Iridium-Catalyzed Homogeneous Hydrogenation and Hydrosilylation of Carbon Dioxide

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Abstract

The knowledge of the potential of transition-metal based complexes as catalysts for the reduction of CO_2 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_2 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_2 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) 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_2 to formic acid. However, Ir(III)-NSiN^{Me} (NSiN = *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl) and Ir(III)-NSi^{Me} (NSi^{Me} = 4-methylpyridine-2-yloxydimethylsilyl) species are not stable under hydrogen atmosphere, but are effective catalysts for the reduction of CO_2 with hydrosiloxanes to silylformate under solvent-free conditions and moderate CO_2 pressures and temperatures. Moreover, while using iridium(III)-DHBP half-sandwich complexes high CO_2 and H_2 pressures are required to achieve the catalytic CO_2 hydrogenation to methanol, Ir-NSi^{Me} species catalyze the reduction of CO_2 to methoxysilane with hydrosiloxanes under low CO_2 pressure.

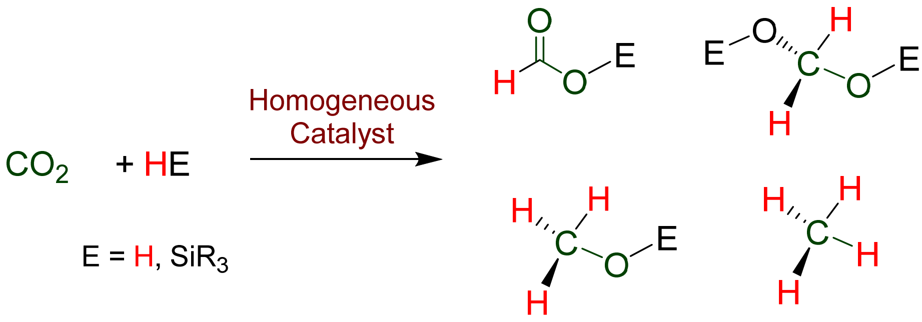
Keywords

Iridium, Homogenous Catalysis, CO_2-reduction, CO_2-hydrogenation, CO_2-hydrosilylation

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_2 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_2 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_2 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_2 stability. Thus, in recent decades, great advances have been made in the field of catalytic CO_2 transformation into value added chemicals [6 – 16]. Particularly, catalytic hydrogenation [6, 9, 10, 17 – 21] and/or hydrosilylation [22 – 25] of CO_2 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 catalytic systems based on iridium complexes have shown high catalytic performance as CO_2 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_2 by using hydrogen and/or hydrosilanes as reducing agents.



Scheme 1. Possible products from the catalytic reduction of CO_2 with hydrogen and/or silicon-hydrides.

2 Recent advances on iridium-catalyzed CO_2 hydrogenation

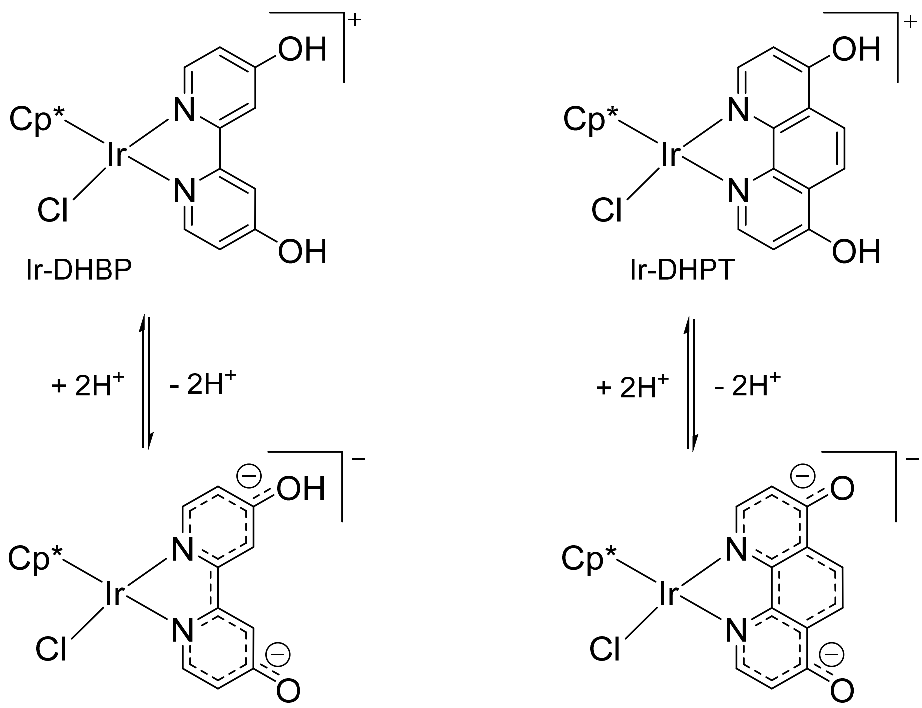
During last decades several examples of homogeneous catalysts effective for the hydrogenation of CO_2 have been reported, most of them are based on ruthenium(II) complexes but some examples of highly active iridium(III) catalysts have also been described. Among them are iridium(III) half-sandwich complexes with 4,4′-dihydroxy-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) ligands, which are excellent catalyst for the hydrogenation of CO_2 to formic acid and also have been used as catalysts for the direct hydrogenation of CO_2 to methanol. Moreover, iridium(III)-PNP pincer complexes have also been used as effective catalysts for the hydrogenation of CO_2 to formic acid. Conversely, the potential of iridium complexes as catalysts for the hydrogenation of CO_2 to formaldehyde, methylcarbonate and/or methylformate remains a challenge.

