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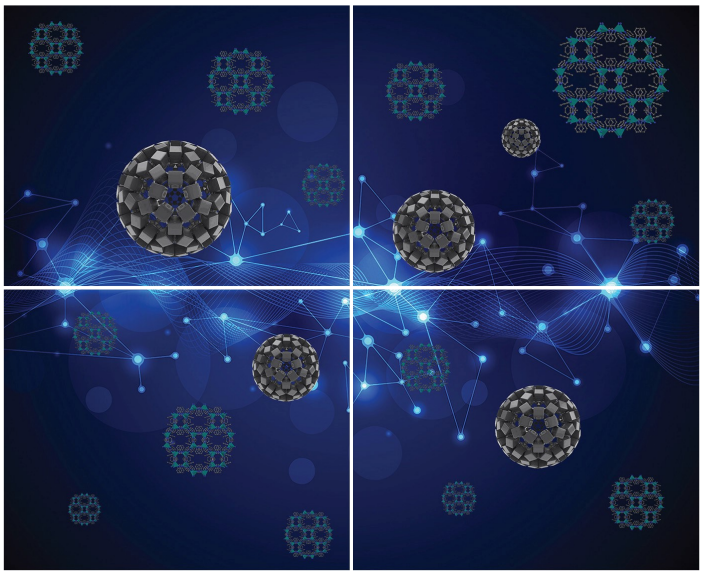

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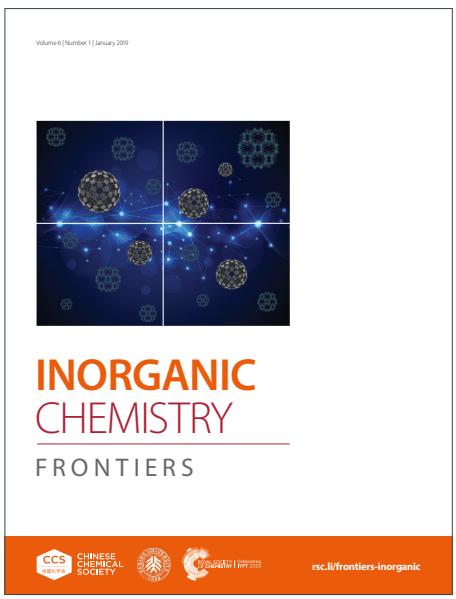

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ARTICLE

Mesoionic Imines: Strong N-Donors, Electronic Ambivalence and Applications in Catalysis

Richard Rudolf[a] and Biprajit Sarkar[a,b*]

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Mesoionic imines (MIIs) based on a 1,2,3-triazole core have been popularized in the past ca. 5 years. In this review article we discuss the synthesis, coordination ability and the structural and spectroscopic properties of these fascinating class of electronically ambivalent compounds. Apart from this, we also discuss the utility of MIIs and their compounds in directed C-H activation reactions, and in the activation and conversion of small molecules such as alkynes and CO_2. Based on the current state of the art, we touch upon possible future developments of the chemistry of these classes of molecules.

Introduction

The first reports on the preparation[1] and isolation of carbenes in the form of N-heterocyclic carbenes (NHCs)[2] fundamentally reshaped the realm of organometallic chemistry. NHCs cemented themselves as powerful tools in synthetic chemistry but also adjacent scientific fields like material sciences. The history, properties and applications of NHCs were extensively reviewed elsewhere.[3–6] Being powerful and intriguing compounds for various applications, finding suitable synthetic methods for tailoring the properties of NHCs by perturbation of the substitution pattern is a leading development in this field. Two concepts for substitution arguably stand out the most: Replacement of the lone-pair with an organic moiety X or interchange of the imidazole-frame with other heterocyclic cores (chart 1).

Besides the "classical" imidazol-2-ylidene, NHCs like pyrrolidin-2-ylidenes[7–9] (commonly referred to as "CAACs") with other heterocyclic backbones garnered a lot of attention as they allowed the introduction of other, different properties.[10]

A currently highly popular heterocycle in the realm of NHC-chemistry is the 1,2,3-triazole. By the Nobel-prize winning

