ARTICLE

Catalytic applications of zwitterionic transition metal compounds

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This frontiers article highlights recent developments on the application of transition metal-based zwitterionic complexes in catalysis. Recent applications of selected zwitterionic catalysts in polymerization reactions, including the carbonylative polymerization of cyclic ethers, carbon-carbon coupling reactions, the asymmetric hydrogenation of unfunctionalized olefins, and the hydrofunctionalization of alkenes are reviewed. In addition, advances in the field of hydrogenation/dehydrogenation reactions related to energy applications, including the hydrogenation of CO_2 and the dehydrogenation of formic acid and N-heterocycles, the functionalization of CO_2 with amines and hydrosilanes, and the valorization of polyfunctional bio-based feedstocks, such as the dehygrogenation of glycerol to lactic acid or the reduction of levulinic acid into γ-valerolactone, are also described.

Introduction

Zwitterionic metal complexes having formal charge separation within an overall neutral molecular framework have attracted considerable attention in the field of organometallic chemistry.[1,2] Zwitterionic metal complexes can be classified into two types depending on the location of the charges in the molecular framework. On one hand, complexes having a formal positive charge on the metal centre associated with an anionic ancillary ligand and, on the other hand, zwitterionic metallates which exhibit reverse polarity due to the presence of a formally negative metal centre associated with a cationic ancillary ligand moiety (Fig. 1). Although formal atom charges do not represent true charges within a complex, the existence of charge separation within the complexes has been recently demonstrated. A combined synchrotron X-ray and theoretical charge-density study on a zwitterionic complex featuring a formally cationic Rh(cod)+ (cod = 1,5-cyclooctadiene) metal fragment and a formally anionic indenide unit incorporated into the backbone of the associated κ^2-P,N ligand, has shown that the electron density and electronic structure in the region of the rhodium centre is similar to the found in the related cationic compound (Fig. 2).[3] It is therefore evident that zwitterionic metal complexes can emulate the charge distribution featured in cationic or anionic transition metal complexes which allow to combine the reactivity properties of the corresponding ionic compounds with the solubility pattern of the neutral complexes in low polarity media, which is particularly attractive in catalysis. In addition, the formal charge separation between the ancillary ligand and the metal fragment in a rigid structure avoids the unwanted ion-pairing

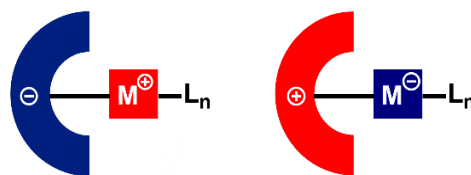that influences the chemical behaviour of the ionic compounds and is responsible for the observed counterion effects.[4]

Fig. 1. Zwitterionic metal complexes with a formally positively charged metal center (*left*) and a formally negatively charged metal center (zwitterionic metallates, *right*).

Zwitterionic complexes can be prepared following several strategies although the most common is the reaction of zwitterionic ligands with suitable metal species.[5,6] Advances in the design of anionic and cationic ancillary ligands have made possible the synthesis a large number of both types of zwitterionic metal complexes. In this context, zwitterionic metallate complexes derived from phosphonium-, ammonium-, iminium- and sulfonium-based ancillary ligands have been reported.[2] On the other hand, borate-,[7] sulfonate-,[8] carbanion-based[9] or anionic N-heterocyclic carbenes (NHC)[10] ancillary ligands have been widely used for the synthesis of zwitterionic metal complexes. The presence of an electrophilic or nucleophilic metal centre in a neutral zwitterionic species offers the opportunity for new reactivity patterns in bond activation and catalysis. In this way, zwitterionic compounds having a metal centre with sufficient Lewis acidity can promote polymerization reactions in the absence of initiators or, alternatively, an electron-rich metallate moiety may promote oxidative addition, a key elementary step for substrate activation.[11] In this context, the application of zwitterionic metal complexes as catalysts for organic transformations has also attracted increased interest. In particular, a number of well-defined transition metal-based zwitterionic catalysts for

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polymerization reactions have been reported. However, there has been notable advances in other applications such as, for example, hydrogenation, dehydrogenation, hydro-functionalization and C-C coupling reactions.
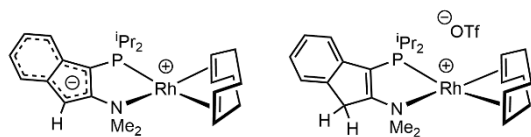

Fig. 2. Stradiotto's indenide-based rhodium zwitterionic neutral complex (*left*) and the related cationic complex (*right*).

Despite the limited number of comparative studies, the catalytic performance of zwitterionic complexes is in many cases analogous to that of conventional ionic related species. However, in some cases, increased activity and/or divergent reactivity has been observed highlighting the potential of zwitterionic transition metal complexes in catalysis. In addition, zwitterionic complexes derived from ligands bearing ionic groups such as carboxylate, ammonium or sulfonate, are water-soluble which expand the range of potential applications of this type of complexes.[12] Finally, the presence of reactive ancillary ligands close to the metal center may allow for metal-ligand bifunctional catalysis.[13]

The aim of this frontier article is to highlight recent developments on the application of transition metal zwitterionic complexes in catalysis. This report, which is not intended to be exhaustive, has been organized by reaction types in which these complexes have been used more frequently. In particular, polymerization, C-C coupling, hydrogenation, dehydrogenation, and hydrofunctionalization reactions.

Polymerization reactions

Transition metal zwitterionic complexes have found wide application as catalysts for polymerization and co-polymerization reactions. Early transition metal-based zwitterionic complexes were shown to be efficient catalysts for the polymerization of ethylene. In particular, group 4 metal-based zwitterionic metallocenes bearing a borate functionality behave as single-component polymerization catalysts exhibiting in some cases comparable activities to related non-zwitterionic analogous.[14] The principle design for these catalysts is the covalent attachment of the counterion to the ancillary or reactive ligands in the metallocene catalysts, ring-type and girdle-type catalysts, respectively, in order to attenuate ion-pairing through enforced physical separation from the metal centre. However, the ethylene polymerization activity of girdle-type catalysts was, in general, poor by virtue of the tight intramolecular ion pairing.[15] Ring-type catalysts, which have a borate functionality attached to one of the cyclopentadienyl moieties in the bent-metallocene structure,

were found to be more effective as the zwitterionic character is maintained throughout the polymerization process.

Although a few zwitterionic early transition metal-based polymerization catalysts have been recently described,[16,17] current advances in this field are dominated by catalysts based on late transition metals.

CO-ethylene copolymerization. A number of zwitterionic palladium and nickel complexes were shown to exhibit catalytic activity for the alternating copolymerization of carbon monoxide and ethylene (Fig. 3).
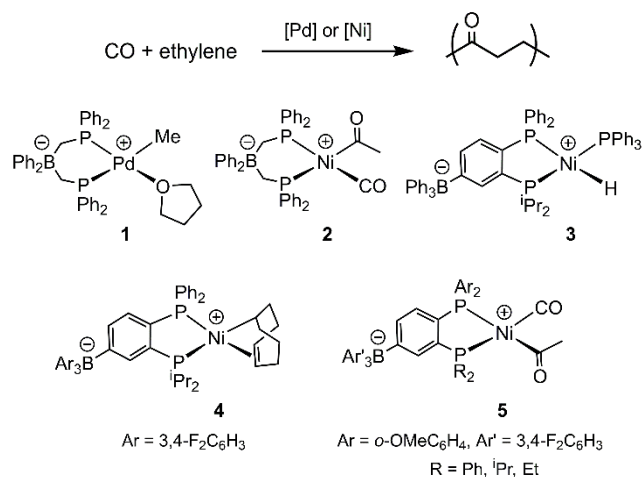

Fig. 3. Palladium- and nickel-based zwitterionic catalysts for the alternating copolymerization of CO and ethylene.

