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Dipyrin based metal complexes: reactivity and catalysis

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Sometimes coined half-porphyrins, the bis-pyrrolic dipyrin ligands endow their metal complexes with unique properties such as the potential to functionalize the heterocyclic backbone or the *meso* position as well as the ability to catalyze interesting chemical transformations. Thus, strategies towards the derivatization of or at the *meso* group and the use of dipyrin metal complexes for the formation of a broad range of polypyrrolic derivatives such as 2,2'-bis-dipyrins, nor-/hetero-corroles and porphynoids have been elaborated. Furthermore, the chelating ability of dipyrins and the possibility to modify the steric and electronic characteristics by functionalization can be exploited for the development of numerous complexes featuring appealing properties. Hence, C-H activation/amination, polymerization or oxidation reactions can be catalyzed by dipyrin metal complexes and classical reagents such as Grignard species, Rh-based or Suzuki-Miyaura catalysts have been revisited by incorporation of dipyrins in the coordination sphere of the metal cations. This contribution aims at reviewing and illustrating all these aspects, highlighting the potential of these complexes for the design and synthesis of valuable organic compounds and metallo-organic architectures.

1. Introduction

The bis-pyrrolic dipyrromethene derivatives, also coined dipyrins (dpm) (Fig. 1),¹ known for almost a century,² have received a revived interest since the 1990s. BODIPYs, their boron difluoride adducts, (Fig. 1), have been particularly studied as they represent an important class of dyes with applications in sensing,³⁻⁴ therapy⁵⁻⁶ or photovoltaics,⁷ among others. The metal complex analogues have, for their part, been investigated for their optical and photophysical properties⁸⁻⁹ as well as for the preparation of coordination polymers,¹⁰ supramolecular assemblies¹¹ and for material applications.¹² Owing to their conjugated bis-pyrrolic nature, dipyrins are often seen as “half-porphyrins”. This analogy is noteworthy, since it suggests that dipyrin metal complexes may also feature interesting reactivity and catalytic activity. Indeed, porphyrins and related tetrapyrrolic macrocycles such as corroles, endowed with unique optical and electrochemical properties, are involved in a variety of biological processes and are capable of catalysing a diversity of reactions.¹³⁻¹⁶ Furthermore, these derivatives can be readily functionalized at the pyrrolic and peripheral positions.¹⁷⁻¹⁸ Over the past decade, the potential of dipyrin metal complexes to act as reactive templates for the formation of more elaborate architectures or to catalytically produce chemicals of high added value, thus paralleling porphyrins and their cousins, has been explored. This contribution aims at giving an overview of these recent efforts. The functionalization or modification of the dipyrin backbone and/or of its peripheral moieties will be first described, highlighting the reactivity of the scaffold and its ability to produce other polypyrrolic systems and assemblies. Catalysis based on dipyrin metal complexes for a wide array of reactions will then be presented, emphasizing the potential of these derivatives in synthetic chemistry.

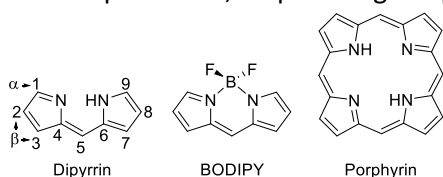


Fig. 1. Representation of a dipyrin, a BODIPY and a porphyrin. No functional groups have been presented at the pyrrolic and *meso* positions for clarity.

2. Functionalization of dipyrin metal complexes

While functionalization of the boron dpm core has been recognized as an efficient approach for the preparation of a diversity of BODIPYs,¹⁹ this strategy has been much less explored for the post-synthetic preparation of derivatized dpm metal complexes.

2.1. Reactivity at the *meso* group

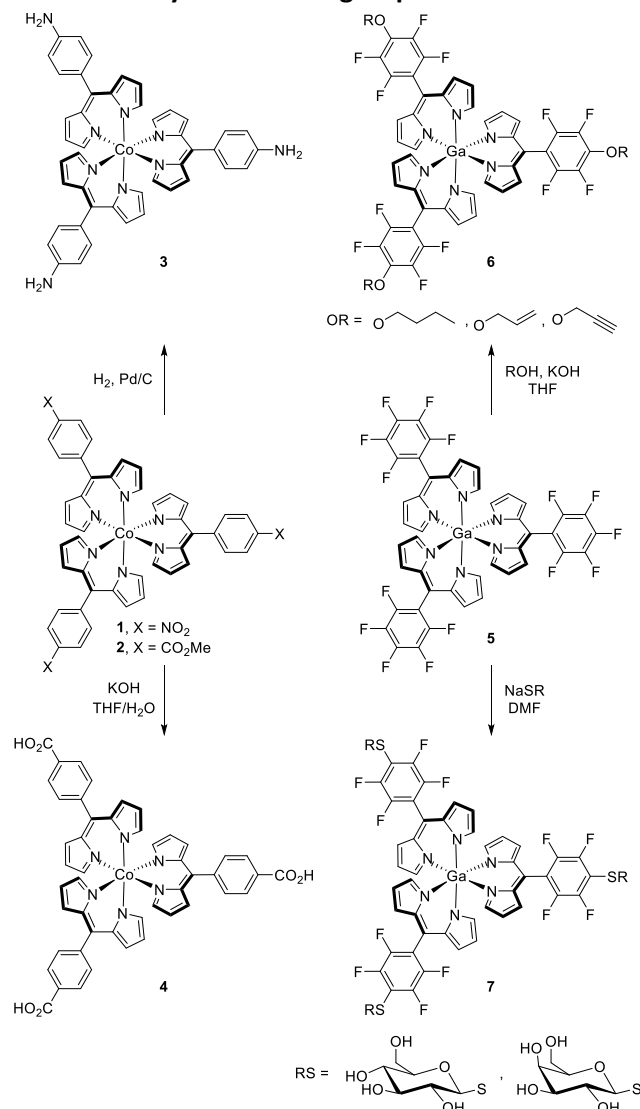


Fig. 2 Post-synthetic functionalization of trivalent $M(\text{dpm})_3$ complexes as described by Dolphin (left)²⁰ and Wiehe (right).²⁵ For all compounds, only one enantiomer of the tris-chelate complex is presented for clarity.

In a seminal article, Dolphin and coworkers took advantage of the inertness of $\text{Co}(\text{dpm})_3$ complexes for their post-synthetic functionalization.²⁰ Thus, the nitro derivative **1** was converted to the amino analogue **3** by hydrogenation (78% yield), while the ester-appended complex **2** was converted to the corresponding carboxylic acid **4** by saponification (90% yield) (Fig. 2 right). The saponification can be taken advantage of to introduce an additional coordinating and reactive group that can be used for the formation of MOFs²¹ and heterometallic assemblies,²² employed for further functionalization such as introduction of hydrogen bonding units²³⁻²⁴ or to separate Δ and Λ enantiomers upon reaction with cinchonidine.^{21, 23-24}

More recently, following an analogous approach, Ga(III), In(III) and Fe(III) complexes based on a penta-fluorophenyl appended dpm have been derivatized to allow the introduction of alcohol or thio-

carbohydrates. These functionalizations proceeded with moderate to good yields (21 to 88 %) and the corresponding conversion of the Ga(III) complex **5** to **6** and **7** respectively is illustrated in Fig. 2. This post-synthetic strategy is valuable as it allowed grafting of thiosugars that would be otherwise prone to oxidation under the conditions classically employed in dpm chemistry (synthesis of dipyrromethane, oxidation to dpm followed by complexation). The Ga(III) complexes of type **7** were shown to feature phototoxic activity towards different cell lines (human epidermoid carcinoma A253, human epithelial carcinoma A431, human oral adenosquamous carcinoma CAL 27 and colorectal adenocarcinoma HT29) and the ability to photodynamically inactivate *S. aureus* bacteria.²⁵ It is worth noting that the Fe(III) analogues were shown to not have any activity owing to their different photophysical properties. A similar functionalization strategy was also employed by the same authors for the derivatization of heteroleptic Ru complexes, for which introduction of alcohol, thiosugar and also amino groups could be performed.