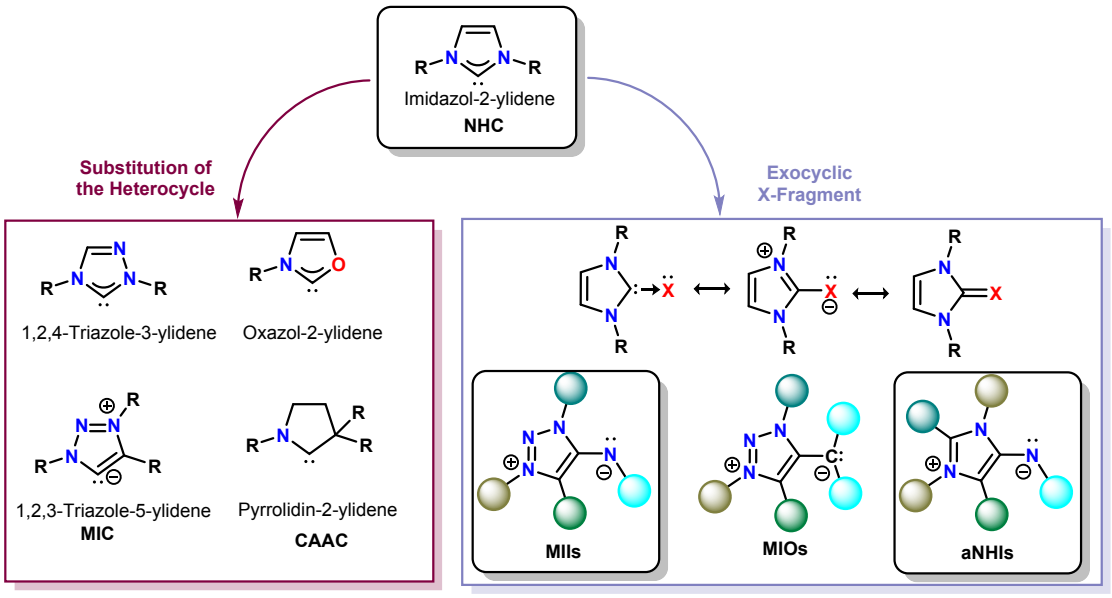

Chart 1 Overview on NHCs and derived compounds.

[a] Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. Email: b.sarkar@fu-berlin.de
[b] Institut für Chemie und Biochemie, Anorganische Chemie, Freie Universität Berlin, Fabeckstraße 34-46, 14195 Berlin, Germany.

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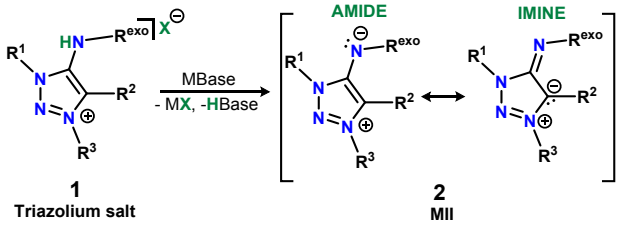
concept of CuAAc (copper-catalysed azide-alkyne cycloaddition reaction)[11–16] 1,2,3-triazoles are synthetically accessible with a large variety of substituents. Further quaternisation of the N3-position on 1,2,3-triazoles with electrophiles like alkyl-halides or bisaryliodonium salts generates the corresponding NHC after deprotonation. Bearing mesoionic characteristics, such 1,2,3-triazol-5-ylidenes are often referred to as mesoionic carbenes (MICs).[17–19] Further information can be found in excellent reviews by Crowley et al, [20] Sarkar et al,[21, 22] Albrecht et al[23–26] and Bugarin et al[27, 28]. Formal replacement of the lone-pair on NHCs with an organic moiety X (X = NR, CR_2, PR, O, Se, …) generates compounds with a highly polarised C-X bond. Such compounds can be described with a zwitterionic canonical structure, which reveals a large electron density at the fragment X. From that, it is no surprise that compounds of the form "NHC-X" are found to be versatile ligand systems and act as potent organocatalysts.[29–34] One prominent representative of this class is the N-heterocyclic imine (X = NR, referred to as "NHI", Chart 1). After fundamental work on NHIs by Kuhn in the 1990s,[35] NHIs found great application in the stabilisation of elusive main-group element fragments like radicals,[36–39] nitrenes[40, 41] or heavier tetrylenes[42–50] or as ligands in transition metal and actinide/lanthanide[51] complexes. Excellent reviews on NHIs in this regard are available by Inoue and coworkers [52] and by Tamm and coworkers[53].

Introduction of an exocyclic fragment X on MICs gives therefore interesting new opportunities. Recent publications on N-heterocyclic olefins of the type MIC-CR_2 (MIOs)[54–60] and MIC-derived NHIs (MIC-NR)[61–69] cement this statement. The corresponding NHIs with a MIC-core are referred to as mesoionic imines (or short as "MIIs") as they also show mesoionic characteristics. After the first report on MIIs in 2020 by Ooi and coworkers,[69] the potential of MIIs as ligands[66, 63–65] and potent organocatalysts[61, 62] was uncovered. In this regard, we herein wish to provide a review and outlook on the work done on MIIs with a 1,2,3-triazole core by us and others. Deprotonation of 5-amino-1,2,3-triazolium salts **1** is the general synthetic approach to MIIs **2** (Scheme 1), which is highly inspired by the parent compounds (NHCs, MICs, NHIs, …). Therefore, we will start with an overview on the synthetic procedures currently established for such 5-amino-1,2,3-triazolium salts and then dive into the electronic structure, reactivity and application of MIIs as organocatalysts, [61, 62] fluorophores[70, 64, 66, 68] and as ligands[66, 63–65, 70].



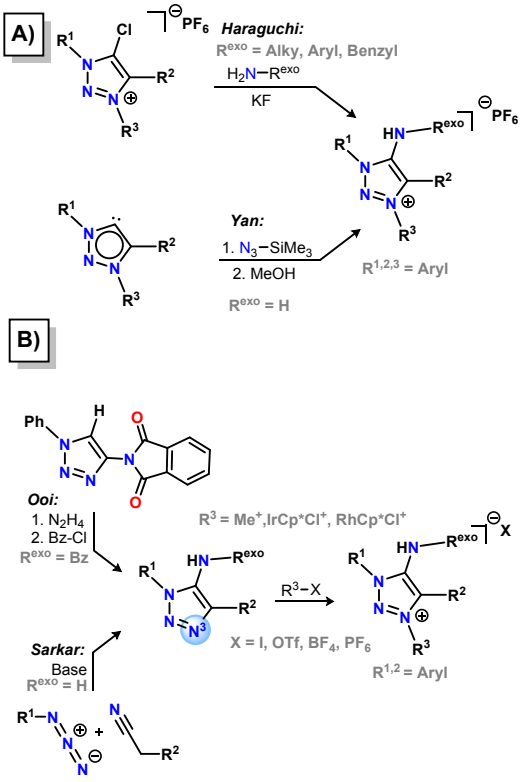
Scheme 1 General approach for the synthesis of MIIs **2** from triazolium salt **1**.

