

# Iridium-Catalyzed Homogeneous Hydrogenation and Hydrosilylation of Carbon Dioxide



Francisco J. Fernández-Alvarez and Luis A. Oro

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**Abstract** The knowledge of the potential of transition metal-based complexes as catalysts for the reduction of CO<sub>2</sub> has grown significantly over the last few decades. This chapter focuses on the progress made during recent years in the field of homogeneous iridium-catalyzed reduction of CO<sub>2</sub> by using hydrogen and/or silicon hydrides as reducing agents, comparing them with homogeneous catalysts based on other transition metals.

The reported studies on iridium-catalyzed CO<sub>2</sub> reduction processes show that an important point to keep in mind when designing a catalyst is the nature of the reducing agent (hydrogen, hydrosilanes, and/or hydrosiloxanes). Thus, iridium(III)

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The original version of this chapter was revised. A correction to this chapter can be found at [https://doi.org/10.1007/978-3-030-69083-0\\_74](https://doi.org/10.1007/978-3-030-69083-0_74)

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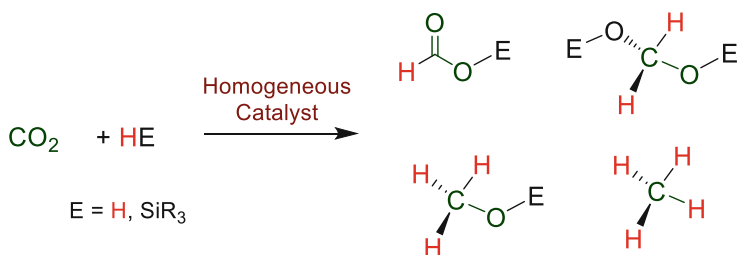
half-sandwich complexes with 4,4'-dihydroxy-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) ligands, and iridium(III)-PNP pincer complexes have proven to be excellent catalysts for the hydrogenation of CO<sub>2</sub> to formic acid. However, Ir(III)-NSiN<sup>Me</sup> (NSiN = *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl) and Ir(III)-NSi<sup>Me</sup> (NSi<sup>Me</sup> = 4-methylpyridine-2-yloxydimethylsilyl) species are not stable under hydrogen atmosphere but are effective catalysts for the reduction of CO<sub>2</sub> with hydrosiloxanes to silylformate under solvent-free conditions and moderate CO<sub>2</sub> pressures and temperatures. Moreover, while using iridium(III)-DHBP half-sandwich complexes, high CO<sub>2</sub> and H<sub>2</sub> pressures are required to achieve the catalytic CO<sub>2</sub> hydrogenation to methanol; Ir-NSi<sup>Me</sup> species catalyze the reduction of CO<sub>2</sub> to methoxysilane with hydrosiloxanes under low CO<sub>2</sub> pressure.

**Keywords** CO<sub>2</sub> hydrogenation · CO<sub>2</sub> hydrosilylation · CO<sub>2</sub> reduction · Homogenous catalysis · Iridium

## 1 Introduction

Carbon dioxide is an abundant, easily available, cheap, and low toxic chemical. On the other hand, during the last decades, the concentration of CO<sub>2</sub> in the earth's atmosphere has reached historical values, which is generally considered one of the main reasons for the global warming. Therefore, both for economic and environmental reasons the development of sustainable processes that allow the transformation of CO<sub>2</sub> on an industrial scale into valuable chemicals could be considered one of the most important tasks for the sustainability of the modern chemical industry [1–5]. In this context, to achieve the goal of using CO<sub>2</sub> as raw material of the chemical industry there are several difficulties to face, among which its great thermodynamic stability stands out.

Catalysis has proven to be essential to overcome the challenge of CO<sub>2</sub> stability. Thus, in recent decades, great advances have been made in the field of catalytic CO<sub>2</sub> transformation into value added chemicals [6–16]. Particularly, catalytic hydrogenation [6, 9, 10, 17–21] and/or hydrosilylation [22–25] of CO<sub>2</sub> have proven to be efficient methodologies for its reduction to formate, formaldehyde, methanol, or methane level (Scheme 1). In this regard, it is remarkable that several homogeneous



**Scheme 1** Possible products from the catalytic reduction of CO<sub>2</sub> with hydrogen and/or silicon hydrides

catalytic systems based on iridium complexes have shown high catalytic performance as CO<sub>2</sub> reduction catalysts [18, 26–28]. This chapter will focus on the progress made during recent years in the field of iridium-catalyzed reduction of CO<sub>2</sub> by using hydrogen and/or hydrosilanes as reducing agents.

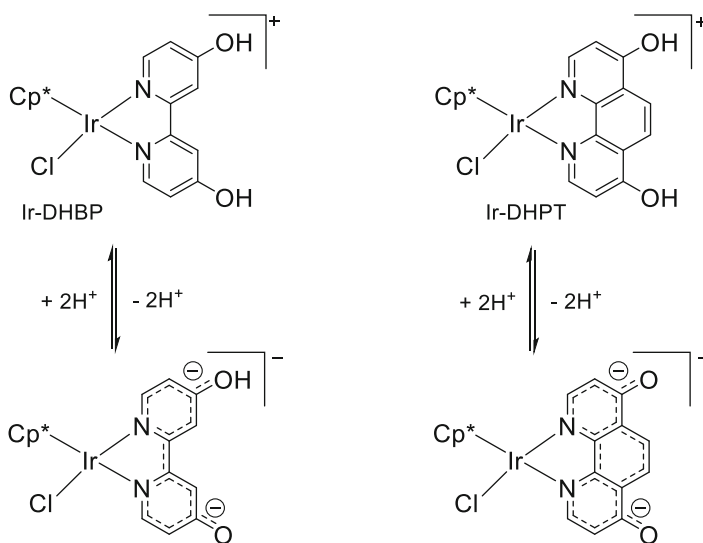
## 2 Recent Advances on Iridium-Catalyzed CO<sub>2</sub> Hydrogenation

During last decades, several examples of homogeneous catalysts effective for the hydrogenation of CO<sub>2</sub> have been reported, most of them are based on ruthenium (II) complexes but some examples of highly active iridium(III) catalysts have also been described. Among them are iridium(III) half-sandwich complexes with 4,4'-dihydroxy-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) ligands, which are excellent catalysts for the hydrogenation of CO<sub>2</sub> to formic acid and also have been used as catalysts for the direct hydrogenation of CO<sub>2</sub> to methanol. Moreover, iridium(III)-PNP pincer complexes have also been used as effective catalysts for the hydrogenation of CO<sub>2</sub> to formic acid. Conversely, the potential of iridium complexes as catalysts for the hydrogenation of CO<sub>2</sub> to formaldehyde, methyl carbonate, and/or methyl formate remains a challenge.