Borate-containing anionic bidentate phosphine ligands have revealed as efficient supporting ligands for the stabilization of zwitterionic metal complexes. The zwitterionic methyl-palladium(II) complex **1** catalyzed the co-polymerization of CO and ethylene with activities comparable to that of structurally related cationic species.[18] The square planar acetyl nickel(II) complex **2** also catalyzed the alternating copolymerization of CO and ethylene albeit with low productivity which was attributed to its instability under high CO pressure. In fact, the square planar acetyl complex is stable in solution under 1 atm of CO but undergoes irreversible decomposition at high CO pressure at room temperature likely due to the high reactivity of the aliphatic borate moiety.[19] Rigid bis-phosphine borate ligands were designed with the aim to improve the stability of the zwitterionic nickel catalysts under co-polymerization conditions. Although the initial catalytic activity of **3** was comparable to that of cationic palladium catalysts, it is much less productive as a consequence of rapid catalyst deactivation. It has been suggested that instability of the tetraphenylborate motif in the ligand framework with respect to electrophilic attack may be the cause of catalyst deactivation.[20] The stability of the borate moiety in the anionic bidentate phosphine was improved by replacing the B-Ph groups with electron-withdrawing B-($3,4$-$F_2C_6H_3$) groups. Although catalyst **4** (Ar = $3,4$-$F_2C_6H_3$) only shows a modest productivity improvement for CO-ethylene copolymerization in comparison to the B-Ph catalyst (Ar = C_6H_5), both were more productive that the related cationic analogues. However,

catalyst **4** still deactivates quickly under polymerization conditions.[21] The catalyst lifetime and overall productivity can be improved by introduction of *o*-methoxyphenyl substituents at the phosphine moiety although it decreases the activity of the catalyst. Thus, catalysts **5** produces the alternating CO and ethylene copolymer with M_n values of polyketone products up to 10^4 g/mol. The improvement of the catalyst stability is attributed to the coordinating ability of the *o*-methoxy group rather than a steric or inductive electronic origin.[22]

Ethylene dimerization and polymerization. Nickel and palladium zwitterionic complexes have shown catalytic activity in the dimerization and polymerization of ethylene (Fig. 4). In particular, methyl-palladium complexes bearing an *o*-aryltrifluoroborate-functionalized phosphine ligand have shown activity in the dimerization of ethylene. The palladium lutidine-based complexes **6** slowly reacted with ethylene at ambient temperature and pressure, to yield a mixture of propene, 1-butene and 2-butenes consistent with ethylene dimerization.[23] In contrast, the 2,4,6-collidine complex **7** slowly dimerized ethylene to 1-butene under ethylene pressure. Addition of $[H(OEt_2)_2][B(3,5-(CF_3)_2-C_6H_3)_4]$ to trap the collidine ligand as the collidinium salt resulted in a 10-fold increase in the dimerization rate. However, under these conditions, the primary product 1-butene was isomerized to cis and trans 2-butene.[24] The nickel complex **8** catalyzed the dimerization of ethylene at a significantly faster rate than its palladium analogue to afford the kinetic 1-butene product which isomerizes into a thermodynamic mixture of 2-butenes once the ethylene has been consumed. Nevertheless, under constant ethylene pressure, the isomerization of 1-butene was significantly suppressed although a 20–30% of hexenes was also produced. This catalyst is quite active reaching a TOF for 1-butene production greater than 2000 h^{-1}.[25] The behaviour of this catalyst contrasts with that of analogous phosphine-sulfonate complexes which are known to be very effective ethylene polymerization catalysts.[26] The tendency toward oligomerization vs polymerization may be related to the electronic deficiency at the nickel centre imparted by the poorly donating trifluoroborate group. The zwitterionic η^3-benzyl-nickel(II) complex **9**, featuring a remotely functionalized bidentate N,O ligand, has revealed as an effective ethylene oligomerization initiator (100 PSI, 308 °C) with an activity of 1450 Kg·mol^{-1}Ni·h^{-1} providing a distribution of ethylene oligomers with an internal olefin structure.[27]

The zwitterionic methyl-palladium complexes **10** containing a phosphine ligand appended with an anionic 10-vertex perchlorinated closo-carborane moiety oligomerized ethylene (2 atm) at room temperature to a mixture of C_4–C_{10} olefins with TOFs of *ca.* 8000 (R = *i*Pr) and 1800 (R = Ph) h[-1], respectively. In contrast, the methoxy-stabilized methyl-palladium complex **11** polymerized ethylene to yield polyethylene wax with a M_n of *ca.* 10^3 g/mol and polydispersity index of 1.5.[28] The related Pd(η^3-allyl) complex bearing the perchlorinated carba-closo-dodecaborate anion (R = *i*Pr) also polymerized norbornene affording soluble polynorbornene with a M_w of $4.4·10^4$ g/mol and a polydispersity index of 1.71.[29] Zwitterionic tetrahedral nickelate(II) complexes bearing a functionalized imidazolium ligand of general formula $NiCl_3(L)$ have revealed as effective catalysts for the oligomerization/polymerization of ethylene. The nickel complexes **12**, featuring a pyrazolyl-ether-imidazolium ligand, showed moderate activity in ethylene oligomerization upon activation with methylaluminoxane (MAO) to afford short-chain olefins in the C_4–C_6 range.[30] The substituent at the C2 position of the imidazolium group strongly influences the catalytic activity which was tentatively attributed to the reaction of the acidic proton at C2 with MAO. In contrast, mixed-halide tetrahedral nickelate(II) complexes **13**, featuring a picolyl-functionalized imidazolium ligand, polymerized ethylene in presence of MAO producing high-density polyethylene with activities of 105 g (PE)·mol^{-1}Ni·h^{-1}.[31]

The α-diimine nickel(II) complex **14**, featuring a borate-functionalized η^3-allyl ligand, polymerized ethylene without any additional activator component to afford polyethylene with a branched structure. Activities of 159 kg (PE)· mol^{-1}Ni[1]·h^{-1}·bar[-1] were attained under 2 bar of ethylene at 25 °C.[32]

Polymerization of phenylacetylene derivatives and carbonylative polymerization. Zwitterionic rhodium complexes bearing diene ligands were shown to exhibit catalytic activity for the polymerization of phenylacetylene (Fig. 5). Notably, the zwitterionic rhodium(I) complexes $[Rh(\eta^6-C_6H_5-BPh_3)(diene)]$ **(15)** (diene = cod, nbd and tfb) featuring an η^6-phenyl ring tethered to an anionic borate centre have shown a remarkable activity in the polymerization of phenylacetylene (PA).[33] Alper's zwitterionic Rh(cod) complex exhibited high catalytic activity in the presence of hydrosilylation reagents, such as triethylsilane, to afford stereoregular polyphenylacetylene (PPA) with M_w up to $3.5·10^4$ g/mol.[33a] Noyori and co-workers demonstrated that the diene ligand in these catalysts plays a key role. In fact, the Rh(nbd) (nbd = 2,5-norbornadiene)
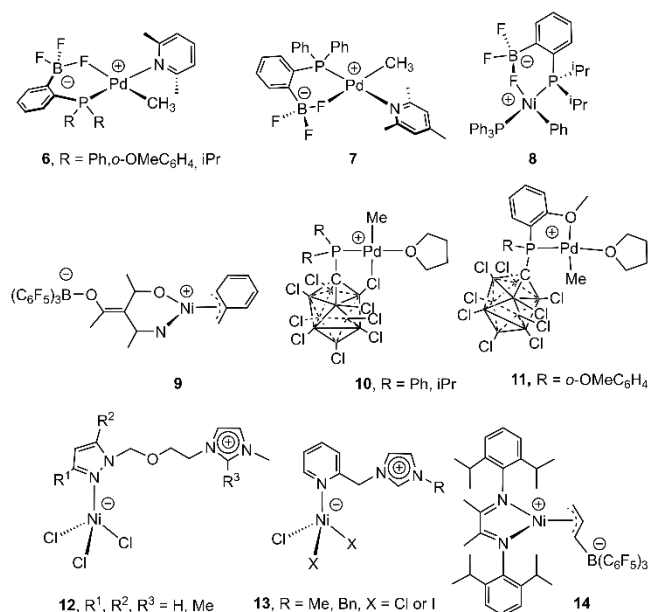

Fig. 4. Zwitterionic palladium and nickel catalysts for the dimerization and polymerization of ethylene.