Lindsey and coworkers have employed divalent metal complexes **8** and **9** (M = Pd(II), Zn(II)) based on a *para*-iodophenyl dpm to build larger architectures using C-C coupling reactions (Fig. 3). Hence, Suzuki-Miyaura coupling of Pd complex **8** with porphyrin **10** led to the formation of triad **11** in 50% yield.²⁶ This heterometallic system was subsequently converted to an all Zn(II) compound showing an efficient energy transfer from the dpm unit to the peripheral macrocycles upon photoexcitation. Similarly, Sonogashira coupling of Zn complex **9** with dipyrromethane **12** led to complex **13** in 84% featuring both the reduced and oxidized forms of the bis-pyrrolic backbone.²⁷

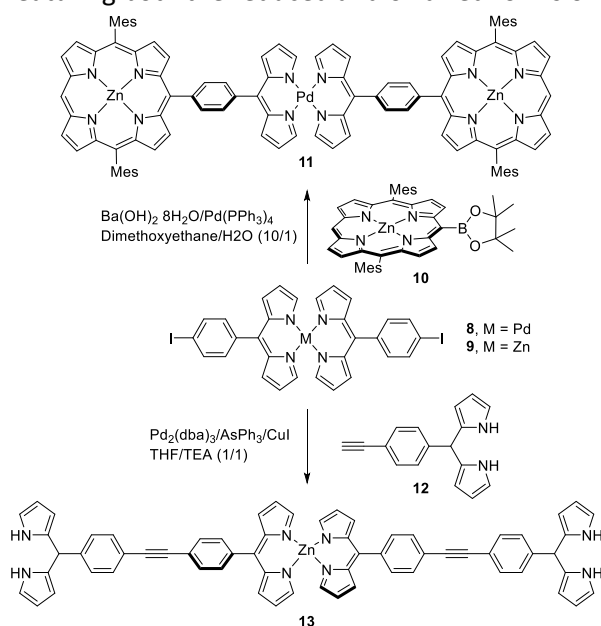


Fig. 3 Pallado-catalyzed couplings on divalent metal complexes based on a *para*-iodophenyl dpm, as described by Lindsey and coworkers.²⁶⁻²⁷ Mes = mesityl.

While the previous examples relied on the presence of an aryl group at the *meso* position, the group of Telfer has described another approach for direct functionalization at this site.²⁸ Inspired by a procedure developed for BODIPYs,²⁹ they have prepared Re(I) complex **14** bearing a thiomethyl group at the *meso* position. The latter is prone to undergo nucleophilic substitution allowing the introduction of other functional groups such as amines. However, unlike for BODIPYs, a high concentration of the nucleophile is necessary for the reaction to proceed, as exemplified in the synthesis of complexes **15** and **16** prepared in neat propylamine and 1-aza-15-crown-5 respectively (Fig. 4). Unfortunately, in contrast with other Re(I) dpm complexes,³⁰ the species prepared using this approach were all found to be non-emissive as a result of intramolecular charge transfer.

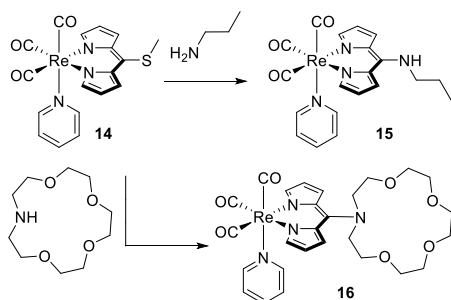


Fig. 4 Nucleophilic substitution on a thiomethyl appended Re(I) dpm complex as described by Telfer.²⁸

2.2. Reactivity at the α positions

The examples presented above described functionalization at the *meso* position. The pyrrolic positions are also prone to derivatization. In particular, alkoxylation of the dpm backbone at the α position has been demonstrated to be activated by complexation.³¹ The group of Cohen reported that upon reaction of the benzonitrile-appended dipyrromethane **17** with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and the $\text{Na}_3\text{Co}(\text{NO}_2)_6$ salt in a mixture of MeOH and NEt_3 , several compounds were concomitantly formed: the target homoleptic Co(III) complex **18**, as expected, along with a heteroleptic Co(III) compound incorporating a dpm bearing a methoxy group at one α position **19**, as well as the corresponding functionalized free alkoxy-dpm ligand **20** (Fig. 5). The reaction was found to only proceed in the presence of the metal. The above-mentioned Co(III) salt gave the best yields, with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Co}(\text{py})_4\text{Cl}_2\text{Cl}$ found to be also effective, albeit to a lesser extent. Other alcohols such as ethanol, 1- and 2-propanol, benzyl alcohol could be employed for the alkoxylation, although with much lower yields. This type of reactivity, that had also been observed on a N-confused Ni porphyrin,³² was also reported for a ferrocene appended dpm and a 2,2'-bis-dpm bearing pentafluorophenyl groups, catalyzed by FeCl_3 .³³⁻³⁴

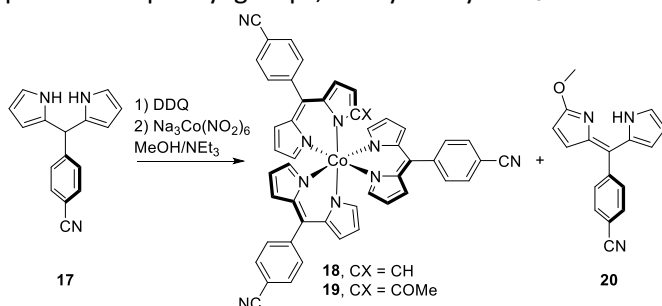


Fig. 5 Alkoxylation at the α position of a dpm as described by Cohen and coworkers.³¹

While α -Me groups have been extensively employed for functionalization of dpm or BODIPY derivatives such as in Knoevenagel reaction,^{19,35} functionalization of dpm metal complexes at these sites remains scarce. Interestingly, Wagler and coworkers have studied the complexation of a Si(IV)cyclobutane complex based on a 1,1-bis(pyrrol-2-yl)ethene and have showed that this compound was prone to a ring opening leading to an attack of the methyl group in the α position of the dpm.³⁶

3. Templates for the formation of polypyrrolic derivatives

The dpm scaffold has been employed as a precursor to polypyrrolic derivatives by taking advantage of the template nature of its metal complexes, thus arranging two dpm moieties in a preorganized fashion. Following this approach, a wide array of compounds has been prepared.

3.1 Template complexes for the formation of [2]catenanes

Since the seminal article by Sauvage and coworkers,³⁷ metal templation has been extensively used for the elaboration of catenanes.³⁸ While 2,2'-bipyridine and 1,10-phenanthroline derivatives have been extensively used for such purposes, the group of Bozdemir has taken advantage of the neutrality and

organization of complexes of α -functionalized dpm with divalent metals (Zn(II), Cu(II)) to prepare a novel class of [2]catenane.³⁹ Thus, complex **21** has been prepared (Fig. 6). It shows a distorted tetrahedral geometry resulting in the favorable arrangement of aryl groups at positions 1 and 9 bearing pendant allyl-terminated diethyleneglycol groups. Upon ring-closing metathesis of the latter moieties in the presence of Grubbs second generation catalyst, the closing of the two ligands hence intertwined is performed in 75% yield leading to complex **22** (Fig. 6). Upon demetallation of **22**, a [2]catenane incorporating two free dpms units is obtained; it can be further used for the preparation of a luminescent BODIPY [2]catenane.

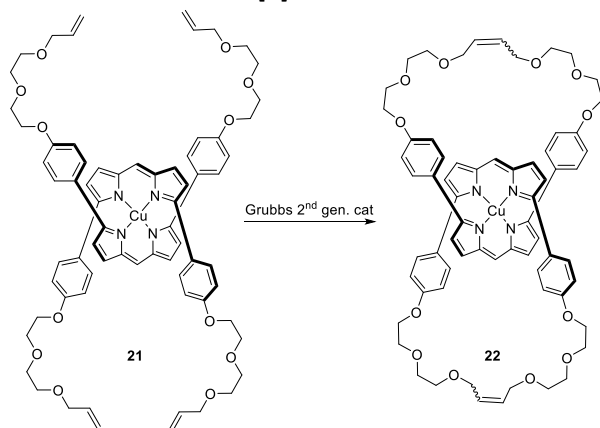


Fig. 6 Ring-closing metathesis for the formation of a [2]catenane precursor, as described by the group of Bozdemir.³⁹

The Zn(II) analogue of **21** has also been prepared but no proper conditions for its demetallation could be found. It is worth noting that ring-closing metathesis was also used by Maeda for connecting strands of binuclear Zn(II) helicates based on functionalized 2,2'-bis-dpm ligands.⁴⁰ These examples benefit from the prearrangement of the dpm ligands but do not fully exploit the intrinsic electronic impact of the metal present in the complex. This has been addressed in the development of a series of conjugated polypyrrolic derivatives.