2.1 Iridium-Catalyzed Formic acid or Formate Preparation from CO_2 and H_2

Catalytic hydrogenation of CO_2 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_2 is endergonic in the gas phase ($\Delta G°_{298}$ = 32.9 kJ mol^{-1}), however, in water solution and in presence of a base (NH_3) this reaction becomes thermodynamically favoured ($\Delta G°_{298}$ = -35.4 kJ mol^{-1}) [29].

The first studies of the potential of transition-metal complexes as homogenous catalysts for the hydrogenation of CO_2 to FA were reported by Inoue et al in 1976 [30]. These studies revealed that using NEt_3 water solutions under 50 atm of mixtures of CO_2 and H_2 (1:1) at r.t. the complex $[IrH_3(PPh_3)_3]$ catalyzes this transformation, however, its catalytic activity is low. Under the same conditions species $[RuH_2(PPh_3)_4]$ 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_2 hydrogenation catalysts improves when using supercritical carbon dioxide [33, 34]. Few years after that Joó, Laurenczy et al reported that the performance of catalytic systems based on water soluble Ir, Rh, Ru and Pd phosphane complexes as CO_2 hydrogenation catalyst is strongly pH-dependent [35]. In this regard, Jessop et al found that using the complex $[RuCl(O_2CMe)(PMe_3)_4]$, which is soluble in supercritical CO_2, as catalysts for the hydrogenation of CO_2 to FA in presence of the appropriate amine and one alcohol that has an aqueous-scale pK_a below that of the protonated amine, it was possible to achieve an initial turnover frequency (TOF) for FA production of 95 000 h^{-1} [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_2 to FA were based on Ru- and Rh-phosphane complexes.

Early examples of highly active iridium CO_2 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_2 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).



Scheme 2. Examples of Ir-DHBP and Ir-DHPT CO_2 hydrogenation catalyst precursors.

Initial turnover frequencies (TOF) of 42 000 and 35 000 h^{-1} were obtained for the Ir-DHPB 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_2/H_2 (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 with *N*, *N*-bidentate ligands different from bipyridine such as picolinamide- [39, 40], azole- [41] and pyridyl-pyrazole-derivatives [42]. Mechanistic studies have found that these catalysts promote the activation of CO_2 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 (Figure 1) or bipyridine derivatives without hydroxy substituents, as catalysts precursors for the hydrogenation of CO_2 lower activities (TOF = 1600 h^{-1}) were observed.

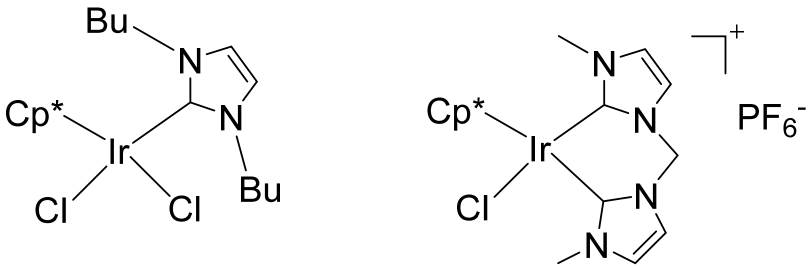
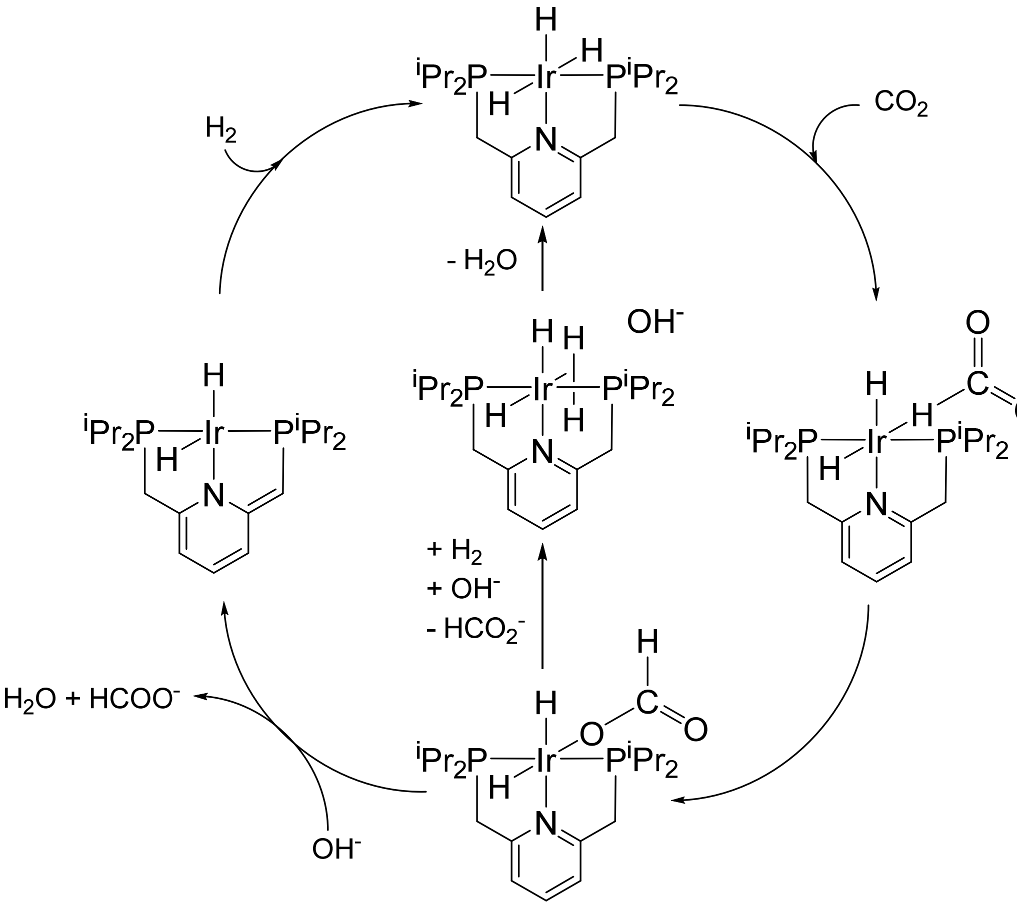