catalyst afforded stereoregular PPA with $M_n > 10^5$ g/mol.[33b] Remarkably, this catalyst effectively polymerized substituted phenylacetylenes which has allowed the preparation of polymers with functional properties.[34] Masuda *et al.* showed that replacement of the diene for the more π-acid tfb diene ligand (tfb = tetrafluorobenzobarralene) resulted in a much higher catalytic activity.[33c] In sharp contrast, the bis-cyclooctene complex [Rh(η^6-C$_6$H$_5$-BPh$_3$)(coe)$_2$] (coe = cyclooctene) showed no catalytic activity illustrating the key role of the diene ligand in the former catalysts.[35] The zwitterionic Rh(cod) complexes **16** consisting of a malonate-based NHCs ligand featuring an endocyclic anionic moiety, have revealed as suitable catalyst for PA polymerization. The negative charge of the zwitterionic Rh(I) species is located on the remote malonate-type backbone whereas in the solid state the coordinative unsaturation of the metal centre is stabilized via an intramolecular η^1-arene interaction between the metal centre and one of the C$_{ipso}$ of the mesityl arms. Catalyst precursors **16** efficiently catalyzed the polymerization of PA affording PPAs with M_n up to $3 \cdot 10^4$ g/mol and polydispersities of 2.2-2.4 with a cis content up to 80%. The catalytic performance of these catalyst is superior to that of the related cationic catalyst resulting from the reaction of **16** with electrophiles E-OTf (E = Me, Tf, H), which produced PPAs of lower molecular weight, higher polydispersities and a cis content up to 40%.[36]
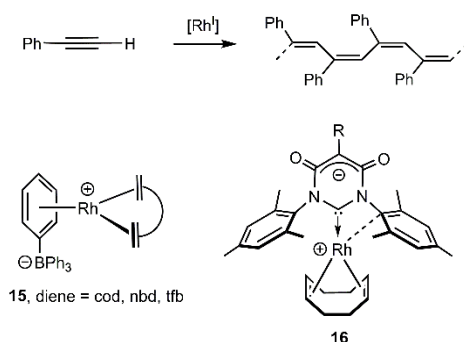

Fig. 5. Zwitterionic rhodium catalysts for the polymerization of phenylacetylene.

The acetyl-nickel(II) catalysts **5** (R = Ph, ^{i}Pr) (Fig. 3) has also been shown to catalyze the carbonylative polymerization (COP) of cyclic ethers (Fig. 6). The design principle of the catalyst is based on the zwitterionic structure in which the electrophilic Ni–acyl bond is able to react with cyclic ethers to give an acyl-cyclic ether oxonium intermediate which is ion-paired with the Ni(0) nucleophile. Carbonylative polymerization of oxetane (EO) or tetrahydrofuran (THF) afforded oligomers in low yield (Fig. 6). However, when the reaction was carried out in the presence of both EO and THF at room temperature and 20 bar of CO a poly(ester-co-ether) copolymer, composed of ester and ether units in a non-alternate way, of M_w $2.1 \cdot 10^4$ and PDI of 2.01 was formed in 16 h.[37] The cationic analogue of **5** bearing the same

bis(phosphine)benzene ligand failed to incorporated carbon monoxide into the polyether structure which supports the key role of the zwitterionic structure of the catalyst. The synthesis of photolytically and hydrolytically degradable polymers by carbonylative copolymerization of ethylene and cyclic ethers catalysed by **5** has recently been reported.[38]
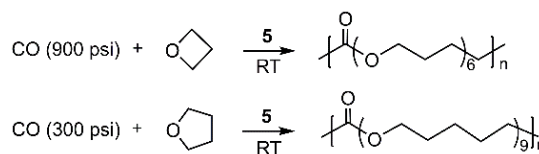

Fig. 6. Carbonylative polymerization of cyclic ethers catalyzed by the acetyl-nickel(II) catalysts **5**.

C-C coupling reactions

Zwitterionic palladate and nickelate complexes have found wide application as catalysts for cross-coupling reactions (Fig. 7). In addition, the catalytic activity of systems based on hybrid phosphine-borate ligands or sulfonate-functionalized NHC ligands have also been explored (Fig. 8).
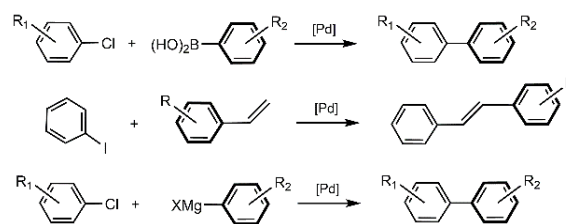

Fig. 7. Palladium-catalyzed Suzuki-Miyaura (i) and Mizoroki-Heck (ii) cross coupling reactions.

Suzuki-Miyaura cross coupling reactions. The sodium salt of the borate-containing caged triarylphosphine hybrid ligand (NaL) in **17** has shown the ability to stabilize allyl-palladium(II) zwitterionic complexes. This bulky anionic phosphine has been applied to the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl chlorides with arylboronic acids. The catalytic system [PdCl$_2$(PhCN)$_2$] (2 mol%)/NaL (P/Pd 2:1) in the presence of K$_3$PO$_4$ at 60 °C in DMF efficiently catalyzed the coupling reaction between 1-butyl-4-chlorobenzene and phenyl-boronic acid affording a 92% yield of the cross-coupling product in 12 h.[39] The water-soluble palladium complex **18**, featuring a sulfonate functionalized CNC pincer ligand, catalyzed the Suzuki-Miyaura coupling between phenylboronic acid and aryl halides. The reactions were carried out in neat water at 110 °C with a 1 mol % of catalyst loading in the presence of K$_2$CO$_3$. Good yields to the coupling products were achieved with aryl bromides in 4 h, however moderate to low yields were attained with the more inert aryl chlorides in 12 h.[40]

The zwitterionic palladate complexes **19**, featuring an imidazolium-functionalized quinoxaline ring σ-bonded to the palladium atom, were found to be highly active in the Suzuki–Miyaura cross coupling between aryl bromides and organoboron reagents in neat water with K$_2$CO$_3$ as base at 70 °C using 0.5 mol% catalyst loading. Under these conditions, a
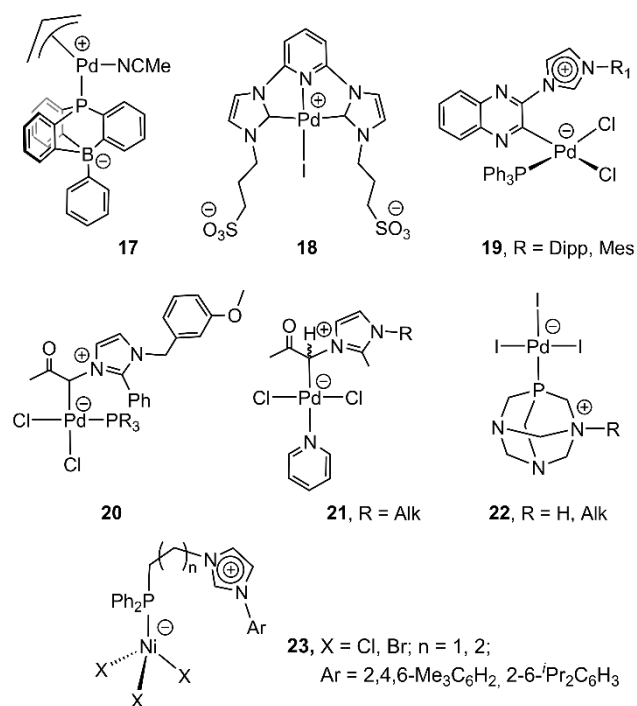
Fig. 8. Zwitterionic palladium catalysts for C-C coupling reactions.

wide range of (hetero)aryl bromides, hydrophilic aryl bromides, benzyl bromides and various organoboron reagents afford the corresponding biaryls/diarylmethanes in excellent yields in 3 h with TON numbers up to 82000. Although deprotonation of the imidazolium moiety could be possible under catalytic conditions, mechanistic investigations ruled out the participation of Pd-NHC species as catalytic intermediates which suggests that the catalytic reaction proceeds in homogeneous phase.[41] The related zwitterionic phosphine-palladate complexes **20**, also featuring an imidazolium moiety, efficiently catalyzed Suzuki–Miyaura reactions between sterically hindered aryl chlorides and arylboronic acids in aqueous medium at room temperature. The reactions were performed in a 1,4-dioxane/water mixture (4/1) employing a 2 mol % of palladium precatalyst and KOH as base. This catalyst allows the coupling of a wide range of aryl chlorides and arylboronic acids with different electronic and steric properties with moderate to good yields in the coupled product in 12 h.[42]

Mizoroki-Heck cross-coupling reactions. In sharp contrast, the related zwitterionic pyridine-palladate precatalysts **21** were successfully applied as metal precursors to generate palladium nanoparticles in the presence of triphenylphosphine under typical Mizoroki-Heck reaction conditions. These palladium nanoparticles stabilized in ionic liquids were effective recyclable catalyst systems for the coupling between 4-iodoacetophenone and n-butyl acrylate with up to nine consecutive catalytic runs. However, the activity and reusability were lower for bromide derivatives.[43]