3.2. Precursors to 2,2'-bis-dipyrins

Scott and coworkers have used Ni(dpm)₂ complexes as templates for the formation of 2,2'-bis-dpm derivatives by oxidative formation of a CC bond owing to the close proximity of the ligands upon complexation as well as the Lewis acidity of Ni(II) cation.⁴¹ For example, dpm Ni complex **23** has been shown to convert to the 2,2'-bis-dpm analogue **24** upon treatment with an oxidant such as DDQ or *p*-chloranil (Fig. 7). Upon reaction, the two dpm chelates are conjugated and afford an environment to the metal center closer to square planar as demonstrated by ¹H-NMR spectroscopy and by crystal structure determination by X-Ray diffraction. Another advantage of the use of Ni(II) for this process is the ease of demetallation of the resulting complex by treatment under acidic conditions thus yielding quantitatively the free 2,2'-bis-dpm ligand. While the original report described this process applied to phenyl and mesityl appended Ni(II) complex, it has been subsequently extended to a wide array of peripheral aromatic groups to afford ligands employed for the formation of more complex assemblies such as Zn(II) linear and circular helicates and macrocycles.^{40, 42-45}



Fig. 7 Formation of a 2,2'-bis-dipyrin complex upon reaction of DDQ with a Ni(dpm)₂ template resulting in conjugation and planarization of the coordination environment, as reported by Scott *et al.*⁴¹ Mes = Mesityl.

3.3 Precursors to nor-/hetero-corroles and porphyrinoids

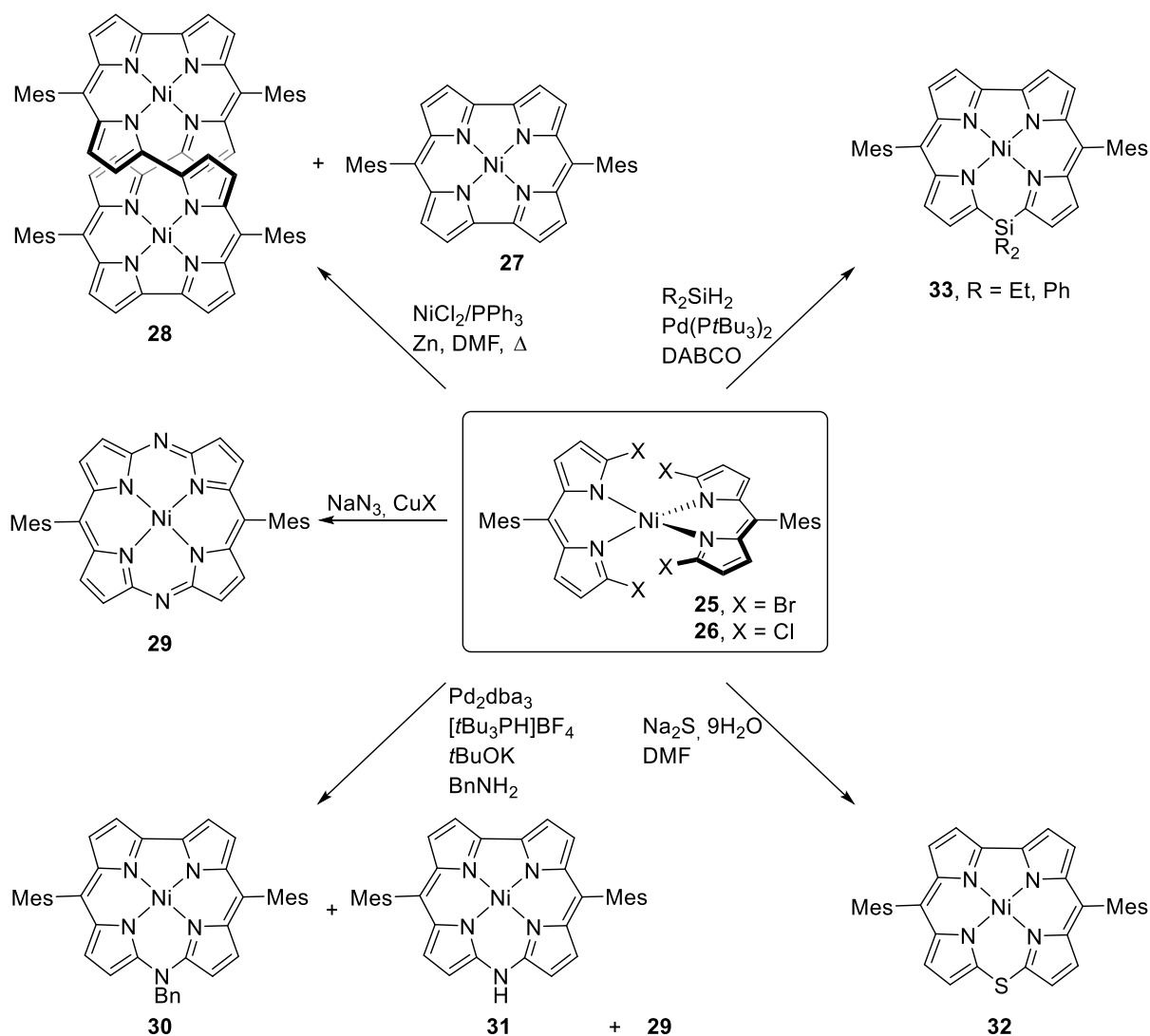


Fig. 8 Homoleptic Ni(II) complexes bearing α -halides as precursors to tetra- and octa-pyrrolic systems. Mes = Mesityl.

Interestingly, while 2,2'-bis-dpm complexes have been shown to allow macrocyclization towards porphyrinoids,⁴⁶⁻⁴⁷ metal dpm complexes can also be employed as templates for such processes. In particular, the homoleptic Ni(II) complexes **25** and **26** based on dpms bearing, respectively, either bromine or chlorine atoms at the α positions (Fig. 8) have been shown to undergo a diversity of transformations leading to valuable polypyrrolic derivatives. The group of Shinokubo has described that **25** could be readily converted to norcorrole **27** in 90% yield upon Ni(0) coupling.⁴⁸ This efficient synthesis differs from the previously described preparation of an highly reactive Fe(III) analogue starting from a 2,2'-bis-dpm complex.⁴⁹ It also allowed the complete characterization of such a unique antiaromatic species,⁵⁰ the properties of which have been shown by theoretical calculations to originate from the dpm moieties within the macrocycle.⁵¹ Furthermore, it was later found that this reaction not only yields the norcorrole but also the octaphyrin(1.0.1.0.1.0.1.0) bis[Ni(II)] complex **28**.⁵² While the latter complex is obtained as a minor product with this process, reaction of the Pd(II) analogue of **25** under the Ni(0) homocoupling conditions affords the Pd version of **28**, in 35% yield. The intramolecular reaction was rationalized to be favored over the intermolecular one in this case as a result of

longer Pd-N distances in the 2,2'-bis-dpm intermediate leading to the remaining reactive α -CBr groups being further apart.

While it has been recognized that metal complexes of β -substituted dpm bearing α -Br atoms were prone to the formation of 5,15-diazaporphyrins upon reaction with sodium azide,⁵³⁻⁵⁵ Matano and coworkers showed that the unsubstituted analogue could be prepared from **25**.⁵⁶ Reaction with sodium azide and Cu(I) halide salts affords **29** in yields above 80%. Interestingly, when the reaction is performed in the absence of Cu(I) salt, the yield drops and pyridazine-fused diazacorrolinoids are also formed. The reaction was found to be also efficient using the Cu(II) analogue of **25** and recently the Zn(II) one.^{57,58} Interestingly, it has been reported that **26** forms **29** only as traces upon Buchwald-Hartwig amination. Under these conditions, the major products are actually azacorroles **30** and **31**.⁵⁹ Compound **31** is the analogue of **30**, where the benzyl group has been cleaved during the synthesis, thus bearing an acidic N-H that can be used for further acylation of the azacorrole.