Figure 1. CO_2 hydrogenation catalysts based on half-sandwich iridium(III) complexes with NHC-ligands.

Iridium-pincer complexes have also found to be active catalysts for the homogeneous hydrogenation of CO_2 to FA. The iridium(III)trihydride-PNP complex shown in Scheme 3 reached a TOF of 150.000 h^{-1} for the hydrogenation of CO_2 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_2 activation step (Scheme 3) [46].



Scheme 3. Mechanism proposed for Ir(III)-PNP catalyzed CO_2 hydrogenation

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 (Figure 2). They have found that under these conditions the dichloro-hydride 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_2 to FA of 160.000 (TOF = 12.000 h^{-1}) was obtained [47].

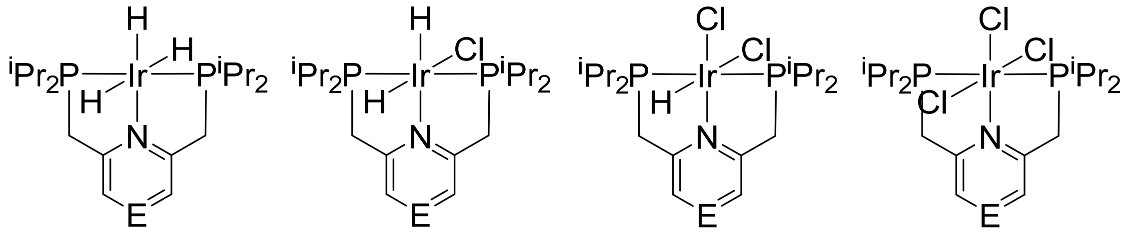
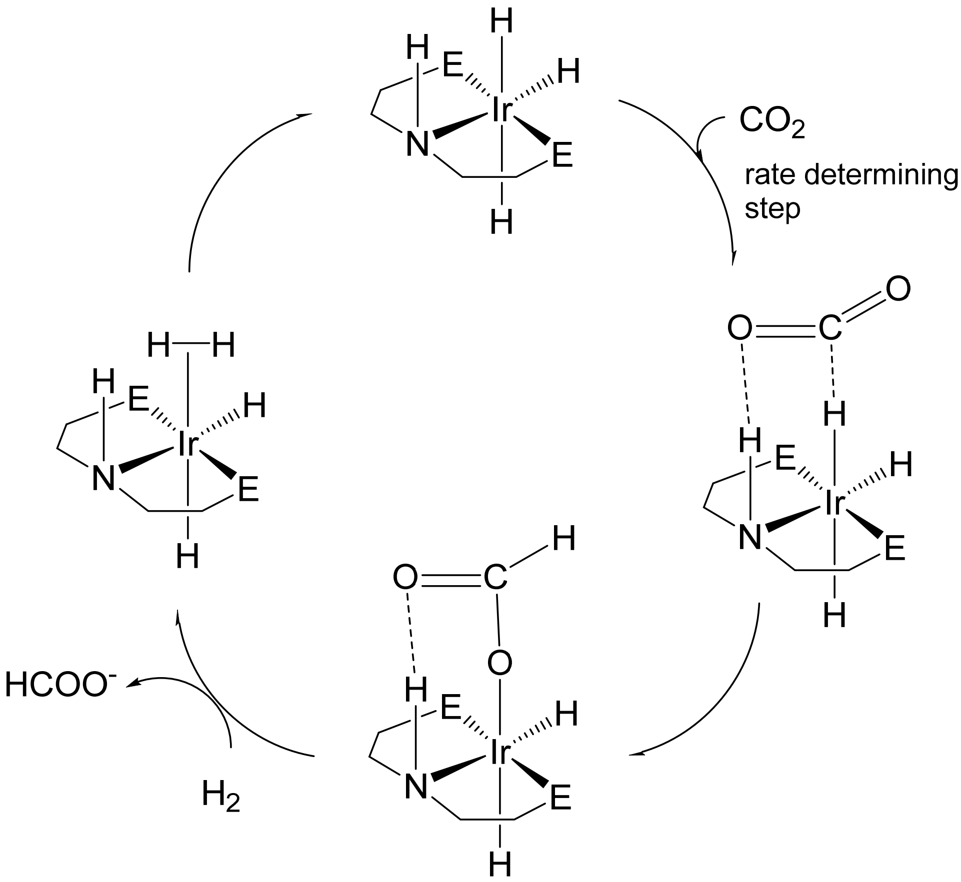