The N-protonated or N-alkyl derivatives of the cage-like 1,3,5-triaza-7-phosphaadamantane ligands, [PTA-R]+ (R = H, Me, Et, nPr, nBu), have allowed the preparation of water soluble zwitterionic palladate compounds **22**. These complexes catalyzed the Mizoroki-Heck coupling of iodobenzene with n-butyl acrylate and substituted styrenes under mild conditions in water using cesium carbonate as base. It was found that the presence of the phase transfer agent tetrabutylammonium bromide in the catalytic system considerably enhance the rate and selectivity of the reaction.[44]

Kumada cross coupling reactions. Poli et al. have reported the synthesis of a series of tetrahedral nickelate(II) complexes based on phosphine-functionalized imidazolium ligands. Catalysts **23** have been proved effective for the Kumada cross coupling of a range of aryl chlorides and arylmagnesium halides. The catalysts possessing a diphenylphosphinopropyl imidazolium ligand (n = 2) were found to be more active. However, the substituent at the imidazolium fragment, mesityl or 2,6-diisopropylphenyl, did not influence activity. Reactivity studies have revealed the formation of chelating phosphine–carbene species, by deprotonation of the imidazolium moiety by the Grignard reagent, which are supposed to be the active species.[45]

Hydrogenation and dehydrogenation reactions

Zwitterionic rhodium, iridium and ruthenium complexes have found application in the hydrogenation and transfer hydrogenation of a range of unsaturated substrates, including the asymmetric hydrogenation of unfunctionalized olefins and the hydrogenation of hindered alkenes. In addition, active catalysts for the hydrogenation of CO_2, bicarbonate salts or levulinic acid have also been designed recently. Moreover, zwitterionic catalysts for the acceptorless dehydrogenation of glycerol and formic acid have been also reported.

Reduction of C=C and C=O bonds. Zwitterionic rhodium and ruthenium complexes featuring a tripodal tris(phosphine)borate [PhBP$_3$]$^-$ ligand were efficient precatalysts for the selective hydrogenation of trans-cinnamaldehyde to the corresponding allyl alcohol under mild reaction conditions (Fig. 9). The dinuclear ruthenium compound **25** in the presence of NEt$_3$ as co-catalyst afforded a 97% selectivity with a TOF of 527 h^{-1}. The mononuclear rhodium compound **24** was somewhat less active, TOF of 219 h^{-1}, and selective (81%). The ruthenium catalyst likely operates via heterolytic activation of hydrogen involving monohydride intermediates, while the rhodium catalyst proceeds through dihydride intermediates resulting from the oxidative addition of dihydrogen.[46] The rhodium complexes **26** and **27** supported by borate-containing anionic bidentate bis-phosphine and bis-amine ligands, [Ph$_2$BP$_2$]$^-$ and [Ph$_2$BN$_2$]$^-$, respectively, have shown activity in the hydrogenation of styrene. These zwitterionic complexes out-performed their cationic counterparts that incorporate a diphenylsilane unit in the ligand backbone. In particular, the zwitterionic bis-amino complex **27** was more active than the both the neutral and cationic bis-phosphine systems, and twice as active as its cationic amine counterpart.[47]

One of the most significant examples of divergent reactivity between zwitterionic and relative ionic compounds is the Stradiotto's indenide-based ruthenium zwitterionic complex **28** (Fig. 9). This compound efficiently catalyzed the transfer hydrogenation of a diversity of alkyl and/or aryl ketone substrates under basic conditions using iPrOH as solvent and hydrogen source at low catalyst loading with impressive TOF values up to 220000 h^{-1}.[48] In sharp contrast, the related cationic complex exhibited only modest activity.

A series of zwitterionic iridium(I) complexes based on chiral P,N-ligands with imidazoline or oxazoline donors and anionic tetraarylborate or aryltrifluoroborate substituents were synthesized by Pfaltz and co-workers and evaluated in the asymmetric hydrogenation of unfunctionalized olefins (Fig. 10). It was found that, in most cases, the anionic derivatization on the back side of the ligands has virtually no influence on the asymmetric induction of the zwitterionic iridium complex compared to that of the related cationic complexes, suggesting that the chiral environment of the cationic metal centre is unaffected by the anionic substituent. However, the zwitterionic catalysts were significantly more reactive than their cationic counterparts in non-polar solvents. The tetraarylborate-based zwitterionic complexes **29** and **30** were found to be slightly less active in dichloromethane although they showed higher activity in aliphatic hydrocarbons in which the cationic analogous are almost inactive. In contrast, the zwitterionic complex **31** featuring an anionic aryltrifluoroborate is more reactive than the cationic relatives even in dichloromethane.[49]

Zwitterionic iridium(I)-cod complexes featuring an anionic NHC ligand containing a weakly coordinating borate moiety (WCA-NHC) exhibited a remarkable catalytic activity for the homogeneous hydrogenation of alkenes (Fig. 10). The electrophilic metal centre in these complexes is stabilized by an intramolecular interaction with the N-aryl groups of the carbene ligands. Compound **32**, in which the WCA-NHC ligand bears a B(C$_6$F$_5$)$_3$ moiety and an 2,6-diisopropyl-phenyl N-substituent, efficiently catalyzed the hydrogenation of hindered alkenes in nonpolar solvents, such as cyclohexane, or in neat alkene substrates. Neat hydrogenation of alkenes proceeded efficiently with catalyst loadings as low as 10 ppm at 8 atm of dihydrogen.[50]
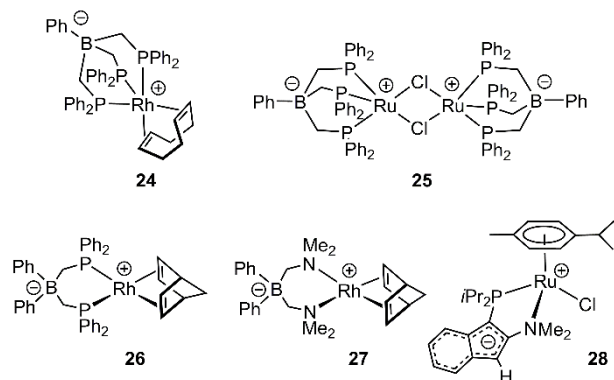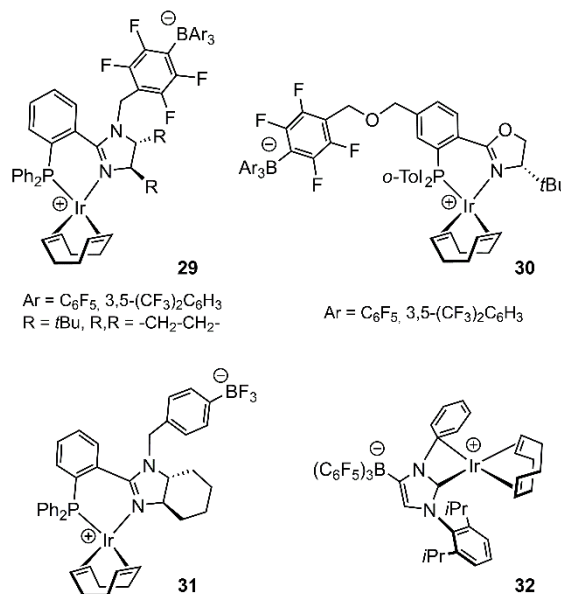

Fig. 10. Zwitterionic iridium catalysts for the asymmetric hydrogenation of unfunctionalized olefins and hydrogenation of hindered alkenes.

