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MINIREVIEW

Homogeneous Catalytic Reduction of CO₂ with Hydrosilanes

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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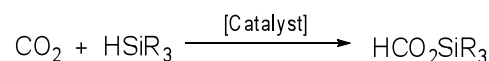
Catalytic CO₂ hydrosilylation is a thermodynamically favored chemical process that could be potentially applied to large-scale transformations of this greenhouse gas. During the last decade, there has been an increasing number of experimental studies regarding metal-catalyzed CO₂ hydrosilylation processes. The first examples of catalytic systems used for CO₂ hydrosilylation employed late transition metals such as ruthenium and iridium. Presently, there are several examples of other catalysts, including transition metal species acting alone or together with B(C₆F₅)₃ as well as metal-free frustrated Lewis pairs (FLP) and organocatalysts which are able to perform this reaction.

Introduction

The world's carbon dioxide emissions from energy related sources reached a record high of 31.6 billion tons in 2012.¹ While numerous strategies are being developed for CO₂ capture, there is an increasing interest in using carbon dioxide as a C1 carbon source. However, the great thermodynamic and kinetic stability of CO₂ is a challenge to overcome in order to achieve its chemical activation. Within this scenario, the catalysis represents a clear alternative that would allow access to new opportunities for large scale CO₂ utilization. Indeed, various reviews on stoichiometric and catalytic reactions involving carbon dioxide and homogeneous catalysts based on transition metal compounds and organocatalysts have been reported.²⁻¹⁹

Several transition-metal catalysts have been found to be effective for the synthesis of formic acid by hydrogenation of carbon dioxide with hydrogen.¹⁵⁻¹⁸ This is a thermodynamically unfavourable reaction and relatively high pressures are required. In contrast, the catalytic reduction of carbon dioxide to silyl formates, methoxysilanes, and methane with silanes¹⁷ is a thermodynamically favoured chemical process, being the ease of activation of the Si-H bond and the strength of the new formed Si-O bond the driving forces behind these transformations. Among the mentioned products silyl formates are of great interest due to their potential application as synthons for the preparation of a wide range of valuable chemicals.¹⁹ In this context, it is worth to mention that a number of cheap and environmentally benign hydrosilanes are available.²⁰ Thus, catalytic CO₂ hydrosilylation to silyl formates (Scheme 1) could represent an alternative methodology for sustainable catalytic CO₂ transformation into useful chemicals. Therefore, a better understanding of the

reaction mechanisms of the catalytic CO₂ hydrosilylation processes is of great importance to allow for the development of sustainable methods for industrial CO₂-reduction.



Scheme 1. Homogeneously catalyzed CO₂ hydrosilylation.

The first examples of metal-catalyzed hydrosilylation of CO₂ were independently reported in 1981 by Koinuma's²¹ and Süs-Fink's²² research groups using homogeneous ruthenium catalysts. These ruthenium-catalyzed processes were selective but required high CO₂ pressures and moderate heating. Some years later, in 1989, Eisenberg and Eisenschmid reported the first example of iridium-catalyzed hydrosilylation of CO₂.²³ Interestingly, this reaction takes place under mild conditions (r.t. and 1 atm). However, this process has a lack of selectivity and silyl formates are obtained together with the corresponding bis(silyl ether), methoxy silane and siloxane.²³ Despite these interesting pioneer results, the studies on metal-catalyzed CO₂ hydrosilylation have been very scarce, but in recent years a significant number of papers have been reported. It is worth mentioning that recently have been published some examples of metal free basic organocatalytic systems able to catalyze the reduction of CO₂ with silanes.²⁴⁻²⁹

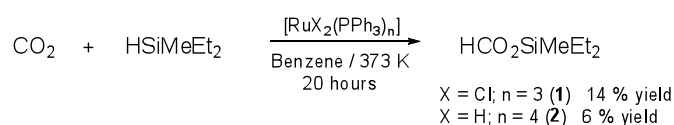
This review arises from the increasing activity in the area, and the growing interest in understanding the parameters that govern the catalytic CO₂ hydrosilylation to silyl formates and related reactions involving CO₂ and hydrosilanes with the aim of designing more active and selective catalytic systems.

1. Late transition metal-catalyzed CO₂ hydrosilylation processes

1.1. Ruthenium-catalyzed CO₂ hydrosilylation processes

1.1.1. Ruthenium phosphane complexes as catalysts.

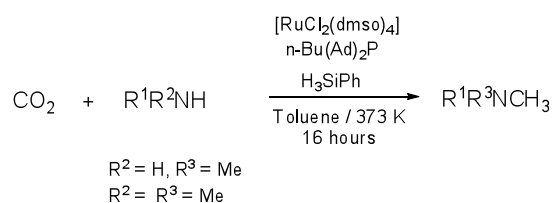
Koinuma et al. reported one of the first examples of homogenous ruthenium-catalyzed hydrosilylation of CO₂.²¹ The authors studied the reaction of CO₂ (30 bar, 373K) with a benzene solution of HSiMeEt₂ in presence of catalytic amounts of the ruthenium(II) species [RuCl₂(PPh₃)₃] (**1**) or [RuH₂(PPh₃)₄] (**2**) (Scheme 2). Under these conditions the expected silyl formate, HCO₂SiMeEt₂, could be isolated from the reaction mixture and characterized by IR and ¹H NMR. It is noteworthy that this reaction is selective while having poor performance, being complex **1** more active than **2** (Scheme 2).²¹



Scheme 2. Examples of Ru-catalyzed CO₂ hydrosilylation processes.

In this context, some years later Jessop, Ikariya and Noyori studied the reaction of CO₂ with HSiMeEt₂ in supercritical CO₂ (200-220 bar) using the complex [RuH₂(PMe₃)₄] (**3**), related to **2**, as catalyst precursor. Interestingly, under these reaction conditions a higher conversion rate (TON = 62) was observed.³⁰ These results show that catalytic systems based on ruthenium(II)-phosphane species are selective to the formation of silyl formates by CO₂ hydrosilylation. However, high CO₂ pressures are required to achieve reasonable reaction rates.

Beller et al. have recently reported an interesting example of catalytic selective methylation of N-H bonds in which secondary and primary amines were transformed into the corresponding tertiary amine by reaction with CO₂ and silanes (Scheme 3).³¹ The authors tested several metal precursors including Ru, Rh, Cu and Fe complexes and twelve different phosphane ligands. The catalytic system formed by the complex [RuCl₂(dmsO)₄] (dmsO = dimethylsulfoxide) as metallic precursor and n-Bu(Ad)₂P (Ad = adamantyl) as phosphane ligand has proved to be the most active (Scheme 3). Interestingly, a clear hydrosilane effect was observed. Indeed, the best yields were always obtained using H₃SiPh as reducing agent.³¹



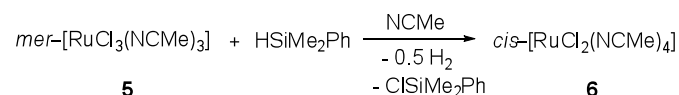
Scheme 3. Examples of Ru-catalyzed methylation of amines using CO₂ and H₃SiPh.

In this regard, Beller's group has also reported the catalytic methylation of amines with CO₂ using hydrogen instead of hydrosilanes as reducing agent. A combination of the ruthenium(III) species [Ru(acac)₃], triphos as phosphane ligand, and either acid additives or LiCl has found to be the best catalytic system for these reactions.³²

1.1.2. Ruthenium acetonitrile complexes as catalysts.

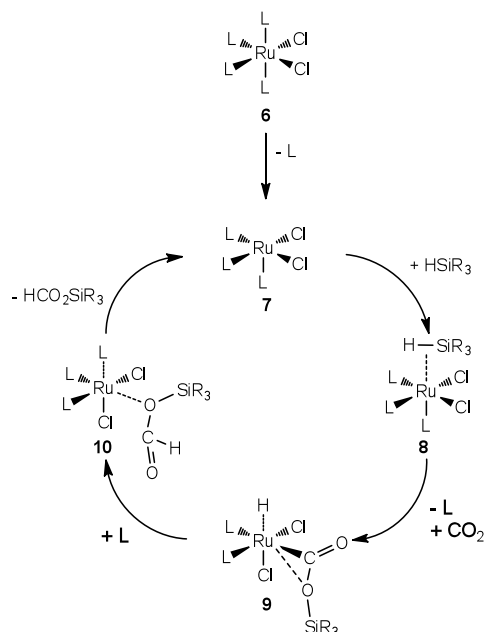
Pitter et al. described that acetonitrile solutions of RuCl₃·nH₂O reacts at 358 K with hydrosilanes to give [Ru^{II}Cl(NCMe)₅][*trans*-Ru^{III}Cl₄(NCMe)₂] (**4**), which was found to be an excellent catalyst for the hydrosilylation of CO₂ to silyl formates at high CO₂ pressures (ca. 70-88 bar).^{33,34} It is worth noting that the activity of this ruthenium-acetonitrile catalytic system was enhanced by adding catalytic amounts of bulky phosphane ligands as PⁱPr₃ and PCy₃.³⁴ Curiously, despite the great excess of reducing agent (HSiR₃) present in the acetonitrile solutions half of the ruthenium remained in its former oxidation state (+III). In this regards, studies carried out by Pitter's research group demonstrated that both the oxidation state of ruthenium and the nature of the halide ligands clearly influence the catalytic activity of neutral ruthenium-acetonitrile complexes in the homogeneously catalyzed hydrosilylation of CO₂ with HSiMe₂Ph.³⁵