Figure 2. Examples of Ir-PNP CO_2 hydrogenation catalysts. The species with E = COMe was found to be the most active catalyst

On the other hand, Hazari and coworkers have studied the activity of Ir-PN^HP (PN^HP = bis{(2-diisopropylphosphanyl)ethyl}amine) pincer species as CO_2 hydrogenation catalysts. They have shown that the insertion of CO_2 into one of the Ir-H bonds of the trihydride derivative [Ir(PN^HP)H_3] gives the corresponding [Ir(PN^HP)(HCO_2)H_2] species, which is stabilized by an intramolecular NH—OCO hydrogen bond (Scheme 4) [48]. This iridium-formate derivative catalyzes the hydrogenation of CO_2, in 1 M aqueous KOH solution at 185 °C, with a TON and TOF values of 348.000 and 18.780 h^{-1}, respectively. DFT calculations show that the Ir-PN^HP-catalyzed CO_2 hydrogenation takes place through an outer-sphere mechanism (Scheme 4). The rate determining step of the overall catalytic process corresponds to the NH-assisted CO_2 activation step [48].



Scheme 4. Mechanism proposal for Ir-PN[H]P catalyzed CO_2 hydrogenation

2.2 Iridium-catalyzed methanol preparation from direct hydrogenation of CO_2

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_2 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_2 to methanol was reported by Tominaga et al in

1993 [53, 54]. They used [$Ru_3(CO)_{12}$] as catalyst precursor, KI as additive to prevent the formation of metallic nanoparticles, and *N*-methylpyrrolidone as solvent at 240ºC under 80 bar of a 1:3 mixture of CO_2 and H_2. 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 behaviour than the parent homogeneous catalysts. Since then only few examples of catalytic systems effective for the direct hydrogenation of CO_2 to methanol have been reported. The reason is that the direct conversion of CO_2 to methanol is thermodynamically hampered at high temperatures due to the negative ΔH and ΔS values of this process.

The first examples of iridium homogeneous catalysts effective for the direct hydrogenation of CO_2 to methanol were reported by Himeda, Laurenczy et al in 2016. They found that the sulfate salt of the iridium half-sandwich cationic complex [IrCp*(DHBP)(OH_2)][SO_4] (DHBP = 4,4´-dihydroxy-2,2´-bypyridine) catalyzes the one pot hydrogenation of CO_2 to methanol. This Ir-DHBP species catalyzes the quantitative hydrogenation of CO_2 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 = 1314), CO_2 and H_2O [55]. In this regard, it is important to be aware that whenever the hydrogenation of CO_2 takes place in basic solution, the question arises whether the actual reactive partner of the catalysts is carbonate, bicarbonate or (hydrated) CO_2.

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_3)(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 complexFe-(κ^3-$^{H}T_{pm}$) ($^{H}T_{pm}$ = tris(pyrazolyl)methane; 44 % yield; TON = 2283) [62].

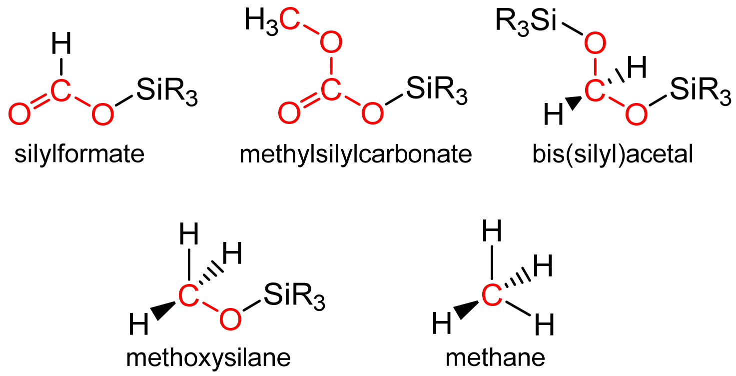
2.3 Miscellaneous

Examples of homogenous catalysts effective for the hydrogenation of CO_2 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_2 to dimethylether [63], formaldehyde [64, 65] or methylformate [66] have been reported. Therefore, the potential of iridium complexes as catalysts for these type of processes remains unexplored.

