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## Carbenes and Nitrenes

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► **To cite this version:**

Emmanuel Gras, Stefan Chassaing. Carbenes and Nitrenes: Chapter 4. Mark G. Moloney. Organic Reaction Mechanisms 2019: An annual survey covering the literature dated January to December 2019, Wiley, pp.141-177, 2023, Organic Reaction Mechanisms Series, 9781119608271. 10.1002/9781119608288.ch4 . hal-03852542

**HAL Id: hal-03852542**

**<https://cnrs.hal.science/hal-03852542>**

Submitted on 15 Nov 2022

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## Chapter 4

### Carbenes and Nitrenes

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### Reviews

The rich metal-free chemistry of tosylhydrazones has been covered illustrating the synthetically usefulness of these precursors of diazo compounds and subsequent carbenes via the Bamford-Stevens reaction.<sup>1</sup> Applications for the synthesis of numerous heterocycles as well as the generation of diverse carbon to main group elements bonds are given illustrating either the carbene chemistry or the sulfonyl anion surrogate characters of these tosylhydrazones. A general review has appeared on catalyst design assisted by computations featuring some examples of carbenes acting either as organocatalysts or *in situ* generated reagents in metal catalyzed reactions.<sup>2</sup> Illustration of the mechanistic insights by quantum

modeling are especially provided in the field of NHC catalyzed CO<sub>2</sub> reduction by silane with computations highlighting a path involving an *in situ* generated NHC imidazolium-carbamate promoting silane activation for hydride transfer to CO<sub>2</sub>. Mechanistic rational for NHC-Ir catalyzed hydrogenation, Rh and Cu catalyzed carbene transfer reactions, formation and reactivity of Au carbenes are also exemplified. Transient carbenes are invoked in the heterogenous ceria and transition metal catalyzed methanation of CO<sub>2</sub> as highlighted in a review on such catalytic processes.<sup>3</sup>

The gold activation of bis alkynes derivatives has been covered and invoked on numerous occasion gold vinylidene complexes.<sup>4</sup>

The prominent impact of stable carbenes (especially NHC and CAAC) for the isolation and characterization of main group atoms and cumulenes has found a detailed illustration in a comprehensive description of chemical bonding of main group elements.<sup>5</sup>

The introduction of carboxylic moieties using CO<sub>2</sub> and catalyzed by copper-NHC complexes has been reviewed.<sup>6</sup> Reactions from arylboronic and alkylborane derivatives as well as through CH activation are described; so are borylative, alkylative and hydrogenative carboxylation of unsaturated compounds. Within a general review dedicated to asymmetric nucleophilic allylic substitution catalyzed by iridium catalysts, the regio- and stereoselectivity outcome of the reaction has been discussed with regard to the nature of the ligand, with a survey of more than 22 ligand scaffolds, 2 being NHC based ligands.<sup>7</sup> Similarly the role of NHC coordinated to palladium has been highlighted for the activation of aryl chlorides, bromide and tosylates for the generation of C–N bonds through Buchwald-Hartwig amination, with a special mention to Pd-PEPPSI precatalysts.<sup>8</sup> Catalytic properties of NHC-containing rhodium complexes has been covered in details.<sup>9</sup> The review carefully details their numerous applications and illustrates the influence of the nature of the carbene upon moving from diaminocarbenes to cyclic alkyl aminocarbenes.

Iron catalyzed cross-coupling has been reviewed from a mechanistic viewpoint incorporating the methods based on NHC iron catalysts, either generated in situ or isolated and structurally well-defined.<sup>10</sup> The latter allowed more detailed investigation of their reactivity in alkyl-alkyl and alkyl-aryl cross-coupling by way of EPR, Mössbauer spectroscopy and X-Ray diffraction (XRD). The role of carbene ligands for iron catalyzed hydrosilylation of carbonyl compounds has been highlighted.<sup>11</sup> The synthesis, coordination and catalytic application of abnormal carbenes complexes derived from triazolium salts featuring a chiral sulfur moiety has been reviewed, with an emphasis on their ability to perform chirality transfer to the metal center and to undergo desulfinylation.<sup>12</sup>

The generation of polymers from diazoacetate has been reviewed detailing the average molecular weight obtained as a function of the diazo activation mode.<sup>13</sup> The latter are achieved mainly by metals or main group catalysts but microwave activation is also encountered. Transition metal assisted synthetic applications of unsaturated carbene has been reviewed comprehensively, providing examples of transformations of diverse complexities leading to carbo- and heterocycles, functionalized unsaturated compounds, hydration and reduction products.<sup>14</sup> NH insertions of  $\alpha$ -diazocarbonyl have been reviewed in Chinese, covering transition metal based transformations as well as enzymatic or organo-catalyzed examples.<sup>15</sup> Difluoromethylation methods have been covered, involving a significant body of references based on difluorocarbenes.<sup>16</sup> Numerous examples have been provided illustrating the various precursors of the difluorocarbene intermediate. Applications are illustrating not only difluoromethylation but also difluoromethylthiolation using thiourea or elemental sulfur. Asymmetric cyclopropanations and Wolff rearrangement-based transformations have been covered from the point of view of photochemical activation of diazo compounds in the presence of transition metals or organocatalysts.<sup>17</sup>

In a review covering the chemistry of propargylic alcohols, various references are made to carbenes as (i) intermediates formed from the alkyne in the presence of transition metal; (ii) NHC as organocatalysts in reactions with isocyanates; (iii) electrophilic rhodium-carbenes reagents *en route* to amino-furans.<sup>18</sup> The transition-metal assisted skeletal editing has been covered highlighting potent transient roles of carbenes in both ring contraction and ring expansion in aromatic rings.<sup>19</sup> Although their intermediacy in arene-to-fulvene transformation remains questionable, the role norcaradiene in Buchner type reaction is outlined.

Numerous reviews have appeared on the use of nucleophilic carbenes as organocatalysts.

A first one deals with the umpolung reaction of aldimines involving aza-Breslow intermediates, and features extensive description of the catalytic cycles of the different reactions considered.<sup>20</sup> Enantioselective examples are provided. Within a general review dealing with the equilibrium acidity of organocatalysts, a section has been specifically dedicated to the cationic heterocycle/NHC equilibrium.<sup>21</sup> Triazolium salts are showing the highest acidities among the precursor considered, by many orders of magnitude compared to thiazoliums and imidazoliums. The role of NHC has been illustrated in a review dealing with multicomponent reactions initiated by nucleophilic addition.<sup>22</sup> NHC are more precisely shown to behave either as stoichiometric reagents or as catalysts.

The nitrene generation by iron catalysis and their subsequent involvement in CH amination has been overviewed with dichotomy between the single-electron transfer approaches and the closed-shell type nitrene transfers.<sup>23</sup>

The involvement of isolable silylene in transition metal catalyzed reaction has been covered, describing the various class of silylene ligands, selected successful examples of application, comparison with phosphines and NHCs.<sup>24</sup> Chemo-, regio- and stereoselectivities of relevant transformations are highlighted and paralleled with the electronic natures of the silylene ligands which can prompt them to cooperative participation in the catalytic transformations.

## Generation, Structure and Reactivity

The decomposition of propylamine and propylammonium in the gas phase has been investigated by DFT and composite quantum chemistry methods.<sup>25</sup> Among the 14 pathways explored, 2 were involving carbenes but were not found to be energetically favored.

The generation of NHC featuring an exocyclic N-boryl substituent has been achieved by deprotonation of the corresponding imidazoliums **(1)** and **(2)** (Scheme 1).<sup>26</sup> N,N'-diborylimidazolium proved unstable toward deprotonation leading to the precursor of **(2)** illustrating the easy N to C migration of the boryl substituent. The NHC derived from **(1)** and **(2)** could be characterized by in situ NMR and trapped with different metal fragment as well as elemental selenium.

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### Scheme.1

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The photoinduced generation of NHC by reaction of 1,3-bis(mesityl)imidazolium tetraphenylborate and isopropylthioxanthone **(3)** upon irradiation at 365 nm has been reported.<sup>27</sup> The reaction has been shown to proceed through electron transfer from BPh<sub>4</sub><sup>-</sup> to an excited state of **(3)**, generating the radical anion from **(3)** and thus enabling the deprotonation of the imidazolium to generate the NHC.

The generation of an osmium-bound vinylidene has been invoked in the course of the metallafulvenallene **(4)** from osmapentalyne **(5)** with terminal alkynes (Scheme 2).<sup>28</sup> The reaction occurs through methoxide addition to the triple bond of **(5)** with concomitant chloride displacement from osmium. The coordination of the alkyne then promotes the isomerization to the bound vinylidene which is further attacked by another methanol promoting access to **(4)** after ring opening and ester coordination. A method has been developed to titrate the number of carbenes generated in the course of heterogeneous molybdenum and tungsten oxide catalyzed metathesis of ethylene with 2-butene by determining

the molar amount of propene formed which correlates the molar amount of metal carbenes formed.<sup>29</sup>

Various reports have been dealing with the generation of carbene bound to transition metal. On the one hand a gold(I) carbene complex has been obtained through first insertion of a diazo derived carbene into the AuCl bond providing a carbenoid that was converted to the carbene by chloride abstraction with GaCl<sub>3</sub>.<sup>30</sup> Dimerization and trimerization of the carbene fragment have been shown to lead to stilbene and cyclopropanes in moderate to good yields. The formation of furan from enynones catalyzed by [Cp\*RuCl]<sub>4</sub> in the presence of hydrogen is representing another example of metal-carbene generation, but here a thorough investigation allowed to identify two reaction paths leading to the furan.<sup>31</sup> A first one arises from  $\pi$ -acid catalytic ring closing to a ruthenium alkylidene furan which formation has been nicely and unambiguously established by XRD. This carbene could be either hydrogenated to the methylene derivative or oxidized under air atmosphere to provide the ketone. The second mechanistic path has been shown to occur through a gem-dihydrogenation of the alkyne, providing the Ru-carbene substituted with an enone which then undergoes a ring closure to the furan. Here again relevant experiments are strongly supporting the proposed mechanism.

Computations have shown that the introduction of fluoride substituents on CAAC as in (6) and (7) significantly lowers the  $\pi$ -LUMO promoting some bonding interaction between the carbene center and the  $\alpha$  carbon, and stabilizing a radical with the unpaired electron in the  $\pi$  orbital (scheme 2).<sup>32</sup> From these considerations computations have been carried on CAAC dimers with C2, C4 and phenylene spacers, exhibiting a diradical character which makes these dimers potential candidates to complete singlet fission, opening fruitful application for organic photovoltaic devices.

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**Scheme.2**

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Oxycarbenes substituted by main group elements are attracting increasing interest. Silyloxycarbenes, iconic examples of such oxycarbenes, have been explored from a computational point of view using dispersion-corrected DFT.<sup>33, 34</sup> Singlet-Triplet energy gaps, enthalpies of hydrogenation of the carbene (leading the silyl ether of the corresponding primary alcohol either directly with H<sub>2</sub> or via protonation and hydride transfer) have been calculated. Results suggested a stabilization of the carbene upon moving from alkyl to aryl to amino substituent at the carbene center and an expected favored singlet state.

Mesoionic carbene (**8**) has been shown to react with 9-BBN to generate a carbene borane complex (**9**) able to reduce CO<sub>2</sub> from air, thus at low CO<sub>2</sub> concentrations, both in solution and in the solid state.<sup>34</sup> The reactivity has been well supported by extensive spectroscopic investigation and X-Ray crystallography correlated with high level DFT calculations.

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### Scheme.3

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## Carbenes in Coordination Chemistry

The coordination chemistry of carbenes, especially NHC, is widely dominated by the formation of transition metal complexes but not only restricted to this. The formation of carbene-borane complexes have found numerous applications in the recent years and allowed to identify unprecedented reactions mechanisms. This is here illustrated in the formation of (**10**) which were obtained by addition of a Grignard reagent on the corresponding chloro-borane and happened with high diastereoselectivities.<sup>35</sup> EPR spectroscopy coupled with DFT analysis strongly supported the formation of a radical anion of the chloro-borane through a single electron transfer from the Grignard which upon heterolytic cleavage generated the boron centered radical which recombine with the organic fragment of the Grignard to provide (**10**) in an overall S<sub>RN</sub>1 process. Chiral NHC-borenium complexe (**11**) have been involved in a frustrated Lewis pair based catalyzed reduction of N-alkyl ketimines in high conversion and

yield and *ees* up to 86%.<sup>36</sup> Cyclic alkyl amino carbenes have been found to complex tin(II) dihalide and cyclopentadienyl tin halides (**12**) in good yields.<sup>37</sup> Although stable in the solid state, the cyclopentadienyl complexes were found to be in equilibrium with the stannocene and carbene tin dihalides in solution according to a stepwise mechanism as suggested by spectroscopic observations and supported by DFT computations.  $\alpha$ -Boryl ester (**13**) was obtained in a swift fashion by iodine mediated reductive addition of NHC-BH<sub>3</sub> to unsaturated ester.<sup>38</sup> This transition metal free transformation was found of high scope and showed excellent diastereoselectivities from chiral ester, giving access after reduction of the ester and oxidation of the C–B bond to chiral diols in high yields (65% overall) and *ees* (97%).