### 2.1 Iridium-Catalyzed Formic Acid or Formate Preparation from CO<sub>2</sub> and H<sub>2</sub>

Catalytic hydrogenation of CO<sub>2</sub> to formic acid (FA) has been a research subject of great interest over the last decades [6, 9, 10, 18, 20, 21, 28]. The hydrogenation of CO<sub>2</sub> is endergonic in the gas phase ( $\Delta G^\circ_{298} = 32.9 \text{ kJ mol}^{-1}$ ), however, in water solution and in presence of a base (NH<sub>3</sub>), this reaction becomes thermodynamically favored ( $\Delta G^\circ_{298} = -35.4 \text{ kJ mol}^{-1}$ ) [29].

The first studies of the potential of transition metal complexes as homogenous catalysts for the hydrogenation of CO<sub>2</sub> to FA were reported by Inoue et al. in 1976 [30]. These studies revealed that using NEt<sub>3</sub> water solutions under 50 atm of mixtures of CO<sub>2</sub> and H<sub>2</sub> (1:1) at r.t. the complex [IrH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] catalyzes this transformation, however, its catalytic activity is low. Under the same conditions species [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] was found to be the most active of the studied catalyst precursors [30]. Some years later, Leitner et al. reported very efficient rhodium phosphane water soluble catalysts, which were able to promote the formation of FA in relatively high yields [31, 32]. After that, Noyori et al. described that the effectivity of ruthenium phosphane complexes as CO<sub>2</sub> hydrogenation catalysts improves when using supercritical carbon dioxide [33, 34]. Few years after that, Joó, Laurency et al. reported that the performance of catalytic systems based on



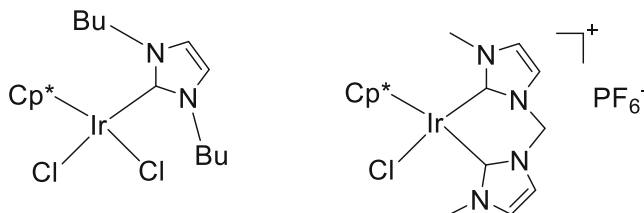
**Scheme 2** Examples of Ir-DHBP and Ir-DHPT CO<sub>2</sub> hydrogenation catalyst precursors

water soluble Ir, Rh, Ru, and Pd phosphane complexes as CO<sub>2</sub> hydrogenation catalyst is strongly pH dependent [35]. In this regard, Jessop et al. found that using the complex [RuCl(O<sub>2</sub>CMe)(PMe<sub>3</sub>)<sub>4</sub>], which is soluble in supercritical CO<sub>2</sub>, as catalysts for the hydrogenation of CO<sub>2</sub> to FA in presence of the appropriate amine and one alcohol that has an aqueous scale p*K*<sub>a</sub> below that of the protonated amine, it was possible to achieve an initial turnover frequency (TOF) for FA production of 95,000 h<sup>-1</sup> [36]. Since then till the development of the highly active Himeda's catalysts [37], based on half-sandwich bipyridine iridium complexes, most of the homogeneous catalysts effective for the hydrogenation of CO<sub>2</sub> to FA were based on Ru- and Rh-phosphane complexes.

Early examples of highly active iridium CO<sub>2</sub> hydrogenation catalysts were based on iridium half-sandwich complexes with 4,4'-dihydroxy-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) ligands (Scheme 2) [38]. These catalysts are highly efficient for the hydrogenation of carbonate, in situ generated from CO<sub>2</sub> in basic KOH aqueous solutions, to formate. The oxyanions generated from the hydroxy group along the catalytic process play a key role on both the catalytic activity and water solubility of these catalysts (Scheme 2).

Initial turnover frequencies (TOF) of 42,000 and 35,000 h<sup>-1</sup> were obtained for the Ir-DHBP and Ir-DHPT (Scheme 2) catalyzed reactions, respectively. The best performance was achieved heating at 120°C aqueous KOH (1.0 M) solutions of the corresponding iridium catalysts under 6 MPa of CO<sub>2</sub>/H<sub>2</sub> (1:1). Moreover, these iridium catalysts could be reused for four cycles maintaining high catalytic performance [38].

Himeda et al. have extended their studies to iridium half-sandwich complexes with *N,N*-bidentate ligands different from bipyridine such as picolinamide- [39, 40],



**Fig. 1** CO<sub>2</sub> hydrogenation catalysts based on half-sandwich iridium(III) complexes with NHC ligands

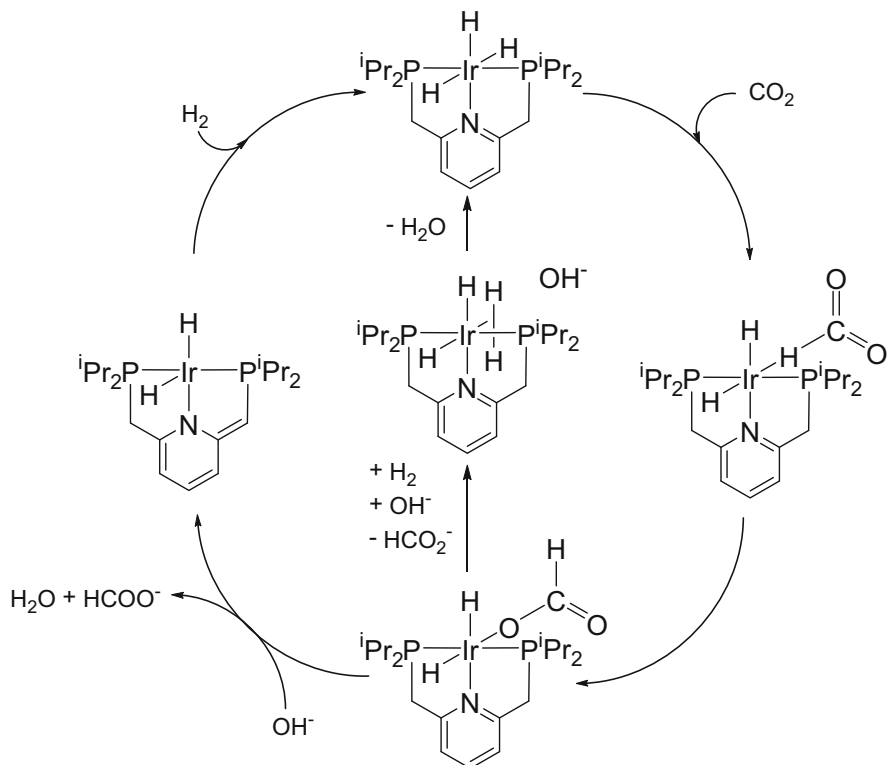
azole- [41] and pyridyl-pyrazole derivatives [42]. Mechanistic studies have found that these catalysts promote the activation of CO<sub>2</sub> via an outer-sphere mechanism [41]. Interestingly, it has been found that using this type of iridium catalysts it is possible to achieve the pH-controlled reversible hydrogen storage [40, 42, 43].