As imiazol-4-ylidenes also bear mesoionic characteristics, the NHI with an imiazol-4-ylidene core can also be characterised as an MII. Work on such NHIs is also quite recent[71] and a short overview on them will be given in the last chapter. In order to avoid misunderstandings, NHIs with imidazol-4-ylidene backbones will be called "aNHIs" in the following, while the term "MII" is reserved for NHIs with a 1,2,3-triazole-5-ylidene scaffold.

Discussion

Synthesis of MIIs

For the construction of 5-amino-1,2,3-triazolium salts two general methods were employed until now (Scheme 2): A) Synthesis of either 5-chloro or 5H-triazolium (further conversion to free MIC in that case) salts followed by amine-functionalisation of the 5-position. [61, 62, 68] B) Quaternisation of the N3-position of 5-amino-1,2,3-triazoles by methylation or coordination of monocationic metal-fragments. [66, 63–65, 70, 69]



Scheme 2 *Hitherto* reported synthetic routes to 5-amino-1,2,3-triazolium salts. A) Amine-functionalisation of 1,2,3-triazolium salts. B) Construction of 5-amino-1,2,3-triazoles followed by quaternisation of N3.

According to the reports by *Haraguchi et al*, 5-chloro-triazolium salts can be aminated with primary or secondary amines under the presence of a fluoride source.[61] Follow-up work highlighted the large scope of triazolium salts and amines, which could be coupled by this methods.[62] Among the amines, either aromatic, benzylic or aliphatic amines were tolerated. Even sterically congested amines like *tert*-butylamine or pyrolidine were successfully employed as the coupling reagent. This method also tolerates quite a scope of functional groups, like alkynes, alkenes, amines or alcohols without the need of prior

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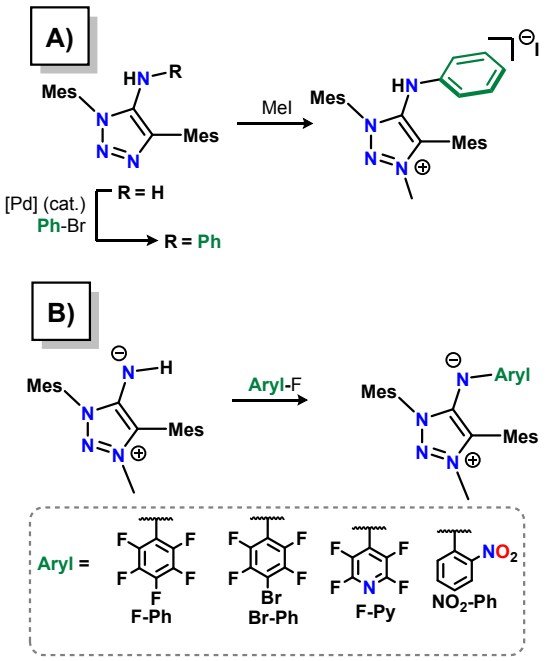
protection. *Yan* et al reported on a *Staudinger*-type reaction of a "free" MIC with trimethylsilyl azide followed by hydrolysis under methanolic conditions. This method generates MIIs with a proton bound to the exocyclic N-position.[68] Being strong nucleophiles, *Yan* et al reported in the same work that the corresponding Me-substituted MII is accessible by reaction of the H-substituted MII with MeI. Until now, both methods have been reported for triply arylated triazolium salts.

The second method revolves around the construction of 5-amino-triazoles, which are then converted to the corresponding triazolium salts *via* quaternisation of the N3-position of the heterocycle. The group of *Ooi* generated a triazole by reaction of a phthalimide substituted alkyne with phenylazide under "classical" CuAAc-conditions.[69] The free amine can then be liberated by deprotection of the thus formed phthalimide protected 1,2,3-triazole by reaction with hydrazine hydrate. Subsequent methylation afforded the desired 5-amino-triazolium salt. *Sarkar* et al constructed several, differently substituted 5-amino-triazoles by a base-mediated cycloaddition reaction between aromatic azides and aryl-substituted acetonitrile derivatives.[66, 63–65, 70] Subsequent methylation or coordination with cationic metal-fragments (such as $[MCp^*Cl]^+$ with M = Rh, Ir)[64] yielded like in the case of *Ooi* et al the desired triazolium salts.



Scheme 3 Possible methods for substitution of Rexo of MIIs. A) Pre-functionalisation of 5-amino-1,2,3-triazoles by Buchwald-Hartwig amination. B) C-F activation with electronpoor arylfluorides.[71]

The prior construction of 5-amino-triazoles gave some peculiar advantages compared to the methods reported by *Haraguchi et al* and *Yan et al*. Quite a variety of arylated substituents were employed as the R^1- or R^2-residues by *Sarkar* et al. Until now, quaternisation of the N3-position of 5-amino-triazoles by a substituent R^3 was only reported with methylating agents or by coordination of a monocationic metal-fragment to the N-N chelating pocket provided by the pyridyl-substituted 5-amino-triazole (R^2 = Pyridyl).[64] In a work of Sarkar and co-workers, methods of R^{exo}-substitution were further investigated (Scheme 3).[70] By *Buchwald-Hartwig* amination of 5-amino-triazoles[72] a phenyl-substituent could be introduced as R^{exo} (Scheme 3 A)). The free N_{exo}-H MIIs were also found to be quite active reagents for C-F activation of electron-poor fluoro-arenes, which yielded the corresponding R^{exo}-substituted congeners as isolable compounds (Scheme 3 A)). [70]