Complex *mer*-[RuCl₃(NCMe)₃] (**5**) has found to be the most active precatalyst (conversion 92 % and selectivity 94 %) of the following series of complexes: *mer*-[RuCl₃(NCMe)₃], *cis*-[RuX₂(NCMe)₄] and *trans*-[RuX₂(NCMe)₄] (X = Cl, Br).³⁵ Experimental evidences revealed that during the reaction complex **5** is reduced to the ruthenium(II) complex *cis*-[RuCl₂(NCMe)₄] (**6**) (Scheme 4). However, when complex **6** was used as precatalyst lower reaction rates were always observed. These results showed that Ru(III) precursors are more active than the related Ru(II) complexes.³⁵



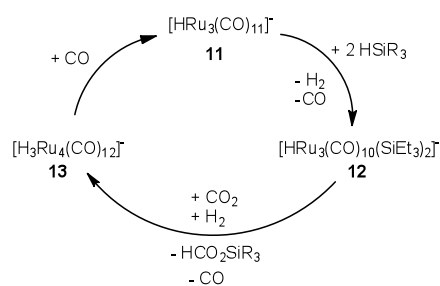
Scheme 4. Reduction of complex **5** to compound **6** in presence of HSiMe₂Ph.

The proposed mechanism based on a modified Chalk-Harrod mechanism³⁶ and supported by DFT calculations³⁵ is shown in Scheme 5. The first step implies dissociation of one NCMe ligand from **6** to generate the active species **7**. The η²-(Si-H) coordination of the silane to the metal centre in **7** affords intermediate **8**, from which successive losing of one additional NCMe molecule and coordination of CO₂ yields the Ru(IV) intermediate **9**. Ligands reorganization in **9** and ulterior coordination of one molecule of acetonitrile yields intermediate **10** from which the corresponding silyl formate is released regenerating the active species **7**.



Scheme 5. Proposed catalytic cycle for the hydrosilylation of CO_2 using **6** as precatalyst.

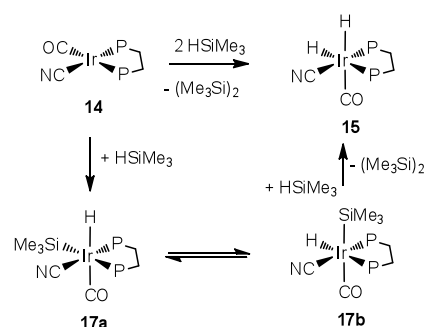
1.1.3. Ruthenium clusters as catalysts. Süss-Fink et al. reported in 1981 the reaction of HSiEt_3 with CO_2 (50 bar at 60°C) in the presence of catalytic amounts of the cluster anion $[\text{HRu}_3(\text{CO})_{11}]^-$ (**11**).²² The resulting product was characterized by ^1H NMR and mass spectrometry as a mixture containing $\text{HCO}_2\text{SiEt}_3$ (81%), HOSiEt_3 (1.4%), $\text{Et}_3\text{SiOSiEt}_3$ (0.8%) and HSiEt_3 (0.8%) together with an unidentified component (16%). Monitoring the reaction by infrared spectroscopy allowed the identification of the cluster anions $[\text{HRu}_3(\text{CO})_{10}(\text{SiEt}_3)_2]^-$ (**12**)³⁷ and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**13**)³⁸ as reaction intermediates. The proposed mechanism based on these experimental evidences is shown in Scheme 6. The authors proposed the addition of two HSiEt_3 molecules to **11** to afford the active species **12** together with H_2 and CO as the initial step of the catalytic process (Scheme 6). Despite there is a lack of knowledge about the CO_2 activation and functionalization steps the authors could observe the formation of the anionic cluster **13** which reacts with CO to regenerate **11**.



Scheme 6. Proposed catalytic cycle for the hydrosilylation of CO_2 using **11** as catalyst.

1.2. Iridium-catalyzed CO_2 hydrosilylation processes.

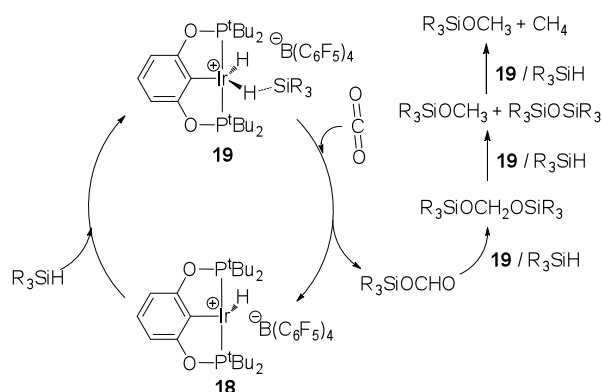
1.2.1. Iridium phosphane complexes as catalysts. Eisenberg and Eisenschmid reported in 1989 the first example of an iridium-catalyzed hydrosilylation of CO_2 process.²³ Interestingly, this reaction takes place under mild conditions (1 atm). The authors used the complex $[\text{Ir}(\text{CN})(\text{CO})(\text{dppe})]$ (**14**) (dppe = 1,2-bis(diphenylphosphano)ethane) as precatalyst. ^1H and ^{13}C NMR studies of the reaction showed that the reduction of CO_2 with HSiMe_3 affords, in a first step, the silyl formate $\text{HCO}_2\text{SiMe}_3$. This species was further hydrosilylated to $\text{Me}_3\text{SiOCH}_2\text{OSiMe}_3$, which finally reacts with an additional equivalent of HSiMe_3 to give $\text{Me}_3\text{SiOSiMe}_3$ and $\text{CH}_3\text{OSiMe}_3$.²³ Study of the iridium containing products allowed identification of $[\text{IrH}_2(\text{CN})(\text{CO})(\text{dppe})]$ (**15**)³⁹ and $[\text{IrH}(\text{CO})_2(\text{dppe})]$ (**16**)⁴⁰ as major iridium components after a week at room temperature. This fact is in agreement with the formation of the iridium(III) $[\text{IrH}(\text{CN})(\text{SiMe}_3)(\text{dppe})]$ (**17a/17b**) isomers as reaction intermediates³⁹ (Scheme 7).



Scheme 7. Reaction of the iridium(I) complex **14** with HSiMe_3 .

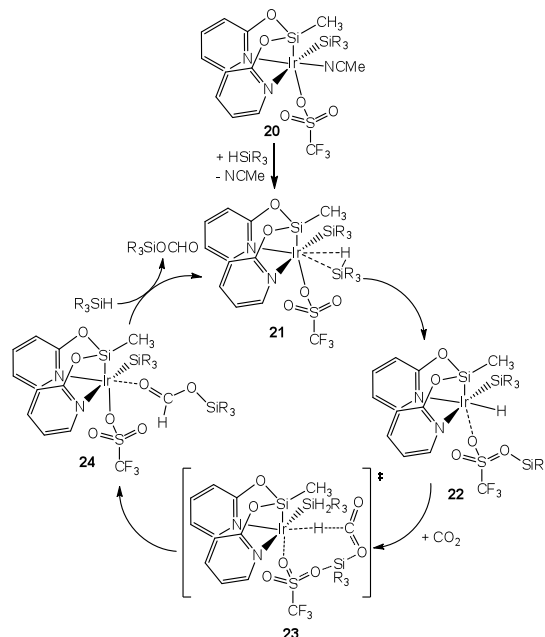
1.2.2. Iridium-POCOP pincer complexes as catalysts.

Recently, Brookhart's group has reported an Ir^{III} -POCOP (POCOP = 2,6-bis((di-tert-butylphosphano)oxy)phenyl) pincer catalyst efficient for the reduction of CO_2 to methane with trialkylsilanes. The authors showed that $\text{Ir}(\eta^1\text{-HSiR}_3)$ cationic species $[\text{Ir}(\text{H})(\eta^1\text{-HSiR}_3)(\text{POCOP})][\text{B}(\text{C}_6\text{F}_5)_3]$ (**19**) catalyzed the reduction of CO_2 to the corresponding silyl formate that under these reaction conditions is not stable and evolves (Scheme 8). Interestingly, the reaction products depend on the nature of the silane. For example, the use of bulky silanes produces mixtures of CH_4 , $\text{R}_3\text{SiOCH}_2\text{OSiR}_3$, CH_3OSiR_3 and $\text{R}_3\text{SiOSiR}_3$. Conversely, less sterically hindered silanes such as HSiEt_3 or HSiPhMe_2 affords selectively CH_4 and $\text{Me}_3\text{SiOSiMe}_3$, with no detection of other products or intermediates.⁴¹

Scheme 8. Iridium(III)-POCOP catalyzed hydrosilylation of CO₂.