Further support to the relevant role of oxyanions in these type of catalysts comes from the studies reported from Peris et al. [44], which showed that using half-sandwich iridium(III) complexes with strong donor NHC ligands (Fig. 1) or bipyridine derivatives without hydroxy substituents, as catalyst precursors for the hydrogenation of CO<sub>2</sub> lower activities (TOF = 1,600 h<sup>-1</sup>) were observed.

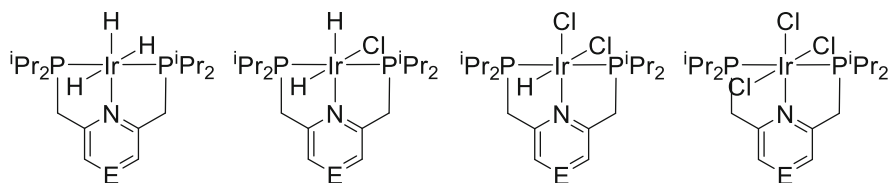
Iridium-pincer complexes have also found to be active catalysts for the homogeneous hydrogenation of CO<sub>2</sub> to FA. The iridium(III)trihydride-PNP complex shown in Scheme 3 reached a TOF of 150,000 h<sup>-1</sup> for the hydrogenation of CO<sub>2</sub> to FA in basic medium. The performance of this catalytic system is strongly influenced by the nature of the base, the temperature and the presence of THF in the reaction medium. Thus, the best results were obtained at 200°C, using 1.0 M KOH aqueous solution and adding 0.1 mL of THF [45]. Mechanistic studies showed that two reactions pathways are possible, one of them involving a deprotonative dearomatization of the pyridinic ring and other a hydroxy-assisted hydrogenolysis as the rate determining step, respectively. Moreover, an outer-sphere mechanism has been found for the CO<sub>2</sub> activation step (Scheme 3) [46].

Iridium-PNP catalysts showed the best performance in KOH aqueous solutions, however, under these conditions, the corresponding formate salt, not FA, is obtained as reaction product. Therefore, a neutralization step of the formate with a strong acid is required to obtain FA. Interestingly, when using amine derivatives as bases a simple distillation of the resulting ammonium formate allows separation of pure FA from the starting base. In this regard, Nozaki's group has studied the effect of both using triethanolamine aqueous solution as base and having different substituents at the pyridinic ring on the activity of Ir-PNP catalysts (Fig. 2). They have found that under these conditions the dichlorohydride derivative with a *p*-MeO substituent is the most active catalyst, indeed, using this species as catalyst precursor in a 1.0 M triethanolamine aqueous solution, in presence of THF and heating at 150°C, a TON for the conversion of CO<sub>2</sub> to FA of 160,000 (TOF = 12,000 h<sup>-1</sup>) was obtained [47].

On the other hand, Hazari and coworkers have studied the activity of Ir-PN<sup>H</sup>P (PN<sup>H</sup>P = bis{(2-diisopropylphosphanyl)ethyl}amine) pincer species as CO<sub>2</sub>



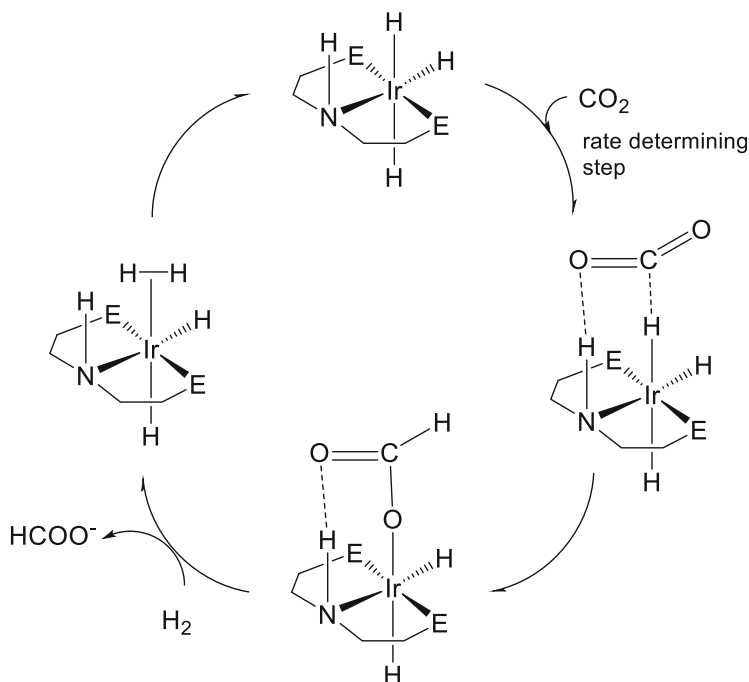
**Scheme 3** Mechanism proposed for Ir(III)-PNP catalyzed CO<sub>2</sub> hydrogenation



E = CH; COMe; N

**Fig. 2** Examples of Ir-PNP CO<sub>2</sub> hydrogenation catalysts. The species with E = COMe was found to be the most active catalyst

hydrogenation catalysts. They have shown that the insertion of CO<sub>2</sub> into one of the Ir-H bonds of the trihydride derivative [Ir(PN<sup>H</sup>P)H<sub>3</sub>] gives the corresponding [Ir(PN<sup>H</sup>P)(HCO<sub>2</sub>)H<sub>2</sub>] species, which is stabilized by an intramolecular NH-OCO hydrogen bond (Scheme 4) [48]. This iridium-formate derivative catalyzes the hydrogenation of CO<sub>2</sub>, in 1 M aqueous KOH solution at 185°C, with a TON and TOF values of 348,000 and 18,780 h<sup>-1</sup>, respectively. DFT calculations show that the Ir-PN<sup>H</sup>P-catalyzed CO<sub>2</sub> hydrogenation takes place through an outer-sphere



**Scheme 4** Mechanism proposal for Ir-PN<sup>H</sup>P catalyzed CO<sub>2</sub> hydrogenation

mechanism (Scheme 4). The rate determining step of the overall catalytic process corresponds to the NH-assisted CO<sub>2</sub> activation step [48].