Spectroscopic and Structural Analysis of MIIs

The C1-N4 bond length can be probed to analyse the bonding situation in MIIs. With a mean bond distance of around 1.30 Å, the C1-N4 bond in "primary" MIIs with a proton bound to the exocyclic N-atom are best characterised with significant double bond character thus justifying naming them "imines"(Scheme 1, description of **2** as imine).[66, 63–65, 68] This is also reflected in the corresponding C1-N4 stretching frequency obtained by IR-spectroscopy. With a frequency > 1700 cm^{-1} such compounds are in the range of reported, "classical" imines. Electron-withdrawing moieties like fluorinated arenes[70] or benzoyl-substituents[69] bound to the exocyclic N-atom elongate the C1-N4 bond to up to 1.35 Å (Figure 1). This can be rationalised by delocalisation of electron-density from the triazole-cycle onto the fluorinated substituent. A *p*-quinone type resonance delivers therefore a significant contribution to the structure. Thus, in such cases the C1-N4 bond is best characterised as a highly polarised single bond (Scheme 1, description of **2** as amide).[70, 69]

In the bis-phenyl substituted derivative **2a** we observed intramolecular H-bonding interactions between *ortho*-protons of the Ph-substituents and the exocyclic nitrogen-atom N4 in solid state by XRD structural analysis on single-crystals (Figure 1). [63] More precise bonding analysis showed that the strength of these contacts differ tremendously: The much shorter contact formed by the *o*-protons of the N1-substituted Ph-moiety (2.31(2) Å) suggest a stronger H-bond compared to the respective contact of the o-proton of the Ph-substituent on C2 (2.91(1) Å). NMR-spectroscopy (^{1}H) confirmed that such interactions are also present in solution as the resonance of the involved protons is significantly down-field shifted.[63, 66, 65] QTAIM-analysis also suggests a critical bonding point between the aforementioned protons and N4 although it's supposedly relatively weak.[65] The corresponding C-H bond is therefore quite activated and can be reacted with appropriate substrates. Such a reactivity is discussed in a later chapter.

In most cases, free MIIs show intense yellow to red colour as solids and in solution (Figure 1). According to (TD-)DFT calculations (Figure 1), the intense colours of the compound is the result of HOMO→LUMO transitions in the visible region of the electromagnetic spectrum.[65, 70] The HOMO is predominantly localised on the Nexo-atom (non-bonding n(Nexo)-orbital) while the LUMO consists of an anti-bonding π*-orbital on the triazole-backbone. After excitation of this main HOMO→LUMO

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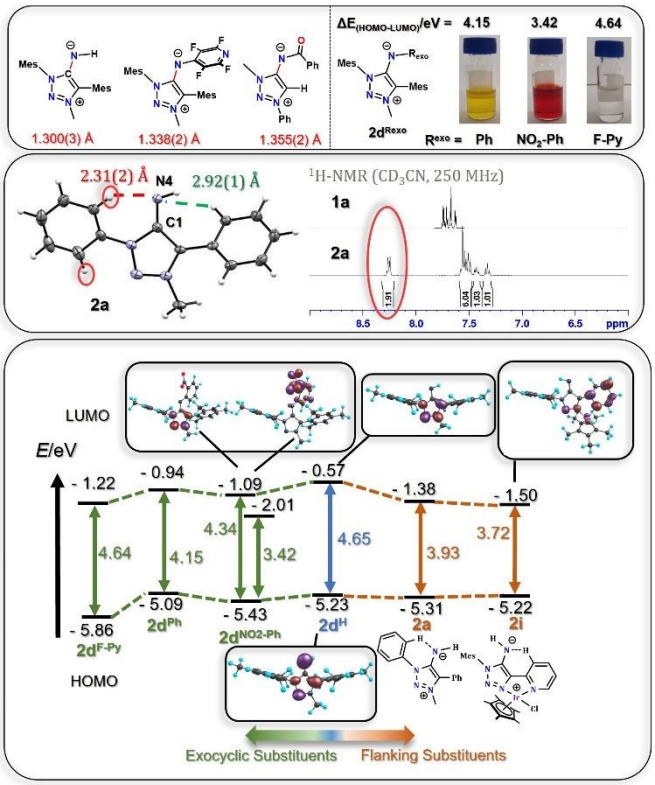


Figure 1 Top: C1-N4 bond lengths and the colours of MIIs with different R^{exo} substituents. Middle: Intramolecular H-bonds are highlighted in solid state and in solution. Bottom: MO-diagram with the frontier orbitals (HOMO, LUMO and LUMO +1) and the corresponding energy levels for differently substituted MIIs. The localised Kohn-Sham orbitals are displayed only for selected compounds to remain clarity of the figure. Level-of-theory: PBE0/def2-TZVP/SARC-ZORA-TZVP(Ir)/CPCM(CH_2Cl_2) [84–87].

transition, MIIs with R^{exo} = H were shown to emit yellow to green light with a quantum yield up to 50%.[68] The authors of this work state, that this property is highly dependent on the degree of conjugation present in the system. As the work of MIIs is still in its infancy, possible photophysical application of MIIs represent therefore an interesting opportunity.