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#### **Scheme.4**

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Transition metal complexes featuring a carbene ligand (predominantly N-Heterocyclic Carbenes) have found many application for chemical transformations, essentially of interest in general organic synthesis. Within this frame alkylation from alcohol has been illustrated. Manganese complexes such as (**14**) have been involved in the monoalkylation of anilines by alcohols at room temperature in good to excellent yields and with a wide scope.<sup>39</sup> The same group has expanded the method to the  $\alpha$ -alkylation of ketones, using the same catalyst (**14**), once again with high yields and wide scope including an extension to the Friedländer synthesis of quinolines.<sup>40</sup> The synthesis of substituted tetrahydrofurans and tetrahydropyrans has been achieved with the catalytic assistance of the cationic NHC-iridium complex (**15**) promoting the cyclodehydration of diols.<sup>41</sup> A mechanistic rationale has been proposed based on Hammett correlation and kinetic isotope effect as well as cross-over and trapping experiments. The mechanism has been shown to highly depend on the electronic properties of the substrates. The dehydrogenation of 1-phenylethanol using (**15**) has been computationally explored highlighting that the dehydrogenation step occurs in an inner-sphere fashion, while the rate determining step is the formation of H<sub>2</sub> from the iridium hydride complex and the

pendant alcohol function.<sup>42</sup> A series of iridium complexes (**16**) featuring a NHC ligand fused with two oxazolines has been applied to the asymmetric transfer hydrogenation of unsaturated carbonyl compounds, providing the reduced compounds in good to excellent yields albeit with poor *ees*.<sup>43</sup> The cationic heteroleptic copper complex (**17**) has been obtained from the parent NHC-copper hydroxide complex.<sup>44</sup> (**17**) was found to promote, after deprotonation of the pendant alcohol both diastereoselective alkyne reduction to the *Z* alkene, and the conjugate reductions of unsaturated ketones and esters.

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### Scheme.5

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Similar diastereoselective semi-hydrogenation of alkynes have also been performed using bis(NHC) pincer complex of cobalt (**18**).<sup>45</sup> (**18**) has also been able to perform semi-parahydrogenation of alkynes and unsaturated ester at 37 °C under 4 atm. The influence of the nature of the ligand in cobalt catalyzed hydrogenation of ketones has been investigated computationally by DFT, and pincer containing NHC proved superior to those featuring phosphines.<sup>46</sup> The heterolytic cleavage of H<sub>2</sub> has been shown to be the rate determining step which is strongly impacted by the ligand, while the hydride transfer to the ketone appears as a facile process not strongly affected. A new mode of H<sub>2</sub> activation has been reported using the manganese (I) complex (**19**).<sup>47</sup> The selective deprotonation of the methylene combined with a formal interconversion between  $\lambda^3$  and  $\lambda^5$  phosphorous appeared to be key features for this activation as illustrated by DFT calculations. The high activity of Amino-NHC manganese complex (**20**) in transfer hydrogenation of ketones with isopropanol was found to be related to the presence of the NH bond in the coordination sphere of the metal.<sup>48</sup> The introduction of a pyridine substituent on NHC involved in ruthenium coordination as in (**21**) have proved to be key to efficiently achieve transfer hydrogenation of aromatic ketone.<sup>49</sup> DFT calculations have indicated that the pyridine promotes an easier formation of catalytically active species by

stabilizing the non-saturated metal center after CO release. This applied to imidazolylidenes as in (21) and to triazolylidenes.

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### Scheme.6

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The serendipitous formation of the NHC ruthenium complex (22) from (23) has provided a catalyst enabling the base-free hydrogenation of esters.<sup>50</sup> DFT calculation have shown that the catalytic cycle is potentially common for (22) and (23), the latter requiring a base activation. Tricoordinated zinc complexes featuring medium ring NHC (24) have been characterized and proved to enable terminal C–H borylation of alkynes as well as hydroboration of alkene, performing a one pot terminal diborylation of alkynes in an efficient fashion.<sup>51</sup> Detailed characterization of numerous complexes and DFT calculations have been performed to provide a significant support to the proposed mechanism. Rhodium NHC complex (25) proved competent for CH borylation of 2-substituted pyridines under blue light irradiation in the presence of B<sub>2</sub>pin<sub>2</sub>.<sup>52</sup>

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### Scheme.7

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Copper-NHC complex encapsulated into cyclodextrin have been successfully engaged in the carboboration of alkynes with B<sub>2</sub>pin<sub>2</sub> and and alkyl iodide, high selectivities being achieved for the borylation of the terminal position, presumably as a consequence of the reaction being confined in the cavity of the cyclodextrin.<sup>53</sup> Interestingly intramolecular carboboration proceeded smoothly with similar regioselectivities. Ruthenium-NHC complex (26) has exhibited high efficiencies and Z-diastereoselectivity in the hydroboration of terminal alkynes with HB(dan), thus by a trans addition.<sup>54</sup> The reaction proved much less diastereoselective for internal alkynes such as diphenylacetylene. The mechanism has been shown to arise from the alkyne insertion into a Ru–B bond through a systematic isolation of relevant intermediates of the catalytic cycle. Cyclometallated NHC platinum complexes (27) have been shown to

undergo, in the presence of primary silanes, a formal insertion of silicon into the C–Pt bond leading to **(28)**.<sup>55</sup> The reaction could be extended to other cationic bis NHC compounds and mechanistic investigations highlighted an initial formation of a cationic platinum silane complex with concomitant release of H<sub>2</sub>. Complex **(29)** has been synthesized and successfully engaged in the catalytic hydrosilylation of aldehydes and ketones in the presence of diphenylsilane and tetramethyldisiloxane.<sup>56</sup> The NHC proved to provide an increased stability toward air and moisture allowing **(29)** to be used even in the presence of water.

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### Scheme.8

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The NHC–nickel(0) catalyzed silylation and germylation has been shown to be strongly dependent on the steric bulk brought by the NHC.<sup>57</sup> Indeed in competition experiments stannylation of pentafluorobenzene through C–H activation was always occurring preferentially against hydroarylation of the competing alkene; but lower bulk was required to achieve germylation and silylation, potentially as a consequence of the more difficult  $\beta$ -elimination step to the product. Metal complexes featuring a NHC ligand have been found able to degrade CC bonds as shown in the overall conversion of benzene to H<sub>2</sub> and CO<sub>2</sub> catalyzed by **(30)**, thus representing a mild process for benzene cracking in water at controlled pH in the presence of Ce(IV).<sup>58</sup> Generation of H<sub>2</sub> from water has also been achieved photocatalytically by photosensitizing homoleptic NHC based Ru complexes.<sup>59</sup> Zwitterionic water soluble iridium NHC complexes enabled water oxidation to produce O<sub>2</sub> in the presence of CAN.<sup>60</sup> Although extensive investigation allowed to conclude on the homogeneous nature of the catalytic process rather than the formation of nanoparticles, the detailed catalytic cycle remains substantially hypothetical. DFT calculations have been carried out to investigate the ability of a range of scandium complexes to activate methane, including NHC complexes which were found to exhibit the lowest energy barrier.<sup>61</sup> Bimetallic oxo-bridged iron complexes featuring macrocyclic tetracarbene iron complexes have been found to promote

autocatalytic oxidation of dihydroanthracene by CH activation through disproportionation in acetonitrile, albeit with moderate efficiency.<sup>62</sup> Detailed mechanistic studies including isolation of tetranuclear adducts opened the route to more efficient iron based homogeneous catalysts.

Generation of Ir(III)- and Rh(III)-NHC complexes (**31**) and (**32**) from theophylline derivatives bearing a coordinating substituent have been reported to occur by C-H activation of the C8 position of theophylline.<sup>63</sup> Bis NHC-PEPSI complexes have been designed to catalyze cascade Sonogashira/Cyclization to benzoxazoles and CH activation of benzothiazoles.<sup>64</sup> A range of NHC-Cu-X complexes have been synthesized, characterized and engaged in the CuAAC reaction highlighting that the reactivity of the complexes was strongly related to the nature of the counteranion X, and its trans effect ability.<sup>65</sup> The catalytic cycle was shown to involve a dissociation of the carbene generating the imidazolium and the copper-alkyne complex. NHC-copper azide complex (**33**) has been synthesized, fully characterized and engaged in a range of dipolar cycloadditions leading to copper coordinated triazole and tetrazoles, azide transfer reactions and dimerization.<sup>66</sup>

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### Scheme.9

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A range of NHC-metal complexes have been designed to perform various CO<sub>2</sub> reduction reactions. A first example is a ruthenium terpyridine pyridyl-NHC involved in the electrochemical reduction of CO<sub>2</sub> to CO.<sup>67</sup> Although the Ru complex could exist under two isomeric forms, the one featuring the NHC trans to the activation site of CO<sub>2</sub> was theoretically shown more stable and more efficient to promote the reduction. The zwitterionic bis carbene iridium complex (**34**) has been shown to generate silylformates by hydrosilylation of CO<sub>2</sub> with a range of organosilanes.<sup>68</sup> Supported by DFT calculation, the catalyst activation was shown to involve a transfer of the silyl group to the carboxylate fragment of the ligand backbone, providing an iridium hydride which performs the reduction of CO<sub>2</sub> to the

corresponding formate which after silylation regenerate the hydride complex. Cobalt complex featuring a macrocyclic bispyridyl-biscarbene ligand (**35**) has been synthesized and engaged in the electrocatalytic reduction of CO<sub>2</sub> to CO in a range of solvents (aqueous or organic) using water as proton source.<sup>69</sup> Selectivity and catalytic activity were shown to increase with the ring strain of the macrocyclic structure. Bidentate NHC-phosphine nickel complexes have proved to be excellent catalysts for the generation of acrylate from CO<sub>2</sub> and ethene.<sup>70</sup> Bulky aryl-substituted NHC were found appropriate ligands to perform a Pd-catalyzed cyclopropanation from allyl carbonates and nitrile nucleophiles in the presence of silver salt.<sup>71</sup> Moderate to high enantioselectivities were achieved with imidazolynilidenes. Pincer rhodium complex (**36**) featuring two NHCs has been shown to efficiently promote the isomerization of epoxides to the corresponding ketone in high yields and excellent functional group tolerance.<sup>72</sup> Deuterium labelling experiments supported the intermediacy of a Rh–H complex in a β-hydride elimination/reductive elimination sequence. Among the numerous application of transition metal complexes featuring a NHC, olefin metathesis remains one of the most widely exemplified. Thus the generation of new ruthenium complexes is still an active field of research to tackle a range of synthetic challenges. A first example is the design of DMSO containing ruthenium complexes for ring opening metathesis polymerization of norbornene in the presence of ethyldiazoacetate (EDA).<sup>73</sup> The reaction mechanism was shown to be dissociative, a first dissociation of DMSO allowing the generation of the ruthenium carbene complex with EDA followed by a second dissociation promoting the coordination of norbornene and its subsequent ROMP. DFT investigations have been carried out on a similar reactivity from RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(Py)<sub>2</sub>.<sup>74</sup> In this case the dissociation of a phosphine was found as the initial event allowing coordination of norbornene followed by displacement of the second phosphine by EDA. ROMP of norbornene with dicyclopentadiene has been carried out through *in situ* photogeneration of the active catalyst from bis(mesityl)imidazolium

tetraphenylborate with the inactive ruthenium dimer ( $[\text{RuCl}_2(\text{p-cymene})]_2$ ) and allowed the formation of cross-linked polymers.<sup>75</sup> The photogeneration of the NHC was significantly optimized by the addition of a photosensitizer such as 2-isopropylthioxanthone and irradiation promoted the decoordination of p-cymene, thus exalting the catalyst activity. Olefin chelation has been shown as a stabilizing factor in the context of NHC-based ruthenium metathesis polymerization.<sup>76</sup> In a very detailed investigation, the intercepted intermediates in the chain propagation has been isolated and fully characterized by NMR and X-ray crystallography. They were shown to achieve a lower dispersity by stabilizing the propagating species and decrease the rate of propagation compared to initiation. Such chelation effect has also been investigated on a range of Grubbs Ru-NHC of the 3<sup>rd</sup> generation by varying the sterics of the NHC and the nature of the monomer.<sup>77</sup> The geometry of the latter and the steric bulk were shown to have a synergetic effect allowing the formation of chelated metallacycles leading to a similar outcome on the propagation rate and on copolymerization. Activation of indenylidene-Ruthenium catalyst has been achieved by converting a commercially available indenylidene catalyst featuring two CAAC ligand into a dimeric structure through CAAC abstraction in the presence of CuCl.<sup>78</sup> This transformation allowed to reach similar activities to more conventional but less scalable benzyliene complexes, establishing that the indenylidene is not causing the lack of reactivity which is due to the poor liability of other ligands. Z-selective cross metathesis catalysts have been obtained from ruthenium complexes featuring fluorinated NHC and incorporating a chelating catecholthiolate ligand.<sup>79</sup> Upon extensive optimization of the reaction condition good yields and diastereoselectivities above 94% *d.e.* were achieved. Molybdenum imido alkylidene complexes (**37**) featuring a NHC ligand were found to perform olefin metathesis.<sup>80</sup> Interestingly a combination of experimental and theoretical investigations established that these 16 electrons complexes (either neutral or solvent-stabilized cationic) undergo an associative mechanism, the substrate coordination

preceding the triflate dissociation, thus contrasting with the acknowledged dissociative mechanism observed with the solvent-stabilized Schrock catalysts.