## 2.2 Iridium-Catalyzed Methanol Preparation from Direct Hydrogenation of CO<sub>2</sub>

Methanol is commonly produced on an industrial scale using fossil fuel-based syngas as the principal feedstock. The annual demand for methanol has grown steadily over the last decade, consequently the CO<sub>2</sub> emissions related to the industrial production of methanol have also grown [49, 50]. Therefore, the development of catalysts effective for the synthesis of methanol from renewable sources is attracting the interest of several research groups [50, 51]. In this regard, the production of methanol through carbon dioxide capture and recycling is one of the keys of the "Methanol Economy" concept [52]. The early example of a homogeneous catalyst effective for the direct hydrogenation of CO<sub>2</sub> to methanol was reported by Tominaga et al. in 1993 [53, 54]. They used [Ru<sub>3</sub>(CO)<sub>12</sub>] as catalyst precursor, KI as additive to prevent the formation of metallic nanoparticles, and *N*-methylpyrrolidone as solvent at 240°C under 80 bar of a 1:3 mixture of CO<sub>2</sub> and H<sub>2</sub>. In this regard, it

should be mentioned that it is of great importance to avoid the decomposition of the homogeneous catalysts to colloidal or nanosized metallic particles, which may have different catalytic behavior than the parent homogeneous catalysts. Since then only few examples of catalytic systems effective for the direct hydrogenation of CO<sub>2</sub> to methanol have been reported. The reason is that the direct conversion of CO<sub>2</sub> to methanol is thermodynamically hampered at high temperatures due to the negative  $\Delta H$  and  $\Delta S$  values of this process.

The first examples of iridium homogeneous catalysts effective for the direct hydrogenation of CO<sub>2</sub> to methanol were reported by Himeda, Laurency et al. in 2016. They found that the sulfate salt of the iridium half-sandwich cationic complex [IrCp<sup>\*</sup>(DHBP)(OH<sub>2</sub>)](SO<sub>4</sub>) (DHBP = 4,4'-dihydroxy-2,2'-bipyridine) catalyzes the one pot hydrogenation of CO<sub>2</sub> to methanol. This Ir-DHBP species catalyzes the quantitative hydrogenation of CO<sub>2</sub> to formic acid in acidic media without any additives, and the subsequent disproportionation of the in situ generated formic acid to give methanol (96% selectivity; 47% yield; TON = 1,314), CO<sub>2</sub> and H<sub>2</sub>O [55]. In this regard, it is important to be aware that whenever the hydrogenation of CO<sub>2</sub> takes place in basic solution, the question arises whether the actual reactive partner of the catalysts is carbonate, bicarbonate, or (hydrated) CO<sub>2</sub>.

The activity of this iridium catalyst is higher than that reported for the Ru-(Triphos) (Triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) species (TON = 221) [56, 57], the ruthenium(II) species [Ru(PNP)(H)(H-BH<sub>3</sub>)(CO)] (PNP = {Bis [2-(diphenylphosphino)ethyl]amine}) [58, 59], Co-(Triphos) (TON = 50) [60] and Mn-(PNP) (TON = 36) [61]. Being surpassed by that of the complex Fe-(κ<sup>3</sup>-<sup>H</sup>T<sub>pm</sub>) (<sup>H</sup>T<sub>pm</sub> = tris(pyrazolyl)methane; 44% yield; TON = 2,283) [62].

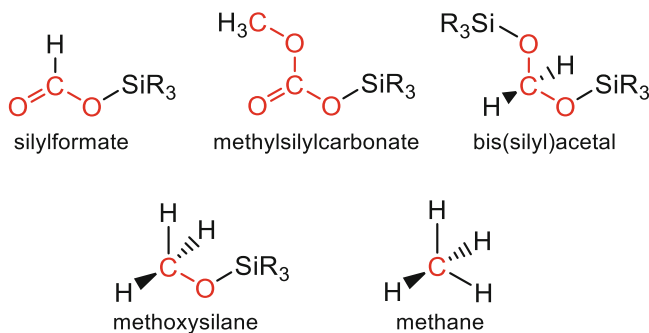
### 2.3 *Miscellaneous*

Examples of homogenous catalysts effective for the hydrogenation of CO<sub>2</sub> to other products, different of formic acid and/or methanol, are scarce. Indeed, to the best of our knowledge only few examples of ruthenium catalysts effective for the hydrogenation of CO<sub>2</sub> to dimethyl ether [63], formaldehyde [64, 65], or methyl formate [66] have been reported. Therefore, the potential of iridium complexes as catalysts for these types of processes remains unexplored.

## 3 Recent Advances on Iridium-Catalyzed CO<sub>2</sub> Hydrosilylation

The catalytic hydrogenation of CO<sub>2</sub> with H<sub>2</sub> requires high H<sub>2</sub> and CO<sub>2</sub> pressures and temperatures, as well as the addition of bases or other additives. Contrariwise, the catalytic reduction of CO<sub>2</sub> with hydrosilanes features several advantages such as





**Scheme 5** Reported products from the catalytic reduction of CO<sub>2</sub> with silicon hydrides

being a thermodynamically favored process and the fact that silanes are easier and safer to handle and to store than molecular hydrogen [22, 23, 25, 26, 67]. However, the utilization of silicon hydrides as reductants for large-scale reduction of CO<sub>2</sub> faces some difficulties. One of them is the high price of hydrosilanes, which could be solved by using cheap hydrosiloxanes instead of hydrosilanes, another is the stoichiometric generation of siloxanes, which is unsustainable due to the challenge of Si-H regeneration from Si-O-Si bonds [24, 68]. Furthermore, differently to hydrogenation processes, the catalytic hydrosilylation cannot be performed in aqueous or alcoholic solutions since homogeneous hydrosilylation catalysts usually catalyzed the dehydrogenative hydrolysis and/or alcoholysis of silicon hydrides [69, 70].