3 Recent advances on iridium-catalyzed CO_2 hydrosilylation

The catalytic hydrogenation of CO_2 with H_2 requires elevated H_2 and CO_2 pressures and temperatures, as well as the addition of bases or other additives. Contrarywise, the catalytic reduction of CO_2 with hydrosilanes features several advantages such as 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_2 face 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_2 with silicon-hydrides allows its selective reduction to the corresponding silylformate, bis(silyl)acetal or methoxysilane, and to methane [22, 23, 25, 26, 70] (Scheme 5). In addition, the formation of methylcarbonates from the iridium-catalyzed reduction of CO_2 with silicon-hydrides has been recently reported (Scheme 5) [71].

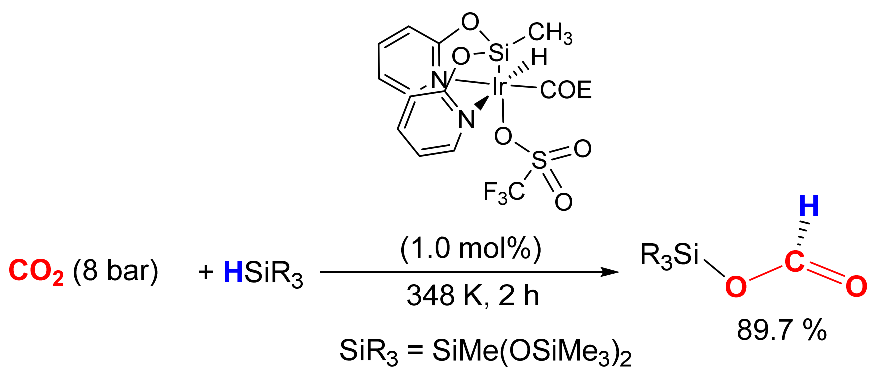


Scheme 5. Reported products from the catalytic reduction of CO_2 with silicon-hydrides.

The first examples of homogeneous catalytic reduction of CO_2 using hydrosilanes as reductants were reported in the 1980s [72, 73, 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_2 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_2 hydrosilylation processes has considerably grow up [8, 22, 23, 24, 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_2 hydrosilylation catalysts have proven to be effective under solvent-free conditions and using hydrosiloxanes as reductants.

3.1 Iridium catalyzed CO_2 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_2. 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_3SO_3)(NSiN)(SiR_3)($NCMe_3$)] (NSiN = *fac*-bis-(pyridine-2-yloxy)methylsilyl; SiR_3 = SiMe($OSiMe_3$)$_2$), efficient for the hydrosilylation of CO_2 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^{-1}) [76]. Interestingly, using species [Ir(CF_3SO_3)(NSiN)(H)(coe)] (coe = *cis*-cyclooctene, Scheme 6), which is easier to prepare than the above mentioned Ir-NSiN-acetonitrile derivative, under the same reaction conditions (3 bar, 298 K) produces an increase of the reaction rate (TOF = 1.2 h^{-1}) [77, 78]. Further studies on the influence of reaction temperature [77] and CO_2 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_2-pressure effect on the activity of the reaction. It is remarkable, that from the point of view of selectivity the CO_2- pressure has proven to be a parameter to consider. Indeed, for each temperature an enhancement of the CO_2-pressure results in increased the selectivity of the process [78]. Thus, using species [Ir(CF_3SO_3)(NSiN)(H)(coe)] as catalyst precursor the best reaction performance was achieved at 344 K and under 8 bar of CO_2 (99.9 % conversion, 89.7 % purity (GC-MS), TOF = 138 h^{-1}; TON = 87.5) (Scheme 6) [78].



Scheme 6. Iridium-NSiN catalyzed solvent-free CO_2-hydrosilylation with HSiMe($OSiMe_3$)$_2$.

The iridium(III) complex [Ir(H)(CF_3CO_2)($NSiN^{Me}$)(coe)] ($NSiN^{Me}$ = *fac*-bis-(4-methyl-pyridine-2-yloxy)methylsilyl), which contains a trifluoroacetate instead of a triflate ligand and a $NSiN^{Me}$ ligand with 4-methylated pyridinic rings (Figure 3) has proven to be a highly effective CO_2 hydrosilylation catalyst [79]. Using this Ir-trifluroacetate-$NSiN^{Me}$ species as catalyst precursor for the hydrosilylation of CO_2 to silylformate with $HSiMe(OSiMe_3)_2$ the best results were achieved at 328 K and under 8 bar of CO_2 (100 % conversion; 98.9 % yield to SF by GC-MS; TOF = 99.3 h^{-1}), at temperatures above 328K a decrease in catalytic selectivity and activity was observed [79].