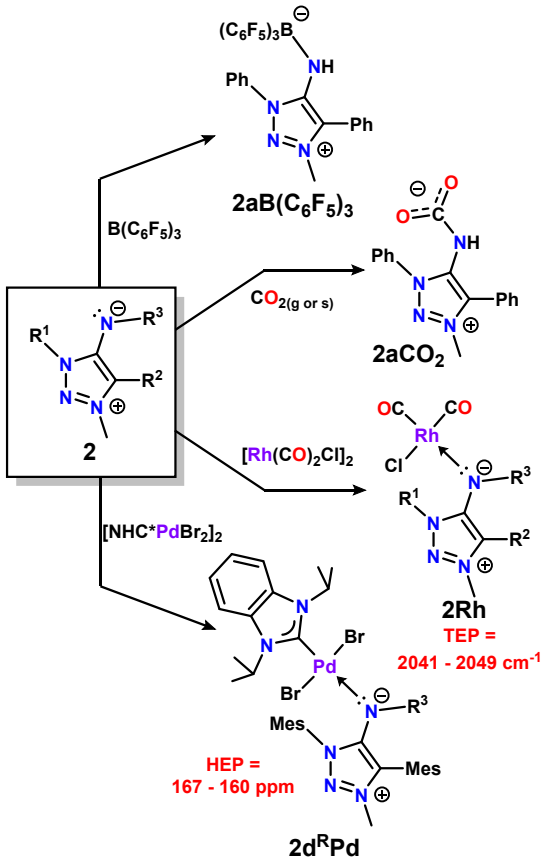
The HOMO/LUMO-energy levels are heavily dependent on the substituent bound to the exocyclic N-atom[70] and on the flanking substituent on the triazole-frame[65, 64]. Electron-withdrawing N-exo-substituents like fluorinated arenes stabilise the HOMO-energy level by partial delocalisation of the HOMO onto the exo-substituent. Likewise, the LUMO-energy is lowered by this effect. This is especially apparent in the MII with the π-acidic (ortho-nitro)phenyl-substituent.[70] In this case, the LUMO is mostly localised on the aryl-substituent, which results in a considerably smaller HOMO-LUMO energy-gap. The corresponding MII therefore has an intense red colour.[70]

The flanking substituents bound to the triazole-scaffold on the other hand have no effect on the HOMO-energy level but tremendously influences the LUMO-energy level (Figure 1).[64] Substituents with a proton bound to the *o*-position, engage in intramolecular contacts between that *o*-proton with the exocyclic N-atom. This interaction was observed not only in solid state but also in solution. AIM-calculation gave further evidence for such an interaction.[65] This interaction induces parallelisation of the said substituent with the triazole-cycle, which in turn increases the conjugation of the system. The result is a lowered LUMO-energy level. The extent of the LUMO stabilisation is highly dependent on the substituent in question. Coordination of an IrCp*Cl-fragment to the N-N chelating pocket of the pyridyl-amino-triazole has a tremendous effect compared to a phenyl-substituent as in the foremost case the LUMO is partially delocalised on the Ir-fragment.[64] The corresponding metallo-MII has a highly nucleophilic site (N_{exo}) as well as a highly electrophilic site (IrCp*Cl).

Further substitution of the IrCp*Cl with an RhCp*Cl fragment shows how this pronounced electrophilicity did not allow for isolation of the compound as such compounds presumably undergo intermolecular reactions owing to their highly ambiphilic nature.[64]

Reactivity of MIIs

Reaction with "simple" Lewis-acids. Being latent amides, MIIs readily react with Lewis-acids LAs under the formation of the corresponding MII-LA adducts (**2LA**, **S**cheme 4). Besides main-group element electrophiles like MeI,[70, 68] fluoro-arenes,[64, 70] boranes[63] or CO_2-gas[63] also "simple" transition metal fragments were coordinated to MIIs. Such reactions were investigated in detail by Sarkar and coworkers. The reaction of MIIs with either a $Rh(CO)_2Cl$- or NHC*-$PdBr_2$-fragment afforded isolable complexes (**2Rh**/**2Pd**), which could be characterised spectroscopically and structurally.[66, 63, 64, 70] The resulting complexes served as probes for the determination of the donor-properties by the established Tolman/Huynh-electronic



Scheme 4 Reactivity of MIIs towards "simple" main-group and transition metal based Lewis-acids. For the Rh/Pd-complexes the ranges of the respective TEPs/HEPs are given.