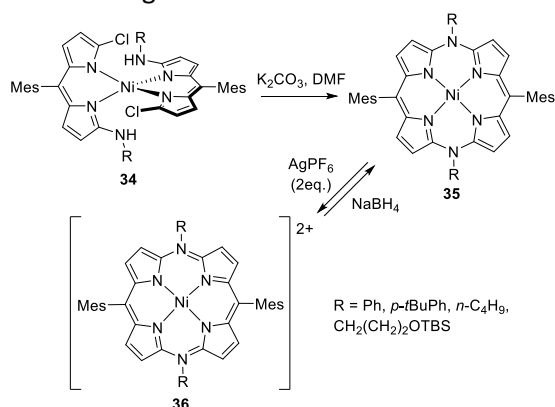


Fig. 9 Template synthesis of redox-active 5,15-diazaporphyrins as reported by the group of Matano.⁶⁰⁻⁶² Mes = Mesityl.

Introduction of nitrogen atoms has been used as a strategy to form 5,15-diazaporphyrins. The interest in these compounds stems from their representing 20π -electron redox-switchable derivatives. Thus, the group of Matano has used Ni(II) complexes **34** based on dissymmetrical dpm ligands as precursors to such 5,15-diazaporphyrins **35** upon treatment under basic conditions (Fig. 9).⁶⁰ This double nucleophilic substitution has been shown to operate with aromatic and alkyl groups on the nitrogen atom as well as on Zn(II) and Cu(II) complexes albeit with a modification of the nature of the base employed.⁶¹⁻⁶² Starting from heteroleptic complexes, dissymmetrical 5,15-diazaporphyrins could also be obtained.⁶³⁻⁶⁴ These compounds were shown to be oxidized by silver salts to produce reversibly the 19π -electron radical cation and the 18π -electron dication, **36**. All these compounds are stable and can be fully characterized allowing an assessment of the effect of redox state on their photophysical properties.

Introduction of sulfur atoms into the tetra-pyrrolic scaffold has been reported by the group of Shinokubo which described that Ni(II) complex **26** reacted with sodium sulfide to produce 10-thiacorrole **32** in 41% yield (Fig. 8).⁶⁵ Interestingly, the same reaction using the Zn(II) analogue of **26** afforded the 5,15-dithiaporphyrin derivative instead, that was shown to be much more distorted than for the planar aromatic **32**. The difference in reactivity is assumed to proceed from the size of the metal cation. The intermediate Ni(II) 5,15-dithiaporphyrin is less folded at the sulfur atoms thus leading to two α -carbon atoms being close for further reaction towards the formation of **32** via an episulfide species. The group of Bröring has shown that a Cu(II) complex based on a α -bromo substituted dpm can lead to a series of 10-heterocorroles incorporating an oxygen, a sulfur or a selenium atom.⁶⁶ It was described that the resulting Cu(II) compounds obtained could be readily demetallated to access the free base ligand. The family of 10-heterocorroles was extended to 10-silacorroles by the group of

Hiroto and Shinokubo who reported that complex **25** could be silylated to afford **33** in 20-22% yield upon reaction with a silane (Fig. 8).⁶⁷ The Ni(II) cation could be removed to produce the free base that could be metallated by Zn(II). These latter derivatives featured emission in the near-infra-red, in CH₂Cl₂ solution and their electronic properties are impacted by the nature of the substituents on the Si(IV) atom.

Metal dpm complexes thus appear as efficient templates for the preparation of nor-/hetero-corroles and other porphyrinoids and can thus be considered in the toolbox of available synthetic methods for the preparation of such pyrrolic species.^{17,68} In these cases, the reaction takes place on the dpm scaffold. Interestingly, the dpm ligands have also been employed for the preparation of complexes featuring reactivity at the metal center, as described in the following sections.

4. Complexes for C-H activation/amination

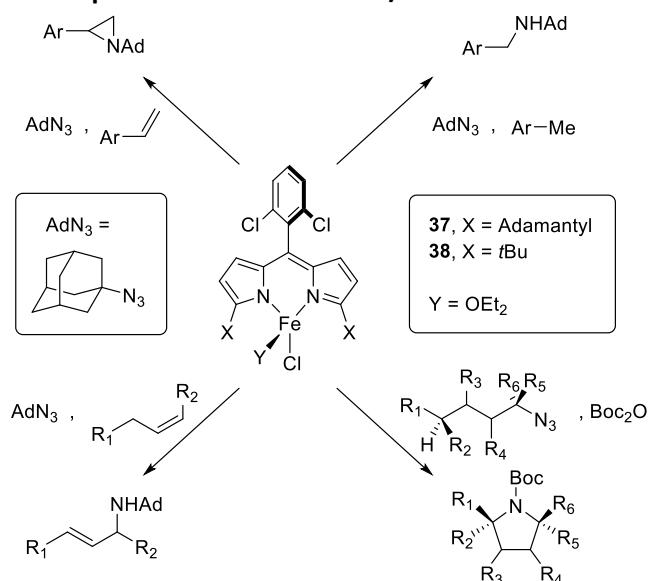


Fig. 10 C-H bond amination based on Fe(II) dpm complexes used in 10-20 mol%, as described by the group of Betley.^{71-72, 73, 75}

Betley and coworkers have reported that a Fe(II) dpm complex with mesityl groups in the α positions is prone to intramolecular C-H amination at the ligand itself in the presence of an arylazide.⁶⁹ It was shown that modification of the functional groups on the bis-pyrrolic backbone not only affects the electronic properties of the complexes⁷⁰ but also can make the reaction proceed in an intermolecular fashion, and even catalytically (Fig. 10).⁷¹⁻⁷² Thus complex **37** bearing adamantyl moieties at the α positions was demonstrated to be efficient to catalyze benzylic amination and aziridination, while **38** bearing *t*-butyl groups was efficient for allylic amination. These reactions were shown to proceed with substrates comprising either electron-withdrawing or donating units. The unique reactivity of these species stems from the formation of a high-spin Fe(III) complex coupled to a nitrogen-based radical, upon reaction with an azide, thus affecting the Fe-N bond. In addition to the spin/radical character, the sterics of the ligand and of the azide is important, as shown in the preference of allylic amination over aziridination with aliphatic olefins. Remarkably, with aliphatic azides, complex **37** catalyzes the formation of pyrrolidines.⁷³ The product inhibition associated with the formation of these heterocycles was circumvented by using Boc₂O as an *in situ* protecting agent. The mechanism of this catalysis has been investigated experimentally as well as theoretically.⁷⁴ It occurs first via exchange of the labile ligand on the metal center (OEt₂ in Fig 10) followed by oxidation of the Fe(II) to Fe(III) center and formation of the nitrene radical, concomitant with the release of dinitrogen. The subsequent hydrogen abstraction and radical rebound afford the desired N-heterocycle. It is worth noting that the latter rebound process shows no energetic barrier hence making the hydrogen abstraction the rate limiting step, consistent with the observation that there is a retention of stereochemical information during

the process thus leading to diastereoisomers. This was further taken advantage of to improve the diastereoselectivity of the amination.⁷⁵ To that aim, a mesityl group was introduced at the *meso* position and phenoxide was substituted for the chloride as ancillary anionic ligand, modifying the electronics⁷⁶ and the sterics of the catalytic pocket. It was further shown that not only Fe iminyl complexes can induce C-H amination but so do the reduced Fe imido counterparts, albeit with a lower rate (see **42** and **43** in Fig. 11).⁷⁷⁻⁷⁹ Furthermore, Fe(I) complex **39** was also demonstrated to react with nitroxyl radicals yielding nitroxido compounds that activate C-H bonds.⁸⁰

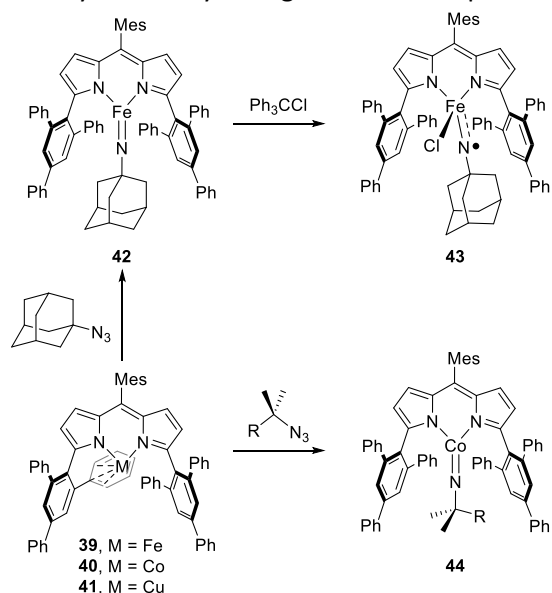


Fig. 11 Fe(I), Co(I), Cu(I) complexes used for C-H activation/amination as described by Betley and coworkers.^{79, 82, 85} Mes = Mesityl.