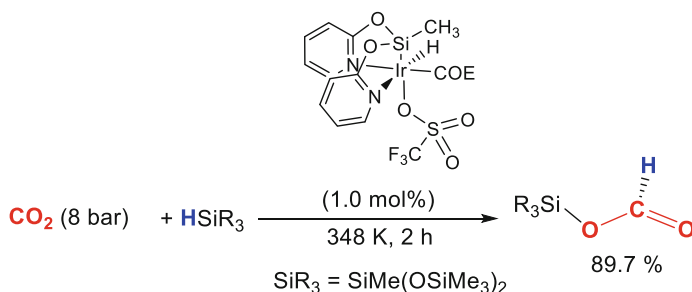
The catalytic reaction of CO<sub>2</sub> with silicon hydrides allows its selective reduction to the corresponding silylformate, bis(silyl)acetal or methoxysilane, and to methane [22, 23, 25, 26] (Scheme 5). In addition, the formation of methyl carbonates from the iridium-catalyzed reduction of CO<sub>2</sub> with silicon hydrides has been recently reported (Scheme 5) [71].

The first examples of homogeneous catalytic reduction of CO<sub>2</sub> using hydrosilanes as reductants were reported in the 1980s [72–74]. However, it was during the year 2012 that the breakthrough of this chemistry took place. Since then until today, the number of catalytic systems effective for the reduction of CO<sub>2</sub> with hydrosilanes based on transition metal complexes as well as on metal-free catalysts or main elements derivatives that have proven to be effective in CO<sub>2</sub> hydrosilylation processes has considerably grow up [8, 22–25, 67, 75]. Among them, catalysts based on iridium complexes stand out not only for their activity but also for their versatility that allows selectivity control by choosing proper ligands and/or tuning the reaction conditions. Furthermore, some examples of iridium-based CO<sub>2</sub> hydrosilylation catalysts have proven to be effective under solvent-free conditions and using hydrosiloxanes as reductants.

### 3.1 Iridium-Catalyzed CO<sub>2</sub> Hydrosilylation to Silylformate

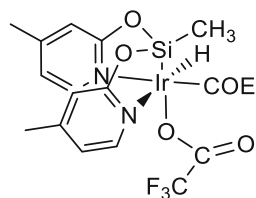
The iridium complex [Ir(CN)(CO)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane), reported in 1989 by Eisenschmid and Eisenberg, is the first example of a homogeneous iridium-based catalyst effective for the hydrosilylation of CO<sub>2</sub>. However, the catalytic activity and the selectivity of this iridium catalyst were low [74]. It was not until 2012 that an example of iridium catalyst, complex [Ir(CF<sub>3</sub>SO<sub>3</sub>)(NSiN)(SiR<sub>3</sub>)(NCMe<sub>3</sub>)] (NSiN = *fac*-bis-(pyridine-2-yloxy)methylsilyl; SiR<sub>3</sub> = SiMe(OSiMe<sub>3</sub>)<sub>2</sub>), efficient for the hydrosilylation of CO<sub>2</sub> to selectively give the corresponding silylformate was reported [76]. This catalytic system allows the solvent-free and gram-scale formation of silylformates under mild reaction conditions (3 bar, 298 K, TON = 97.5) but is slow (TON = 0.7 h<sup>-1</sup>) [76]. Interestingly, using species [Ir(CF<sub>3</sub>SO<sub>3</sub>)(NSiN)(H)(coe)] (coe = *cis*-cyclooctene, Scheme 6), which is easier to prepare than the abovementioned Ir-NSiN-acetonitrile derivative, under the same reaction conditions (3 bar, 298 K) produces an increase of the reaction rate (TOF = 1.2 h<sup>-1</sup>) [77, 78]. Further studies on the influence of reaction temperature [77] and CO<sub>2</sub> pressure [78] on the catalytic performance of this catalytic system showed that the activity is directly proportional to the temperature; however, increasing the temperature reduces the selectivity to silylformate [77]. On the other hand, it is more difficult to generalize the CO<sub>2</sub>-pressure effect on the activity of the reaction. It is remarkable, that from the point of view of selectivity the CO<sub>2</sub>-pressure has proven to be a parameter to consider. Indeed, for each temperature an enhancement of the CO<sub>2</sub>-pressure results in increased the selectivity of the process [78]. Thus, using species [Ir(CF<sub>3</sub>SO<sub>3</sub>)(NSiN)(H)(coe)] as catalyst precursor the best reaction performance was achieved at 344 K and under 8 bar of CO<sub>2</sub> (99.9% conversion, 89.7% purity (GC-MS), TOF = 138 h<sup>-1</sup>; TON = 87.5) (Scheme 6) [78].

The iridium(III) complex [Ir(H)(CF<sub>3</sub>CO<sub>2</sub>)(NSiN<sup>Me</sup>)(coe)] (NSiN<sup>Me</sup> = *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl), which contains a trifluoroacetate instead of a triflate ligand and a NSiN<sup>Me</sup> ligand with 4-methylated pyridinic rings (Fig. 3), has proven to be a highly effective CO<sub>2</sub> hydrosilylation catalyst [79]. Using this Ir-trifluoroacetate-NSiN<sup>Me</sup> species as catalyst precursor for the hydrosilylation of CO<sub>2</sub> to silylformate with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> the best results were achieved at 328 K

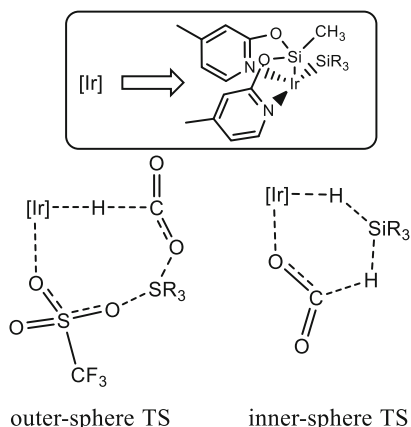


**Scheme 6** Iridium-NSiN catalyzed solvent-free CO<sub>2</sub>-hydrosilylation with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub>

**Fig. 3** Iridium(III) complex  
 $[\text{Ir}(\text{H})(\text{CF}_3\text{CO}_2)(\text{NSiN}^{\text{Me}})]$   
 (coe)



**Fig. 4** Outer- and inner-sphere transition state (TS) found for Ir-triflate- $\text{NSiN}^{\text{Me}}$  and Ir-trifluoroacetate- $\text{NSiN}^{\text{Me}}$  catalysts precursors, respectively