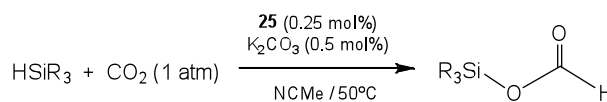
It is remarkable the η^1 -silane coordination proposed for complex **19** (Scheme 8). This coordination mode towards iridium has been proven spectroscopically as well as crystallographically by Brookhardt and coworkers.⁴² Interestingly, a *Natural Bond Orbitals* (NBO) analysis conducted on the modeled Ir-silane complexes **19**- η^1 -(Si-H) and **19**- η^2 -(Si-H) shows a greater electrophilicity at the Si atom in [Ir]- η^1 -(Si-H) species compared to its [Ir]- η^2 -(Si-H) analogue.⁴²

1.2.3. Iridium-NSiN complexes as catalysts. We have recently reported the iridium-catalyzed hydrosilylation of CO₂ with HMTS (HMTS = 1,1,1,3,5,5,5-heptamethyltrisiloxane). This reaction affords selectively the corresponding silyl formate under mild conditions (3 atm of CO₂, HMTS as solvent and 295 K) and generates no waste.⁴³ The air and moisture stable [Ir(SiMe(OSiMe₃)₂)(CF₃SO₃)(NSiN)(CH₃CN)] (**20**) (NSiN = bis(pyridine-2-yloxy)methylsilyl *fac*-coordinated) species was used as precatalyst for this reaction. This reaction proves the potential large-scale applicability of the catalytic reduction of CO₂ to silyl formates.⁴³ This process has a good performance, close to 99%, and a TOF_{1/2} of 0.17 h⁻¹. Theoretical calculations and experimental evidences show that the acetonitrile ligand substitution by a η^2 -(Si-H) coordinated silane is energetically much more favorable than CO₂ coordination. Thus, the CO₂ hydrosilylation process is initiated by silane coordination to the iridium centre, followed by silyl transfer from the Ir- η^2 -(Si-H) moiety to the triflate ligand and simultaneous Ir-hydride bond formation and ends with transfer of silyl and hydride ligands to CO₂ in a concerted way (Scheme 9). Therefore, as is shown in Scheme 9 activation and functionalization of CO₂ occur through an outer-sphere mechanism.⁴³

Scheme 9. Iridium(III)-NSiN catalyzed hydrosilylation of CO₂.

1.3. Rhodium-catalyzed CO₂ hydrosilylation processes.

Mizuno et al. have recently published that the combination of [Rh₂(OAc)₄] (**25**) with inorganic bases (M₂CO₃, M = K, Cs) generates an efficient catalytic system for CO₂ hydrosilylation to silyl formates under mild conditions (1 atm, 50-70 °C) (Scheme 10).⁴⁴ The reaction is selective to the formation of the corresponding silyl formate with only traces (8%) of R₃SiOSiR₃ as subproduct. It is remarkable that this catalytic system is effective with a wide range the silanes.

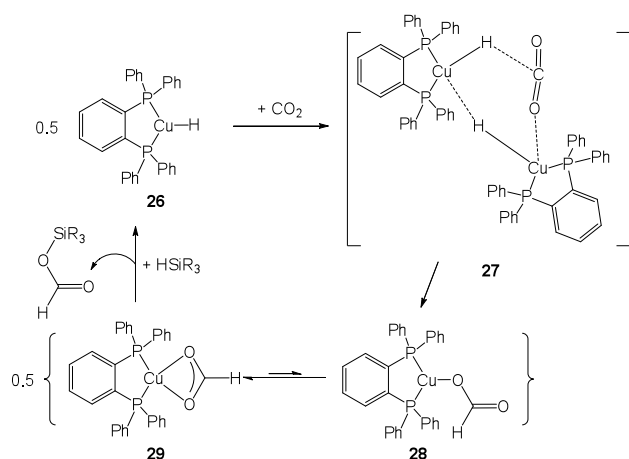
Scheme 10. [Rh₂(OAc)₄] (**25**) catalyzed hydrosilylation of CO₂.

It is worth noting that the silyl formates thus obtained have been used *in situ* for the preparation of value-added chemicals as for instance formamides.⁴⁴ Therefore, this reaction constitutes an interesting and promising example of transition metal-catalyzed utilization of CO₂ as C1 building block for catalytic synthesis of value added chemicals.

1.4. Copper-catalyzed CO₂ hydrosilylation processes

1.4.1. Copper phosphane complexes as catalysts. The reaction of Cu(OAc)₂·H₂O with dppp (dppp = 1,2-bis(diphenylphosphino)benzene) and excess of HSiMePh₂ leads to the formation of the copper(I) complex [CuH(dppp)] (**26**) which has been characterized in solution (Scheme 11).⁴⁵ This catalytic system has demonstrated to be highly active for the

CO₂ hydrosilylation to silyl formates under mild conditions (1 atm, 100 °C). ¹H, ¹³C and ¹⁸O NMR studies of the reaction with CO₂, ¹³CO₂ and C¹⁸O₂ suggest the initial formation of a monodentate [Cu(η¹-OCHO)] (**28**) species (Scheme 11). Intermediate **28** evolves to the more stable bidentate complex [Cu(η²-OCHO)] (**29**) which is the only copper containing species observed in solution after 10 min. Interestingly, this copper-based catalytic system allows CO₂ reduction to silyl formates using polymethylhydrosilane (PMHS) as reducing agent.⁴⁶ Kinetic studies of the reaction suggest a mechanism involving a binuclear species (**27** in Scheme 11) formed by interaction between two molecules of **26** and one molecule of CO₂.⁴⁶

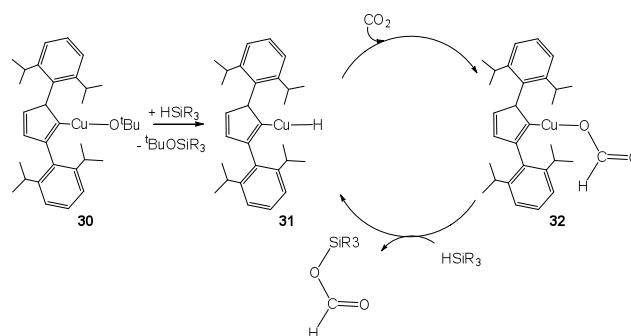


Scheme 11. Proposed reaction pathway for CO₂ hydrosilylation catalyzed by **26**.

Ligand screening shows that the substituents of the phosphane moiety notably influence the catalytic activity. Copper species with the 1,2-bis(diisopropylphosphane)benzene ligand have proven to be the most active catalysts.^{45,46}

1.4.2. Copper complexes with N-heterocyclic-carbene ligands as catalysts. Copper(I) *N*-heterocyclic carbene (NHC) complexes have been used as catalyst for the hydrosilylation of CO₂ to silyl formates. These catalytic systems are highly efficient and afford the corresponding silyl formate in a multigram amount under mild conditions (1 atm, 60 °C).⁴⁷ Copper complexes with high sterically demanding NHC ligands as **IPr** (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) are more active than the corresponding species with the less sterically hindered **IMes** (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene). It is worth mentioning that the performance of the Copper-phosphane catalyst **26** is higher (TON = 8100) than that reported for [Cu(O^tBu)(IPr)] (**30**) (TON = 7489).⁴⁷ Experimental studies using [Cu(O^tBu)(IPr)] (**30**) as catalyst precursor evidenced the initial formation of [CuH(IPr)] (**31**) which reacts with CO₂ to give [Cu(η¹-OHCO)(IPr)] (**32**). In a final step, the reaction of **32** with HSiR₃ affords the corresponding silyl formate and

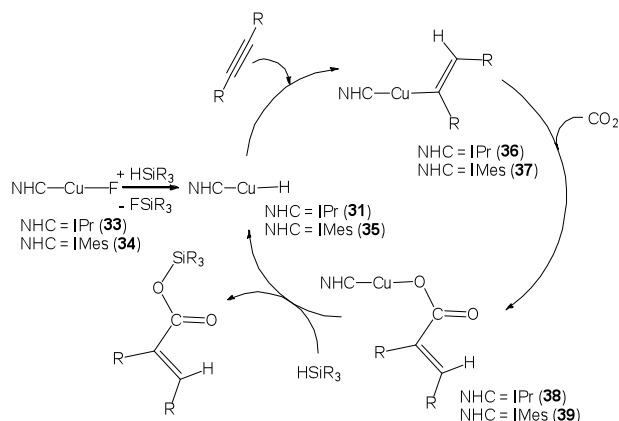
regenerates **31** (Scheme 12).⁴⁷ Complex **32** could be isolated from the reaction mixture and characterized by an X-ray diffraction. Despite the η²-coordination of the formate ligand to copper(I) is thermodynamic favored, the η¹-coordination observed in **32** could be attributed to the steric hindrance and the strong electron σ-donor character of the **IPr** ligand. The formate complex **32** reacts instantaneously with one equivalent of HSiR₃ to give **31** and also shows high catalytic activity for the hydrosilylation of CO₂, both facts agree with the mechanism proposed in Scheme 12.



Scheme 12. Proposed reaction pathway for CO₂ hydrosilylation catalyzed by **31**.