The Co(I) analogue, **40**, reacts with azides to form Co(III) imido species such as **44** (Fig. 11) as observed for the iron species.⁸¹ With such complex, C-H amination towards pyrrolidine is competing with the formation of tetrazido compounds.⁸² The latter compounds are catalytically inactive. To avoid their formation and favor amination, the group of Betley has studied the reaction of **40** with benzylic derivatives in order to kinetically facilitate the bond activation step and has employed pyridine as a ligand to hamper generation of tetrazido based species. This approach proved successful with excellent yields and rates of amination for this system. An alternative strategy relied on modifying the steric hindrance of the groups at the α -positions by using trityl moieties. With such complex, amination was shown to be highly effective while limiting the formation of tetrazene but also led to a modification of the arrangement of the imide group during the process facilitating the hydrogen atom abstraction.⁸³ This family of complexes prepared by reaction of the Li(dpm) intermediate⁸⁴ with the desired metal cation followed by reduction was extended to the Cu(I) species **41** (Fig. 11).⁸⁵ This compound is also active for C-H amination of cyclohexene, cyclohexane and toluene in the presence of stoichiometric amount of electron-poor aryl azide with yields up to 77%. With a modified dpm scaffold bearing highly sterically demanding units in positions 1 and 9, a dinitrogen adduct could be isolated and fully characterized. Interestingly, when a Pacman structure was constructed using two dpm chelates bridged by a dimethylxanthine unit (*vide infra*), the resulting binuclear Cu complexes were demonstrated to form imide compounds upon reaction with aryl azides that could be reduced to the iminyl species.⁸⁶ However, neither nitrene nor hydrogen atom abstraction were observed with these complexes. Recently, a Ni(I) analogue based on a dpm with a pentafluorophenyl group and adamantyl moieties at the *meso* and α positions respectively has been shown to also form an iminyl complex upon reaction with 1-adamantylazide, prone to further reaction with toluene to afford an imine.⁸⁷

5. Reactivity of oxygen based species

In addition to compounds for nitrene transfer, oxo and oxygen adducts of dpm metal complexes have been described and their reactivity has been explored. For example, the above-mentioned Cu(I) complex **41** reacts with dioxygen to form compound **45** that has been characterized in solution and in the crystalline state (Fig. 12).⁸⁸ This complex was shown to induce hydrogen atom abstraction upon reaction with 1,4-cyclohexadiene. Furthermore, this latter process was observed coupled to oxygen atom transfer when **45** was treated with 2,4,6-tri-*tert*-butylphenol for example. The model reaction with a radical trap suggests a rearrangement of the O₂ binding mode to a terminal one leading to these two processes. Interestingly, analogous reaction with phenol led to the generation of hydrogen peroxide and formation of the phenolate Cu complex. Finally, oxygen atom transfer was also observed upon reaction with triphenylphosphine (Fig. 12).

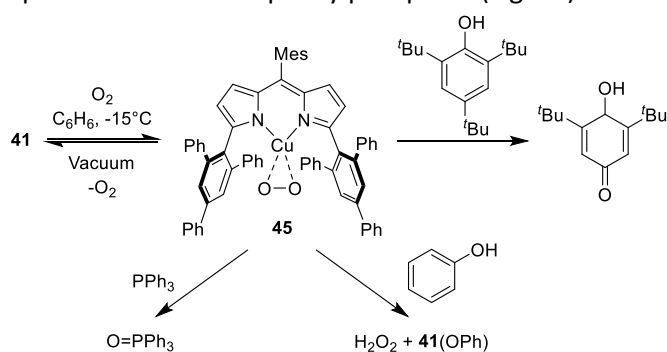


Fig. 12 Reactivity of **45**, the oxygen adduct of **41**, as described by the group of Betley.⁸⁸

The μ -oxo binuclear Fe complex, **46**, based on a Pacman bis-dpm ligand was shown to convert into the {Fe(III)}₂, **47**, and mixed valent {Fe(II)Fe(III)}, **48**, form (Fig. 13).⁸⁹ These oxo complexes were investigated for their basicity towards the formation of μ -hydroxide analogues. Compound **48** was found to not react with weak C-H bonds but it was rather revealed that this species was sensitive to water.

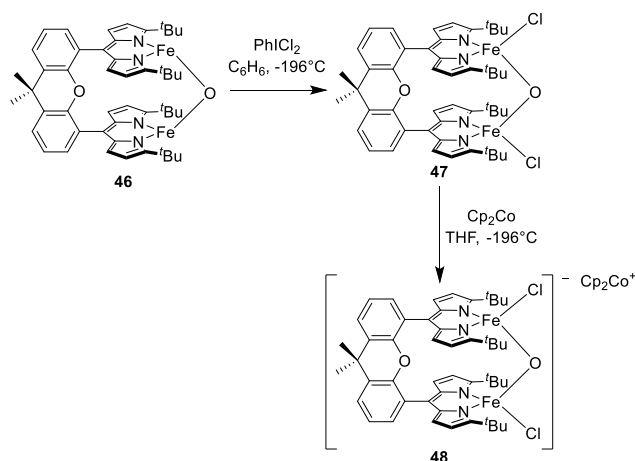


Fig. 13 Binuclear μ -oxo bridge Fe complexes described by Betley and coworkers.⁸⁹

It is worth noting that the group of Love also reported a μ -oxo binuclear Fe(III) complex, **49**, analogous to **47** (Fig. 14).⁹⁰ The reactivity of this compound has, to the best of our knowledge, not been described. The difference between **47** and **49** is that the latter comprises two unbridging mono-dpm ligands featuring imine groups at the α positions. Katayev and coworkers have similarly appended the dpm scaffold with imines showing that the formally Pd(0) and Pt(0) complexes **50** (Fig. 14) were prone to dioxygen activation leading to complexes with modification of the functional groups at the α or *meso* positions; the imine was shown to convert to a carboxylate unit in the case of the Pd compound, for

example.⁹¹ The dpm-diimine backbone was also shown to complex not only uranyl but more generally to stabilize the uranium cation in the oxidation states IV, V and IV as illustrated for **51** (Fig. 14).⁹²⁻⁹³ The stabilization of these different redox states involves the non-innocent nature of the ligand allowing its reduction and the capacity to use the axial oxygen atom upon reaction with [TiCp₂Cl]₂ or borane functionalization. Interestingly, with dpm unfunctionalized at the α positions, the uranyl complexes were not studied for such reactivity but were demonstrated to be emissive.⁹⁴ The group of Bowman-James has reported that the binuclear Mn(II) complex **52** based on two dpm- α -diimine moieties bridged by flexible propyl groups features mono-oxygenase like activity. In the crystal structure of this compound, the Mn(II) cations are bridged by an acetate anion and their coordination sphere is completed by either a water molecule or a chelating acetate (Fig. 14). The epoxidation of either cyclohexene or stilbene could be performed using this complex in yields up to 40%.⁹⁵ It was later demonstrated that **52** also shows a catalase-like activity thus catalyzing the disproportionation of H₂O₂.⁹⁶ The bound water and acetate anions were demonstrated to play an active part in the reactivity of this complex.