Reduction of CO$_2$, carbonate salts and acceptorless dehydrogenation. The water-soluble anionic rhodium(III), iridium(III) and ruthenium(II) compounds featuring a bis-NHC doubly functionalized with 3-sulfonate-propyl wingtips were found to be efficient catalysts for the hydrogenation of bicarbonate to formate (Figs. 11 and 12). The rhodium catalyst **33** was the more active with a TON of 1300 and a 64% yield using 1 mM of catalyst in 2 M aq. KHCO$_3$ at 100 ºC for 24 h under a hydrogen pressure of 50 bar. Catalysts **34** and **35** lead to slightly lower conversions of 54 % and 62 %, respectively, under the same conditions. Decreasing the concentration of **33** to 0.2 mM and increasing the reaction time to 72 h resulted in a 36 % conversion with a TON of 3600.[51] Interestingly, these complexes have also shown activity in the dehydrogenation of formic acid (Fig. 11). The rhodium compound **33** was again the more active with a TOF of 6700 h^{-1} at 80 ºC and a catalyst concentration of 1 mM. Lower activities were observed for **34** and **35** with TOFs of 50 h^{-1} and 30 h^{-1}, respectively. Reduction of the catalyst concentration resulted in TOF values of 27000 h^{-1} (0.1 mM) and 37100 h^{-1} (0.01 mM). The high activity of catalyst **33** both in the hydrogen storage and release processes shows its potential for a total hydrogen storage cycle.[51]

Jiménez, Pérez-Torrente and co-workers reported on the synthesis and reactivity of carboxylate-functionalized bis-NHC zwitterionic rhodium and iridium complexes.[52] The water-soluble zwitterionic iridium(I) catalyst **36**, [Ir(cod){(MeIm)$_2$CHCOO}] (MeIm = 3-methylimidazol-2-yliden-1-yl), displayed good catalytic activity for the hydrogenation of CO$_2$ (Figs. 11 and 12). The reactions were carried out under 60 atm of 2:1 H$_2$/CO$_2$ in a 1.8 M solution of NEt$_3$ in water in the presence of 0.07 mol % of iridium catalyst at 110 °C, to afford

Fig. 9. Zwitterionic rhodium and ruthenium catalysts for the hydrogenation and transfer hydrogenation of unsaturated substrates.

exclusively the triethylamine/formic acid adduct as product. The highest TOF of 279 h^{-1} was observed at 2 h with a 39% conversion, and full conversion was attained after 42 h with an average TOF of 34 h^{-1}.[53] Mechanistic investigations and related studies have shown the ability of the carboxylate-funcionalized bis-NHC ligand to stabilize iridium(III) octahedral species through the κ^3-C,C',O coordination mode. Compound **36** reacted with CO_2 in methanol in the presence of traces of water to afford the iridium(III) hydrido species [IrH(cod){(MeIm)$_2$CHCOO}][HCO$_3$] which is likely formed by the direct protonation of the iridium centre by the carbonic acid generated under reaction conditions. In fact, protonation of **36** by HOTf, a strong acid, resulted in the clean formation of [IrH(cod){(MeIm)$_2$CHCOO}]OTf. Compound **36** also reacted with H_2 to afford the iridium(III) dihydride species [IrH$_2$(coe){(MeIm)$_2$CHCOO}] (Fig. 13). DFT studies on the mechanism, assuming the compound [IrH$_2$(H$_2$O){(MeIm)$_2$CHCOO}] as the catalytic active species which is formed under catalytic reaction conditions, showed that a base-involved mechanism in which the base assists the proton transfer in heterolytic cleavage of the H_2 molecule is more favourable than one in which the base neutralizes the produced formic acid. However, the energy barrier obtained from kinetic experiments suggests that both mechanisms could be operative under the experimental reaction conditions.
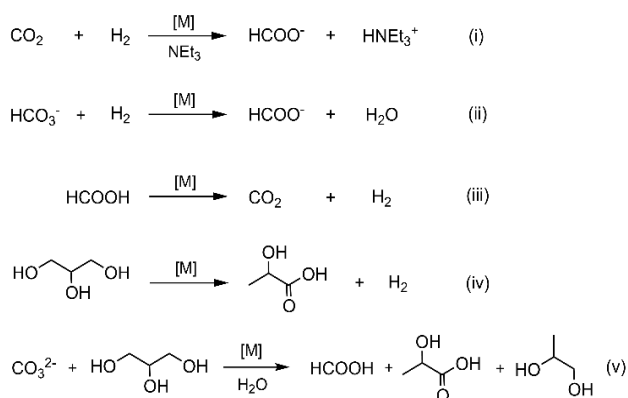

Fig. 11. Hydrogenation of CO_2 and bicarbonate salts (i and ii), acceptorless dehydrogenation of formic acid (iii) and glycerol (iv), and transfer hydrogenation of carbonate salts with glycerol (v).

Voutchkova-Kostal et al. studied the application of a series of water soluble zwitterionic iridium(I), iridium(III), and ruthenium(II) NHC complexes with sulfonate-functionalized wingtips, including **34** and **35**, in the selective acceptorless dehydrogenation of glycerol to lactic acid in water (Fig. 11). The iridium(I) carbonyl bis-NHC complex **37** (Fig. 12), featuring aryl-sulfonate wingtips, afforded a TOF of 42500 h^{-1} at 150 ^{o}C (microwave heating) in glycerol:water (1:1) solution with KOH (42 mmol) as base and a catalyst loading as low as 1.8 ppm.[54] Compound **37** was found to be an efficient catalyst for the transfer hydrogenation of carbonate salts using glycerol as hydrogen source (Fig. 11). Under the optimized reaction conditions, 150 °C under microwave heating in a 1:1water:glycerol and a catalyst loading of 10 ppm, the reduction of potassium carbonate afforded formic acid (FA),

lactic acid (LA) and the dehydration-transfer hydrogenation product, 1-2-propanediol (1,2-PDO), in a selectivity ratio of ~2 : 4: 1.[55]

Reduction and reductive amination of ketoacids. Fischmeister et al. disclose the utility of dipyridylamine ligands in the design of efficient hydrogenation/dehydrogenation catalysts (Fig. 14). The zwitterionic iridium(III)-dipyridylamine complex **38** bearing a coordinated sulfato ligand was found to be very efficient in transfer hydrogenation and direct hydrogenation of levulinic acid into γ-valerolactone (Fig. 14). Transfer hydrogenation of levulinic acid (1 M) was carried out in water at 110 °C in the absence of base using formic acid as hydrogen donor (2:1 ratio). Full levulinic acid conversion was attained in 16 h using a 0.1 mol% catalyst loading. It was demonstrated that, under transfer hydrogenation conditions, the reaction essentially proceeded by hydrogenation involving formic acid dehydrogenation. Compound **38** also catalyzed the hydrogenation of levulinic acid in water. TON numbers up to 174000 were achieved at 130 ^{o}C in 72 h at 5 bar of H_2 and a catalyst loading of 10 ppm. Remarkably, the proposed mechanism involves the participation of the sulfato moiety in the heterolytic H_2 splitting leading to the formation of the key Ir(III) hydrido catalytic active species.[56]

Compound **38** also catalyzed the reductive amination of levulinic acid into pyrrolidone derivatives using H_2 (5 bar) as
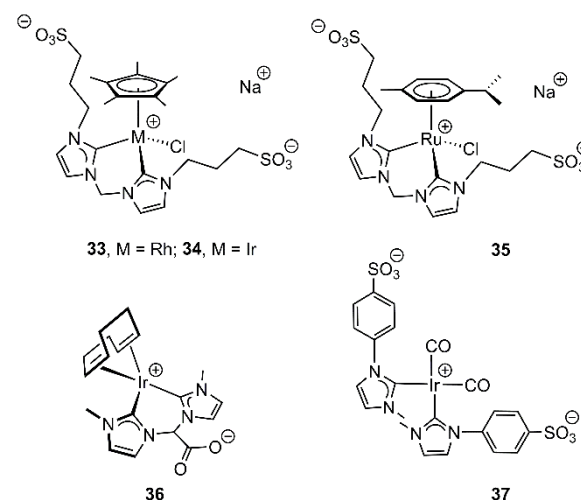

Fig. 12. Zwitterionic ruthenium, rhodium and iridium catalysts for the hydrogenation of CO_2 and bicarbonate salts, and acceptorless dehydrogenation of glycerol.
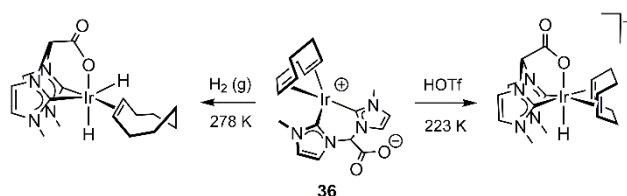

Fig. 13. Reactivity of **36** leading to octahedral iridium(III) complexes.

hydrogen source. A broad range of pyrrolidone derivatives were efficiently synthesized from aliphatic and aromatic amines at 110 ^{o}C under neat conditions using a catalyst loading of 0.05 mol%.[57] The related compound **39** featuring an

electron-donating dimethylamino-group into the dpa ligand (Fig. 14) allowed to carried out the reductive amination of levulinic acid and 2-formylbenzoic acid in water under hydrogen transfer conditions using formic acid as hydrogen source.[58]