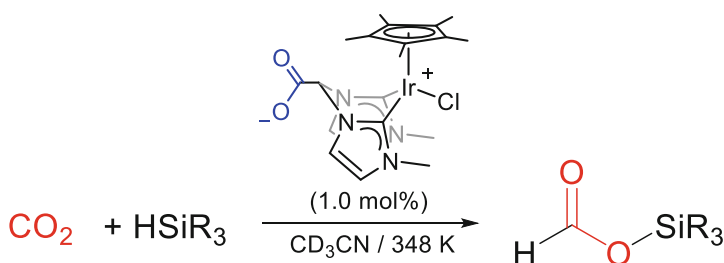
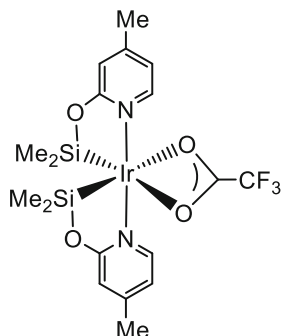
and under 8 bar of  $\text{CO}_2$  (100% conversion; 98.9% yield to SF by GC-MS;  $\text{TOF} = 99.3 \text{ h}^{-1}$ ), at temperatures above 328 K a decrease in catalytic selectivity and activity was observed [79].

Mechanistic studies based on theoretical calculations at DFT level showed that while Ir-trifluoroacetate- $\text{NSiN}^{\text{Me}}$  species catalyzes the  $\text{CO}_2$  activation via an inner-sphere mechanism, an outer-sphere mechanism is favored for Ir-triflate- $\text{NSiN}^{\text{Me}}$  derivatives (Fig. 4) [80].

The presence of the Ir-silyl group of the  $\text{NSiN}^{\text{R}}$  ( $\text{R} = \text{H}, \text{Me}$ ) ligand *trans*-located to the trifluoroacetate (or triflate) ligand plays a key role on the catalytic activity of Ir- $\text{NSiN}^{\text{R}}$  catalysts. Based on this knowledge the catalyst precursor  $[\text{Ir}(\text{CF}_3\text{CO}_2)(\kappa^2\text{-NSi}^{\text{Me}})_2]$  ( $\text{NSi}^{\text{Me}} = 4\text{-methylpyridine-2-ylmethoxydimethylsilyl}$ ), containing two Ir-Si bonds *trans*-located to the catalyst active positions was designed (Fig. 5) [81].  $^1\text{H}$  NMR studies on the activity of  $[\text{Ir}(\text{CF}_3\text{CO}_2)(\kappa^2\text{-NSi}^{\text{Me}})_2]$  as  $\text{CO}_2$  hydrosilylation catalyst using  $\text{HSiMe}(\text{OSiMe}_3)_2$  show that at 298 K under 4 bar of  $\text{CO}_2$  this catalyst is more active ( $\text{TOF} = 28.6 \text{ h}^{-1}$ ) [81] than the previously reported Ir- $\text{NSiN}$  species, which at 298 K independently of the  $\text{CO}_2$ -pressure are low active with TOF values in the range of  $1.2\text{--}1.6 \text{ h}^{-1}$  [78]. The higher activity of  $[\text{Ir}(\text{CF}_3\text{CO}_2)(\kappa^2\text{-NSi}^{\text{Me}})_2]$  allows the selective formation methoxysilane from  $\text{CO}_2$  and  $\text{HSiMe}(\text{OSiMe}_3)_2$  as it is shown below [81].

Other iridium complex which have proven to be an active catalyst for the selective hydrosilylation of  $\text{CO}_2$  (3 bar) to silylformates is the zwitterionic iridium (III) half-sandwich species  $[\text{IrClCp}^*\{(\text{MeIm})_2\text{CHCOO}\}]$  ( $(\text{MeIm}) = 3\text{-}$

**Fig. 5** Iridium(III) complex  
 $[\text{Ir}(\text{CF}_3\text{CO}_2)(\kappa^2\text{-NSi}^{\text{Me}})_2]$



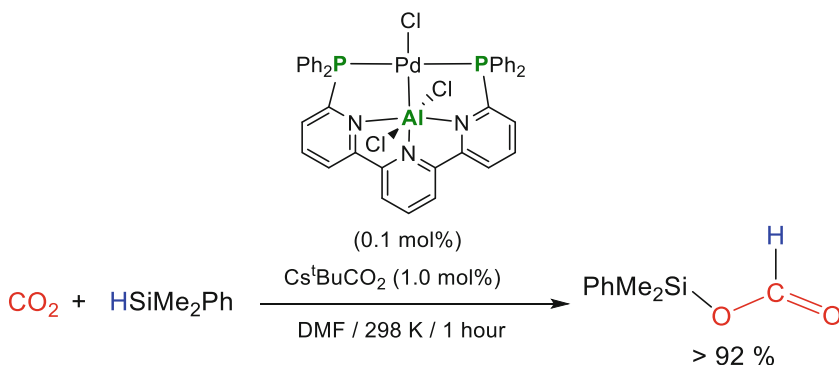
$\text{SiR}_3 = \text{SiEt}_3, \text{SiMe}_2\text{Ph}, \text{SiMePh}_2$   
 no reaction when  $\text{SiR}_3 = \text{SiMe}(\text{OSiMe}_3)_2$

**Scheme 7**  $\text{CO}_2$  hydrosilylation catalyzed by the zwitterionic iridium species  $[\text{Cp}^*\text{IrCl}\{(\text{MeIm})_2\text{CHCO}_2\}]$

methylimidazol-2-yliden-1-yl;  $\text{Cp}^* =$  pentamethylcyclopentadienyl) (Scheme 7) [82]. However, this catalytic system requires the use of acetonitrile as reaction solvent. It is relatively high active for the hydrosilylation of  $\text{CO}_2$  with  $\text{HSiMe}_2\text{Ph}$  ( $\text{TOF} = 51 \text{ h}^{-1}$ ), but under the same reaction conditions is not active when the hydrosiloxane  $\text{HSiMe}(\text{OSiMe}_3)_2$  is used as reductant instead of  $\text{HSiMe}_2\text{Ph}$  [82].

Other transition metal-based catalysts including Ru [83, 84], Co [85], Rh [86], Pd [87], Pt [88], Cu [89, 90], and Zn [91, 92] complexes effective for the selective hydrosilylation of  $\text{CO}_2$  to the formate level have been reported. Among them, the catalytic system based on the Pd-PAIP complex shown in Scheme 8 has proven to be the most active catalyst for  $\text{CO}_2$ -hydrosilylation reported so far [87]. Indeed, using this Pd-PAIP catalyst in DMF as solvent in presence of  $\text{Cs}^t\text{BuCO}_2$  (1.0 mol%) at 298 K, the selective reaction of  $\text{CO}_2$  with  $\text{HSiMe}_2\text{Ph}$  to give  $\text{HCO}_2\text{SiMe}_2\text{Ph}$  (92%,  $\text{TOF} = 19,300 \text{ h}^{-1}$ ) was achieved in 1 h (Scheme 8) [87].