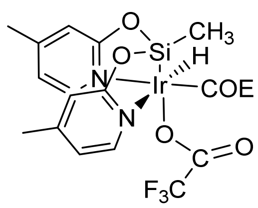


Figure 3. Iridium(III) complex [Ir(H)(CF_3CO_2)($NSiN^{Me}$)(coe)].

Mechanistic studies based on theoretical calculations at DFT level showed that while Ir-trifluroacetate-$NSiN^{Me}$ species catalyzes the CO_2 activation via an inner-sphere mechanism, an outer-sphere mechanism is favored for Ir-triflate-$NSiN^{Me}$ derivatives (Figure 4) [80].

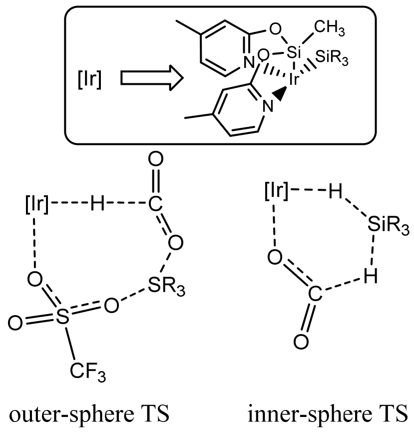


Figure 4. Outer- and inner-sphere transition state (TS) found for Ir-triflate-$NSiN^{Me}$ and Ir-trifluroacetate-$NSiN^{Me}$ catalysts precursors, respectively.

The presence of the Ir-silyl group of the $NSiN^R$ (R = H, Me) ligand *trans*-located to the trifluoroacetate (or triflate) ligand plays a key role on the catalytic activity of Ir-$NSiN^R$ catalysts. Based on this knowledge the catalyst precursor $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ (NSi^{Me} = 4-methylpyridine-2-yloxydimethylsilyl), containing two Ir-Si bonds *trans*-located to the catalyst active positions was designed (Figure 5) [81]. ^1H NMR studies on the activity of $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ as CO_2 hydrosilylation catalyst using $HSiMe(OSiMe_3)_2$ show that at 298 K under 4 bar of CO_2 this catalyst is more active (TOF = 28.6 h^{-1}) [81] than the previously reported Ir-NSiN species, which at 298 K independently of the CO_2-pressure are low active with TOF values in the rage of 1,2 – 1,6 h^{-1} [78]. The higher activity of $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ allows the selective formation methoxysilane from CO_2 and $HSiMe(OSiMe_3)_2$ as it is shown below [81].

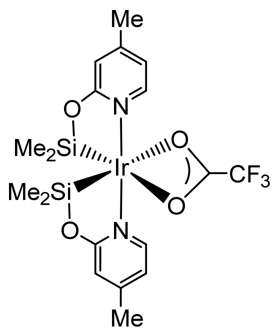
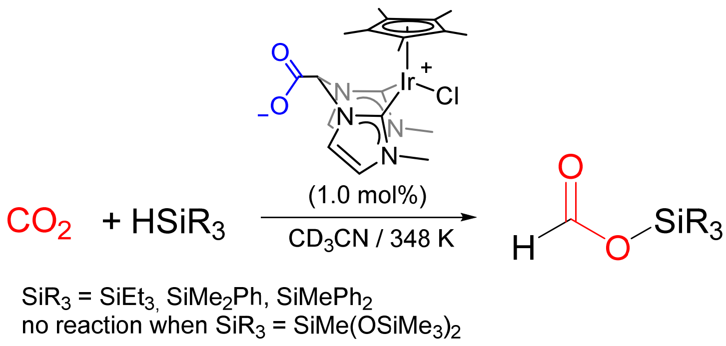


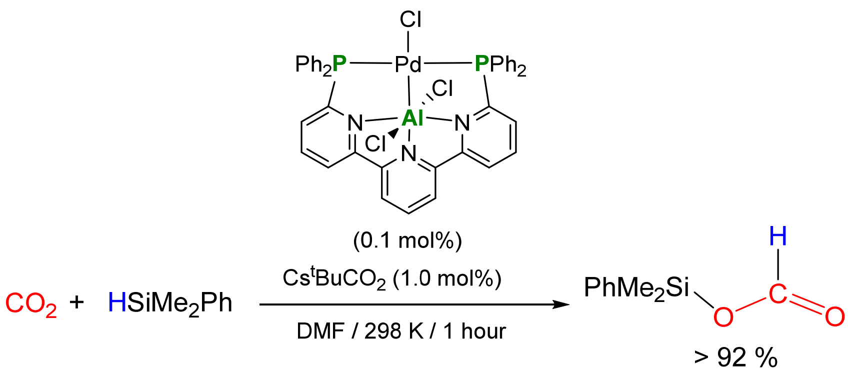
Figure 5. Iridium(III) complex $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$.

Other iridium complex which have proven to be an active catalyst for the selective hydrosilylation of CO_2 (3 bar) to silylformates is the zwitterionic iridium(III) halfsandwich species [IrClCp*{$(MeIm)_2CHCOO$}] ((MeIm = 3-methylimidazol-2-yliden-1-yl; 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 CO_2 with $HSiMe_2Ph$ (TOF = 51 h^{-1}) but under the same reaction conditions is not active when the hydrosiloxane $HSiMe(OSiMe_3)_2$ is used as reductant instead of $HSiMe_2Ph$ [82].