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**Scheme.10**

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Some approaches have also highlighted the impact of NHC coordination on gold chemistry. As such, dinuclear NHC gold complexes have been synthesized, characterized and proved able to release slowly the cationic gold NHC species.<sup>81</sup> Interestingly higher catalyst loading allowed to intercept the enol ether during the hydroalkylation of alkynyl diols while lower catalyst loading yielded the spiroderivatives. NHC-gold complexes have been tethered to  $\beta$ -cyclodextrins using either copper or ruthenium catalyzed alkyne-azide-cycloaddition.<sup>82</sup> A full characterization of the complexes has been achieved and their use and recyclability for the cyclizations of allenes and alkynes in water has been established. Moderate *ees* have been achieved in the cycloisomerizations of hydroxyallenes. A NHC-pyridyl gold complex has been designed to perform an hydrative synthesis of amide from an aromatic alkyne and sodium azide in water.<sup>83</sup> The reaction is a formal insertion of nitrogen into a C–C bond combined with the hydration of the alkyne into the corresponding C=O, and is supposed to occur through a cascade of alkyne hydration with assistance of the pyridyl moiety followed by gold assisted azide attack on the corresponding acetophenone and a Curtius rearrangement. The stabilization nature of NHCs has also been advantageously used to promote the generation of a surface active, air and thermal stable Au<sub>25</sub> nanocluster which proved superior to molecular catalyst for the cycloisomerization of alkynyl sulfonamides.<sup>84</sup> NHC-Nickel tricarbonyl complex has been engaged in the dimerization of phosphalkynes yielding diphosphatetrahedranes (**38**), limiting the oligomerization of phosphalkynes. Varying the NHC structure allowed to isolate intermediates involved in the formation of the tetrahedranes such as the 1,3-diphosphacyclobutadiene complex (**39**). A range of silyl bridged dinuclear cobalt complexes stabilized by the coordination of NHCs have been isolated from the reaction

of cobalt(II)-NHC complexes with phenylsilane.<sup>85</sup> The treatment of the same complex with diphenylsilane provides a dinuclear silylhydridocobalt complex highlighting the influence of the silane sterics on reaction outcome. The sterics of the N-aromatic substituents of ethylene-bridged bis NHC precursors has been shown to be instrumental in the outcome of their reaction with palladium acetate.<sup>86</sup> Indeed the less hindered compounds yielded a homoleptic bidentate complex, whereas the bulkier ones lead to a monocoordinated complex with a pendant imidazolium group. Interestingly an intermediate bulk promoted the formation of a mixture of complexes featuring either a homoleptic bidentate ligand or a tricyclic monodentate ligand (**40**) arising from the reductive elimination of a bidentate heteroleptic normal/abnormal carbenes complex. Detailed computations have been carried out to determine the mechanism of the formation of acyclic diaminocarbene iridium complexes by addition of an amine to an aromatic isocyanide iridium complex followed by insertion of the metal into a C<sub>ar</sub>-H bond.<sup>87</sup>

The great stability of metal-carbene complexes has also led to fruitful application in various fields. A first example is the design of copper and gold complexes featuring a CAAC and a carbazole based dendritic architecture for photoluminescent applications such as OLED.<sup>88</sup> Their high quantum yields and short excited state lifetimes combined with their good solubility and amorphous properties allowed to obtain OLED via a solution process which forecast processing techniques such as inkjet printing to produce flexible OLEDs. It has also been applied for the generation of nanoparticles of copper which were readily accessed in a straightforward approach by combining a NHC-borane compound featuring long alkyl chains with copper mesitylene.<sup>89</sup> Another illustration is the use of purine based carbene (**41**) for palladium complexation and the subsequent biological assessment of these complexes with regards to their antiproliferative activity and pro-apoptotic effects.<sup>90</sup>

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**Scheme.11**

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## Addition/Fragmentation Reactions involving Carbenes

Free carbenes or main group carbenoids reactions

Computational studies have been led on the reaction mechanism of lithium and magnesium carbenoid cyclopropanations.<sup>91</sup> Various reactions between halogen-containing carbenoids and ethylene have been scrutinized and the resulting calculations have revealed a new reaction mechanism. In fact, all reactions have been found stepwise, exoenergetic and with low barriers.

The reactions between electron-deficient dimethyl *E*- and *Z*-2,3-butenedioates and various diaryldiazomethanes have been experimentally and computationally investigated.<sup>92</sup> The product distribution proved to be dependent on the nature of diazo precursor. While the use of diphenyldiazomethane and its 4-methoxylated derivative led to the corresponding cyclopropanes, pyrazoles resulting from a formal [3+2]-cycloaddition have been formed when using (trimethylsilyl)diazomethane. Based on calculations, all reactions have been suggested to take place in a stepwise manner, with the formation of a C-N bond as initial step.

A covalent cross-linking has been found to occur in the gas phase *via* the photoactivation of complexes of diazirine-tagged peptides and various DNA dinucleotides.<sup>93</sup> Mass-spectrometry analyses of the resulting conjugates have shown that the cross-linking mainly occurred in the 3'-nucleotide *via* the formation of an aziridine motif. From a mechanistic viewpoint, the formation of this aziridine has been suggested to take place in a two-step manner, with the nucleophilic addition of the photogenerated peptide carbene intermediates to the 3'-guanine as first step.

Also based on a nucleophilic addition step, the synthesis of a series of dihydropyridines (**42**), corresponding to 2,6-diphenyl-*N*-arylpiperidinium-carbene hybrids, has been successfully achieved.<sup>94</sup> Remarkably, the so-formed hybrids proved to be unique organic (super) electron donors, with three stable and air-stable oxidation states.

The synthesis of novel mesoionic, fused heterocyclic systems (**43**) has been accomplished *via* the simple coupling between malonate or arylacetate esters and 5-bromoimidazo[1,5-*a*]pyridinium salts as carbene sources.<sup>95</sup> Based on mechanistic investigations, a nucleophilic addition of the carbenic centre of a transient NHC to an ester group has been proposed as key step. The nucleophilic addition has been shown to proceed intramolecularly through intermediate (**44**) in the case of malonates, while intermolecularly in the case aryl acetates.

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**Scheme.12**

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The nucleophilicity of other carbenes has been efficiently exploited for the formation of C-B adducts as key intermediates or products. While carbene borane adducts (**45**) and (**46**) have been suggested as key intermediates during the C-C bond functionalization of allyl alcohols,<sup>96</sup> and the ring-expansion of a 1,4,2,3-diazadiborinine,<sup>97</sup> the carbene borane adduct (**47**) has been successfully synthesized and used in imine hydrogenation.<sup>98</sup> In a similar way, carbene diborane adducts (**48**) have been shown to undergo a spontaneous trans-selective transfer hydrogenation with dimethyl borane.<sup>99</sup> Based on calculations, the unprecedented trans-selectivity has been rationalized by a stepwise mechanism involving a  $[\mu\text{-H-B}_2\text{R}_2\text{L}_2]^+[\text{Me}_2\text{NBH}_3]^-$  ion pair as key intermediate.

Other carbene-small molecule adducts have been reported. In the case of dinitrogen, its efficient activation by persistent carbene pairs has been computationally demonstrated using methylene as model carbene,<sup>100</sup> whereas the carbon-boron frustrated Lewis pair (**49**) has been shown to enable the dinitrogen activation both thermodynamically and kinetically.<sup>101</sup> Both works correspond to ‘green’ metal-free approaches.

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**Scheme.13**

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In the case of carbon dioxide, two works dealing with mechanisms related to its reduction have been reported. On one hand, the mechanism of carbon dioxide electroreduction in

imidazolium-based ionic liquids has been scrutinized by means of cyclic voltammetry, in operando infra-red and sum-frequency generation spectroscopies.<sup>102</sup> The obtained spectroscopic results have evidenced the formation of the carbene-carbon dioxide adduct (**50**) during the electrocatalytic process. On the other hand, the carbon dioxide photoreduction on defected anatase TiO<sub>2</sub>(101) has been computationally studied using DFT techniques.<sup>103</sup> In addition to other non-carbene pathways, the resulting calculations have revealed a carbene-like deoxygenation pathway to form methane.

The NHC-radical adduct (**51**) has been employed as a probe to support the efficient photoinduced release of NHC from a mixture of isopropylthioxanthone as photosensitizer and an air-stable imidazolium salt as NHC precursor.<sup>104</sup> Accordingly, such a mixture has been shown to be a new class of NHC photogenerator enabling polyurethane, polyester and ROMP polymers synthesis.

The formation of ylides through an addition reaction exploiting here the electrophilic behavior of carbenes has been demonstrated as key step in the synthesis of tetrahydrofuran derivatives,<sup>105</sup> and *IH*-1,2,4-diazaphospholes.<sup>106</sup>

The reaction of difluorocarbene, as electrophilic carbene, and isocyanide, as nucleophilic carbene, has led to the formation of the unprecedented difluoroketinimine (**52**) as analogue of the elusive difluoroketene.<sup>107</sup> The so-formed difluoroketinimine proved to smoothly undergo [2+2] cycloaddition with imine, thus furnishing valuable  $\alpha,\alpha$ -difluoro- $\beta$ -amino amides.

Other valuable compounds, including  $\gamma,\delta$ -unsaturated ketones and skipped dienes possessing both a quaternary carbon centre, have been selectively prepared from a single cyclopropane-based  $\alpha$ -silylated carbinol intermediate (**53**), depending on reaction conditions.<sup>108</sup> The selective access to skipped dienes, using dibutylmagnesium as carbometallating agent, has been mechanistically rationalized by the involvement of the carbene (**54**) as key intermediate, which is formed prior to an addition and a  $\beta$ -fragmentation as last steps.

By means of computational methods, a predictive physical model of the self-assembly of halogen carbene layers on graphene has been postulated.<sup>109</sup>

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## Scheme.14

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### Transition metal-assisted reactions

Efforts are still underway to extend the scope of transition metal-catalyzed olefin cyclopropanation reactions, with rhodium, gold and iron as the main reported metals.

In the case of rhodium, the intermolecular cyclopropanation of unactivated olefins has been achieved under Rh<sup>III</sup> catalysis using *N*-enoxyphthalimides as rhodium carbene sources.<sup>110</sup> Based on mechanistic studies, the required metal carbene intermediate has been suggested to be formed by initial C-H activation of the alkenyl moiety of the *N*-enoxyphthalimide partner. By exploiting the well-established potential of the 1-tosyl-1,2,3-triazole as rhodium carbene source, the Rh<sup>II</sup>-catalyzed synthesis of cyclopropano[*cd*]indoles (**55**) has been accomplished from cyclohexa-2,5-dienones (**56**, X = N).<sup>111</sup> Shifting from a nitrogen to an oxygen atom (**56**, X = O) as connecting linker changed the reaction outcome with the formation of benzofuran derivatives. In both cases, the corresponding  $\alpha$ -imino rhodium carbene has been suggested to be formed as the key intermediate, prior to an intramolecular cyclopropanation or an oxy-Cope rearrangement depending on the linking heteroatom X.

The divergent synthesis of three structurally complex tetracyclic indolines has been achieved from the tryptamine-based precursor (**57**) using a Rh<sup>II</sup>/In<sup>III</sup> catalytic system.<sup>112</sup> Mechanistic studies have revealed that the reaction starts with the Rh<sup>II</sup>-catalyzed cyclopropanation of the alkene moiety of (**57**) and the so-formed cyclopropane derivative then evolves to the polycyclic scaffolds under In<sup>III</sup>-catalysis. Still using rhodium, the synthesis of chiral fluorocyclopropanes has been achieved from  $\alpha$ -fluoroacrylates and a diazo ester as carbenoid source.<sup>113</sup> The chiral Rh<sup>II</sup>-based catalyst (**58**) has been found to enable this

challenge and a computational mechanistic investigation has been led to rationalize the peculiar reactivity of the donor-acceptor diazo compounds with electron-deficient  $\alpha$ -fluoroacrylates.

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### Scheme.15

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Regarding gold, a series of novel gold sulfonium benzyliide complexes (**59**) has been prepared and these thermally stable gold carbenoid species proved to be efficient cyclopropanating agents *via* benzyliidene transfer to alkenes.<sup>114</sup> The di- and enantioselectivities of a Au<sup>I</sup>-catalyzed cyclopropanation reaction between propargylic esters as gold carbene sources and styrene has been computationally studied by means of DFT methods.<sup>115</sup> With the biphenylphosphine (**60**) as chiral ligand, the resulting calculations have evidenced a [2+1]-cheletropic reaction as the stereoselective rate-determining step.

In the case of iron, metalloprotein engineering has allowed the identification of myoglobin-based systems as powerful catalysts for asymmetric olefin cyclopropanation reactions. A particular engineered myoglobin, *i.e.* Mb(H64V,V68A), has been found to enable benzofuran cyclopropanation with excellent efficiency and stereoselectivity.<sup>116</sup> A stereochemical model for this reaction has been formulated by means of computational and structure-reactivity studies. Also efficient for asymmetric vinylarene cyclopropanation, the stereoselective features of this Mb(H64V,V68A)-catalyzed reaction have also been determined in a parallel work.<sup>117</sup> In a similar way, a myoglobin-based system incorporating a redesigned iron-porphyrin cofactor has been identified as an efficient catalyst for the asymmetric cyclopropanation of challenging electron-poor alkenes.<sup>118</sup> Mechanistic studies have revealed a radical reactivity of this catalytic system, thus diverging from the classical electrophilic reactivity of myoglobin. In parallel, DNA/RNA G-quadruplexes have been shown to enhance the catalytic activity of Fe<sup>II</sup>-heme in cyclopropanation reactions.<sup>119</sup>

Copper carbenes (**61**) have been successfully generated from *N*-propargyl ynamides (**62**) as a new source of metal carbenes.<sup>120</sup> Based on mechanistic studies, such donor/donor carbenes have been shown to be involved in a cascade reaction, furnishing chiral tetracyclic pyrroles (**63**) *via* an asymmetric intramolecular cyclopropanation step. DFT studies have been led on a related cycloisomerization reaction leading to cyclopropane sesquiterpenoids.<sup>121</sup> In that case, 1,5-enynes bearing a propargyl acetate moiety have been employed as metal carbene sources.