$\text{Ir-NSiN}$  and  $\text{Ir-NSi}^{\text{Me}}$  species are comparatively less active than some of the abovementioned catalysts; however, they have the advantage of being active under solvent-free conditions and are highly effective when using hydrosiloxanes, instead



**Scheme 8** Palladium-PAIP catalyzed CO<sub>2</sub>-hydrosilylation with HSiMe<sub>2</sub>Ph

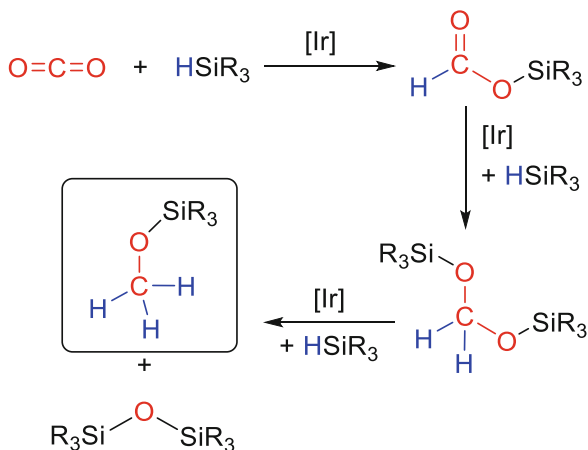
of hydroorganosilanes, as reductants. Therefore, from the point of view of sustainability iridium species based on Ir-NSi<sup>n</sup> and Ir-NSi<sup>Me</sup> species could be considered promising for future applications of the catalytic reduction of CO<sub>2</sub> with silicon hydrides.

### 3.2 Iridium-Catalyzed Reduction of CO<sub>2</sub> to Methoxysilanes with Silicon-Hydrides

Only few examples of homogeneous catalysts effective for the reduction of CO<sub>2</sub> to methanol level using silicon hydrides as reducing agents have been published to date. The first one was the abovementioned iridium complex [Ir(CN)(CO)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) [74]. This catalyst promotes the reduction of CO<sub>2</sub> with HSiMe<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> at 313 K to the corresponding methoxysilane, CH<sub>3</sub>OSiMe<sub>3</sub>. This reaction is slow, and 2 weeks are required to achieve the conversion of the starting hydrosilane into CH<sub>3</sub>OSiMe<sub>3</sub>. <sup>13</sup>C NMR studies of this process using <sup>13</sup>CO<sub>2</sub> confirm that it entails in a stepwise progression with the initial formation of the corresponding silylformate HCO<sub>2</sub>SiMe<sub>3</sub>, which is further reduce to bis (silyl)acetal CH<sub>2</sub>(OSiMe<sub>3</sub>)<sub>2</sub>, the later finally reacts with one equivalent of HSiMe<sub>3</sub> to give CH<sub>3</sub>OSiMe<sub>3</sub> and O(SiMe<sub>3</sub>)<sub>2</sub> (Scheme 9) [74].

The iridium(III) complex [Ir(CF<sub>3</sub>CO<sub>2</sub>)(κ<sup>2</sup>-NSi<sup>Me</sup>)<sub>2</sub>] (Fig. 5) has proven to be an effective catalyst for the reduction of CO<sub>2</sub> with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> to the methoxysilane CH<sub>3</sub>OSiMe(OSiMe<sub>3</sub>)<sub>2</sub> under mild reaction conditions. <sup>1</sup>H NMR studies of the reaction of CO<sub>2</sub> (1 bar) with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 298 K evidenced the selective formation of the corresponding methoxysilane after 16 h (99.0%; TON = 33.6; TOF = 2.1 h<sup>-1</sup>) [81]. Interestingly, increasing the CO<sub>2</sub> pressure to 4 bar the reaction stops in the corresponding silylformate, which under 4 bar is the major reaction product (93%; TON = 93; TOF = 2.9 h<sup>-1</sup>) together with a 7% of CH<sub>3</sub>OSiMe(OSiMe<sub>3</sub>)<sub>2</sub> after 3.5 h. <sup>1</sup>H and <sup>13</sup>C NMR studies and theoretical

**Scheme 9** Iridium-catalyzed reduction of CO<sub>2</sub> to the methoxysilane level with HSiR<sub>3</sub>

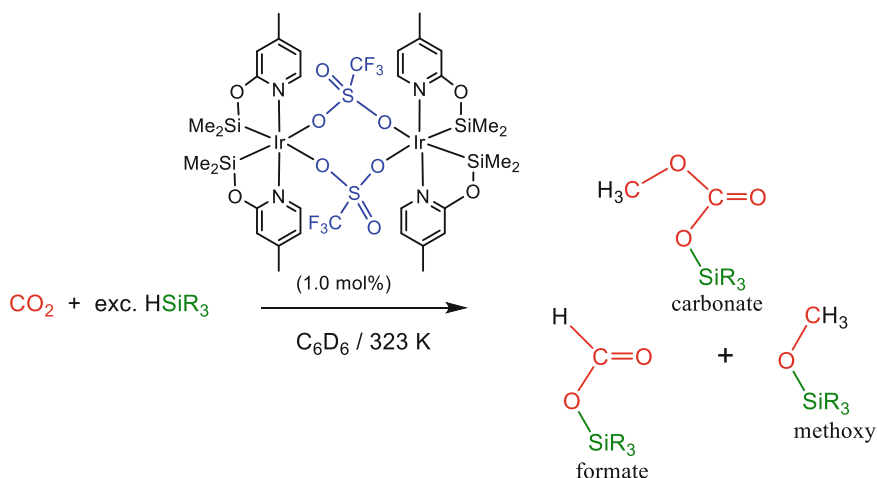


calculations at the DFT level on the Ir-NSi<sup>Me</sup> catalyzed CO<sub>2</sub> reduction to methoxysilane with silicon hydrides, agree with an stepwise mechanism similar to that shown in Scheme 9.