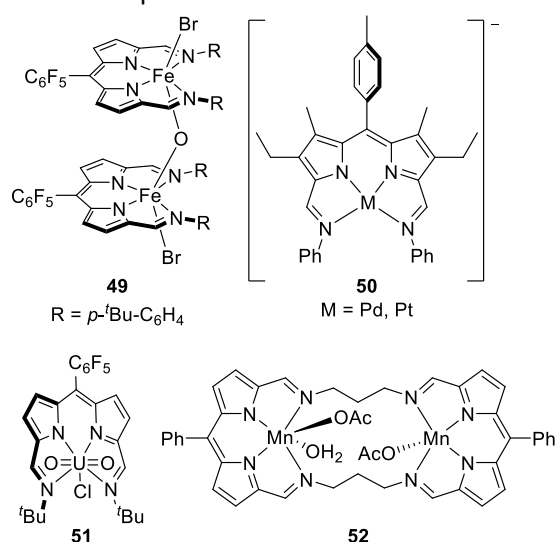


Fig. 14 Reactive complexes **49-52** based on the dpm α -diimine scaffold. Note that, in the crystal structure of **52**, one of the acetate anions is bridging the two Mn(II) cations.

6. The dipyrin-bisphenol scaffold

Another class of α -functionalized dpm has been intensively investigated over the past few years: the dpm-bisphenol (dpmPhO), bearing phenol units at positions 1 and 9. This scaffold is a hybrid between the porphyrin and the salen backbones and bears some analogy with corroles.⁹⁷ Described in the 1970s,⁹⁸ it was used for the preparation of the corresponding luminescent boron complex⁹⁹ and then for a series of emissive metal complexes.¹⁰⁰⁻¹⁰⁴ Interestingly, this type of ligand was shown to have a non-innocent character as the Co,¹⁰⁵⁻¹⁰⁷ Ni,¹⁰⁵ Cu¹⁰⁸ and Pt¹⁰⁹ complexes can be formulated (dpmPhO)²⁻M(II) on the basis of electrochemical data, single-crystal X-ray diffraction, EPR and UV-visible spectroscopies combined with theoretical calculations. With trivalent metal cations such as Au(III), the complex is better described as (dpmPhO)³⁻Au(III) with an electrochemical behavior different from the one of the corrole analogues as reduction involves both the metal center and the ligand.¹¹⁰ Several complexes of dpm-bisphenolate have been investigated for their reactivity, in particular Mn(III) compounds (Fig. 15).

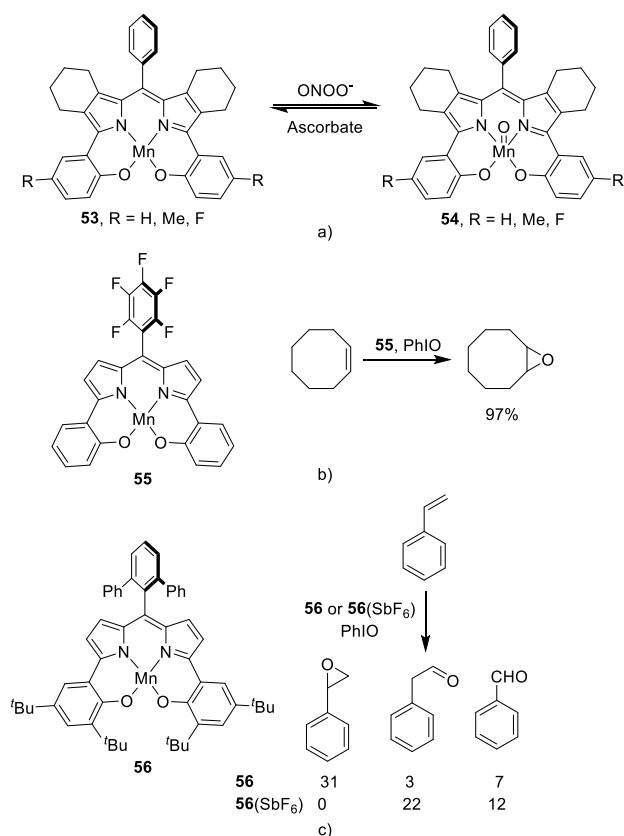


Fig. 15 Reactivity of Mn(dpmPhO) complexes.

Since Mn(III) porphyrin and corroles have been shown to decompose peroxynitrite,¹¹¹⁻¹¹² the group of Neumann has investigated the reactivity of complex **53** towards this oxidant (Fig 15a).¹¹³ This high-spin Mn(III) compound was demonstrated, by absorption spectroscopy and LC-MS, to convert to Mn(V)O complex **54** in the presence of peroxynitrite. This behaviour was further confirmed by the ability of **53** to inhibit the arylboronic oxidation by peroxynitrite as well as hyperalgesia in rats. Using a similar scaffold, the groups of Andrioletti and Aukauloo have prepared **55** and studied its catalytic activity for the epoxidation of alkenes (Fig. 15b).¹¹⁴ This compound, present as a dimer in the crystalline state, is in a monomeric form in solution. In acetonitrile, a yield up to 97% has been observed for the epoxidation of cyclooctene in the presence of iodosylbenzene, PhIO. The group of Thomas has expanded this family of compounds by preparing **56** (Fig. 15c) that bears *t*Bu group on the phenolic moieties and additional phenyl units at the *meso* positions, hence preventing dimerization.¹¹⁵ This complex catalyzes the epoxidation of styrene with yields up to 31% with small amounts of phenylacetaldehyde and benzaldehyde as additional products. Interestingly, they have investigated the redox properties of this compound and have isolated and characterized the oxidized species (**56**)⁺(SbF₆)⁻, featuring a Mn(III) center coupled to the ligand in its radical form. This oxidized species features a different activity towards styrene, since it does not lead to the formation of epoxide but rather to phenylacetaldehyde (Fig. 15c). Furthermore, (**56**)⁺(SbF₆)⁻ was found to catalyze the anti-Markovnikov isomerization of styrene oxide to phenylacetaldehyde. The group of Thomas also reported the properties of **57**, the Cu(II) analogue of **56** (Fig. 16).¹⁰⁸ In this complex, the metal center is in the divalent state and the ligand in its radical form. Compound **57** catalyzes the oxidation of alcohols under aerobic condition and in the presence of a base. Derivatives such as benzylalcohol, 1- and 2-phenylethanol were converted to the corresponding aldehydes (Fig. 16). Though with a smaller TON, the conversion of the latter unactivated primary alcohol is worth noting.

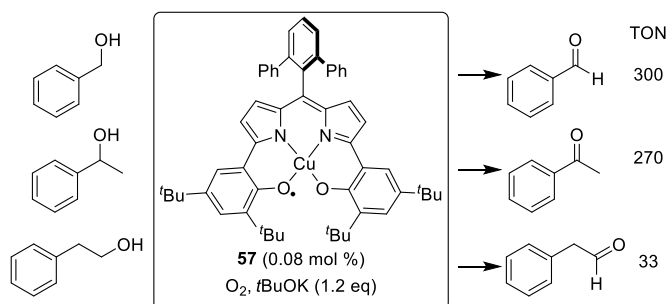


Fig. 16 Oxidation of alcohols catalyzed by Cu(II) complex **57**, as described by the group of Thomas.¹⁰⁸ TONs are given after 24 hours of reaction. Only one of the canonical forms of **57** has been presented for clarity.

Nozaki and coworkers have reported complexes **58** and **59** based on a similar ligand with tetravalent metal cations Ti(IV) and Ge(IV), respectively (Fig. 17).¹¹⁶ The coordination sphere of the metal center is completed by a chloride anion as well as a THF molecule in the case of **58**. Both compounds catalyze the copolymerization of propylene oxide with CO₂ at 60°C in the presence of [PPN]Cl to yield poly(propylene carbonate) and propylene carbonate (PPN = bis(triphenylphosphine)iminium). The selectivity towards the polymer could be tuned by modifying the number of equivalents of [PPN]Cl. The Zr(IV) and Sn(IV) analogues were found to be less efficient in this catalysis. In a following report, the same group has provided mechanistic insights concerning the selectivity of these catalysts towards poly(propylenecarbonate) (PPC) over poly(propyleneoxide) (PPO) or propylene carbonate.¹¹⁷ This has led to the design of novel Ge(IV) catalysts, analogues of **59** where a hydrogen atom or a methoxy group substitutes for the *t*-butyl moiety at the *para* position of each phenolic moiety. It was thus demonstrated that the selectivity as well as the TOF could be rationally modulated by modifying these functional groups.