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### Scheme.16

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The construction of various relevant (hetero)cyclic scaffolds has been achieved *via* a key C-C bond formation step based on a nucleophilic addition to an *in situ* generated metal carbene. Gold catalysis has allowed access to functionalized heterocyclic scaffolds, including chromones,<sup>122</sup> chroman-2-ones,<sup>123</sup> and chromenoquinolines,<sup>124</sup> from the appropriate metal carbene source, while 5-amino-1*H*-pyrrole-3-carboxamide and 2-iodo-1*H*-indene derivatives have been produced under silver and rhenium catalysis respectively.<sup>125,126</sup> Similarly, the construction of  $\gamma$ -butenolides fused with cyclohexanones,<sup>127</sup> and dihydrocyclopenta[*b*]indoles,<sup>128</sup> has been accomplished with diazo compounds as sources of ruthenium, and respectively copper, carbenes. Group 6 alkynyl Fischer carbene complexes have been shown to undergo the vinylogous addition of various *C*-nucleophiles, such as anthrone and 3-hydroxy-2-pyrone.<sup>129</sup> The formation of ketenimines through cobalt-catalyzed reaction between diazo compounds and isocyanides has been reported.<sup>130</sup> Computational investigations have revealed that the formation of C=C bond between both partners starts by the nucleophilic addition of the isocyanide to an *in situ* formed high-valent cobalt carbene.

The reaction outcome of  $\alpha$ -oxo metal carbenes (**64**) generated by *N*-oxide oxidation of alkynes has been shown to be highly catalyst-dependent.<sup>131</sup> While an intramolecular C-C bond formation step has been suggested to take place with zinc-based catalysts, gold-based catalysts have been shown to favor an intermolecular addition of a second equivalent of *N*-

oxide, thus forming a C-O bond. Such a C-O bond formation step has also been suggested for rationalizing the synthesis of gold allyloxysulfonium complexes with a sulfoxide in place of an *N*-oxide as the nucleophilic partner.<sup>132</sup>

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**Scheme.17**

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Similar additions of *O*-nucleophiles to metal carbenes, thus resulting in the formation of oxonium ylides as intermediates, have been efficiently exploited to achieve the synthesis of chiral 2,3-dihydrobenzofurans,<sup>133</sup> and diaza macrocycles,<sup>134</sup> but also to rationalize the mechanism of controlled carbene polymerization.<sup>135</sup> A gold-catalyzed method for preparing indenols has been developed based on an unprecedented vinylogous addition of alcohols to the intermediate gold carbene.<sup>136</sup>

Shifting from *O*- to *N*-nucleophiles, thus from oxonium to ammonium ylides as intermediates, has been also employed as a key tactic to access relevant nitrogen heterocycles, including indolizines,<sup>137</sup> indolo[3,2-*c*]quinolinones,<sup>138</sup> 2-fluoroalkyl-1,3-azoles,<sup>139</sup> octahydro-1*H*-purines,<sup>140</sup> and  $\beta$ -lactams,<sup>141</sup> but also unique ruthenium complexes linked to indole and indoli(zine) moieties.<sup>141</sup>

The chemistry of related onium ylides has been further exploited to access alkylidenephénylthiopropán-2-ones *via* key sulfonium ylides,<sup>142</sup> and selenoketals *via* related selenium ylides.<sup>143</sup>

An unprecedented radical addition to a copper carbene has been exploited as key step for accessing original perfluoroalkanesulfinate esters.<sup>144</sup> This novel radical method has enabled the synthesis of a large scope of perfluoroalkanesulfinate esters under mild conditions.

Allylic sulfones have been found to be powerful partners in cross-metathesis reactions with sterically hindered alkenes.<sup>145</sup> In particular, the first example of a cross-metathesis with a tetrasubstituted alkene has been reported. DFT calculations have revealed the key role played

by the sulfonyl moiety as coordinating site during the [2+2] cycloaddition step leading to the metallacyclobutane intermediate.

## **Insertion/Abstraction Reactions involving Carbenes**

### Free carbenes or carbenoids reactions

The reactivity of photogenerated diphenylcarbene has been found to be controlled by the presence of additional protic molecules.<sup>146</sup> Joint experimental and theoretical investigations have revealed that the reaction pathways highly depend on the nature of the protic molecules. The O-H insertion reaction has been identified as one the most privileged reaction pathways.

The one-step photo-triggered methanol-to-ethanol conversion has been reported for the first time, using an ultra-stable gallium nitride semiconductor as catalyst.<sup>147</sup> Mechanistic studies have revealed the *in situ* generation of methyl carbene as key intermediate which then inserts into a C<sub>sp3</sub>-H bond of methanol, thus resulting in the formation of ethanol. Remarkably, the methanol-to-propan-1-ol conversion has been achieved using the same catalyst by simply adjusting the reaction temperature.

Another C-H insertion reaction has been put forward as key step in order to rationalize the unexpected rearrangement of dilithiated isoindoline-1,3-diols into 3-aminoindan-1-ones.<sup>148</sup>

The B-H insertion reactions of various dihalocarbenes into deprotonated nido-undecaborane (B<sub>11</sub>H<sub>13</sub><sup>2-</sup>) has been experimentally and computationally investigated.<sup>149</sup> The resulting data have allowed to rationalize the different behavior of difluorocarbene compared to dichloro- and dibromo-carbenes.

### Transition Metal assisted reactions

The insertion of transition metal carbenes into C-H bonds remains a powerful tactic in organic synthesis. Diverse intramolecular C<sub>sp3</sub>-H insertion reactions providing 4-membered,<sup>150</sup> 5-membered,<sup>151</sup> and 6-membered *N*-heterocyclic systems have been developed

using palladium and/or ruthenium catalysis.<sup>152</sup> An unprecedented iron-catalyzed intramolecular C<sub>sp3</sub>-H insertion method has been elaborated by combining an electrophilic iron complex with a pre-activated form of alkyl diazo esters using a lithium cation source.<sup>153</sup> Remarkably, the so-elaborated catalytic system has been found to exhibit activity/selectivity levels like those of common rhodium carboxylate catalysts. Iron catalysis has also been successfully employed for tryptamine synthesis *via* an intermolecular C<sub>sp2</sub>-H functionalization of indoles with diazoacetone.<sup>154</sup> This biorelevant transformation has been achieved with an iron porphyrin as catalyst, thus constituting a proof-of-concept work for translating such processes under enzymatic conditions. A similar C-H functionalization of indoles has been performed under rhodium catalysis, with a new triisopropylsilyl-protected  $\gamma$ -substituted enoldiazoacetate as an efficient metal carbene source.<sup>155</sup>

Gold catalysis has also been successfully applied to relevant C-H insertion reactions. An intramolecular C<sub>sp3</sub>-H insertion of Au<sup>I</sup>-carbenes generated by a retro-Buchner process has been developed for accessing indanes and dihydronaphthalenes.<sup>156</sup> A new C<sub>sp2</sub>-H insertion strategy based on gold catalysis has also been developed for achieving the regioselective C<sub>2</sub>- vs C<sub>4</sub>-H functionalization of unprotected naphthols with diazo esters as carbene sources.<sup>157</sup> Mechanistic studies have revealed that the regioselectivity of the insertion is mainly governed by the interaction between the free hydroxy group of the phenol derivative and the gold catalyst.

A silver-catalyzed method allowing this time the insertion into the O-H bond of phenols has been reported.<sup>158</sup> This asymmetric method relies on the bifunctional activity of an *in situ* generated chiral homobinuclear silver complex playing two key roles in the process, that are (i) precursor of the required silver carbene thanks to one silver atom of the complex, and (ii) Lewis acid with the second silver atom. These cooperative catalytic reactions allowed the efficient synthesis of a series of valuable chiral  $\alpha$ -aryl- $\alpha$ -aryloxy esters. In parallel,

mechanistic studies have been computationally led on the asymmetric insertion into the O-H bond of carboxylic acids using  $\text{Rh}_2(\text{OAc})_4$  and a chiral guanidine-amide as the catalytic system.<sup>159</sup> The obtained computational results have suggested a cooperative behavior of the catalytic system and a model has been proposed to rationalize the stereoselectivity of the reaction.

The nucleophilic  $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$  iron complex has been found ineffective for catalyzing the carbene insertion into the O-H bond of alcohols.<sup>160</sup> Nevertheless, this catalyst proved to enable the carbene transfer reactions into polar S-H bonds of thiols and N-H bonds of secondary amines, as well as into the Si-H bond of silanes but with lower activity. A mechanistic dichotomy depending on the acidity of the X-H bond has been suggested for rationalizing these results.

The insertion into Si-H bonds has been found to be efficiently promoted by iron(II) triflate as simple catalyst and in dimethyl carbonate as sustainable solvent.<sup>161</sup> Based on kinetic studies, the extrusion of  $\text{N}_2$  prior to the formation of the iron carbene intermediate has been put forward as the rate-determining step. On the other hand, the mechanism of insertion reactions into Si-H bonds promoted by heme protein biocatalysts has been investigated by means of DFT tools.<sup>162</sup> The obtained results have confirmed the relevance of a  $\text{Fe}^{\text{II}}$ -based concerted hydride transfer mechanism with early transition state feature.

By combination of directed evolution with computational studies, a novel heme protein variant has been identified as a powerful catalyst enabling the asymmetric B-H insertion of 5- and 6-membered lactone carbenes.<sup>163</sup>

The transition metal carbene migratory insertion still constitutes a powerful tactic for achieving innovative transformations, including C-H functionalization,<sup>164-167</sup> coupling,<sup>168,169</sup> multi-component,<sup>170-172</sup> internal alkyne semihydrogenation,<sup>173</sup> and cascade transformations.<sup>174</sup>

Two examples of abstraction reactions based on the hydrogen-atom transfer reactivity of transition metal carbenes have been reported. Whereas substituted piperidines have been prepared *via* a cobalt-catalyzed radical cyclization involving an intramolecular 1,2-hydrogen-atom transfer step,<sup>175</sup> an intermolecular hydrogen-atom transfer process has been exploited as key step to achieve the iridium-catalyzed C<sub>sp3</sub>-H insertion reaction of quinoid carbene.<sup>176</sup>

## Rearrangements of Carbenes

### Free carbenes or carbenoids reactions

The gas-phase unimolecular 1,1-HX (X=F, Cl) elimination reactions of C<sub>2</sub>D<sub>5</sub>CHFCl have been investigated by experimental and theoretical methods.<sup>177</sup> The obtained results have put forward the key role played by the carbene:HF and carbene:HCl adducts in the reaction mechanism.

The hetero-Wolff rearrangement of six-membered  $\alpha$ -diazosulfoxides (**65**) to five-membered  $\alpha$ -oxo sulfines (**66**) has been promoted under photochemical and microwave conditions, involving the rearrangement of  $\alpha$ -sulfinyl carbenes (**67**) as key step.<sup>178</sup> The resulting  $\alpha$ -oxo sulfines (**66**) have been further employed as 1,3-dipoles in 1,3-dipolar cycloadditions with nitrile oxides to provide spirocyclic 1,2,5-oxathiazole-S-oxide-based heterocyclic systems (**68**). The one-pot domino version of the hetero-Wolff rearrangement/1,3-dipolar cycloaddition sequence has been found as efficient as the sequential approach and allowed to prepare a series of relevant scaffolds (**68**) under batch and flow conditions. Remarkably, conditions allowing access to either the kinetic or the thermodynamic isomer of (**68**) have been set up.

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### Scheme.18

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The acid-catalyzed conversion of 4-diazotetrahydrofuran-3-ones (**69**) to regioisomeric 3(*2H*)furanones (**70**) has been experimentally and computationally investigated.<sup>179</sup> The regioselectivity of the process has been found to be dependent on the solvent polarity and the electronic effects of R<sup>1</sup>/R<sup>2</sup> substituents. Based on computational results, the reaction pathway has been suggested to involve the positively charged transition state (**71**) rather than the free carbene.

Experimental and theoretical studies have also been led on the transformation of  $\alpha$ -hydroxytetrazoles (**72**) to alkynes under dehydrative conditions.<sup>180</sup> According to the results obtained, the reaction mechanism has been suggested to commence with the dehydration of (**72**), furnishing tetraazafulvenes (**73**) that next undergo elimination of two molecules of N<sub>2</sub>. The resulting vinyl carbene finally evolves towards the expected alkynes via a Fritsch-Buttenberg-Wiechell rearrangement.

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### Scheme.19

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#### Transition Metal assisted reactions

1,2-Shift migration rearrangements are often taking place in the case of transition metal carbenes. Uncommon 1,2-migration reactions of transition metal NHCs (**74**) have been scrutinized using DFT calculations.<sup>181</sup> The obtained results have shown that electronic effects, the ring strain of the four-membered ring, as well as the aromaticity of the NHC have significant contributions in the thermodynamics of this rearrangement.

1,2-Migration rearrangement reactions of transition metal carbenes have also been employed as key step during the development of new methodologies. Depending on the nature of the transition metal, the reactions between diazo esters and imines have been found to selectively form  $\alpha$ -aryl- or  $\beta$ -aryl- $\beta$ -aminoacrylates.<sup>182</sup> Whereas  $\alpha$ -arylated derivatives result from a Roskamp reaction under gold catalysis, the  $\beta$ -arylated derivatives have been

found to be formed under silver catalysis *via* a 1,2-hydrogen shift involving a silver carbene. In parallel, a 1,2-allene shift rearrangement of a gold carbene has been employed as key step to achieve the [4+1]-annulation reactions between 4-methoxy-1,2-dienyl-5-yne and anthranils.<sup>183</sup>

Computational studies have been led on the gold-catalyzed oxidation of the indolyl propargylic alcohol (**75**) by a *N*-oxide in the presence of an imine.<sup>184</sup> Based on the calculations, the mechanistic pathway towards the product (**76**) has been suggested to involve a 1,2-aryl shift in a  $\alpha$ -carbonyl gold carbene intermediate as key step.