Scheme 7. CO_2 hydrosilylation catalyzed by the zwitterionic iridium species [Cp*IrCl{$(MeIm)_2CHCO_2$)}].

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 CO_2 to the formate level have been reported. Among them, the catalytic system based on the Pd-P**Al**P complex shown in Scheme 8 has proven to be the most active catalyst for CO_2-hydrosilylation reported so far [87]. Indeed, using this Pd-P**Al**P catalyst in DMF as solvent in presence of Cs^tBuCO_2 (1.0 mol%) at 298 K, the selective reaction of CO_2 with $HSiMe_2Ph$ to give HCO_2SiMe_2Ph (92%, TOF = 19300 h^{-1}) was achieved in one hour (Scheme 8) [87].

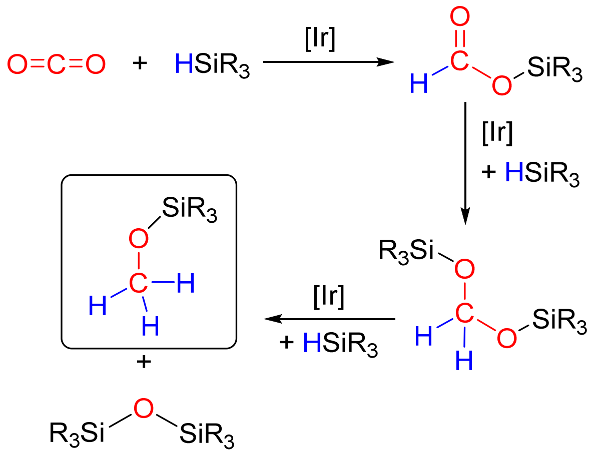


Scheme 8. Palladium-P**Al**P catalyzed CO_2-hydrosilylation with $HSiMe_2Ph$.

Ir-NSiN and Ir-NSi^{Me} species are comparatively less active than some of the above-mentioned catalysts, however they have the advantage of being active under solvent-free conditions and are highly effective when using hydrosiloxanes, instead of hydroorganosilanes, as reductants. Therefore, from the point of view of sustainability iridium species based on Ir-NSiN and Ir-NSi^{Me} species could be considered promising for future applications of the catalytic reduction of CO_2 with silicon-hydrides.

3.2 Iridium catalyzed reduction of CO_2 to methoxysilanes with silicon-hydrides

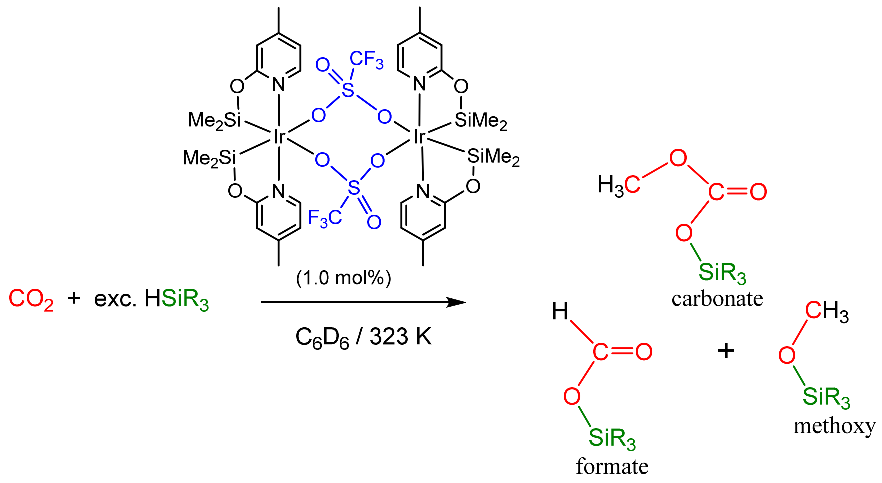
Only few examples of homogeneous catalysts effective for the reduction of CO_2 to methanol level using silicon-hydrides as reducing agents have been published to date. The first one was the above-mentioned iridium complex [Ir(CN)(CO)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) [74]. This catalyst promotes the reduction of CO_2 with $HSiMe_3$ in C_6D_6 at 313 K to the corresponding methoxysilane, CH_3OSiMe_3. This reaction is slow, and two weeks are required to achieve the conversion of the starting hydrosilane into CH_3OSiMe_3. ^{13}C NMR studies of this process using $^{13}CO_2$ confirm that it entails in a stepwise progression with the initial formation of the corresponding silylformate HCO_2SiMe_3, which is further reduce to bis(silyl)acetal $CH_2(OSiMe_3)_2$, the later finally reacts with one equivalent of $HSiMe_3$ to give CH_3OSiMe_3 and $O(SiMe_3)_2$ (Scheme 9) [74].