Tsuji's group reported in 2011 the copper-catalyzed hydrocarboxylation of alkynes using CO₂ and hydrosilanes.⁴⁸ Interestingly, this reaction is applicable to a wide variety of internal alkynes. The complexes [CuF(IPr)]⁴⁹ (**33**) and [CuF(IMes)] (**34**) were found to be the best catalyst precursors for such processes.

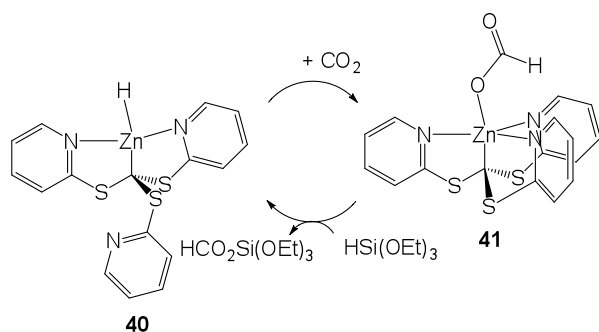
The authors proposed the copper-hydride complex [CuH(NHC)] generated *in situ* by reaction of the corresponding compound [CuF(NHC)] (NHC = IPr **33**, IMes **34**) with hydrosilane, as the active catalyst for the process. The catalytic cycle depicted in Scheme 13 shows the insertion of the alkyne into the Cu-H bond as the first step of the catalytic reaction. Followed by the reaction of the corresponding Cu-alkene intermediate with CO₂ to afford a Cu-carboxylate complex which in a last step reacts with hydrosilane to regenerate the [CuH(NHC)] species and the corresponding silyl formate.⁴⁸ In this regard it is remarkable that Lin's group has recently reported DFT studies on these catalytic systems which confirm the mechanism proposed in Scheme 13.⁵⁰



Scheme 13. Proposed reaction pathway for copper catalyzed hydrocarboxylation of alkynes using CO₂ and hydrosilanes.

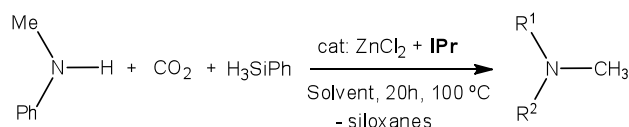
1.5. Zinc-catalyzed CO₂ hydrosilylation processes.

1.5.1. Zinc complexes with N-donor ligands as catalysts. The complex [ZnH(κ^3 -tptm)] (**40**) (tptm = tris(2-pyridylthio)methyl) is an effective catalyst for the formation of HCO₂Si(OEt)₃, by reaction of CO₂ with HSi(OEt)₃ at 100°C (Scheme 14).⁵¹ Remarkably, this reaction can be performed on gram-scale, with a TON of 10³ and a TOF of 2.9 h⁻¹. The proposed mechanism for the catalytic cycle is illustrated in Scheme 14. In a first step, the hydride complex **40** reacts with CO₂ to give the corresponding formate [Zn(η^2 -OCHO)(κ^3 -tptm)] (**41**)⁵² which was observed by ¹H NMR as the resting state. In a final step, **41** reacts with HSi(OEt)₃ to give HCO₂Si(OEt)₃ and regenerates the active species **40**.



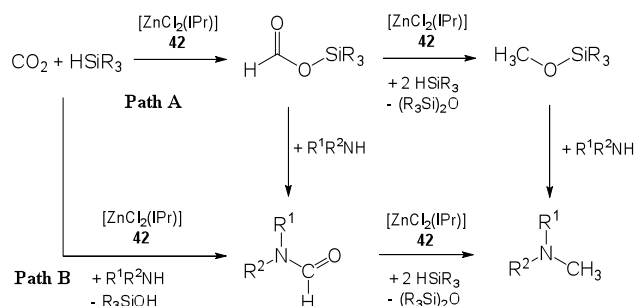
Scheme 14. Proposed reaction pathway for CO₂ hydrosilylation catalyzed by **40**.

1.5.2. Zinc complexes with N-heterocyclic-carbene ligands as catalysts. N-Heterocyclic carbene zinc complexes are effective catalysts for the catalytic methylation of N-H bonds in the presence of hydrosilanes (Scheme 15). The activity of these catalytic systems depends on both the ligand and silane nature. The more sterically hindered IPr ligand led to somewhat more reactive catalyst than the IMes analogue. Regarding the silane, H₃SiPh is more reactive than H₂SiPh₂, HSiPh₃, HSiEt₃ and HSi(OEt)₃.⁵³



Scheme 15. Catalytic methylation of amines using Zn-IPr species as catalyst precursor.

Based on experimental data two main pathways were proposed for the methylation of N-H bonds using CO₂ and hydrosilanes (Scheme 16). In path A, methylamines are obtained by reaction of methoxysilanes with amines. In path B, hydrosilylation of formamides affords the corresponding methylamine. Interestingly, CO₂ was found to be stable in the presence of [ZnCl₂(IPr)] (**42**) and H₃SiPh and no traces of the corresponding silyl formate or methoxysilane were observed. However, formamides were detected as reaction intermediates and were isolated together with the methylated final product. Additionally, complex **42** is an active catalyst for the hydrosilylation of methylphenylformamide to dimethylphenylamine.⁵³ These evidences point to path B (Scheme 16) as a possible mechanistic model for this process.



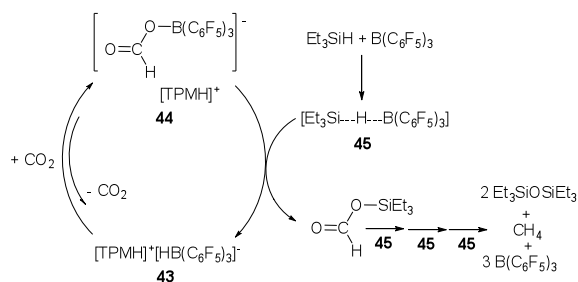
Scheme 16. Proposed reaction pathways for the catalytic methylation of amines using **42** as catalyst precursor.

2. Reactions involving B(C₆F₅)₃ and related catalysts for CO₂ reduction with hydrosilanes.

The strong Lewis acid B(C₆F₅)₃ is becoming the borane of use for some special reactions.⁵⁴ It is relatively inert, hydrolytically more stable than BF₃ and able to act as acid catalysts in organic synthetic transformations.⁵⁵ Although, several examples of B(C₆F₅)₃-catalyzed hydrosilylation of carbonyl bonds are known,⁵⁶⁻⁵⁹ this Lewis acid is not capable to catalyze the hydrosilylation of CO₂ by itself. In this regard, there have been described some examples of catalytic systems formed by B(C₆F₅)₃ acting together with frustrated Lewis pairs (FLPs) or transition metal complexes which are effective for CO₂ hydrosilylation.

2.1. Lewis Pair/ $B(C_6F_5)_3$ catalytic systems.

During the last years FLPs have led to the development of new strategies for the activation of a wide variety of small molecules including CO_2 .⁶⁰ In this context, Piers et al reported in 2010⁶¹ that the ion pair **43** (Scheme 17), formed by treatment of a stoichiometric mixture of $B(C_6F_5)_3$ and 2,2,6,6-tetramethylpiperidine (TMP) with hydrogen, reacts reversibly with CO_2 to afford the previously reported⁶² formateborate anion of **44** (Scheme 17). 1H and ^{19}F NMR studies revealed that under these reaction conditions, stoichiometric amount of $B(C_6F_5)_3$, $HSiEt_3$ is unable to reduce CO_2 . Interestingly, when the reaction was carried out under the same conditions but using one additional equivalent of $B(C_6F_5)_3$ the immediate conversion of **43** into **44** together with the appearance of the corresponding CO_2 hydrosilylation products was observed (Scheme 17).⁶¹

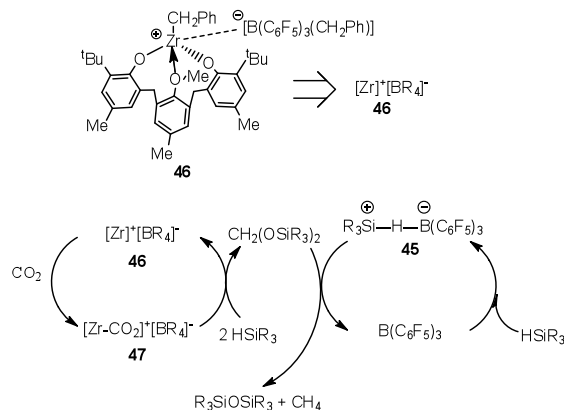


Scheme 17. Ion pair **43**/ $B(C_6F_5)_3$ catalyzed CO_2 reduction to methane with $HSiEt_3$.