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### **Scheme.20**

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The gold-catalyzed annulation of *N*-propargyl ynamides with anthranils has enabled the synthesis of two distinct scaffolds depending on the nature of ynamide.<sup>185</sup> The use of an ynamide featuring an internal alkyne has been found to trigger a reaction mechanism involving a 1,6-carbene transfer rearrangement.

An *E/Z* isomerization process involving a manganese carbene anion intermediate has been suggested as key step in a manganese-catalyzed coupling reaction between arenes and 1,6-enynes.<sup>186</sup>

## **Nucleophilic Carbenes – Carbenes as organocatalysts**

### Transformations mediated by Breslow-type intermediates

*N*-Heterocyclic carbene (NHC) organocatalysis is still developed as a powerful umpolung tactic to reverse the usual mode of reactivity of electrophiles, such as aldehydes, enals and  $\alpha$ -brominated enals.

In the case of aldehydes, their reaction with NHCs result in the formation of usual Breslow intermediates (**77**) as nucleophilic acyl anion equivalents. Breslow intermediates derived from

the heterocyclic thiazolium scaffold of vitamin B<sub>1</sub>, the Nature's umpolung catalyst postulated as soon as in 1958 by Breslow himself, have been formed and characterized for the first time.<sup>187</sup> Whereas the structure of the Breslow intermediate (**78**) derived from pentafluorobenzaldehyde has been confirmed by means of NMR spectroscopy and X-ray diffraction analysis, the first stable Breslow intermediate (**79**) derived from an aliphatic aldehyde (*i.e.*, trifluoroacetaldehyde) has been reported and characterized by NMR spectroscopy in solution. The reversibility of the process furnishing Breslow intermediates has been demonstrated and nicely exploited for converting aldehydes to their C1 deuterated analogues.<sup>188</sup> The success of this method has relied on the fine-tuning of the NHC catalyst to favor the wished reversible process to the detriment of the usual benzoin condensation process. The so-elaborated method will allow the facile, straightforward synthesis of new deuterated compounds for drug discovery. In parallel, 1,2,3-triazolylidene-based mesoionic carbenes have also been found to exhibit the required reactivity profile allowing the reversible H/D exchange reaction rather than the benzoin condensation reaction.<sup>189</sup>

The benzoin reaction has been used as a model reaction to prove a new concept, that is the *in situ* modification and optimization of NHC organocatalysts at their secondary sphere *via* dynamic covalent binding.<sup>190</sup> Using boronic acids as secondary sphere modifiers of NHCs bearing a hydroxy anchor, the asymmetric benzoin reactions of challenging electron-poor substrates has been achieved for the first time.

An intramolecular NHC-catalyzed benzoin process has been successfully exploited to accomplish the asymmetric synthesis of 2-hydroxy-2,3-dihydronaphthalene-1,4-diones.<sup>191</sup>

The benzoin and the intramolecular Stetter-type hydroacylation reactions have been mechanistically investigated by means of experimental and theoretical methods.<sup>192</sup> EPR experiments have revealed in both cases the involvement of radical intermediates, namely Breslow-type radicals.

The reaction mechanisms of the aldehyde carboxylation with CO<sub>2</sub> have been scrutinized by means of DFT methods.<sup>193</sup> Among a lot of options, the feasibility of a NHC-catalyzed version of this reaction, involving a Breslow intermediate, has been envisaged. Unfortunately, the resulting calculations have revealed that the benzoin process is energetically favored to the detriment of the Stetter-type aldehyde carboxylation process, both thermodynamically and kinetically.

An NHC-catalyzed retro-benzoin process has been suggested as key step in the mechanism of the intercepted dehomologation of aldoses.<sup>194</sup> In that case, the Breslow intermediate is trapped *via* a secondary Stetter-type reaction using chalcone as sacrificial reagent, thus regenerating the required NHC organocatalyst.

An intramolecular Stetter approach has also been employed for the construction of 3-amino- and 3-alkyl-chromones under green conditions.<sup>195</sup> The mechanistic studies conducted have suggested the involvement of the corresponding Breslow intermediate. Noteworthy is that the obtained library of compounds has been evaluated for their anticancer potential, with promising activities for some of them.

Theoretical calculations have been led to rationalize the mechanism of the NHC-catalyzed asymmetric addition of 2*H*-azirines with aldehydes.<sup>196</sup> The Stetter-type mechanism has been confirmed by the resulting calculations and the stereoselectivity-determining step has been further identified as the rate-determining step. Interestingly, relationships between efficiency of the reaction and nucleophilicity of the Breslow intermediates have been also established.

An NHC-catalyzed dual Stetter reaction has been reported for the first time.<sup>197</sup> This formal annulation method has been found suited to the synthesis of a large array of relevant (hetero)cyclic scaffolds, including naphthoquinones, isoflavanones and sugar derivatives.

Various NHC-catalyzed annulation reactions have been reported. DFT studies have been led on the switchable selectivity of NHC-catalyzed [3+2] and [3+3] annulation reactions.<sup>198</sup>

The chemoselectivity has been found to be controlled by the nature of the base. DFT studies have also been led on oxidative annulation reactions of aliphatic aldehydes with ketimines,<sup>199</sup> and azomethine imines.<sup>200</sup>

An elegant fragmentation/Stetter-type reaction cascade has been developed for preparing hydroxytrifluoromethyl ynones and allenones.<sup>201</sup> The required sensitive aliphatic aldehydes have been in situ generated *via* a base-mediated Grob-type fragmentation of cyclic vinylogous hemiacetal triflates.

The vicinal alkylacylation of alkenes has been achieved under NHC organocatalysis using aldehydes and redox-active esters.<sup>202</sup> A radical relay mechanism involving the enolate form of the aldehyde-derived Breslow intermediate has been proposed.

Breslow intermediates (**80**) derived from enals have been also successfully exploited, this time as powerful homoenolate equivalents. Whereas a synthetic method towards chiral cyclohepta[b]furan-2-ones (**81**) has been developed *via* a NHC-catalyzed [8+2] annulation of tropones,<sup>203</sup> the reaction mechanisms and stereoselectivities of other annulation reactions leading to spirocyclic products using isatin derivatives have been investigated computationally.<sup>204,205,206</sup> Similar theoretical studies have also been conducted on NHC-catalyzed asymmetric dearomatization reactions of *N*-alkylisoquinolinium derivatives.<sup>207</sup>

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## Scheme.21

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Enal-derived Breslow intermediates (**80**) have also been employed as efficient intermediates prone to undergo an asymmetric  $\beta$ -protonation/ $\alpha$ -fluorination cascade process.<sup>208</sup> A suited balance between the relative rates of the  $\beta$ -protonation and the  $\alpha$ -fluorination steps has been demonstrated as the key factor for the success of the method. The reaction mechanisms of a similar cascade fluorination process starting here from epoxy enals has also been computationally investigated.<sup>209</sup> The computational results have revealed that the stereo- and regioselective step is the C-F bond formation step.

A method allowing the  $\gamma$ - or  $\epsilon$ -alkylation of enals has been reported.<sup>210</sup> The success of the method relies on the merging of NHC and photoredox catalyses, thus combining the usual umpolung chemistry peculiar to NHC catalysis with the radical chemistry specific to photoredox catalysis.

Shifting to 2-bromo-enals results in the formation of the brominated form (**82**) of (**80**), which further gives birth to the  $\alpha,\beta$ -unsaturated acylazolium intermediate (**83**) *via* elimination of the bromide anion. The resulting electrophilic profile of such acylazolium intermediates (**83**) has been smoothly exploited for the synthesis of chiral thiazinones *via* a [3+3] annulation approach,<sup>211</sup> and indole-containing  $\beta$ -biaryl methylene-type esters (**84**) *via* a challenging dual addition approach.<sup>212</sup>

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### Scheme.22

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The outcome of the NHC-catalyzed [3+3] annulation of 2-bromo-enals with enaminones has been found to be highly temperature-dependent.<sup>213</sup> Whereas fused quinolones have been formed at 80 °C, decreasing the temperature to 35 °C led to a regioselectivity shift to fused pyranones.

The NHC-catalyzed ring expansion of oxaziridines resulting from their reaction with  $\alpha$ -acyloxy aldehydes has been computationally examined by means of DFT methods.<sup>214</sup> According to the calculated results, the enolate azolium species (**86**) *in situ* generated from Breslow intermediate (**85**) has been suggested as the nucleophilic intermediate of this process.

The NHC-catalyzed umpolung of functional groups that are different from the aldehyde function is also conceivable. An imine umpolung tactic has thus been exploited for the development of a new aza-Stetter process allowing access to chiral 3-functionalized dihydrocoumarin derivatives (**87**).<sup>215</sup> Two examples of umpolung of Michael acceptors have also been reported. First, a powerful method has been developed to achieve all-carbon [5+1]

annulation reactions with a Breslow-type intermediate equivalent to vinyl dianion.<sup>216</sup> On the other hand, a novel NHC-catalyzed method allowing the intramolecular cyclization of acrylamides containing a 2-fluorophenyl group has been set up.<sup>217</sup> Computational studies have indicated that the reaction involves a concerted nucleophilic aromatic substitution of aryl fluorides as key step.

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**Scheme.23**

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Transformations non-mediated by Breslow-type intermediates

NHC organocatalysis can also allow the development of relevant synthetic methods, still using the nucleophilicity of NHC species but *via* intermediates different from usual Breslow intermediates.

A stereoselective [4+2] annulation tactic has been elaborated to construct the dihydrobenzoxazinone scaffold through an unprecedented aza-*o*-quinonedimethane species as non Breslow intermediate.<sup>218</sup>

Computational studies have been led on the NHC-catalyzed umpolung of ketones and benzonitriles when both coexist.<sup>219</sup> The resulting calculations have revealed that a selective umpolung can be performed depending on the substitution pattern of the reactants.

The direct carboxylation of aryl acetylenes has been accomplished via a NHC-catalyzed multicomponent method, involving a terminal alkyne, an organic halide and carbon dioxide as reaction partners.<sup>220</sup> Computational studies using DFT methods have revealed that the reaction is initiated by the nucleophilic addition of the NHC to carbon dioxide.

A dual catalytic system employing a NHC as nucleophilic species and lithium chloride has been successfully developed for the synthesis of poly(oxazolidine-2-one)s starting from diepoxides and diisocyanates.<sup>221</sup> The NHC has been suggested to act as a nucleophilic species

reacting with the diisocyanate *via* a nucleophilic addition or with an activated form of the epoxide *via* a  $\text{S}_{\text{N}}2$  ring opening process.

Another NHC-catalyzed ring-opening process has been reported.<sup>222</sup> The ring-opened systems are here bicyclic amidine systems related to DBU and the resulting process has allowed access to  $\epsilon$ -caprolactam- and  $\gamma$ -lactam derived imines.

The hydrophosphination of alkynes catalyzed by nickel-NHC complexes has been computationally examined by means of DFT calculations.<sup>223</sup> The resulting calculations have indicated the involvement of the free NHC ligand as catalytically active species, which act as a Lewis base forming an imidazolium phosphide species as key intermediate.

A new mechanism has been suggested for the NHC-catalyzed hydroboration of aldehydes/ketones.<sup>224</sup> A direct hydride transfer step has been proposed as key step.

## Nitrenes

### Free nitrenes - generation and reactivity

Nitrene transfer reactions to olefins under metal-free conditions are still challenging. The gas phase aziridination of olefins by organic azides has been computationally investigated at the B3LYP/6-31G level.<sup>225</sup> Various pathways have been proposed but none of them suggest the involvement of a free nitrene species.

A novel nitrene transfer reaction has been developed for the synthesis 2,2-diaryl enamides from stilbenes as substrate and using an iminoiodinane as nitrene reagent.<sup>226</sup> Based on mechanistic studies, an aziridine species has been suggested as key intermediate.

Another metal-free aziridination method has been reported, again using iminoiodinane as nitrene reagent.<sup>227</sup> The iminium tetrafluoroborate (**88**) has been utilized as organocatalyst and is suggested to react with the iminoiodinane to form the diaziridinium salt (**89**) as nitrene equivalent.

The generation of (iso)nicotinoyl nitrenes by photolysis of the corresponding nitrenes has been confirmed by matrix-isolation infrared spectroscopy.<sup>228</sup> While both nitrenes have been found to undergo a Curtius rearrangement under visible light irradiation (400 nm), their UV irradiation (193 nm) has resulted in the elimination of carbon monoxide and the ring-expansion of the pyridine moiety. Similarly, the light-induced reactivity of diverse cyclic vinyl azides has also been examined.<sup>229</sup> The low-temperature generation of the corresponding vinyl nitrenes under UV light (> 250 nm) has been confirmed by means of electron paramagnetic resonance spectroscopy. Interestingly enough, the resulting triplet nitrenes have been found to be stable at cryogenic temperature. The further formation of keteneimines (**90**) and azirine (**91**) have been supported by IR spectrometry and DFT calculations.

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#### **Scheme.24**

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The mechanism of the photochemical reaction leading to azoarenes from aryl azides on a single-crystal copper surface has been scrutinized.<sup>230</sup> The results obtained have revealed the concurrent formation of an unreactive copper nitrene intermediate and a reactive triplet nitrene prone to dimerize.

In contrast, the gas phase cleavage of the azo bond of 1-phenylazo-2-naphthol (Sudan I) has been studied.<sup>231</sup> A combination of mass spectrometry and DFT calculations have been employed to identify the fragment pathways of the protonated form of Sudan I. The free naphthol nitrene has been detected by mass spectrometry, thus suggesting its probable involvement as intermediate.

#### Transition Metal assisted reactions

The development and optimization of aziridination reactions under transition metal catalysis are still attracting much attention.

