which are converted under relatively mild conditions, while primary amines provide mixtures of reaction products.^[81]

Some examples of metal-free catalytic system have been reported to be able to promote the N-methylation of N-H bonds. Dyson et al. have shown that using IMes (5.0 mol%) as catalyst is possible to achieve the methylation of secondary and primary amines in DMF at 323 K with CO₂ (1.0 bar) and H₂SiPh₂. The reactions require 24-48h to produce the corresponding methylation products in 63-91 % yield.^[82] In this regard, He and collaborators have reported that using glycine betaine as catalyst in acetonitrile is possible to achieve the selective transformation of secondary amines into the corresponding formamide, aminal or methylamine by their reaction with CO₂ and H₂SiPh₂. The selectivity of this catalytic system could be easily tuned by changing the reaction conditions.^[83] Thus, while formamides were obtained at 323 K using a 10 mol% of catalyst and 10 bar of CO₂, the selective formation of methylamines is favored at 343 K using 5.0 mol% of catalyst and 1.0 bar of CO₂.^[83] In this context, Nguyen and coauthors have recently shown that guanidine-catalyzed the reductive amination of CO₂ with hydrosilanes to give formamides, aminals or methyl amines.^[73] Mechanistic studies on these reactions evidenced that the formation of the corresponding aminal or methylamine does not follow a sequential mechanism. Thus, the formation of the aminal could take place directly by reaction of the corresponding bis(silyl)acetal with the N-H bond of the amine.^[73] Interestingly, using the Lewis acid B(C₆F₅)₃ (5.0 mol%) as catalyst has been possible to perform the methylation of N-methylaniline derivatives in acetonitrile at 413 K with CO₂ (5.0 bar) and H₃SiPh.^[84] Carboxylates have also found to be effective catalyst for the methylation of amines. Thus, cesium formate (5.0 mol%) promotes the N-methylation of secondary amines in acetonitrile at 323 K with CO₂ (1.0 bar) and H₂SiPh₂ to afford the corresponding product in 56-94 % yield.^[85]

Finally, it should be mentioned that examples of solvent-promoted N-methylation of amines have also been reported. Lei, Chiang and co-workers found that secondary and primary amines reacts with CO₂ (1.0 bar) and H₃SiPh in DMF at 363 K to yield the corresponding methylation product which were isolated in 45-95% yield.^[86]

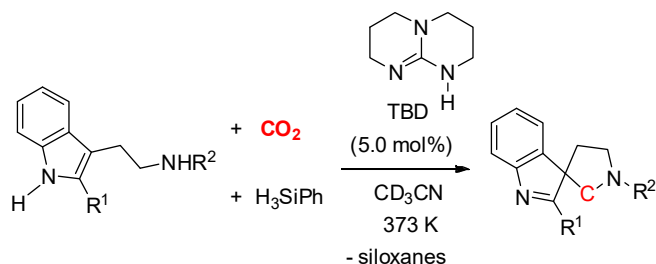
3.3. Synthesis of aminals from amines, CO₂ and hydrosilanes

The catalytic formation of aminals from reaction of amines with CO₂ and silicon-hydrides, which could be considered as a four electrons reduction of CO₂, was first reported in 2015 by Cantat and collaborators. They showed that using an organocatalyst such as TBD (5.0 mol%) was possible to transform secondary amines into the corresponding aminal by their reaction with CO₂ and two equivalents of H₃SiPh in acetonitrile at 353 K. It should be noted that this methodology could be also used to prepare unsymmetrical aminals (Scheme 25).^[87]



Scheme 25. TBD-catalyzed reduction of CO₂ to amins with amines and H₃SiPh.