Experimental studies showed that the nucleophilic attack from the hydridoborate moiety of **43** to the CO_2 molecule to afford intermediate **44** constitutes the rate limiting step of the process. Once compound **44** is generated, the silylium ion transfer to the formate fragment of **44** from **45** produces the corresponding silyl formate and regenerates the active ion pair **43**. Finally, the three steps reduction of the silyl formate by successive reactions with the $B(C_6F_5)_3$ -activated silane species **45** produces CH_4 and $Et_3SiOSiEt_3$ (Scheme 17).⁶¹

2.2. Zirconium/ $B(C_6F_5)_3$ catalytic systems.

Matsuo and Kawaguchi reported in 2006 the hydrosilylation of CO_2 to CH_4 level using the *in situ* generated zirconium cationic complex **46** (Scheme 18).⁶³ The authors found that the silane plays a double role, as reducing agent and oxygen acceptor. Interestingly, higher reaction conversions were observed using an excess of $B(C_6F_5)_3$. Additionally, the authors demonstrated that the cation-free system $B(C_6F_5)_3/HSiR_3$ is not active for CO_2 hydrosilylation.⁶³

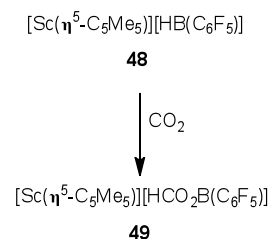


Scheme 18. Ion pair **46**/ $B(C_6F_5)_3$ catalyzed CO_2 reduction to methane with $HSiEt_3$.

Despite scarce experimental evidences available, based on the known electrophilic character of zirconium(IV) cationic species in their reactions with CO_2 ,⁶⁴ the authors proposed a mechanism in which the zirconium cationic complex **46** coordinates the CO_2 molecule to afford the corresponding Zr- CO_2 adduct **47** (Scheme 18), which reacts with two equivalents of $HSiR_3$ to give the corresponding bis(silyl ether). Simultaneously, $B(C_6F_5)_3$ reacts with $HSiR_3$ to afford the Lewis pair $[R_3Si^+ \cdots H \cdots B(C_6F_5)_3^-]$ (**45**) which by reaction with the previously produced bis(silyl ether) gives CH_4 and $R_3SiOSiR_3$ and regenerates $B(C_6F_5)_3$.⁶¹

2.3. Scandium/ $B(C_6F_5)_3$ catalytic systems.

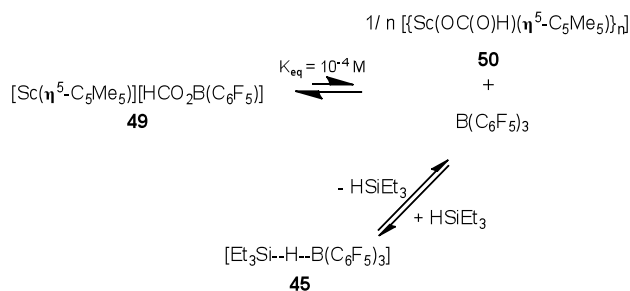
Analogously to **46** the ionic pair $[Sc(\eta^5-C_5Me_5)_2][BH(C_6F_5)_3]$ (**48**), recently described by Piers and Maron,⁶⁵ catalyzed the deoxygenative reduction of CO_2 to CH_4 with silanes.⁶⁶ The cationic moiety of the ion pair **48**, $[Sc(\eta^5-C_5Me_5)_2]^+$, is a highly active Lewis acid which activates CO_2 towards acceptance of the hydride from the anionic fragment $[BH(C_6F_5)_3]^-$ to afford the ion-pair **49** which could be isolated and was characterized by X-ray diffraction methods (Scheme 19).⁶⁶ DFT calculations show that the formation of **49** from the reaction of **48** with CO_2 is exergonic and without significant barriers.



Scheme 19. Reaction of the ion-pair **47** with CO_2 .

In solution, the ion-pair **49** is in equilibrium with $B(C_6F_5)_3$ and the oligomer **50** (Scheme 20). $B(C_6F_5)_3$ reacts reversibly with $HSiEt_3$ to give the Lewis pair $[R_3Si^+ \cdots H \cdots B(C_6F_5)_3^-]$ (**45**)

which acts as hydrosilylation catalyst. Therefore, ion-pair **49** in presence of an excess (4 equ.) of $B(C_6F_5)_3$ constitutes a highly active catalytic system for the reduction of CO_2 to methane level.⁶⁶

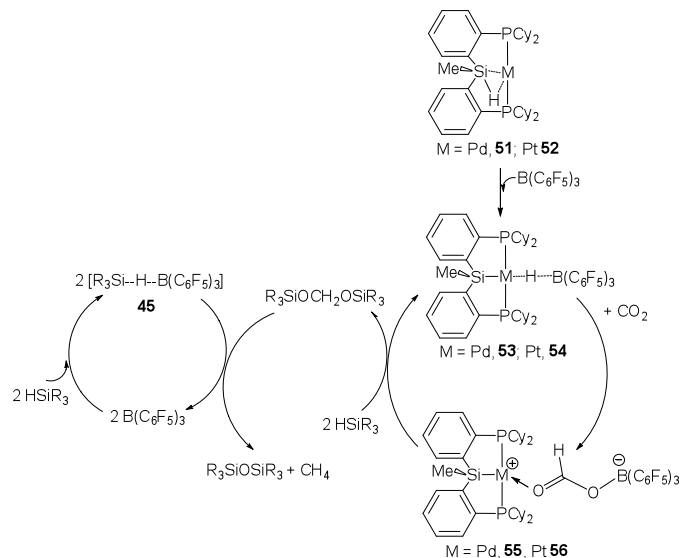


Scheme 20. Evolution of the ion-pair **49** in the presence of $HSiEt_3$.

It seems interesting to compare the activity of the ion-pair **48** with the metal-free ion-pair $[TMPh][HB(C_6F_5)_3]$ **43**, also reported by Piers's group. The metal containing ion-pair is more active because the carbon atom of carbon dioxide becomes highly electrophilic due to its interaction with the cationic scandium center.

2.4. Platinum and palladium/ $B(C_6F_5)_3$ catalytic systems.

Mitton and Turculet have recently demonstrated that group 10 (Pd, Pt) silyl pincer compounds in combination with $B(C_6F_5)_3$ catalyzed the reduction of CO_2 to methane using hydrosilanes as reducing agents.⁶⁷ The authors reported the preparation of $[(Cy-PSiP)M]$ ($M = Pd$ **51**; Pt **52**) complexes, containing an interesting intramolecular (η^2 -Si-H) interaction, which react with $B(C_6F_5)_3$ to give the corresponding borate derivate $[(Cy-PSiP)M-H-B(C_6F_5)_3]$ ($M = Pd$ **53**; Pt **54**) (Scheme 21). The *in situ* generated **53** or **54** complexes are effective catalysts for the CO_2 reduction to methane with $HSiMe_2Ph$ being species **54** more active than **53**. The activity of these catalytic systems is comparable to that reported by Brookhart for the cationic iridium pincer complex **18**.⁴¹

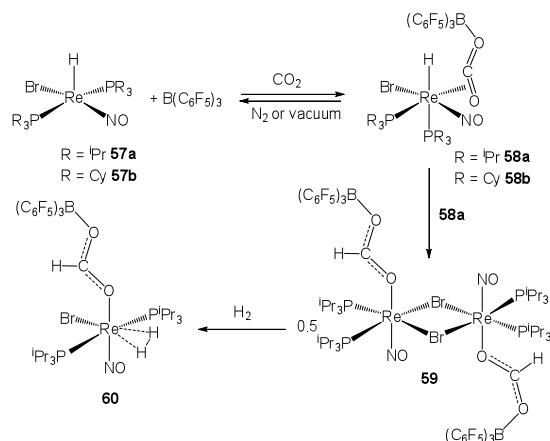


Scheme 21. Palladium and Platinum catalyzed- CO_2 reduction to methane with silanes.

The reaction of species **53** (or **54**) with CO_2 leads to the corresponding formateborate complex $[(Cy-PSiP)M-O-CHO-B(C_6F_5)_3]$ ($M = Pd$ **55**; Pt **56**) which reacts with $HSiR_3$ to yield the bis(silyl ether) $R_3SiOCH_2OSiR_3$. The authors proposed that the reaction of the bis(silyl ether) with two equivalents of **45** affords methane and the corresponding siloxane.⁶⁷

2.5. Rhenium/ $B(C_6F_5)_3$ catalytic systems.

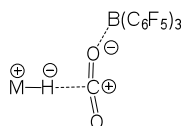
Berke's group has recently reported some examples of catalytic CO_2 activation processes assisted by a rhenium hydride complex and $B(C_6F_5)_3$.⁶⁸ Interestingly, C_6D_6 solutions of the rhenium compounds $[ReHBr(NO)(PR_3)_2]$ ($R = iPr$ **57a**, Cy **57b**) and $B(C_6F_5)_3$ react with CO_2 to produce *in situ* the corresponding species $[ReHBr(NO)(PR_3)_2(\eta^2-O=C=O-B(C_6F_5)_3)]$ ($R = iPr$ **58a**, Cy **58b**) which were characterized by means of 1H , $^{13}C\{^1H\}$, ^{31}P and ^{19}F NMR spectroscopy. Complexes **58** are not stable and gradually evolved into several species. In the case of benzene solutions of **58a**, it was possible to isolate the new dinuclear species **59** which was characterized by X-ray diffraction methods (Scheme 22).^[68]



Scheme 22. Reactivity of species **57** and $B(C_6F_5)_3$ with CO_2 .