The aziridinating catalytic activity of iron phenolate complexes has been finely tuned regarding the substitution pattern of the ligand.<sup>232</sup> Various diphenolate ligands have been evaluated and the combined experimental and theoretical results have confirmed the key influence of the electron affinity of the catalytically active iron species.

A formal rhodium-catalyzed [4+1] cycloaddition reaction between unactivated olefins and a suited nitrene source has been developed as a powerful tool to prepare pyrrolidines.<sup>233</sup> Mechanistic studies have revealed the involvement of a cascade process commencing with the rhodium-catalyzed aziridination of the olefin partner.

An intramolecular regiodivergent oxyamination approach has been achieved under iridium catalysis.<sup>234</sup> In the course of mechanistic studies, a strained aziridine-based azabicyclo[3.1.0] derivative has been isolated, thus suggesting the involvement of an iridium-nitrene-mediated aziridination reaction as key step. On the other hand, the rhodium-catalyzed synthesis of functionalized tetrahydropyridines has been accomplished via a formal [5+1] cycloaddition reaction of aryl-substituted vinylcyclopropanes and benzyl tosyloxycarbamate as nitrene source.<sup>235</sup> A nitrene transfer aziridination reaction has been suggested as plausible step to rationalize the reaction mechanism.

Computational investigations have been led on various transition metal-catalyzed reactions employing an aziridination process as key step.<sup>236-239</sup>

Other addition reactions involving a transition metal nitrene have been reported as key steps. A rhodium-catalyzed three-component C-H amidation reaction has been developed and the resulting mechanistic studies have revealed that the amides are formed *via* a key rhodium nitrene intermediate prone to add to carbon monoxide.<sup>240</sup>

A stereoselective method for accessing  $\gamma$ -lactams has been developed via an iridium-catalyzed olefin difunctionalization approach.<sup>241</sup> This approach relies on the *in situ* generation

of an iridium nitrene intermediate which acts as a 1,3-dipole enabling the amido transfer process.

Olefin-diazene cross-metathesis has been found to be feasible between usual ruthenium-based olefin-metathesis catalysts and aryl diazenes.<sup>242</sup> The formation of the imine has been mechanistically investigated using DFT methods and the resulting calculations have revealed the viable involvement of ruthenium carbenes and nitrenes as intermediates.

Another method for producing imines has been elaborated through the iron-catalyzed nitrene transfer reaction of 4-hydroxystilbenes with aryl azides.<sup>243</sup> Mechanistic studies have indicated the involvement of a radical pathway. The *in situ* generated iron carbene has been suggested to promote the formation of the stable phenoxy radical form of the hydroxystilbene precursor *via* a hydrogen atom abstraction process. Noteworthy is that the so-elaborated nitrene transfer process has been successfully linked to diverse relevant organic transformations, thus resulting in sequential one-pot processes.

The synthetic potential of nitrene insertion reactions continues to be exploited. Diverse intramolecular C-H amination methods have been reported. The enantioselective intramolecular C-H amination of aliphatic azides has been achieved under dual ruthenium and phosphine catalysis,<sup>244</sup> whereas ruthenium catalysis has also enabled a similar nitrene insertion process with the cleavage of an existing geminal C-N bond as unprecedented event.<sup>245</sup> The peculiar place of silver catalysis in nitrene insertion reactions has been further illustrated by the formation of benzosultams with a regioselectivity complementary to other transition metal catalysts.<sup>246</sup> Moreover, the regioselectivity proved to be switchable by tuning the ligand steric effects.

Although rhodium-catalyzed nitrene insertion reactions have been known for over 40 years, the first X-ray crystal structure of a reactive rhodium nitrene has only now been described.<sup>247</sup> Getting this remarkable structural characterization data has been possible thanks

to the use of crystalline matrix confinement. In addition, a computational study has been conducted on rhodium-catalyzed C-H amination reactions using *N*-mesyloxycarbamates as rhodium nitrene sources.<sup>248</sup> The involvement of a concerted pathway based on a rhodium nitrene intermediate proved to be the more favored pathway, and the rate-limiting step has been found to be the C-H insertion process rather than the nitrene formation.

A computational study has also been conducted on the mechanism and the regioselectivity of iron-dipyrinato-catalyzed intramolecular C-H amination of alkyl azides.<sup>249</sup> The resulting calculations have suggested that a radical pathway takes place with a hydrogen atom abstraction step as the regioselectivity-determining step. Iron catalysis has also been nicely exploited to achieve the intramolecular C-H amination of sulfamate esters.<sup>250</sup> Noteworthy is that the addition of a second ligand has been found to enhance the catalyst activity.

Novel cytochrome P450-based hemoproteins have been reported as powerful biocatalytic systems for achieving C-H amination reactions, including the C2-amidation of indoles,<sup>251</sup> and the asymmetric amination of primary, secondary and even tertiary C<sub>sp3</sub>-H bonds.<sup>252</sup>

The chemoselective nitrene insertion into an amide bond over a C-H bond has been achieved under rhodium catalysis.<sup>253</sup> The origin of this chemoselectivity has been rationalized by means of experimental and theoretical studies.

Although still much less exploited than their carbene equivalents, examples of migratory insertion reactions involving transition metal carbenes have been reported. The three-component copper-catalyzed synthesis of *N*-acyl amidines from amines, aryl acetylenes and 1,4,2-dioxazol-5-ones has been suggested to take place via a migratory insertion process as key step.<sup>254</sup> In addition, computational studies conducted on a cobalt-catalyzed C-H amination reaction,<sup>255</sup> and on a rhodium-catalyzed synthesis of pyridines,<sup>256</sup> have revealed the involvement of a migratory insertion process as key step in both cases.

## Heavy-atom Carbene Analogues

Cyclic (Alkyl)(amino)silylene (**92**) has been engaged in dehydrogenative reactions of cyclohexadiene and dihydroanthracene at 150 °C.<sup>257</sup> The dehydrogenation is thought to occur via a stepwise hydrogen abstraction leading to the aromatic compounds and the cyclic aminosilane. The reaction of NHC stabilized dichlorosilylene with 1-disilagermirene (**93**) has been investigated both theoretically and experimentally establishing the nucleophilicity of the silylene.<sup>258</sup> The NHC stabilized silyliumylidene cation (**94**) has found an elegant application in the catalytic hydroboration of carbonyls, CO<sub>2</sub> and pyridine.<sup>259</sup> This reduction has been shown to take place by the Si(II) activation of the substrate to promote the hydroboration. Alternatively a NHC-Borylsilyliumylidene (**95**) was also isolated and also proved catalytically efficient.

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### Scheme.25

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Acetamides have been synthesized from CO and primary amines or ammonia through their reaction with the ferrocene based disilylene (**96**).<sup>260</sup> The reaction proceeds through a disilaketene by unprecedented Si–C and Si–O bond cleavages. Bis(pyrido)silylene hydrido iron complex (**97**) has been synthesized and proved highly competent to catalyze the hydroboration of carbonyl compounds at room temperature with an exquisite 1,2 selectivity on unsaturated substrates.<sup>261</sup> A range of low valent silicon compounds corresponding to species engaged in the disilene (R<sub>2</sub>Si=SiR<sub>2</sub>)-silylsilylene (**98**) equilibrium have been identified. The equilibrium was shown to be modulated by the nature of the Lewis base (from pyridine to NHC) performing the stabilization.<sup>262</sup>

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### Scheme.26

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The *Z/E* isomerization of a stable silene has been investigated experimentally and computationally through the syntheses of both diastereoisomers.<sup>263</sup> The isomerization was

shown to occur via one migration of one substituent generating a silylene intermediate, followed by a rotation and a migration of the substituent back, providing an overall diastereo-inversion.

Diarylstannylene have been shown to react with ethylene by a formal insertion of ethylene into a Sn–Ar bond.<sup>264</sup> The reaction has been shown to occur through Lewis acid activation of ethylene by the stannylene followed by migration of one aryl group from tin to carbon. The influence of the halogen substituent on the skeletal rearrangement of germacyclopropylidenoids (**99**) and (**100**) to germaallenes has been investigated computationally. It was found that (**99**) undergoes a concerted rearrangement whereas it is stepwise for (**100**); and the ring opening of the former was found comparatively thermodynamically favored. Structure modulation of silyl substituted germylene has been achieved by Si–H/Si–C bond metathesis involving cyclic (alkyl)(amino)germylenes and a range of hydrosilanes.<sup>265</sup> The metathetic transformation was shown to be catalyzed by electron deficient borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> through Lewis acid activation of the Si–H bond followed by trapping of the silyl cation by the germylene and silyl cation exchange. The generation of silylene, germylene and stannylene in the coordination sphere of platinum complexes has been performed by the action of cationic platinum complex (**101**) with dihydrosilane, dihydrogermane and dihydrostannane respectively without any Lewis acid promoted methyl abstraction.<sup>266</sup> The reactivity of a ferrocene based diaminoplumbylene has been investigated highlighting a rare reversible dimerization to (**102**).<sup>267</sup> This has been shown to occur through a CH bond activation of one ferrocene moiety leading the formation of a Pb–C bond and one Pb–N bond.

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**Scheme.27**

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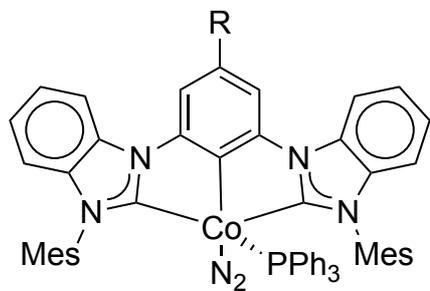
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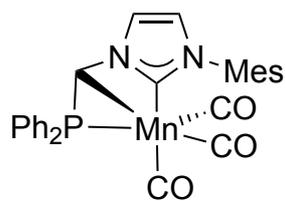
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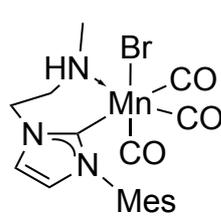
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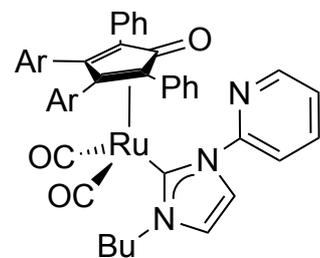
(18)



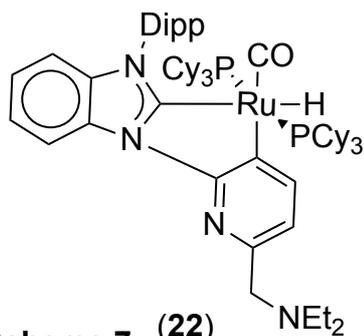
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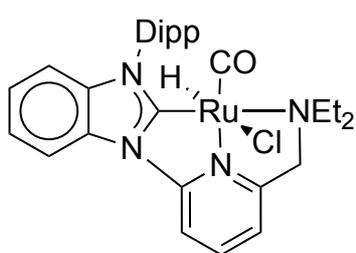
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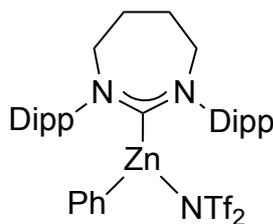
(21)

**Scheme.6**


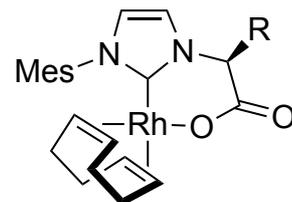
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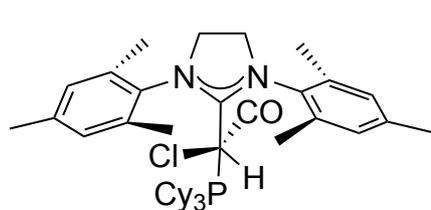
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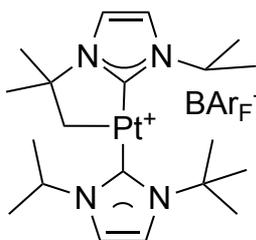
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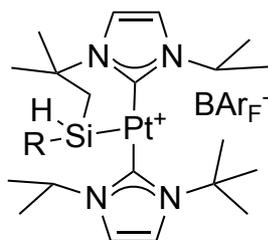
(25)

**Scheme.7**


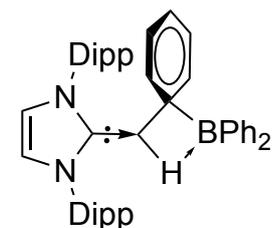
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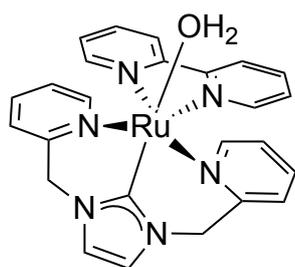
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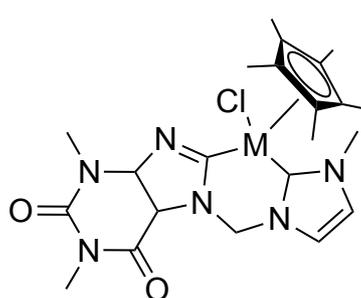
(28)



(29)

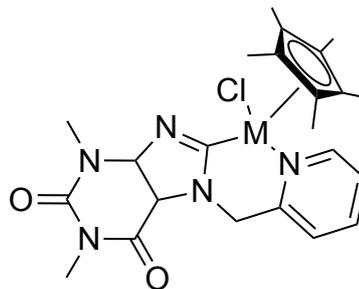
**Scheme.8**


(30)

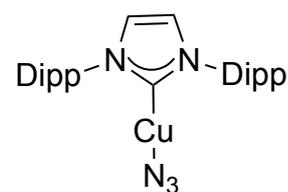


(31)