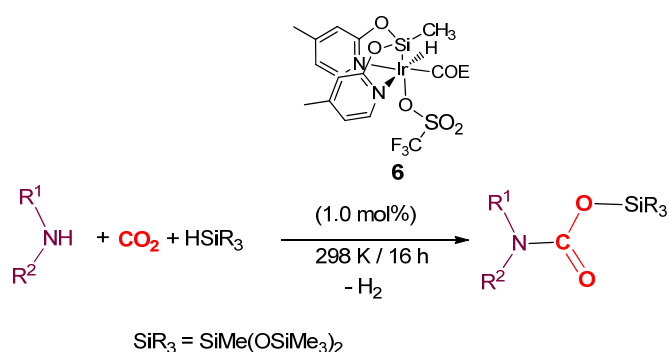
This methodology has been recently successfully employed to prepare spiroindolepyrrolidines via dearomatization of tryptamine derivatives by tandem C–C and C–N bond-forming reaction with CO₂ and H₃SiPh as reducing agent. These reactions were applied to a wide range of substrates allowing the formation of the desired products in high yield (Scheme 26).^[88]



Scheme 26. TBD-catalyzed reduction of CO₂ to amins with amines and H₃SiPh.

3.4. Synthesis of silylcarbamates from amines, CO₂ and hydrosilanes

The formation of silylcarbamates as by-products of the catalytic formylation of amines with CO₂ and hydrosilanes was first reported by Garcia and collaborators in 2013.^[63] They found that the catalytic system based on the complex [(dippe)Ni(μ-H)]₂ (**55**) (1.0 mol%) and BEt₃ (10 mol%) catalyzed the reaction of secondary amines, pyrrolidine and dibenzylamine, with CO₂ (1.0 bar) with HSiEt₃ in THF at 353K to afford the expected formamide together with the corresponding silylcarbamate in around 30% yield. One year later, we found that in presence of catalytic amounts (1.0 mol%) of [Ir(H)(CF₃SO₃)(NSiN)(coe)] (**6**) (NSiN = *fac*-bis-(pyridine-2-yloxy)methylsilyl), various aliphatic secondary amines react with CO₂ (3.0 bar) and one equivalent of HSiMe(OSiMe₃)₃ under solvent-free conditions to selectively afford the corresponding silylcarbamate in high yield after 16 h of reaction at 298 K (Scheme 27).^[89]



Scheme 27. Ir-catalyzed reduction of CO₂ to silylcarbamates with secondary amines and HSiMe(OSiMe₃)₃.

In this regards, it should be mentioned that heterogeneous catalytic systems based on 15% wt Pd catalyst on matrix carbon have also shown to be effective for the formation of silylcarbamates from the reaction of amines with CO₂ and HSiPr₃.^[90]

4. Conclusions

The catalytic reduction of CO₂ with silicon-hydrides could be considering a promising technology for the selective reduction of CO₂ to silylformates, bis(silyl)acetals, methoxysilane or methane. In addition, this methodology could be also applied for the formylation and/or methylation of secondary and primary amines by reaction of the corresponding N–H bonds with CO₂ and hydrosilanes.

The first examples of this type of catalytic transformations of CO₂ were reported during the eighties of the last century, but it is not until 2012 that the breakthrough of this chemical methodology took place. Since then several catalytic systems have been found to be active and selective for the reduction CO₂ with hydrosilanes. It is difficult to establish a general mechanism for these processes. The reason is that the activity and selectivity of these catalytic processes depend not only on the catalyst but also on the nature and concentration of the silicon-hydride, the solvent, the CO₂ pressure and the temperature. For example, for transition metal catalyzed CO₂ hydrosilylation inner- and/or outer-sphere mechanisms have been proposed. Thus, in the case of Ir-NSiN catalyzed CO₂-hydrosilylation to silylformates small changes on the catalytic active site favour inner-sphere versus outer-sphere mechanisms.

It is worth mentioning that some of the reported processes operate under neat conditions, using cheap and stable hydrosiloxanes obtained as side products from the silicone industry such as polyhydromethylsiloxane. The discovery of new active and selective catalysts that allow the use of hydrosiloxanes as well as the clarification of the factors that determine the reaction mechanism of the above mentioned catalytic processes are research fields that are being studied by various research groups around the world. Therefore, it should be expected that in the coming years new and interesting research on this field will come to light.

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Keywords: Carbon dioxide • formylation of amines • methylation of amines • hydrosilylation • homogeneous catalysis

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