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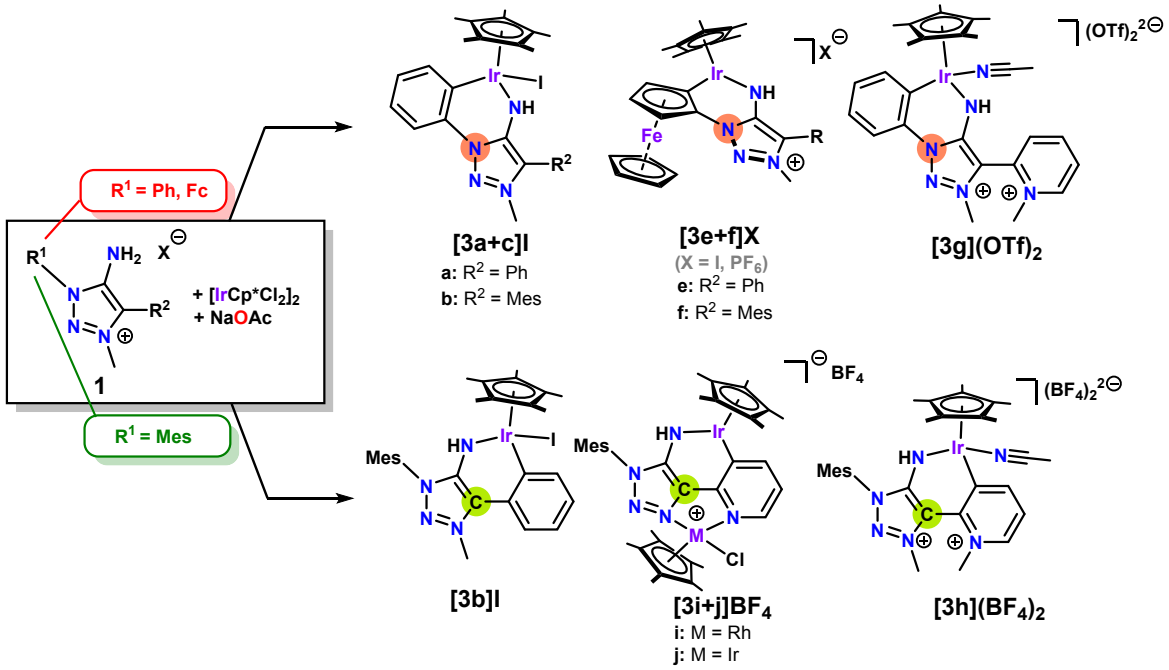
parameter (TEP[73]/HEP[74–76]).[77] In conjugation with theoretically calculated methyl-cation-affinities (MCAs) the data published by Sarkar and co-workers[70] not only represents the first thorough study on the donor-properties of NHIs, it also provides more insight into the high-electron donating nature of MIIs. The TEP of MIIs are in the range of other latent amides like pyridylidene-amides[78–81] and cyclopropenyl-carbeneimines[82]. As discussed in the previous chapter, electron-withdrawing substituents will increase the TEP value as the donating ability is likewise decreased while the HEP value decreases accordingly. The calculated MCAs also reflect this trend.



Scheme 5 Synthesis of cyclometalated complexes **3** with MII-ligands as C-N chelates starting from the corresponding triazolium salts **1**.

C-H activation reactions with Ir-precursors and correlations between crystallographic and NMR data. The intramolecular H-contacts as discussed in more detail in an earlier chapter were also found to have strong implication for the reactivity of MIIs towards substrates, which are active in C-H activation reactions. Reaction of any MII bearing a C-H acidic flanking substituent with either $[Ir(COD)Cl]_2$ or $[IrCp^*Cl_2]_2$ resulted in the immediate C-H activation and cyclometalation of the MII-ligand with the corresponding Ir-containing substrate.[65] According to thorough spectroscopic and structural investigation, the MII acts as a C-N chelating ligand under the formal depletion of one equivalent of HCl. As MIIs are strong bases, residual MII is protonated by the formed HCl in solution which results in a 1:1-mixture of cyclometalated complex **3** and triazolium chloride salt **2**. This direct metalation method did not allow for isolation of the complexes as the Ir-complexes were not separable from the triazolium salt. Sarkar and co-worker therefore reacted the triazolium salt as a pro-ligand under basic conditions with $[IrCp^*Cl_2]_2$ (Scheme 5). These conditions not only resulted in full conversion of the MII-proligand to the desired complexes, the Ir-complexes could also be isolated in good to very good yields from the reaction mixtures.[66, 63–65] It stands out, that depending on the substitution pattern the C-H activation follows a profound regio- and chemoselectivity: substituents on the N1-atom undergo the C-H activation far more preferentially than the respective site substituted to the C2-atom of the triazole-frame. This behaviour becomes especially obvious with the Fc-substituted derivative or the pyridinium-substituted congener. In both cases, the respective C-H bond on the C2-substituent (Fc-H vs. Ph-H or Ph-H vs. $[Py-H]^+$)[23, 83–87] should be far more acidic but still the C-H activation occurs preferably on the N1-substituent.