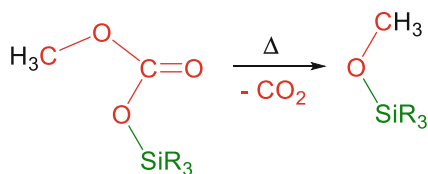
The related complex [Ir(μ-CF<sub>3</sub>SO<sub>3</sub>)(κ<sup>2</sup>-NSi<sup>Me</sup>)<sub>2</sub>]<sub>2</sub>, which is a rare example of an iridium dinuclear species with triflate groups acting as bridges, catalyzed the reaction of CO<sub>2</sub> (3 bar) with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 323 K to afford, after 3 h, a mixture of the corresponding silylformate (65.2%), methoxysilane (8.1%) and methylsilylcarbonate (26.7%) (Scheme 10) [71].

<sup>1</sup>H and <sup>13</sup>C NMR studies of the reaction shown in Scheme 10 evidenced that at 323 K, once all the starting hydrosilane is consumed; the methylsilylcarbonate is slowly transformed into the corresponding methoxysilane. These outcomes prove that the formation of methoxysilanes during the catalytic reduction of CO<sub>2</sub> with silicon hydrides, which traditionally has been explained by the stepwise process shown in Scheme 9, could also be consequence of thermal decomposition of the corresponding methylsilylcarbonate (Scheme 11) [71].

Few examples of other homogeneous catalysts effective for the reduction of CO<sub>2</sub> to methanol level using silicon hydrides as reductants have been described, which include the anionic rhenium complex [N(hexyl)<sub>4</sub>][ReO<sub>4</sub>] [93], the cationic zinc derivative [Zn(Me)(IDipp)][C<sub>6</sub>F<sub>5</sub>]<sub>3</sub> (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) [94] and metal-free NHC-catalysts [95]. In this context, it is noteworthy that the activity of the Ir-trifluoroacetate-NSi<sup>Me</sup> catalyst is similar to that reported for these Re-, Zn-, and NHC-based catalytic systems.



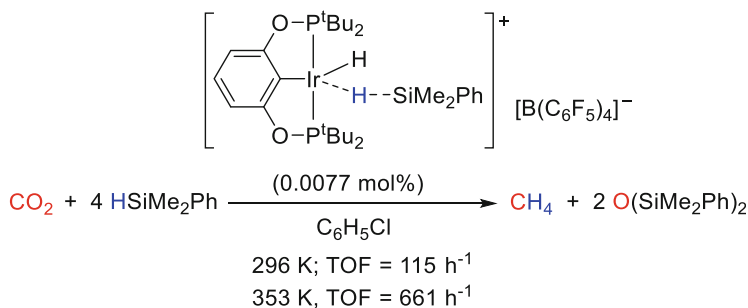
**Scheme 10** Iridium-catalyzed reduction of  $\text{CO}_2$  to the methoxysilane level with  $\text{HSiR}_3$



**Scheme 11** Thermal decomposition of methylsilylcarbonates to give methoxysilanes and  $\text{CO}_2$

### 3.3 Iridium-Catalyzed Reduction of $\text{CO}_2$ to Methane with Silicon-Hydrides

The catalytic reduction of  $\text{CO}_2$  to methane using hydrosilanes as reducing agents remains a challenge. Examples of transition metal catalysts based on Zr [96, 97], Hf [97], Ir [98], Pd [99] and Pt [99] complexes as well as transition metal-free catalysts such as the frustrated Lewis pair  $\text{B}(\text{C}_6\text{F}_5)_3/\text{TMP}$  (TMP = 2,2,6,6-tetramethylpiperidine) [100] and other Lewis acids and ionic pairs [101–104]. Among them stands out the iridium(III) cationic species  $[\text{Ir}(\text{H})(\eta^1\text{-HSiR}_3)(\text{POCOP})][\text{B}(\text{C}_6\text{F}_5)_4]$  (POCOP = 2,6-bis((di-tert-butylphosphanyl)oxy)benzen-1-yl) reported by Brookhart et al. in 2012 [98], which has proven to be effective for the reduction of  $\text{CO}_2$  (1 bar, 296 K) to methane with different hydrosilanes ( $\text{HSiEt}_3$ ,  $\text{HSiPh}_3$ ,  $\text{HSiMe}_2\text{Et}$ ,  $\text{HSiMe}_2\text{Ph}$ , and  $\text{HSiEt}_2\text{Me}$ ) using  $\text{C}_6\text{H}_5\text{Cl}$  as solvent. This catalytic system works reasonably well with  $\text{HSiMe}_2\text{Ph}$  at 296 K (TOF =  $115 \text{ h}^{-1}$ ), moreover, increasing the temperature to 333 K produces a positive effect of the catalytic activity (TOF =  $661 \text{ h}^{-1}$ ) (Scheme 12) [98].



**Scheme 12** Ir-(POCOP) catalyzed CO<sub>2</sub> reduction to methane with HSiMe<sub>2</sub>Ph

## 4 Concluding Remarks

This chapter illustrates the progress made during recent years in the field of iridium-catalyzed reduction of CO<sub>2</sub> with hydrogen and/or silicon hydrides as reductants. It is difficult to draw general conclusions since not only the characteristics of the ligands but also the nature of the reducing agent (hydrogen, hydrosilanes, and/or hydrosiloxanes) strongly influences the reaction conditions and the mechanism. It has been observed that most of the iridium CO<sub>2</sub> hydrogenation and hydrosilylation catalysts are based on Ir(III) species. The selectivity is one of the challenges of homogeneous catalytic CO<sub>2</sub> reduction with hydrogen and silicon hydrides, this is because mixtures of different reduction products are frequently obtained. In this regard, it is worth mentioning that iridium(III) half-sandwich-DHBP species and iridium(III)-PNP pincer complexes have found to be highly efficient and selective CO<sub>2</sub> hydrogenation catalysts and that Ir(III)-NSiN and Ir(III)-NSi<sup>Me</sup> species have proven to be highly selective CO<sub>2</sub> hydrosilylation catalysts. From the point of view of the mechanism, it is difficult to establish a general behavior trend. Thus, although most of the reported homogeneous Ir(III) catalysts follow an outer-sphere CO<sub>2</sub> activation mechanism, when using Ir-NSiN and Ir-NSi<sup>Me</sup> trifluoroacetate derivatives as CO<sub>2</sub> hydrosilylation catalysts, an inner-sphere CO<sub>2</sub> activation mechanism is preferred. Therefore, it could be concluded that iridium(III) complexes have great potential as homogeneous CO<sub>2</sub> reduction catalysts; however, there are still many mechanistic questions to answer and future applications to unveil.

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