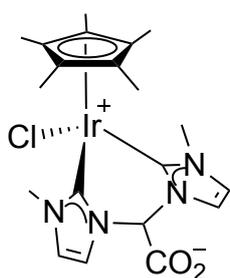
M = Rh, Ir



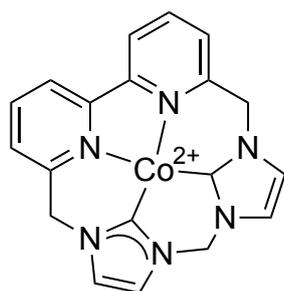
(32)



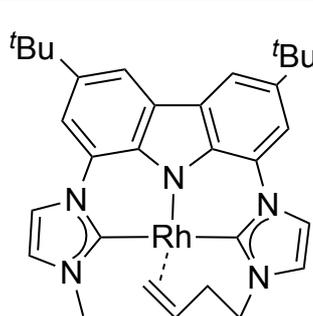
(33)

**Scheme.9**


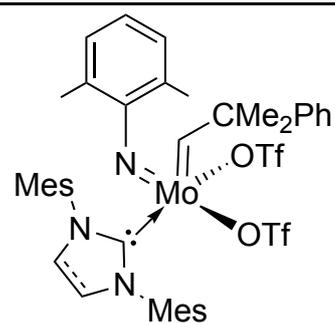
(34)



(35)



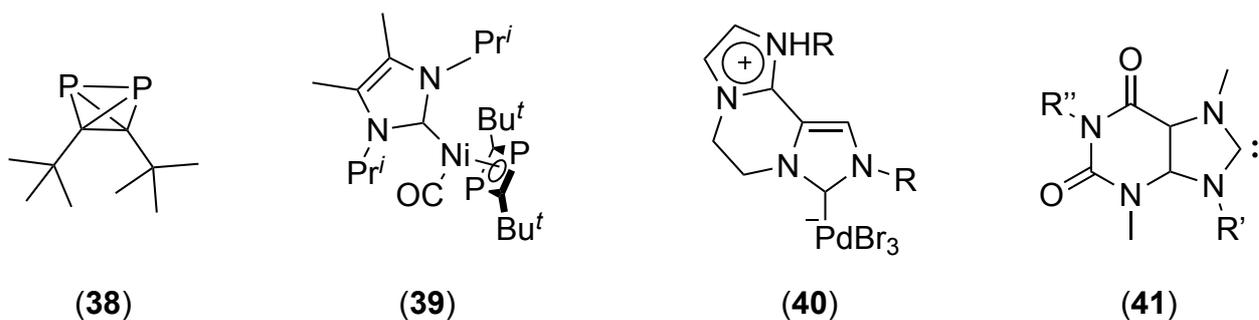
(36)



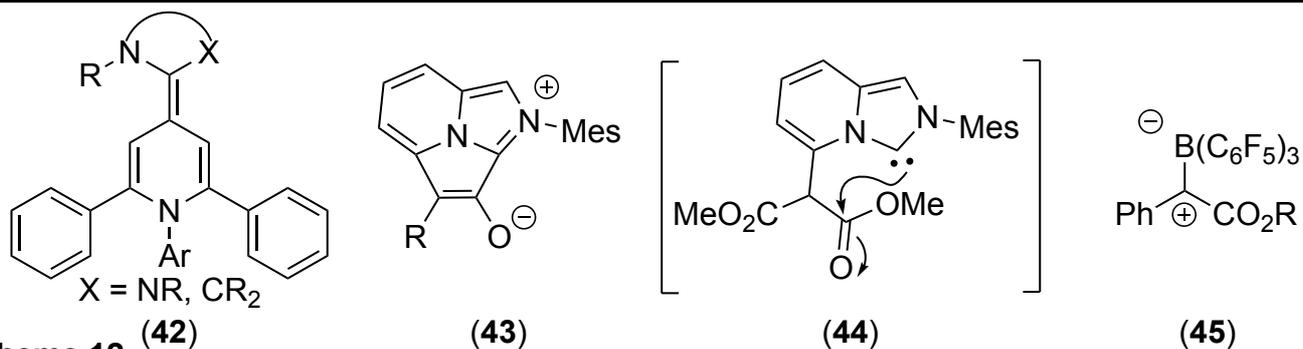
(37)