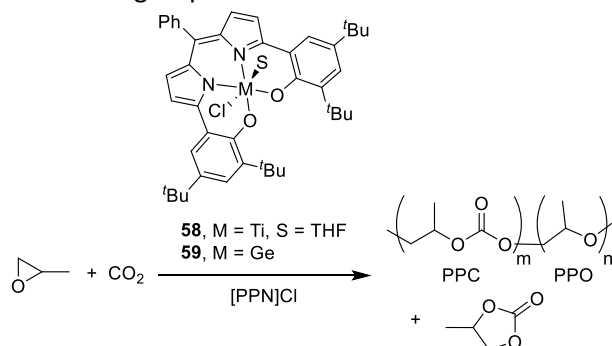


Fig. 17 Copolymerization of propylene oxide with CO₂ catalyzed by Ti(IV) and Ge(IV) complexes **58** and **59**, as described by Nozaki and coworkers.¹¹⁶

7. Reactivity of Mg(II) and Al(III) complexes

Other dpm complexes have also been explored for polymerization purposes. Indeed, Chisholm *et al.* have reported Mg(II) complex **60** based on a tris-mesityl dpm (Fig. 18).¹¹⁸ This ligand was considered in light of its sterically demanding structure and low lability in order to modify the reactivity of the resulting Grignard reagent and, in particular, to prevent its involvement in the Schlenk equilibrium. The compound was described to react with alcohols, leading to a kinetic replacement of the alkyl group (*n*-butyl in this case) and to form amides upon reaction with amines. Furthermore, it was demonstrated that the complex could act as an initiator for the ring opening polymerization of lactide and ϵ -caprolactone thus producing polylactide and polycaprolactone, respectively (Fig. 18). The solvent, either THF or CH₂Cl₂, was found to have an influence on the formation of heterotactic polylactide, with a more important stereocontrol in non-coordinating media. The role of the dpm is crucial in this

observation. Interestingly, the specific sterics of this particular ligand was recently taken advantage of to isolate and identify a magnesium isocyanide compound and a germylene monochloride species.¹¹⁹⁻¹²⁰

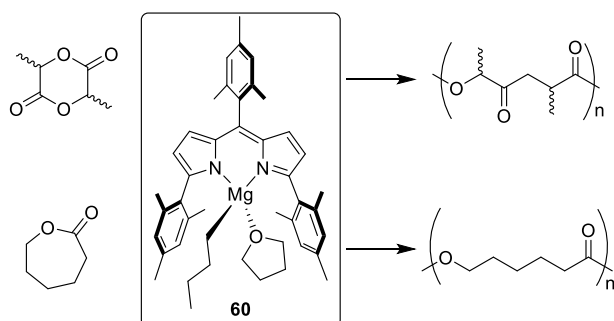


Fig. 18 Mg(II) complex **60** as initiator of ring opening polymerization of lactide (top) and ϵ -caprolactone (bottom) as described by Chisholm et al.¹¹⁸

The group of Mason has investigated the ring-opening polymerization activity of Al(III) analogues of **60**, with a phenyl at the *meso* position and either alkoxide or amide ligands.¹²¹⁻¹²² However, polymerization of ϵ -caprolactone was observed with rather poor conversion, as a result of the sterics imposed by the dpm ligand. Also, decomposition of the dimethylamide complex in the course of the catalysis was suggested.

8. Rh(I)/Rh(III)-based catalysts

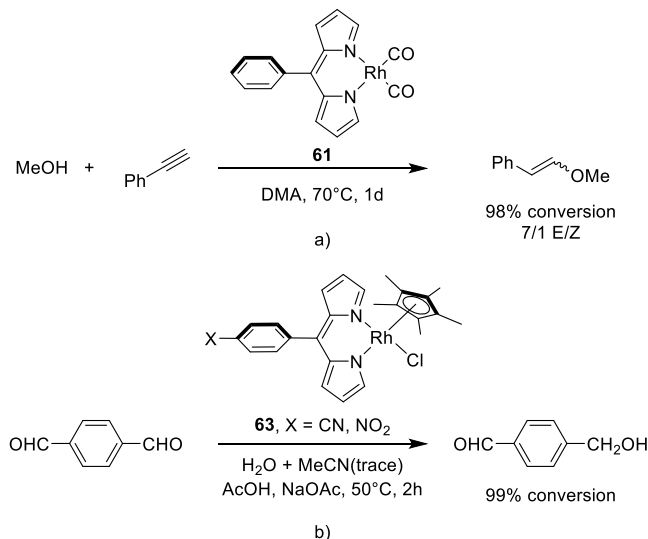


Fig. 19 Reactions catalyzed by Rh(I) or Rh(III) dpm complexes.

Compounds incorporating Rh are widely explored in the literature for their reactivity.¹²³⁻¹²⁴ While a Rh(I) dpm complex has been described in 1974,¹²⁵ the catalytic activity of such species has been investigated much later. Messerle and coworkers reported Rh(I) complex **61** (Fig. 19a) active for the catalytic hydroalkoxylation of phenylacetylene and MeOH.¹²⁶ The reaction with 1 mol% of **61** in *N,N*-dimethylacetamide (DMA) proceeded with a conversion of 98% and a clear preference for the *E* product. Interestingly, the substrate scope was found to be wide, since neither electron-donating nor electron-withdrawing group in the *para* position of the aromatic unit of the substrate impacted negatively the conversion rate. The favored formation of the *E* isomer of (2-methoxyvinyl)benzene was rationalized by less steric hindrance between the methoxy and phenyl group in the *trans* arrangement by DFT calculations.¹²⁷ This theoretical investigation also suggests that DMA facilitates the addition of

MeOH and that the mechanism involves a vinyl Rh(III)-H hydride intermediate. Khoroshutin and coworkers also described the activity of a Rh(I) compound based on dpm albeit with the bis-pyrrolic chelate not at the rhodium center.¹²⁸ The heterometallic catalyst was obtained by combination of (acac)Rh(CO)₂ with **62**, the analogue of Co(III) complex **1** where X = PPh₂ (Fig. 2). This compound led to the formation of a mixture of isomers of aldehyde upon hydroformylation of 1-octene.

The group of Pandey has reported a series of organometallic Ru(II), Ir(III) and Rh(III) complexes incorporating dpm ligands focusing on their biological activity, supramolecular assembly as well as their catalytic activity.¹²⁹⁻¹³⁴ In particular, Rh(III) complexes of type **63** (Fig. 19b) were shown to catalyze the transfer hydrogenation of terephthalaldehyde leading to the mono-reduced derivative 4-hydroxymethylbenzaldehyde with complete conversion.¹³⁰ Interestingly, the Ir(III) analogues of **63** were found to be less efficient for this process. A similar reactivity was observed for compounds where the metal center (Ru(II), Ir(III) or Rh(III)) is coordinated to a peripheral pyridyl unit of a dipyrromethene ligand rather than by the dpm chelate itself.¹³¹

9. Pd(II) based catalysts

The Suzuki-Miyaura cross-coupling is an important tool in organic chemistry with active research in the development of new palladium catalysts.¹³⁵ Surprisingly, while homo- and heteroleptic Pd(II) dpm complexes have been extensively investigated,^{33,136-145} only one report described the potential of these compounds for C-C bond formation.¹⁴⁰ Mono- and bi-nuclear heteroleptic complexes **64** and **65** (Fig. 20) were shown to be active for the cross-coupling of arylboronides with phenylboronic acid. Yields were found to reach up to 81% with aromatic substrates bearing an electron-withdrawing substituent and when using the binuclear species. Compound **64** gave a conversion rate around *ca.* 70%. Whereas the analogue of **65** with an azaBODIPY moiety substituting for one Pd(II) complex has been reported, its catalytic activity has not been described.¹⁴¹