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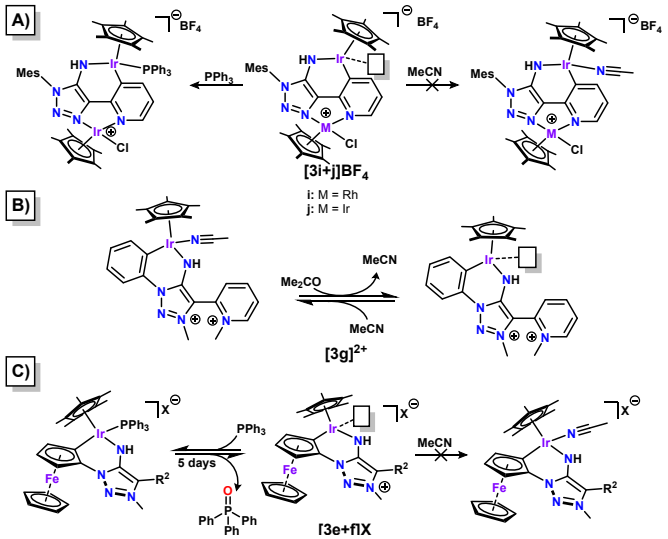
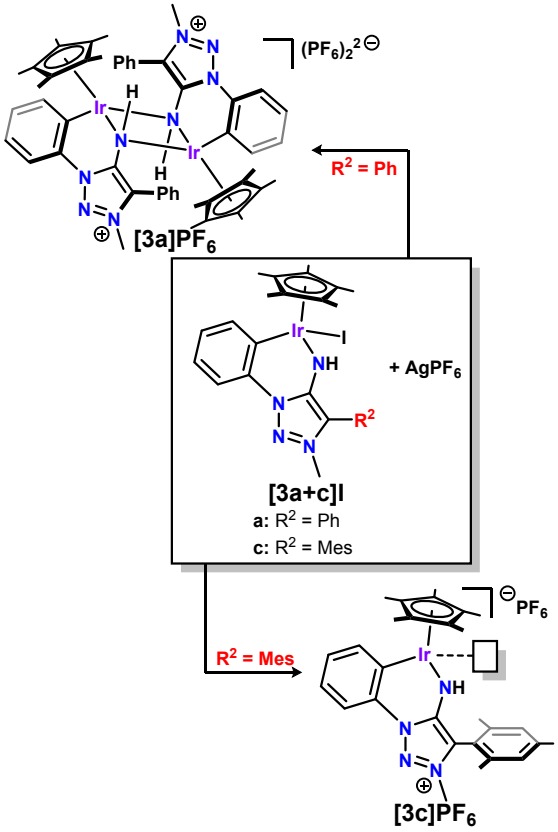
Such profound electronic differences by either C- or N-substitution on MIC-ligands were previously investigated[88–90] and derived from these insights the observed regio- and chemoselectivity is connected to higher C-H acidity induced by the N-substitution and to the preferential stronger H-bonding interaction between the imine-N and the C-H bond of the N1-substituent. The cyclometalated iridium-complexes **3** obtained *via* this route usually contain the Ir-centre coordinated in a three-legged piano-stool geometry. Exceptions to that are the ferrocenyl-substituted derivatives [66] **[3e]I** and **[3f]I** and the Rh/Ir-based metallo-MIIs [64] **[3i]BF$_4$** and **[3j]BF$_4$**, in which the Ir-centre in question is obtained as a two-legged piano-stool complex after work-up. Even the presence of potentially coordinating solvent (MeCN) or coordinating counter-anions (I^- in the case of **[3e]I** and **[3f]I**, Scheme 6) did not result in the occupation of the free coordination site. Only stronger donors, such as Ph_3P, occupied this free coordination site, although in the case of the ferrocenyl-substituted derivatives **[3e]I** and **[3f]I**, oxidative dissociation of the phosphine-ligand was observed over time (Scheme 6).[66]



Scheme 6 Observed reactivity of MII-IrCp* complexes towards association/dissociation of the sixth ligand. [61–63]

This behaviour points to the high electron-donating nature of MII-ligands as they provide the platform to stabilise coordinatively unsaturated Ir(III)-centres as the thermodynamically favoured species. The cyclometalated MII-IrCp* complexes **[3a]I** and **[3c]I** with a covalently bound iodide-counter anion can undergo halide-abstraction reaction with $AgPF_6$ under the formation of two different products dependent on the substitution pattern on the triazole-frame (Scheme 7). The Ir-complexes bearing the MII-ligand with a phenyl-substituent on the C2-atom of the triazole-frame undergoes halide-abstraction under the formation of a dimeric, molecular complex **[3a]PF$_6$**, in which two MII-ligands act as μ^2-ligands for two IrCp*-fragments. The halide-abstraction reaction of the Ir-complexes containing the MII-ligand with the sterically more demanding Mes-substituent on C2 yielded the corresponding monomeric coordinatively unsaturated Ir-complex **[3c]PF$_6$**.

The reactivity of such coordinatively unsaturated complexes were investigated in greater detail on the derivative **[3c]PF$_6$**



Scheme 7 Chemical abstraction of the covalently bound iodide-counteranion from **[3a]I** and **[3c]I** with $AgPF_6$.[66]

(Scheme 8).[65] In this case neutral donors such as CO-gas or Ph_3P reacted instantaneously with the MII-IrCp* complex under occupation of the respective free coordination site. Reaction with NaN_3 resulted in the formation of an azide-bound IrCp* complex while the reaction of **[3c]PF$_6$** with Li[$HBEt_3$] resulted in the formation of an ethylide-bound as a carbanion to the Ir-centre. Both the CO and the ethylide bound IrCp* are extremely rare examples of structurally characterized complexes with those constellations.

With the electron-poor alkyne DMAD (DMAD = Dimethylacetylenedicarboxylate) an unexpected reaction was observed: In total, three equivalents of DMAD were activated and added to the Ir-complex under the formal depletion of "HPF_6". Two of the three DMAD-molecules dimerised under C-C coupling.

This fragment now bridges the N_{exo}-atom and the Ir-centre under the formation of a new six-membered iridacycle. The third DMAD-molecule inserted into the C-Ir bond of the Ph-substituent, which underwent the C-H activation reaction previously. This way a new and rare eight-membered iridacycle was formed. This unusual and unprecendented structure could be elucidated by sc-XRD in combination with ^{1}H-NMR-spectroscopy. Based on these results *Sarkar* and co-worker