The μ -Br bridges in **59** break in presence of H_2 (1 bar) to afford complex **60**. The systems **57a**/ $B(C_6F_5)_3$ and **57b**/ $B(C_6F_5)_3$ as well as complexes **59** and **60** were used as catalysts precursors for the catalytic hydrosilylation of CO_2 with $HSiEt_3$. The best performance was achieved with **60** and **59** which allowed the formation of $Et_3SiOCH_2OSiEt_3$ in 89 % and 87 % yield, respectively. In both cases traces of CH_3OSiEt_3 and $Et_3SiOCH_2OSiEt_3$ were observed.⁶⁸

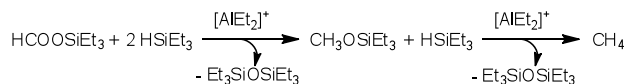
Interestingly, the authors develop the notion that metal hydrides can be considered as "isolobal" to the free electron pair of a Lewis base (Scheme 23). Indeed, their results demonstrates that the Re-H bonds can act as a Lewis base in the Re-H/ $B(C_6F_5)_3$ FLP to activate and reduce CO_2 .⁶⁸



Scheme 23. FPL-Type CO_2 activation by a M-H/ $B(C_6F_5)_3$ system were the M-H unit acts as the Lewis base.

3. $[AlEt_2]^+$ as Lewis acid catalyst for CO_2 hydrosilylation

The previous section includes examples of reactions involving the Lewis acid $B(C_6F_5)_3$ which have found application for catalytic hydrosilylation of CO_2 . In connection with this, it is remarkable that a stronger Lewis acid, such as $[Et_2Al]^+$, catalyzed the reduction of CO_2 by $HSiEt_3$ in C_6D_6 at $80^\circ C$ to afford CH_4 (70 %), $C_6D_5CH_3$ (26 %) and $(C_6D_5)_2(CH_2)$ (4 %) together with $SiEt_4$ as the major silicon containing product.⁶⁹ The authors demonstrated that the reaction of freshly prepared HCO_2SiEt_3 with 3.0 equivalents of $HSiEt_3$ (1h, $80^\circ C$) in presence of catalytic amounts of $[Et_2Al][CH_6B_{11}I_6]$ yielded CH_4 , being CH_3OSiEt_3 the only intermediate observed during the reaction (Scheme 24).



Scheme 24. Reactivity of $HCOOSiEt_3$ with $HSiEt_3$ in presence of $[AlEt_2]^+$.

The Lewis acid mediated alkylation of aromatic compounds⁷⁰ can explain the formation of $C_6D_5CH_3$ and $(C_6D_5)_2(CH_2)$. Indeed, the reaction of $PhCH_2OSiEt_3$ with C_6D_6 in presence of catalytic amounts of $[Et_2Al][CH_6B_{11}I_6]$ produced $PhCH_2C_6D_5$, $Et_3SiOSiEt_3$ and D_2O .⁶⁹ Analogously, $[AlEt_2]^+$ could catalyzed the reaction of CH_3OSiEt_3 with C_6D_6 and $C_6D_5CH_3$ to afford $C_6D_5CH_3$ and $(C_6D_5)_2(CH_2)$, respectively. Additionally, the formation of $SiEt_4$ instead of $(Et_3Si)_2O$ as silicon containing product was explained assuming a Lewis acid-catalyzed ligand exchange process. Accordingly, heating of $Et_3SiOSiEt_3$ solutions in presence of $[AlEt_2]^+$ gave a mixture of $SiEt_4$ and $1/n (Et_3SiO)_n$.⁶⁹

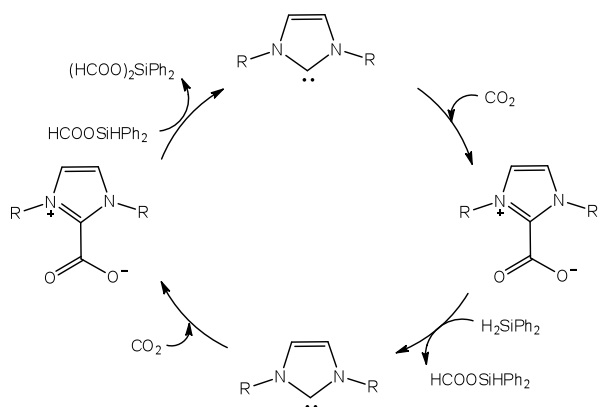
It is interesting to mention that the related $[ZnEt]^+$ Lewis acid is also active, although $[ZnEt][CHB_{11}Cl_{11}]$ is slower than $[Et_2Al][CH_6B_{11}I_6]$.⁶⁹

4. Metal free organocatalysts for CO_2 hydrosilylation

In the previous section have been described some examples in which reagents with strong electrophilic character, such as Lewis acids, catalyze the hydrosilylation of CO_2 . Contrary, this section includes examples of CO_2 hydrosilylation processes in which the role of active catalyst is played by a strong Lewis base, as for instance a carbene.

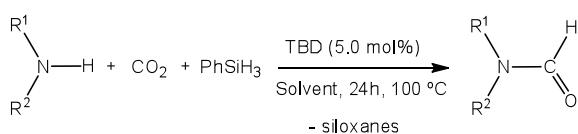
In this sense, it is remarkable that the first example of NHC-catalyzed CO_2 reduction with hydrosilanes was reported in 2009 by Riduan, Zhang and Ying.²⁴ The authors described that the treatment of a solution of 1,3-bis(2,4,6-trimethylphenyl)imidazolium carboxylate ($IMes-CO_2$) in N,N -dimethylformamide (DMF) with H_2SiPh_2 under CO_2 atmosphere (1 bar) at room temperature yields after 24 h the methoxide species $(CH_3O)_2SiPh_2$ and $[(CH_3O)SiPh_2O]_n$ as major reaction products together with traces of $Ph_2HSiOCH_2OSiHPh_2$ (Scheme 25). Hydrolysis of the CO_2 -reduction product with $NaOH$ (aq) affords methanol which was obtained over 90 % yield (based on silane).²⁴

It is worth noting that the efficiency of this type of organocatalysts is exceeded only by copper based catalytic systems, reaching a TON and TOF values of 1840 and $25.5 h^{-1}$, respectively. However, they are considerable less active than the copper phosphane-based systems which reach TON and TOF values of 8100 and $1350 h^{-1}$, respectively. Interestingly, NHC-catalyzed CO_2 hydrosilylation depends very much on the hydrosilane nature. Thus, it was observed that trisubstituted hydrosilanes such as $HSiR'_2R''$ ($R' = R'' = Ph$, Et ; $R' = Me$, $R'' = Ph$; $R' = Ph$, $R'' = Me$) reacted slowly or were not reactive.²⁵



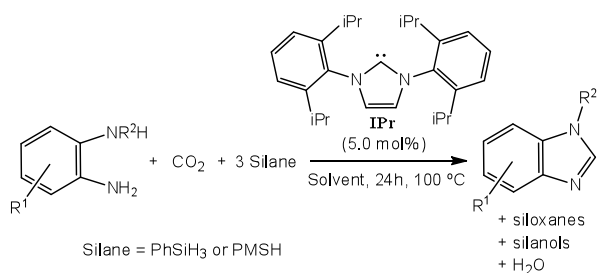
Scheme 25. NHC-catalyzed hydrosilylation with H_2SiPh_2 proposed mechanism (R = phenyl, mesityl).

Not only NHC but also other strong nucleophiles as for instance nitrogen containing bases are effective catalysts for CO_2 hydrosilylation. Cantat and collaborators have recently reported an organocatalytic system that uses nitrogen bases such as 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) as organocatalyst which catalyzes the reduction of CO_2 to formamides using a wide spectrum of amines and H_3SiPh (Scheme 26). Interestingly, these reactions proceed at low pressure (< 3 bar) and under solvent free conditions.²⁶⁻²⁸



Scheme 26. TBD-catalyzed reduction of CO_2 to formamides with PhSiH_3 .

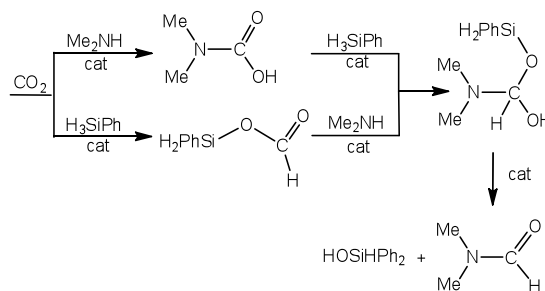
This reaction has found application for the synthesis of benzimidazole derivatives by the reductive functionalization of CO_2 in the presence of *ortho*-diamines and hydrosilanes such as H_3SiPh or poly(methylhydrosiloxane) (PMSH) replacing TBD with **IPr** as catalysts (Scheme 27).²⁶



Scheme 27. NHC-catalyzed synthesis of benzimidazole derivatives by the reductive functionalization of CO_2 .

In this regard, Cao and Wang have recently reported a detailed theoretical study about NHC-catalyzed formylation of N-H

bonds using carbon dioxide and silane.²⁹ The authors proposed two possible reaction pathways (Scheme 28), one of them through the formation of carbamic acid and the other through the formation of the corresponding silyl formate.



Scheme 28. Proposed mechanism for NHC-catalyzed formylation of N-H bonds using CO_2 and H_3SiPh .