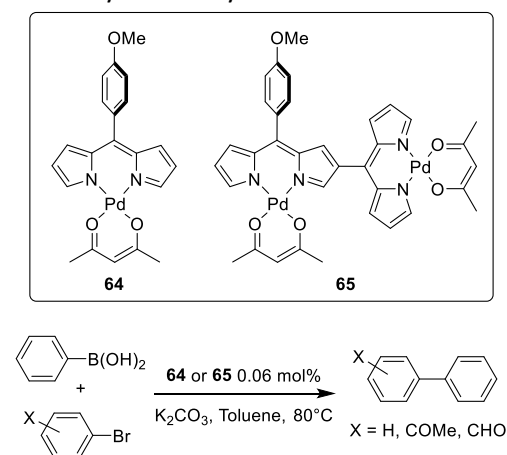


Fig. 20 Pd(II) based Suzuki Miyaura catalysts **64** and **65**, described by Ravikanth and coworkers.¹⁴⁰

10. Heterogeneous catalysts

So far, all the examples described herein have been homogeneous catalysts. Interestingly, the group of Liras has developed an heterogeneous porous polymer as a visible light photocatalyst for the aza-Henry reaction (Fig. 21).¹⁴⁶ Following an earlier report of an all-BODIPY porous polymer,¹⁴⁷ removal of boron led to deprotected dpm available for complexation of the [Ru(bpy)₂]²⁺ fragment (bpy = 2,2'-bipyridine). Whereas heteroleptic [Ru(bpy)₂(dpm)]⁺ derivatives have been described for their photophysical properties and potential applications in solar cells, their catalytic properties had not been explored.^{137,148-153} The resulting polymer was found to photocatalyze, under visible light, the reaction of tetrahydroisoquinoline with nitroalkanes such as nitromethane, as presented in Fig. 21, with a 98% conversion and the presence of a small amount of an oxidation product. Other nitroalkanes could be employed with high conversion rates but afford more of the undesired oxidation adduct. It is

noteworthy that the reaction did not proceed in the absence of light and that the polymer retained its efficiency and selectivity through seven cycles, corresponding to more than 350 hours of irradiation.

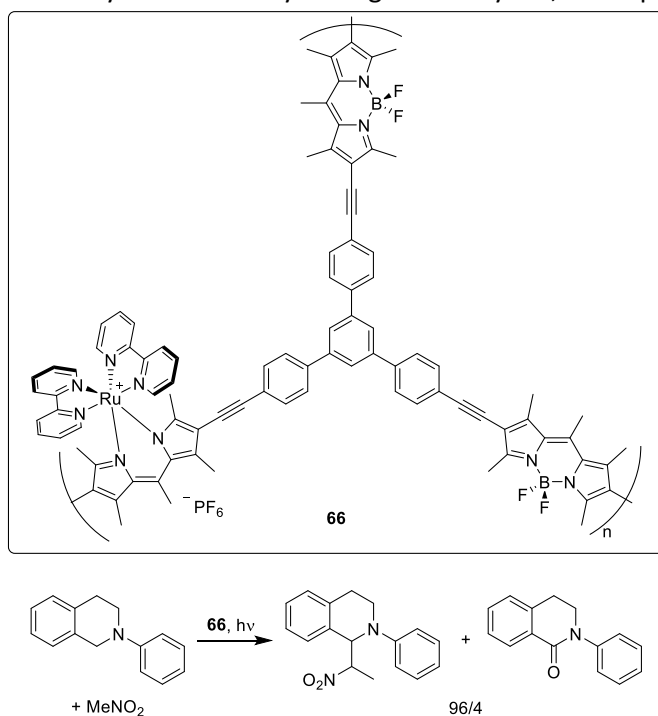


Fig. 21 Representation of a fragment of the BODIPY-based porous polymer **66** enriched with Ru(bpy)₂(dpm) units (top) and photocatalyzed aza-Henry reaction as reported by Liras and coworkers.¹⁴⁶ Only one enantiomer of the Ru complex is shown but both are present in the polymer.

Another approach for the development of heterogeneous catalysts incorporating metal dpm complexes has been reported by the group of Pandey.¹⁵⁴⁻¹⁵⁵ Heteroleptic Ni(II) complexes comprising both a pyridine-appended dpm and a dithiocarbamate ligand were found to stabilize and functionalize Ag and Au nanoparticles. However, the role of the metal complexes in the investigated catalyses (reduction of 4-nitrophenol to 4-nitrophenolate for Ag nanoparticles and of Cr(VI) to Cr(III) for Au nanoparticles) has not been fully detailed. It clearly appears that they stabilize the metal aggregates but their actual mechanistic involvement in the catalyzed reaction has not been fully addressed.

Conclusions

Dipyrin based metal complexes have been extensively investigated for a wide array of properties and applications such as in luminescent or porous materials, in supramolecular chemistry or in biology, for example. Interestingly, the study of the reactivity and catalytic activity of these compounds represents a more recent development. Sometimes coined half-porphyrins, dipyrins analogously endow their complexes with unique properties such as the potential to functionalize the pyrrolic backbone or the *meso* position as well as the ability to favor interesting chemical transformations. Thus, while the derivatization of or at the *meso* group has been successfully explored, the α -positions of the dpm chelate were also shown to be reactive. Indeed, not only alkoxylation is possible at this site, but the reactivity of these positions has also been taken advantage of for the formation of a broad range of polypyrrolic derivatives such as 2,2'-bis-dpms, nor-/hetero-corroles and porphyrinoids. The elaboration of these architectures relies on the use of template metal complexes. These compounds favor the close proximity of the pyrrolic rings and the metal cation exerts an electronic role facilitating the reaction. Beyond the modification of the bis-pyrrolic backbone, the dipyrin-complexed metal cations play a role in a diversity of catalytic transformations. The chelating ability of dpm and the possibility to modify its

steric and electronic characteristics by functionalization has been exploited for the development of numerous complexes featuring appealing activity. Hence, it has been demonstrated that Fe, Co, Cu and Ni dpm complexes can be employed for C-H activation/amination; a reactivity currently especially sought after. Furthermore, introduction of functional groups like phenolic moieties leads to non-innocent tetradentate species. The corresponding complexes have been demonstrated to catalyze efficiently polymerization or oxidation reactions. Finally, classical reagents such as Grignard species, Rh or Suzuki-Miyaura catalysts have been revisited by incorporation of dpm in the coordination sphere of the metal center, with convincing outcomes. In light of all these results, dipyrin metal complexes appear as an interesting addition to the toolbox of catalysts required for the design and synthesis of valuable organic compounds. While additional reactivity under homogeneous conditions may be reported in the future, it seems that one promising area to be explored is the possibility to develop heterogeneous catalysts. For example, whereas dpm have been successfully used for the preparation of crystalline porous materials of the metal-organic frameworks type, the heterogenization of catalytically active dpm metal complexes into such crystalline architectures remains to be uncovered. This area and other potential endeavors suggest a great future for this research field.

Conflicts of interest

There are no conflicts to declare.

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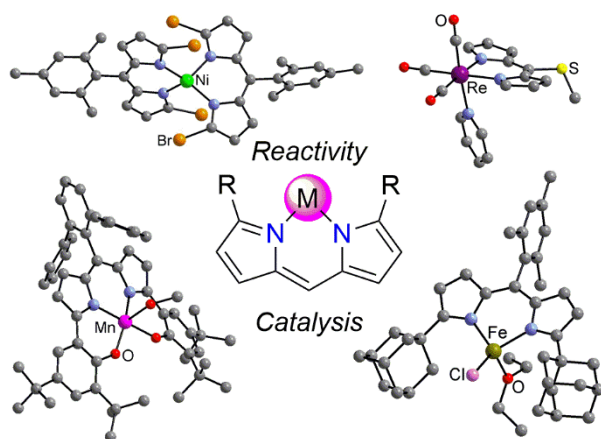


Table of contents This Perspective reviews the use of dipyrin based metal complexes as catalysts and as templates towards polypyrrolic architectures.