The electron-rich iridium complex **39** efficiently catalyzed the dehydrogenation of formic acid under base free conditions. This catalyst achieved a TOF of 12320 h⁻¹ at 80 °C and pH 1.8, with no added sodium formate, and was operative in a concentration range from 2 M to 8 M. The catalyst could also be used in pure formic acid exhibiting a TOF of 4800 h⁻¹.[59] Zwitterionic compound **39** has shown catalytic activity for the hydrogenation of N-heterocycles under mild conditions in water without any co-catalyst. This catalyst also promotes the reverse reaction of dehydrogenation of N-heterocycles and then, it could have potential application in a hydrogen economy based on liquid organic hydrogen carriers (LOHCs).[60]
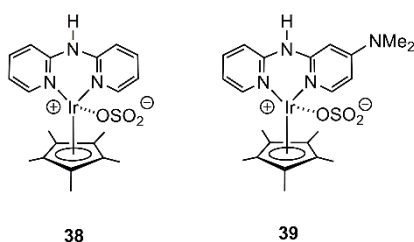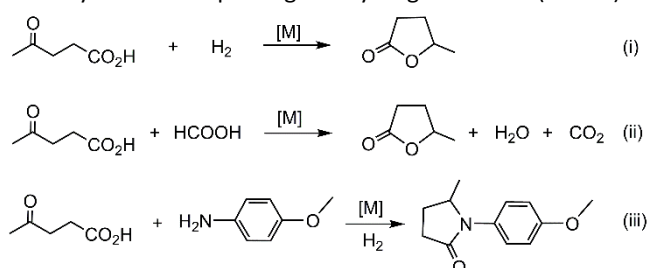
Fig. 14. Zwitterionic iridium(III)-dipyridylamine sulfato complexes for the hydrogenation (i) and transfer hydrogenation of levulinic acid (ii), reductive amination of levulinic acid (iii).

Hydrofunctionalization reactions

Rhodium and iridium zwitterionic complexes were shown to be efficient catalyst for the hydroboration and hydrosilylation of unsaturated derivatives including olefins, ketones and aldehydes. More recently, the application of these type of complexes for the selective hydrosilylation of terminal alkynes, the reduction of CO_2 with hydrosilanes, and the coupling of hydrosilanes with secondary amines has been reported.

Hydroboration reactions. Zwitterionic rhodium complexes [Rh(η^6-catBcat)(P-P)] featuring an arylspiroboronate ester were reported as efficient alkene hydroboration catalysts (Fig. 15). These compounds were proposed to be the catalyst resting state in the hydroboration of alkenes using HBcat (catecholborane) by Rh(acac)(P-P) (acac = acetylacetonate) catalysts. In fact, the rhodium compounds **40** (R = H, P-P = dippe, 1,2-bis(diisopropylphosphino)ethane) catalyzed the hydroboration of 4-vinylanisole using HBcat to selectively afford the unusual branched product.[61] The catalysts having a

t-butyl-substituted arylspiroboronate ester ligand (R = *t*Bu, P-P = dppm, 1,1-bis(diphenylphosphino)-methane; dppe, 1,2-bis(diphenylphosphino)ethane) were less selective due to the formation of dehydrogenative borylation reaction products.[62] In contrast. the related zwitterionic iridium-diphosphine complexes **41** catalyzed the hydroboration of vinylarene derivatives with HBpin (pinacol borane) to selectively afford the corresponding linear hydroboration products.[63]
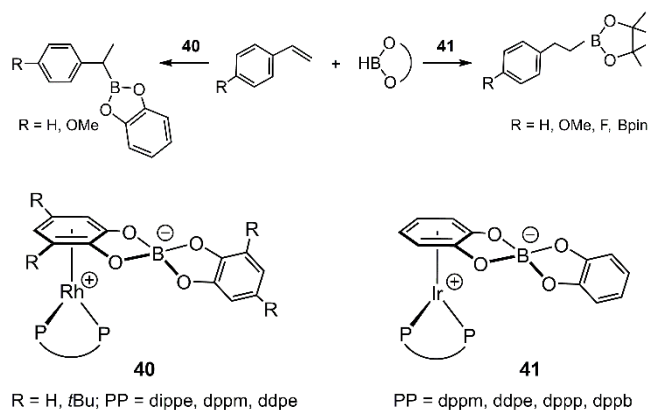
Fig. 15. Zwitterionic rhodium and iridium catalyst for the hydroboration of vinylarene derivatives.

Hydrosilylation reactions. Zwitterionic complexes have also found application in the hydrosilylation of unsaturated derivatives such as aldehydes, alkenes, alkynes or CO_2. For example, the zwitterionic zinc(II) hydride complex **42**, based on a rigid and bulky heteroscorpionate ligand (Fig. 16), efficiently catalyzed the hydrosilylation of aldehydes under mild conditions, featuring excellent functional group tolerance. The reactions were typically conducted in C_6D_6 at room temperature using $PhSiH_3$ (1:3) and a catalyst loading of 1 mol% to afford the corresponding silyl-ether derivatives $(RCH_2O)_3SiPh$ in 5-10 h.[64] On the other hand, the iron(II) zwitterionic complex **43**, featuring an anionic NHC ligand with a malonate backbone, showed good efficiency and excellent chemoselectivity in the hydrosilylation of a range of aldehydes, ketones and aldimine and ketimine derivatives. The reactions
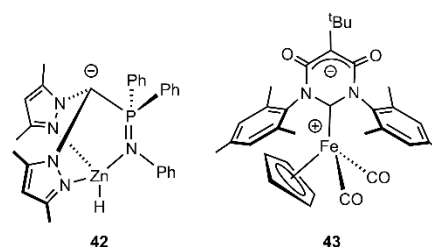
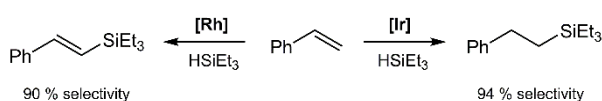Fig. 16. Zwitterionic complexes for the hydrosilylation of unsaturated derivatives.

Fig. 17. Hydrosilylation of styrene by the Stradiotto's indenide-based zwitterionic rhodium(I) and iridium(I) complexes.

were performed under neat conditions ($PhSiH_3$) or in THF (Ph_2SiH_2) using a catalyst loading of 1 mol % under visible light irradiation in order to create coordinative unsaturation in the catalyst precursor by loss of CO.[65]

The hydrosilylation of styrene by the Stradiotto's indenide-based zwitterionic rhodium(I) and iridium(I) catalysts (Fig. 2) showed divergent chemoselectivity. The hydrosilylation of styrene with $HSiEt_3$ at 60 °C in THF using un 5 mol% of the rhodium catalyst afforded the terminal dehydrogenative silylation product with a 90% selectivity whereas the related zwitterionic iridium complex afforded the lineal hydrosilylation addition product with a 94% selectivity under the same conditions (Fig. 17).[66]

The carboxylate-functionalized bis-NHC zwitterionic rhodium(III) catalyst **44** (Fig. 18) efficiently catalyzed the hydrosilylation of terminal alkynes with excellent regio- and stereoselectivity toward the less thermodynamically stable β-(Z)-vinylsilane isomer under mild reaction conditions (Fig. 19). A broad range of linear 1-alkynes, cycloalkyl acetylenes, and aromatic alkynes underwent the hydrosilylation with $HSiMe_2Ph$ under an argon atmosphere in $CDCl_3$ at 333 K with 1 mol % catalyst loading to afford the corresponding β-(Z)-vinylsilanes in quantitative yields in short reaction times. Interestingly, the related cationic compound **45**, featuring an unfunctionalized bis-NHC ligand, was completely inactive under the same reaction conditions, pointing to the impact of the carboxylate function on the catalytic activity of **44**.[67]

In this regard, an ionic outer-sphere mechanism pathway in which the carboxylate fragment of **44** acts as a silyl carrier was proposed, which is supported by DFT calculations, mass spectrometry and labeling studies (Fig. 20). The hydrosilylation mechanism entails the heterolytic activation of the hydrosilane assisted by the carboxylate function to give the hydrido intermediate $[Cp*RhH\{(MeIm)_2CHCOO-SiR_3\}]^+$, which features a silylcarboxylate functionalized bis-NHC ligand. Then, the direct transference of the silylium moiety from the carboxylate group to the alkyne results in the formation of a flat β-silyl carbocation intermediate that undergoes a hydride transfer from the Rh(III) centre to generate the vinylsilane product. The
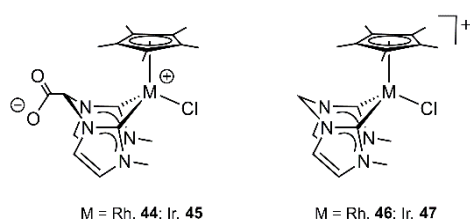
excellent β-(Z) selectivity results from the minimization of the steric interaction between the silyl moiety and the ligand system in the hydride transfer transition state.[67]