Scheme 9. Iridium-catalyzed reduction of CO_2 to the methoxysilane level with $HSiR_3$

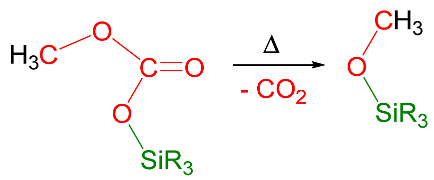
The iridium(III) complex $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ (Figure 5) has proven to be an effective catalyst for the reduction of CO_2 with $HSiMe(OSiMe_3)_2$ to the methoxysilane $CH_3OSiMe(OSiMe_3)_2$ under mild reaction conditions. ^1H NMR studies of the reaction of CO_2 (1 bar) with $HSiMe(OSiMe_3)_2$ in C_6D_6 at 298 K evidenced the selective formation of the corresponding methoxysilane after 16 h (99.0 %; TON = 33.6; TOF = 2.1 h^{-1}) [81]. Interestingly, increasing the CO_2 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^{-1}) together with a 7% of $CH_3OSiMe(OSiMe_3)_2$ after 3.5 h. ^1H and ^{13}C NMR studies and theoretical calculations at the DFT level on the Ir-NSi^{Me} catalyzed CO_2 reduction to methoxysilane with silicon-hydrides, agree with an stepwise mechanism similar to that shown in Scheme 9.

The related complex $[Ir(\mu\text{-}CF_3SO_3)(\kappa^2\text{-}NSi^{Me})_2]_2$, which is a rare example of an iridium dinuclear species with triflate groups acting as bridges, catalyzed the reaction of CO_2 (3 bar) with $HSiMe(OSiMe_3)_2$ in C_6D_6 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].



Scheme 10. Iridium-catalyzed reduction of CO_2 to the methoxysilane level with $HSiR_3$

^{1}H and ^{13}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_2 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].

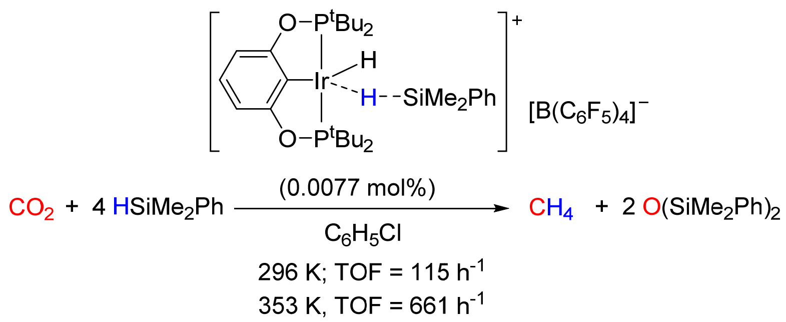


Scheme 11. Thermal decomposition of methylsilylcarbonates to give methoxysilanes and CO_2

Only few examples of other homogeneous catalysts effective for the reduction of CO_2 to methanol level using silicon-hydrides as reductants have been described, which include the anionic rhenium complex [N(hexyl)$_4$][ReO$_4$] [93], the cationic zinc derivative [Zn(Me)(IDipp)][C$_6$F$_5$)$_3$] (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[Me] catalyst is similar to that reported for these Re, Zn and NHC based catalytic systems.

3.3 Iridium catalyzed reduction of CO_2 to methane with silicon-hydrides

The catalytic reduction of 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 $B(C_6F_5)_3$ / TMP (TMP = 2,2,6,6-tetramethylpyperidine) [100] and other Lewis acids and ionic pairs [101, 102, 103, 104]. Among them stands out the iridium(III) cationic species $[Ir(H)(\eta^1\text{-}HSiR_3)(POCOP)][B(C_6F_5)_4]$ (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 CO_2 (1 bar, 296 K) to methane with different hydrosilanes ($HSiEt_3$, $HSiPh_3$, $HSiMe_2Et$, $HSiMe_2Ph$, and $HSiEt_2Me$) using C_6H_5Cl as solvent. This catalytic system works reasonably well with $HSiMe_2Ph$ at 296 K (TOF = 115 h^{-1}), moreover, increasing the temperature to 333 K produces a positive effect of the catalytic activity. (TOF = 661 h^{-1}) (Scheme 12) [98].



Scheme 12. Ir-(POCOP) catalyzed CO_2 reduction to methane with $HSiMe_2Ph$.

Concluding Remarks

This chapter illustrates the progress made during recent years in the field of iridium-catalyzed reduction of CO_2 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_2 hydrogenation and hydrosilylation catalysts are based on Ir(III) species. The selectivity is one of the challenges of homogeneous catalytic CO_2 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_2 hydrogenation catalysts and that Ir(III)-NSiN and Ir(III)-NSi^{Me} species have proven to be highly selective CO_2 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_2 activation mechanism, when using Ir-NSiN and Ir-NSi^{Me} trifluoroacetate derivatives as CO_2 hydrosilation catalysts an inner-sphere CO_2 activation mechanism is preferred. Therefore, it could be concluded that iridium(III) complexes have great potential as homogeneous CO_2 reduction catalysts, however there are still many mechanistic questions to answer and future applications to unveil.

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