**Scheme.10**

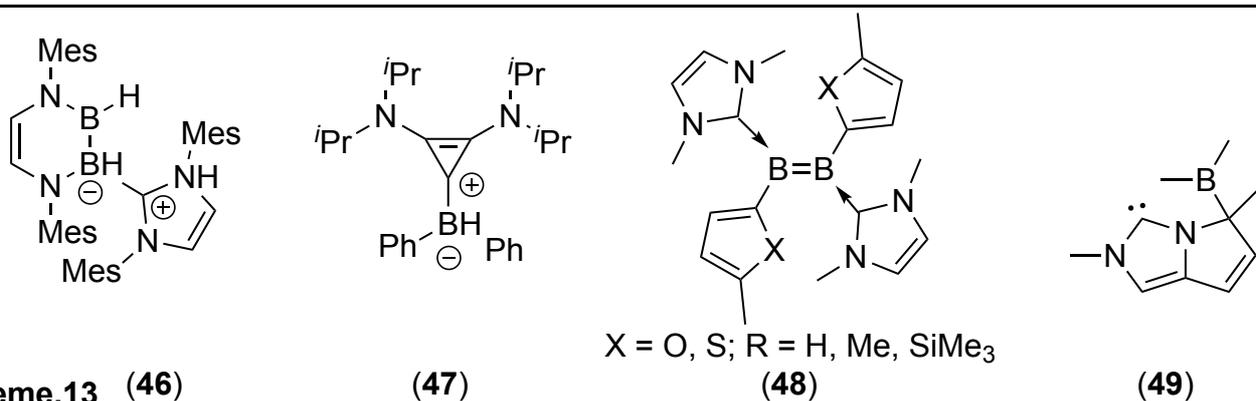




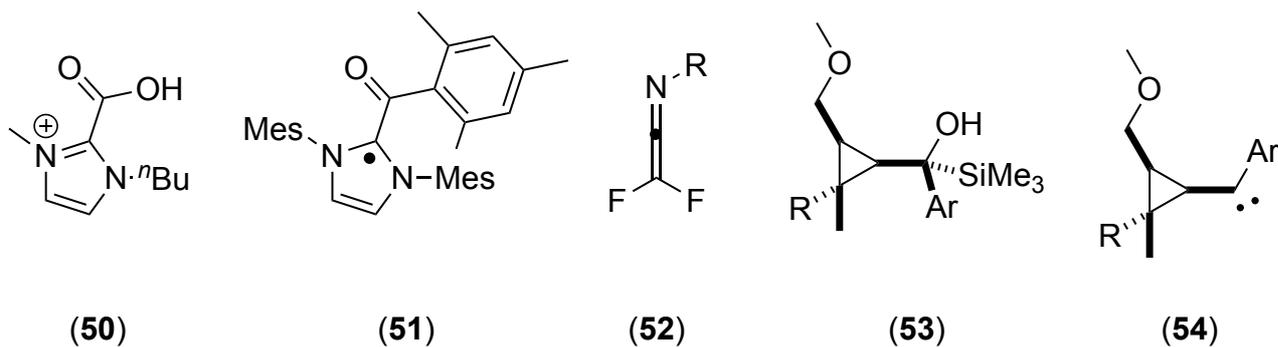
Scheme.11



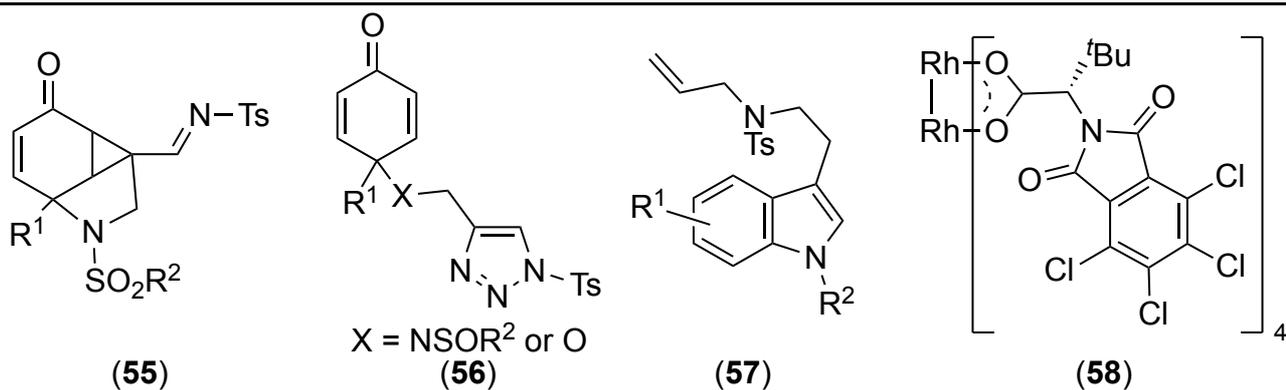
Scheme.12



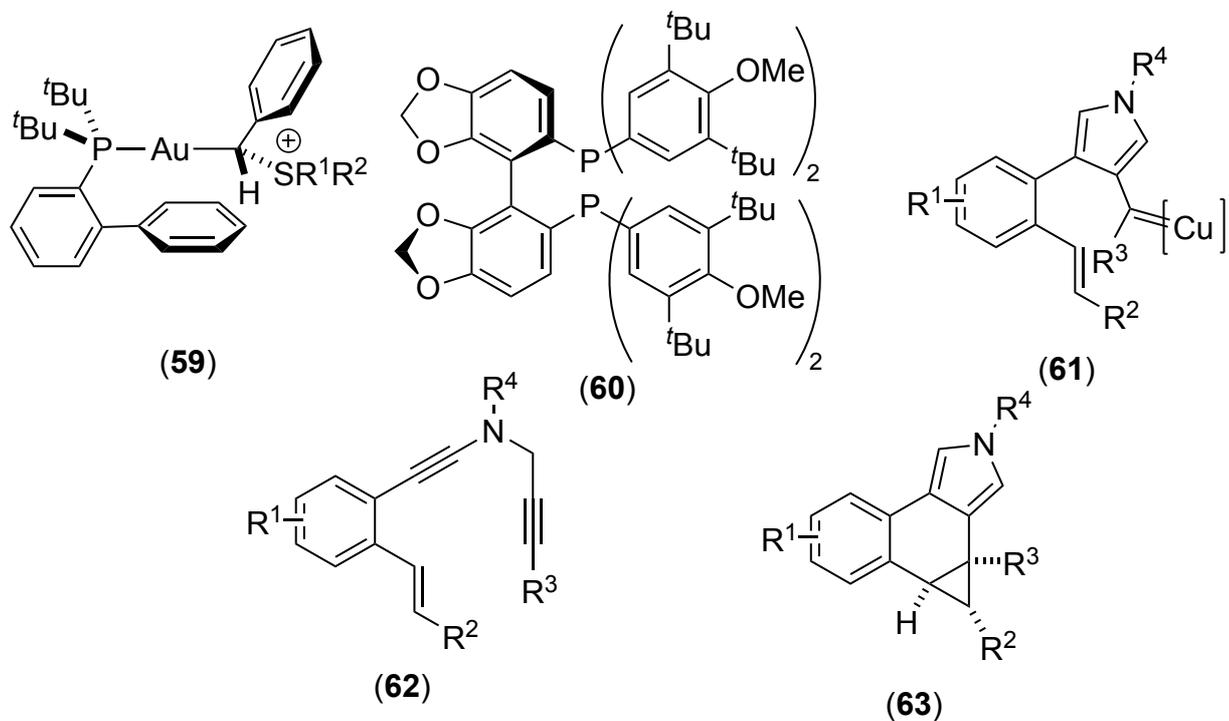
Scheme.13



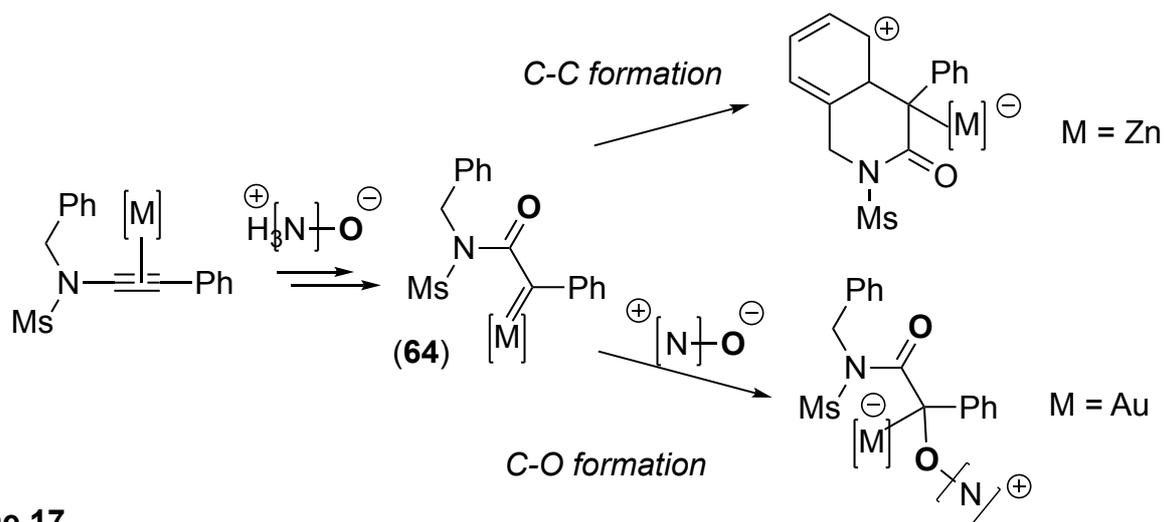
Scheme.14



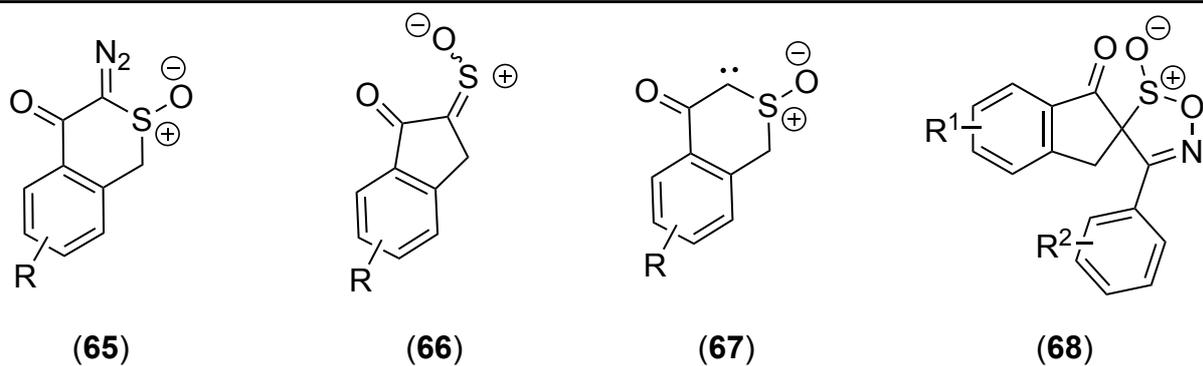
Scheme.15



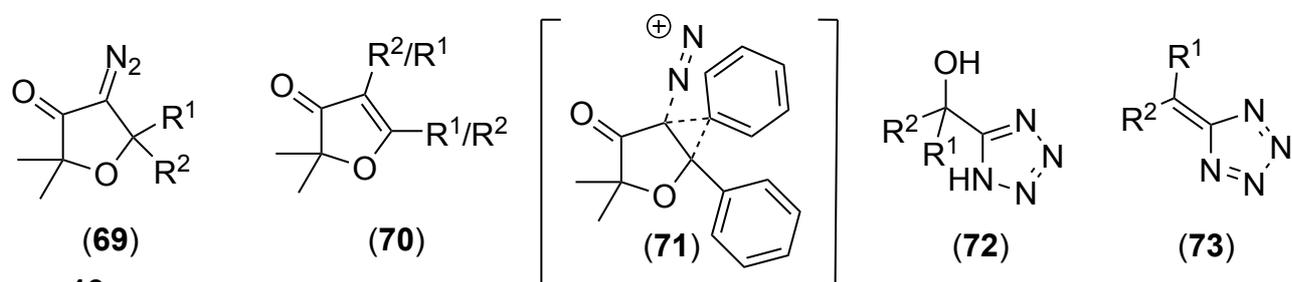
**Scheme.16**



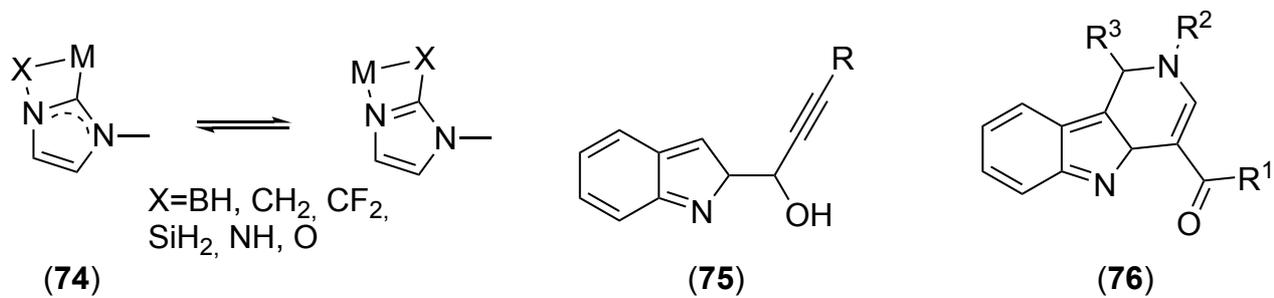
**Scheme.17**



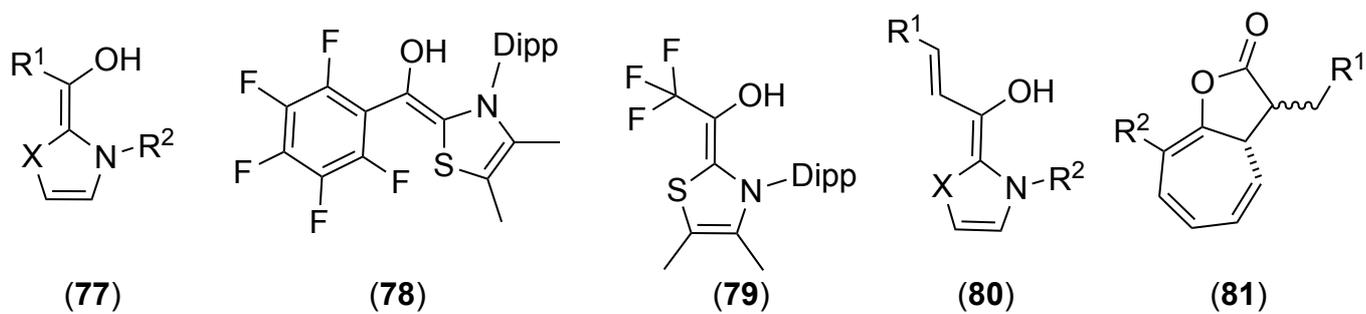
**Scheme.18**



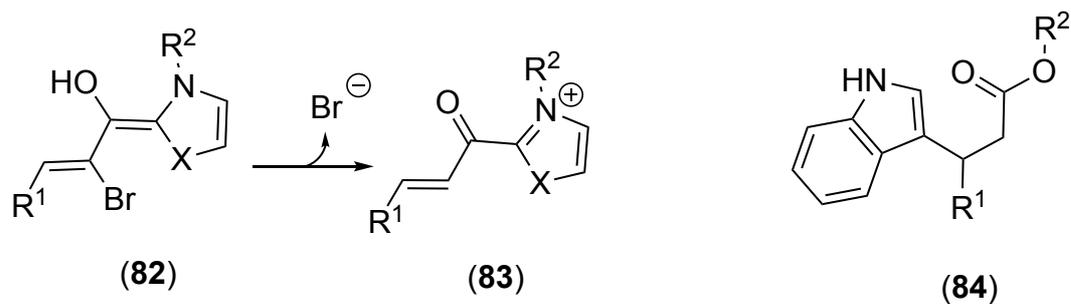
**Scheme.19**



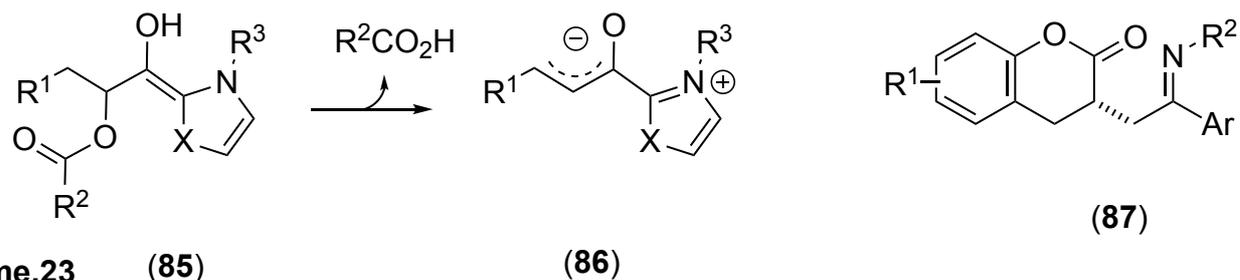
**Scheme.20**



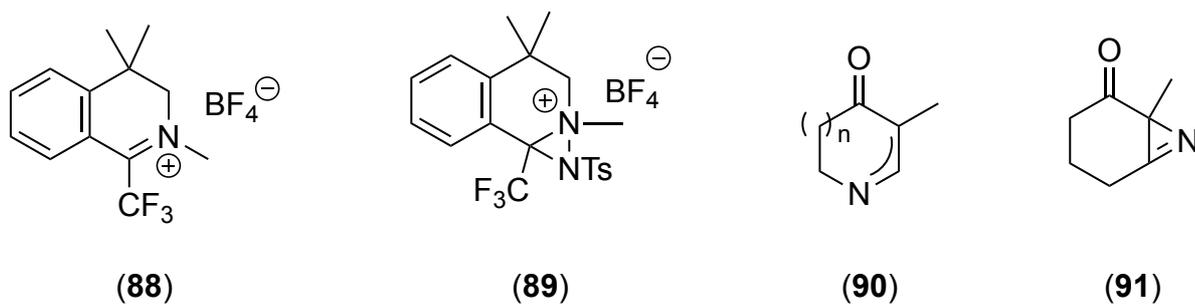
**Scheme.21**



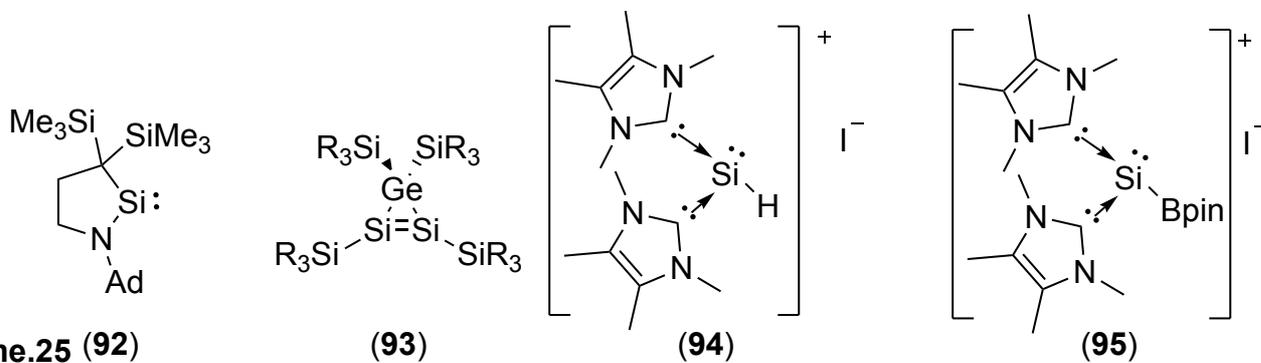
**Scheme.22**



**Scheme.23**



**Scheme.24**

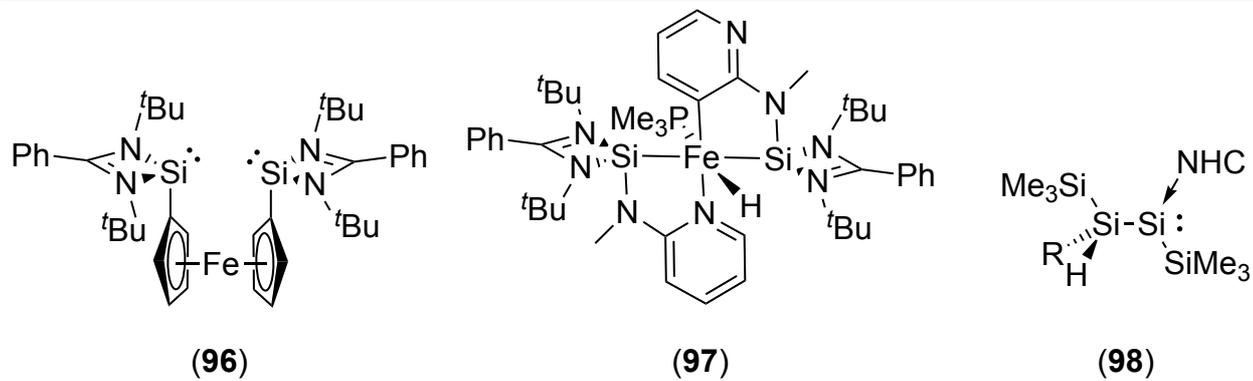


Scheme.25 (92)

(93)

(94)

(95)

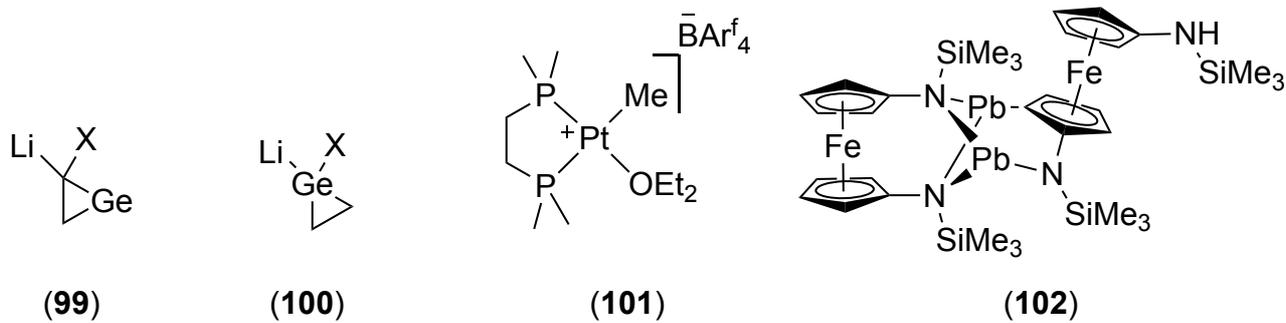


Scheme.26

(96)

(97)

(98)



Scheme.27

(99)

(100)

(101)

(102)