The related zwitterionic iridium(III) catalyst **46**, having a carboxylate-functionalized bis-NHC ligand (Fig. 18), was found to be an active catalyst precursor for the selective reduction of CO_2 with hydrosilanes to afford the corresponding silylformate derivatives. The reactions were carried out in acetonitrile-d_3 at 348K under CO_2 (3 bar) using a catalyst loading of 1 mol%. Full conversion of $HSiMe_2Ph$ to the corresponding silylformates was accomplished in less than two hours. However, the reaction proceeded much slower with bulky hydrosilanes such as $HSiMePh_2$ for which 8 h were required, probably due to the steric hindrance around the Si–H bond. In sharp contrast, the carboxylate-free iridium(III) species **47** was much less efficient affording only a 39 % conversion in the hydrosilylation of CO_2 with $HSiMe_2Ph$ after 6 h under the same reaction conditions. Therefore, the uncoordinated carboxylate moiety at the linker of the bis-NHC ligand in **46** seems to play a role on the mechanism. The proposed reaction mechanism, substantiated by DFT calculations, also entails a pre-activation step of the hydrosilane leading to the catalytic active species. As it has been shown before, the high oxophilicity of silicon in combination with the presence of an available oxygen atom in the uncoordinated carboxylate group allow the activation of the Si–H bond leading to the iridium(III) hydride species, which actually is the catalytic active species, with concomitant formation of a silylcarboxylate moiety at the linker of the bis-NHC ligand. Then, hydride transfer to the CO_2 molecule affords a formate ligand which is κ^1O-coordinated to the iridium centre. Finally, the silylformate reaction product is generated by means of a σ-complex assisted metathesis (σ-CAM) between the Ir–O bond of the metallic complex and the Si–H bond of the hydrosilane (Fig. 21). It is worth noting that the transition state leading to product formation displays a Cp* ligand η^1-coordinated which is stabilized by an acetonitrile solvent molecule.[68]

Fig. 18. Zwitterionic rhodium and iridium(III) complexes based on carboxylate-functionalized bis-NHC ligands and related cationic complexes with unfunctionalized bis-NHC ligands.
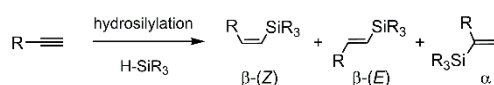

Fig. 19. Possible vinylsilane products in the hydrosilylation of terminal alkynes.
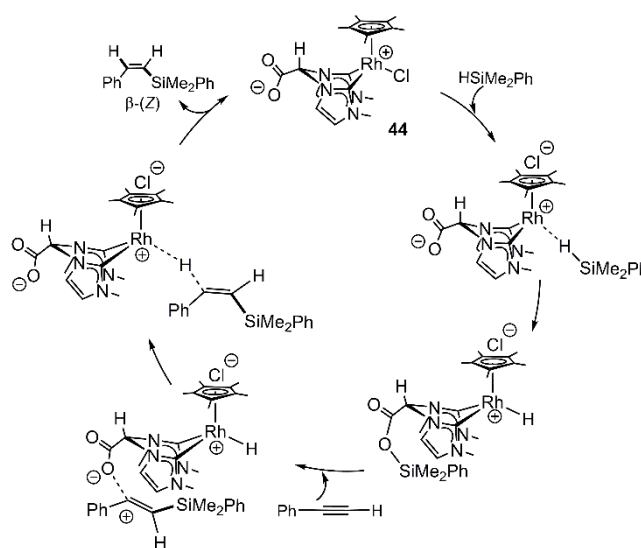

Fig. 20. Proposed mechanism for the β-(Z) selective hydrosilylation of alkynes catalyzed by **44**
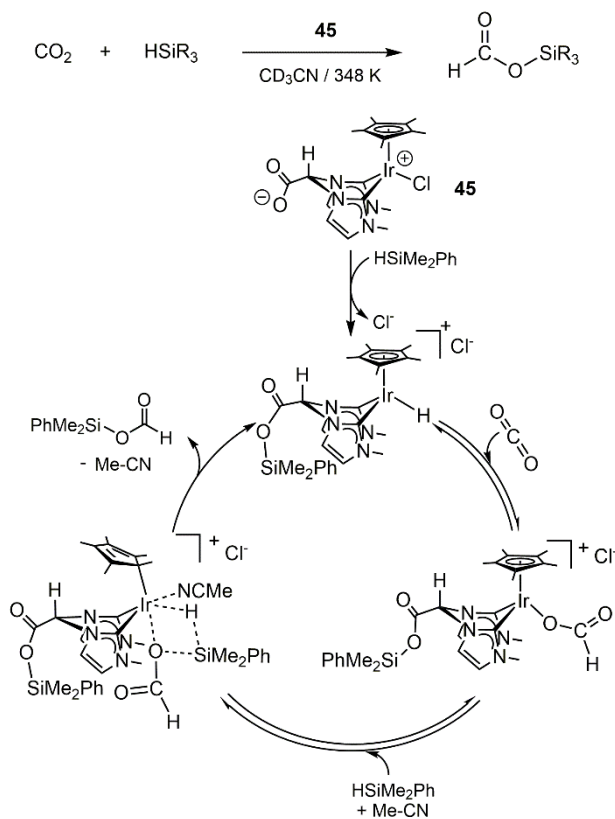
Fig. 21. Proposed mechanism for the hydrosilylation of CO_2 catalyzed by **41**.

The zwitterionic compound **46** has revealed as an efficient catalyst for the dehydrogenative silylation of secondary amines to afford silylamine derivatives with the release of molecular hydrogen (Fig. 22). The reaction of secondary amines HNR_2 containing cyclic or acyclic aliphatic substituents with $HSiMePh_2$ in the presence of 1 mol% of **46** in acetonitrile-d_3 at 348 K gave conversions close to 95% into the corresponding silylamines, $Me_2PhSi-NR_2$, within 10 h. The addition of CO_2 (3 bar) to the solutions containing the freshly prepared silylamines at 298 K allows for the quantitative formation of the corresponding silylcarbamates, $Me_2PhSiOC(O)NR_2$, resulting from the insertion of CO_2 into the Si-N bond of silylamines (Fig. 22).[68]

DFT calculations on the reaction mechanism support a direct amine silylation mechanism through a concerted process which is depicted in Fig. 23. The first step consists of the ligand exchange between the chlorido ligand and the hydrosilane to afford the catalytic active species. Then, the nucleophilic attack of the amine nitrogen atom to the η^1-coordinated
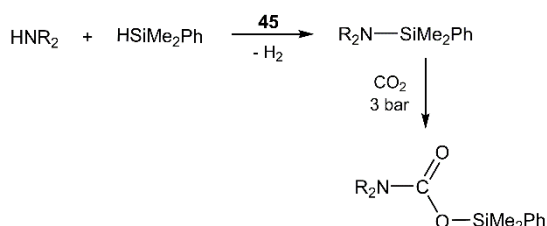

Fig. 22. Dehydrogenative silylation of secondary amines and formation of the corresponding silylcarbamates.

hydrosilane according to a S_N2 type mechanism results in the formation of the zwitterionic hydrido intermediate $[Cp*IrH\{(MeIm)_2CHCOO\}]$ with the release of the silylammonium, $[Me_2PhSi-NHMe_2]^+$, species. Proton transfer from the N-H bond of the silylammonium to the hydride results in the elimination of the silylamine reaction product and formation of an iridium-dihydrogen zwitterionic intermediate. Finally, the catalyst is regenerated by release of molecular hydrogen and the subsequent η^1-coordination of a molecule of hydrosilane. It was found that the dehydrogenative coupling of pyrrolidine with $HSiMe_2Ph$ under low CO_2 pressure (1 bar) catalyzed by **47** showed a comparable product selectivity to that of **46**, thereby suggesting that the carboxylate moiety at the bis-NHC ligand in **46** plays a minor role in the mechanism, which is agreement with the DFT calculations.[68]
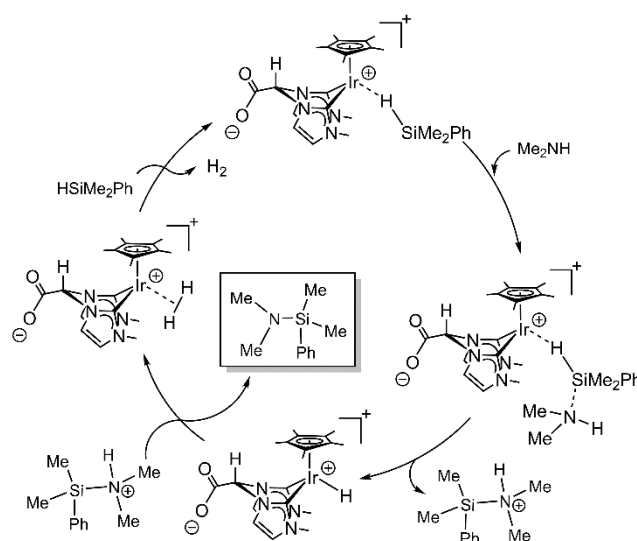

Fig. 23. Proposed mechanism for the dehydrogenative silylation of secondary amines catalysed by **41**.