Theoretical calculations showed that the pathway with initial formation of the silyl formate is remarkably favorable over the pathway via the intermediate carbamic acid.²⁹

5. Theoretical insights on the mechanisms of homogeneous catalytic CO_2 hydrosilylation

Carbon dioxide hydrosilylation catalyzed by late transition metals may be a concerted or stepwise process in which metal-hydride bonded ligands could play a relevant role; the nucleophilic hydride being responsible of the interaction with the electrophilic carbon atom of CO_2 . Very recently, Berke and coworkers have suggested that the classical CO_2 insertion into a transition metal-hydride bond could be viewed as a bifunctional activation or a FLP-type activation process, proposing that the metal-hydride bond can be taken as “isolobal” to the free electron pair of a Lewis base.⁶⁸

Interestingly, Oestreich and Robert have recently pointed out the parallelism between $\text{B}(\text{C}_6\text{F}_5)_3$ and the cationic iridium(III) complexes reported by Brookhart acting as catalysts in the reductive cleavage of ethers with HSiEt_3 .⁷¹ These authors propose an unified catalytic cycle based on the capability of the iridium(III) pincer complex and other Lewis acids, such as $\text{B}(\text{C}_6\text{F}_5)_3$, to activate Si-H bonds through η^1 -(Si-H) interaction. In this regards, it is remarkable that $\text{B}(\text{C}_6\text{F}_5)_3$ has found to be active catalyst for the hydrosilylation of ketones.⁷² Interestingly, tandem reactions involving $\text{B}(\text{C}_6\text{F}_5)_3$ or the strong Lewis acid $[\text{AlEt}_2]^+$ are active catalytic systems for the reduction of CO_2 with hydrosilanes. Remarkably, not only Lewis acids but also metal-free Lewis bases have found application as organocatalysts for CO_2 reduction with hydrosilanes.

However, for a better understanding of the reaction mechanisms which operate in each case theoretical studies seems to be needed. There have been reported some interesting examples of theoretical studies giving insights into mechanistic details involving homogeneous-catalyzed CO_2 hydrosilylation processes. Herein, we briefly summarize some of these studies

with emphasis on key mechanistic details and activation barriers.

5.1. Late transition metal catalyzed processes.

5.1.1. Iridium-catalyzed CO₂ hydrosilylation mechanisms.

Theoretical calculations show that the triflate ligand plays a non-innocent role in the CO₂ hydrosilylation using the Ir-NSiN complex **20** as precatalyst (Scheme 9). Hence, interaction of the triflate ligand with the Ir- η^2 -(Si-H) moiety in intermediate **21** leads to **TS-1** (Figure 1) which is 79.1 kJ mol⁻¹ less stable than **21**. The Si-H bond activation in **TS-1** gives intermediate **22**. Interaction of **22** with CO₂ through an outer sphere mechanism has been found as the most energetically favourable path. This step involves both electrophilic attack of the silyl moiety to the oxygen atom and nucleophilic attack of the hydride ligand to carbon atom of carbon dioxide. This process occurs in a concerted way through an eight member cycle **TS-2** (Figure 1).⁴³ This finding is consistent with the general observation for homogenous iridium CO₂ catalytic reactions which in most of the reported examples follow an outer-sphere mechanism.¹⁷

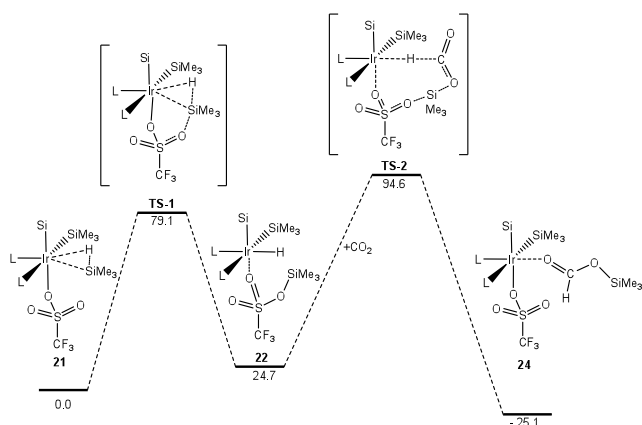


Figure 1. Representation of the energetic profile (ΔE , kJ mol⁻¹) for CO₂ hydrosilylation using complex **20** as precatalyst. The coordination sites of the tridentate NSiN ligand are represented by L and Si.

5.1.2. Ruthenium-catalyzed CO₂ hydrosilylation mechanisms.

DFT studies revealed that the first step in the catalytic hydrosilylation of CO₂ with ruthenium-nitrile complexes is the dissociation of one acetonitrile ligand to generate the catalytic active species **7** (Scheme 5).³⁵ Which interacts with HSiMe₃ through a σ -bond metathesis process to afford intermediate **61** which after dissociation of one additional acetonitrile ligand gives intermediate **62** which is 27.6 kJ mol⁻¹ more stable than **7** (Figure 2).³⁵

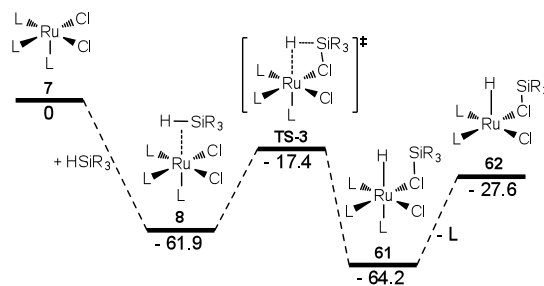


Figure 2. Representation of the energetic profile (ΔE , kJ mol⁻¹) for the Si-H bond activation stage using complex **6** as precatalyst (L = NCMe).

The authors proposed an inner-sphere mechanism for the CO₂ activation. Thus, ligand isomerization in intermediate **62** and subsequent η^2 -CO₂ coordination affords intermediate **63** (Figure 3). The silyl transfer to the CO₂ moiety in **63** to generate the ruthenium(IV) intermediate **9** via **TS-4** is the rate limiting step of the overall process. From the intermediate **9** a reductive elimination step via **TS-5** gives **10** which evolves to regenerate the active species **7** and the corresponding silyl formate (Figure 2, Scheme 5). The higher energetic barrier of the overall process corresponds to the energy difference between intermediate **61** and **TS-4** (146.5 kJ mol⁻¹).

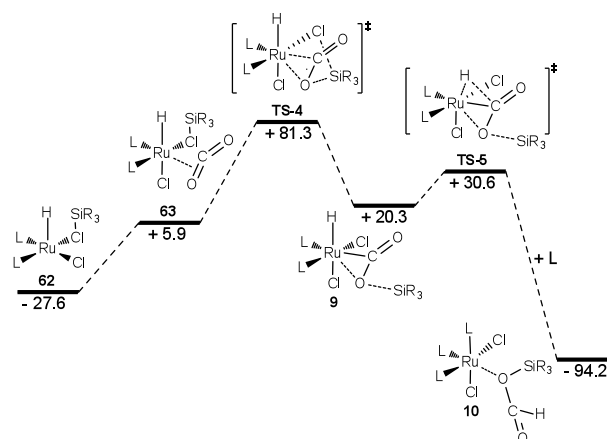


Figure 3. Representation of the energetic profile (ΔE , kJ mol⁻¹) for CO₂ fixation and activation stages using complex **6** as precatalyst (L = NCMe).

5.1.3. Copper-catalyzed CO₂ hydrosilylation mechanisms.

On the bases of the experimental studies of Tsuji and co-workers⁴⁸ Lin et al. have recently reported DFT studies on hydrocarboxylation of alkynes with CO₂ and hydrosilanes using the [CuF(NHC)] complexes **33** and **34** as catalyst precursors.⁵⁰ These studies reveal that the first step of the reaction is the generation of the active species, [CuH(NHC)], which evolves by insertion of the alkyne into the Cu-H bond to afford the corresponding copper alkenyl intermediate **64** (Figure 4). The authors have proposed an inner sphere mechanism for the CO₂

activation process (Figure 4). This process involves both nucleophilic attack of the β -hydrogen of the alkenyl ligand to carbon atom and electrophilic attack of the copper center to the oxygen atom of the $O=C=O$ to afford the copper carboxylate complex **65** (Figure 4), which reacts with the silane to yield the corresponding silyl ester.

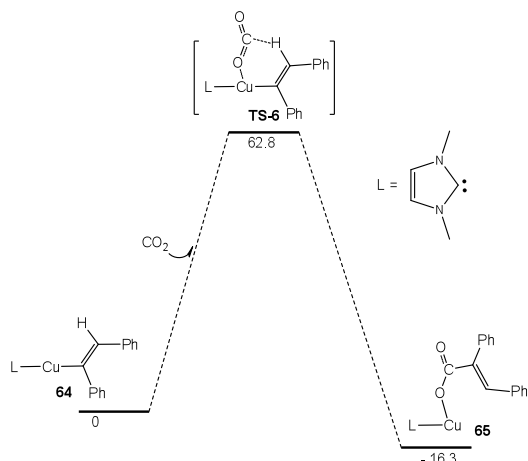


Figure 4. Representation of the energetic profile (ΔE , kJ mol^{-1}) for copper catalyzed hydrocarboxylation of alkynes with CO_2 and hydrosilanes.