Miscellaneous applications

The zwitterionic Rh(nbd) complex **48**, based on a borate-containing anionic bidentate chiral ligand with pholane scaffold, was reported to catalyze the asymmetric carbon-carbon bond activation of cyclobutanones (Fig. 24).[69] Remarkably, a range of cyclobutanones with tethered olefins were efficiently transformed into the corresponding chiral bicyclic ketones in dichloroethane at 90 °C a 10 mol% of catalyst. Moderate to good isolated yields were attained with enantiomeric ratios up to 91:9.

The water-soluble carboxylate-functionalized bis-(NHC) zwitterionic iridium(I) and iridium(III) compounds, **36** and **46** (Fig. 12 and 18, respectively) efficiently catalyzed water oxidation using ammonium cerium(V) nitrate (CAN) or sodium periodate as sacrificial oxidants. Excellent yields with TOF_{50} numbers up to 1000 h^{-1} were achieved using CAN as electron acceptor at [CAN]/[Ir] ratios higher than 700. The similarity of

the oxygen evolution profiles at moderate oxidant/catalyst ratios for both catalyst precursors in combination with experimental studies evidenced that both catalyst precursors were transformed into the same active molecular species resulting from the degradation of the hydrocarbon ligands.[70] A mechanism involving high-valent $Ir^{III}/Ir^{IV}/Ir^{V}$ intermediate species stabilized by the carboxylate functionalized bis-NHC ligand was proposed based on the observation of the of the hydroperoxo species $[Ir\{(MeIm)_2CHCOO\}(OOH)(H_2O)_x]^+$ in the mass spectra of the reaction of **36** with CAN.
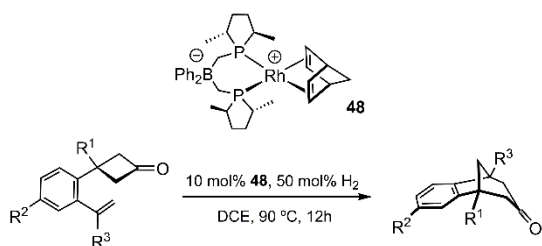

Fig. 24. Carbon-carbon bond activation of olefin-tethered cyclobutanones catalyzed by the zwitterionic rhodium complex **43**.

The zwitterionic octahedral rhodate(III) complex **49**, featuring two 1-butyl-2-diphenylphosphino-3-methyl imidazolium ligands, has found application in olefin hydroformylation (Fig. 25). Hydroformylation of neat oct-1-en in presence of water (CO/H_2 (1/1), 4.0 MPa, 0.05 mol % Rh) afforded 97% conversion in 2 h with 82 % aldehyde selectivity and a linear to branched ratio of 2.2.[71] This catalyst in the presence of an hemilabile P,N ligand and a functionalized ionic liquid allows the biphasic hydroformylation of oct-1-ene. The catalytic system could be recycled for 7 runs with decreasing TOF values while maintaining good selectivity for aldehydes.[72]
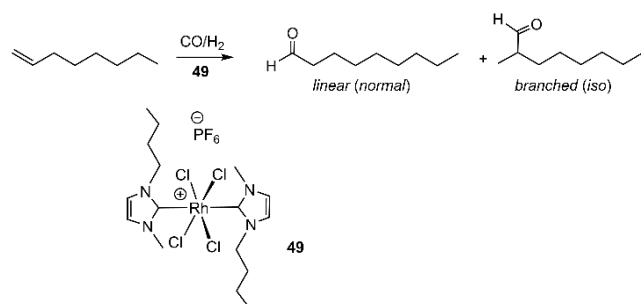

Fig. 25. Oct-1-ene hydroformylation catalyzed by the zwitterionic rhodium compound **49**.

Anionic NHC ligands containing a weakly coordinating borate moiety (WCA-NHC) have also been applied to the design of zwitterionic gold(I) catalysts (Fig. 26). Compound **50** bearing a labile tetrahydrothiophene (tht) ligand efficiently catalyzed the skeletal rearrangement of a 1,6-enyne model compound to selectively afford the 1-vinylcyclopentene derivative in only 5 min (1 mol % catalyst).[73] On the other hand, the SMe_2 complex catalyzed the hydration of alkynes without the need for silver and Bronsted acid additives. A range of terminal and internal alkynes were transformed into the corresponding carbonyl compounds,

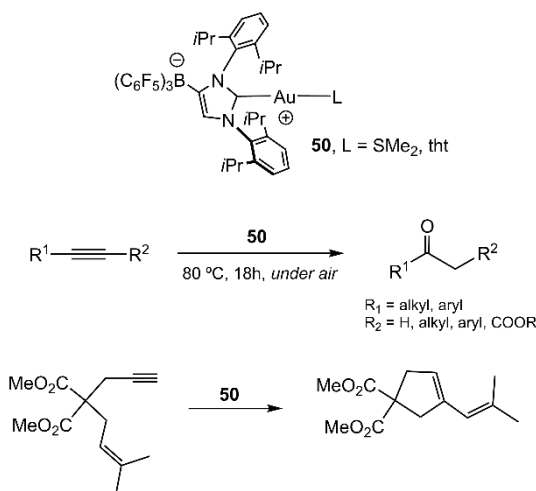aldehydes and ketones, respectively, in a mixture of 1,4-dioxane and water (2:1) at 80 ºC at 1 mol% catalyst loading.[74]

Fig. 26. Hydration of alkynes and skeletal rearrangement by zwitterionic gold catalysts **50**.

Summary and future perspectives

The field of catalytic applications of transition metal-based zwitterionic complexes has been expanded considerably in recent years. Although progress has been made in traditional catalytic applications such as CO-ethylene co-polymerization, phenylacetylene polymerization, olefin hydrogenation and transfer hydrogenation, or the hydrofunctionalization of unsaturated substrates, the last years have witnessed the development of novel catalysts for new applications such as the carbonylative polymerization of cyclic ethers, the asymmetric hydrogenation of unfunctionalized olefins, the hydrogenation of hindered alkenes, or cross coupling reactions. However, the greatest advances have been made in the field of hydrogenation/dehydrogenation reactions related to energy applications, in particular, the utilization of liquid organic hydrogen carriers for hydrogen storage. In this context, zwitterionic catalysts for the hydrogenation of CO_2 and the dehydrogenation of formic acid and N-heterocycles have been recently reported. Also, of great interest has been the development of zwitterionic catalysts for the functionalization of CO_2 with amines and hydrosilanes and the valorization of polyfunctional bio-based feedstocks by transformation into useful chemicals, such as the dehygrogenation of glycerol to lactic acid, a versatile platform chemical with a rich portfolio of applications, or the reduction of levulinic acid into γ-valerolactone.

From the point of view of catalyst design, the placement of anionic groups at the periphery of the coordination sphere of the metal centre remains a well-established strategy that in favourable cases allows the preparation of water-soluble zwitterionic complexes. However, the potential of anionic NHCs ligands for the preparation of zwitterionic complexes is remarkable, although the study of their applications in

catalysis is yet to be developed. Interestingly, a step forward in catalyst design has been the location of anionic groups in the vicinity of the metal centre. This configuration confers hemilabile properties to the ligand and allows stabilization of catalytic intermediates by simple changing the coordination mode of the ligand. In addition, these anionic groups have the potential to behave as reactive sites and assist non-classical activation pathways that have shown to be relevant in hydrogenation and hydrosilylation reactions. In this context, experimental mechanistic studies supported by theoretical calculations should guide the design of new catalysts with the ability to promote unconventional mechanisms for particular catalytic applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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