Although, Hou's group reported that $[\text{CuH}(\text{NHC})]$ species are active for CO_2 hydrosilylation to silyl formates,⁴⁷ the hydrosilylation of CO_2 did not occur under the experimental conditions reported by Tsuji and co-workers and only hydrocarboxylation of alkynes was experimentally observed.^[48] In this sense, should be noted that the theoretical calculations of Lin's group show that the reaction of CO_2 with $\text{HSi}(\text{OMe})_3$ is exergonic by 29.3 kJ mol^{-1} following a pathway initiate by CO_2 insertion into the Cu-H bond to form a copper carboxylate intermediate that undergoes σ -bond metathesis with hydrosilane.⁵⁰ Nonetheless, the insertion of the alkyne into the Cu-H bond to give the copper-alkene species **64** is preferred to the CO_2 insertion, initial step for CO_2 hydrosilylation, due to entropic reasons.

5.2. NHC-catalyzed CO_2 hydrosilylation mechanisms.

Zhang and co-workers have reported the **IMes**-catalyzed CO_2 hydrosilylation with H_2SiPh_2 .²⁴ DFT calculations and experimental studies allowed elucidation of the reaction mechanism. The authors proposed for this reaction a three-step cascade process, with the energy level of each intermediate step lower than the previous one (Figure 5).²⁵

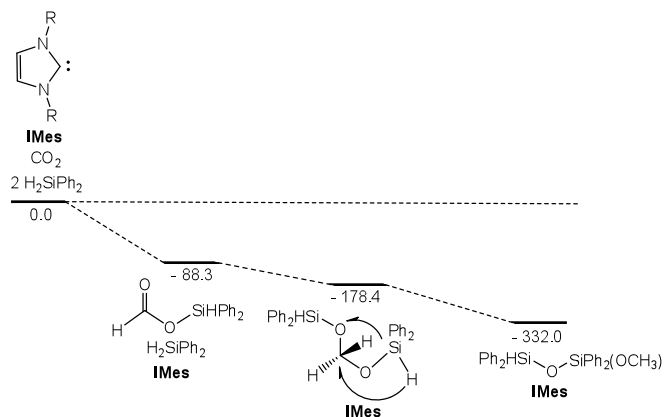


Figure 5. Representation of the energetic profile (ΔE , kJ mol^{-1}) for the **IMes**-catalyzed CO_2 hydrosilylation with H_2SiPh_2 .

The results of this study, in agreement with the experimental observations, show the first hydrosilylation step as the rate-limiting step of the overall process with an energy barrier of 82.1 kJ mol^{-1} corresponding to the energy difference between the **IMes**- $\text{CO}_2 + \text{H}_2\text{SiPh}_2$ and **TS-7** (Figure 6).²⁵ It is worth mentioning that a detailed computational mechanism study of this reaction was reported in 2010 by Wang and co-workers which proposed the second step of the process (Figure 5) as the rate limiting step.⁷³

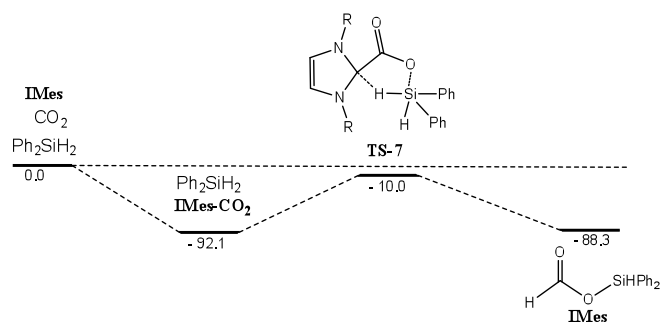


Figure 6. Representation of the energetic profile (ΔE , kJ mol^{-1}) for the first step of the **IMes**-catalyzed CO_2 hydrosilylation with H_2SiPh_2 .

NHC's also catalyze the formylation of N-H bonds using carbon dioxide and silane.²⁹ The overall reaction mechanism can be divided in four steps, including silane activation through covalent interaction with the NHC (**TS-8** in Figure 7) followed by CO_2 insertion into the activated Si-H bond via **TS-9** (Figure 7) to afford the corresponding silyl formate. In a last step, **IMes** catalyzed the coupling between the Me_2NH and the silyl formate (**TS-10**) and subsequent C-O bond breaking to afford the final reaction products (Figure 7).

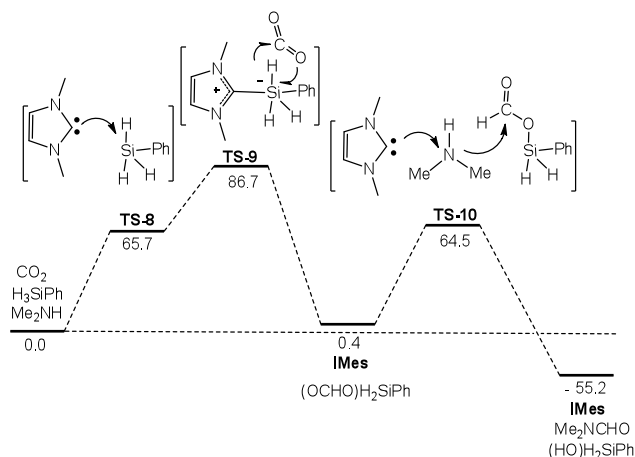


Figure 7. Representation of the energetic profile (ΔE , kJ mol^{-1}) for the IMes-catalyzed formylation of amines with CO_2 and silane.

Conclusions

Catalytic CO_2 hydrosilylation is a thermodynamically favored chemical process that could be potentially applied to large-scale transformations of this greenhouse gas. In spite of the limited data available, it could be possible to make a general classification of the reviewed studies in three general categories i) late transition metal-catalyzed processes, ii) processes involving Lewis acids, commonly $\text{B}(\text{C}_6\text{F}_5)_3$ and iii) metal free Lewis bases organocatalysts. Looking at the bibliographic reports it could be concluded that the first category is the most studied and that catalysts based on copper-phosphane complexes are the most active, so far. Recent observations suggest that transition metal-based catalysts could be designed following activation strategies analogous to FLPs. In any case the recent discovery of active metal free carbene catalysts seems to be rather promising offering the possibility of operating under mild conditions.

The catalytic systems included in the first category are based on late transition metal complexes with phosphane, *N*-donor or NHC ligands. In this group of catalysts it could be mentioned that as a general rule the active species contains a metal-hydride, which activates the incoming CO_2 molecule via either inner- or outer-sphere mechanisms, although the later seems to be dominant. For instance, in the case of iridium complexes it has been established that the outer-sphere mechanisms are preferred meanwhile NMR and theoretical studies suggest that the highly active copper based catalysts prefer inner-sphere mechanisms. It is worth noting that the use of strong donor ligands, which enhance the nucleophilic character of the hydride ligand, facilitate the CO_2 activation process.

The second category includes examples of reactions promoted by metal-free FLP, as well as Zr, Sc, Pd, Pt or Re species acting together with a Lewis acid such as $\text{B}(\text{C}_6\text{F}_5)_3$ which are effective catalysts for CO_2 hydrosilylation. Remarkably, the related strong Lewis acid $[\text{AlEt}_2]^+$ catalyzes the hydrosilylation of CO_2 with HSiEt_3 .

Interestingly, not only Lewis acids but also metal free strong Lewis bases such as carbenes has a great potential as organocatalysts for the catalytic reduction of CO_2 with hydrosilanes, due to the relatively mild and flexible reaction conditions required.

In summary, CO_2 hydrosilylation is an important and feasible challenge for CO_2 reduction. In any case the initial reaction product, silyl formate, is interesting in its own or as intermediate towards others interesting compounds including formic acid, CH_4 , CH_3OH and formamides. The results summarized here are encouraging and show that these catalytic reactions have great potential. Future advances on this research field include a better understanding of CO_2 hydrosilylation mechanisms which would allow for the development of more efficient catalysts.

Acknowledgements

The authors express their appreciation to the support from the Ministry of Higher Education, Saudi Arabia, in establishment of the Center of Research Excellence in Petroleum Refining & Petrochemicals at King Fahd University of Petroleum & Minerals (KFUPM) and the support from KFUPM-University of Zaragoza research agreement. Financial support from MINECO/FEDER projects CONSOLIDER INGENIO-2010 MULTICAT CSD2009-00050 and CTQ2011-27593 and DGA/FSE (group E07) is also acknowledged.

Notes and references

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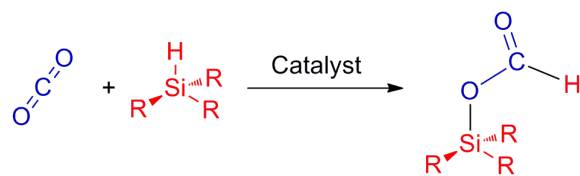
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DOI: 10.1039/b000000x/

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Picture for Table of Contents**Abstract for Table of Contents**

Catalytic CO₂ hydroxylation is a chemical process that could be potentially applied to large-scale transformations.