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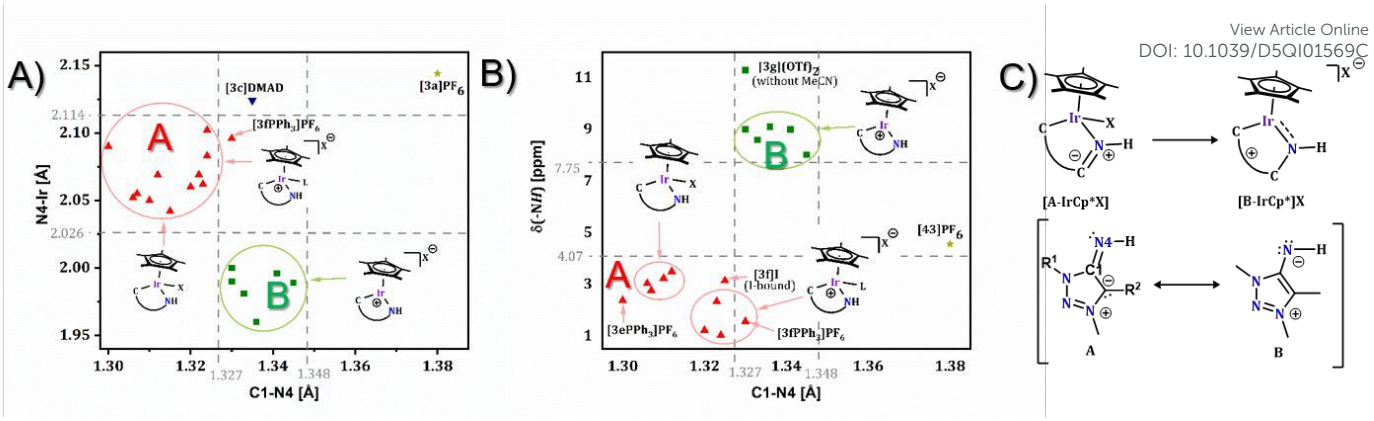
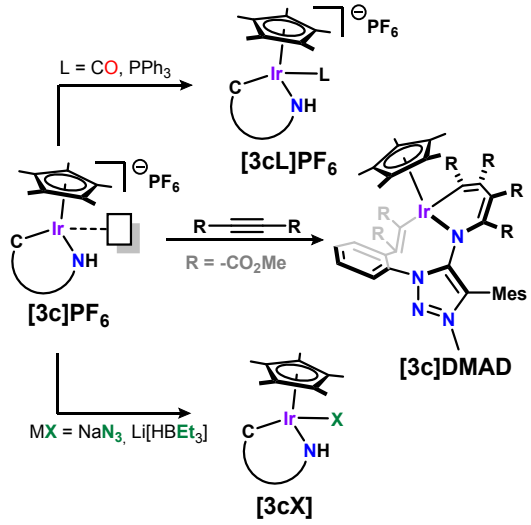


Figure 2: A) Graphical relation of the N4-Ir and the C1-N4 bond length in the IrCp*-complexes **3**. B) Graphical relation of the resonance of the -N*H* in the ^{1}H-NMR spectra and the C1-N4 bond length in the IrCp*-complexes **3**. C) Possible coordination modes in the discuseed MII-IrCp* complexes.

were able to show that also other MII-IrCp*-complex undergo such a reaction.



Scheme 8 Reactivity of the coordinatively unsaturated Ir-complex **[3c]PF$_6$** with neutral donors **L**, coordinating anions **X** and DMAD (= Dimethylacetylenedicarboxylate). [65]

As several MII-IrCp* complexes were reported with different MII-ligands including different coordination modes and coordination numbers, it is worthwhile to look deeper into some crystallographic and spectroscopic data of these complexes and find possible correlations (Table S1, Figure 2). Plotting the N4-Ir bond length over the C1-N4 bond length (Figure 2 A)) shows indeed that the structurally similar Ir-complexes with the Ir-complex ligated by 3 ligands beside the Cp*-ligand have similar bond parameters. Upon dissociation of one of those ligands, the C1-N4 is elongated while the corresponding N4-Ir bond is shortened substantially.

It is therefore reasonable to describe the MII-ligand in complexes of the form **A-IrCp*X** (figure 2 C)) as an imine-type ligand (Scheme 1, description of **2** as imine) with short C1-N4 bonds. In such a case, the corresponding N4-Ir bond is in the ball park of a single-bond. Upon dissociation of X, the MII-ligand will compensate the loss of electron-density of the Ir-atom by shifting more electron density onto the exocyclic N-atom (N4). Thus, in such a case, the MII-ligand accepts more electron density from the heterocycle which results in an elongated C1-N4 bond. Such a bond now shows the characteristics of an amide-bond (Scheme 1, description of **2** as amide). At the same time, the higher electron count on N4 results in a shorter N4-Ir bond, which now has double-bond character. By shortening this bond, the loss of electron density can be compensated as the MII-ligand now offers more than one electron-pair for the coordination. This vividly shows the versatility of the MII-ligand as the ligands can adapt to the electronic situation of the bonding partner. Such a switch from imine to amide also has a strong effect on the resonance of the proton bound to N4 as derived by ^{1}H-NMR spectroscopy (Figure 2 B)). Upon dissociation of X, the resonance of the said proton is significantly down-field shifted, as more electron-density is transferred away from N4.

It stands out that **[3a]PF$_6$** and **[3c]DMAD** do not follow these trends as they do not fit the given model. In **[3a]PF$_6$** the MII-ligand acts as a bridging ligand over the N4-atom. In such a case, "only one" electron pair per N4-atom can be provided per Ir-atom. Accordingly, the N4-Ir is quite long and such a bond is presumably best described as a dative bond. To afford enough electron density to allow for the coordination of two Ir-atoms at the same time, the corresponding C1-N4 bond is also significantly elongated to provide the electron density necessary. Also the (Ir-N4)$_2$-coordination motif is sterically quite congested, which is believed to also contribute to the long (C1-N4/N4-Ir) bond lengths. For **[3c]DMAD** the structural data are not precise enough to further discuss the bonding situation. It will be interesting to see which trends might emerge once more such compounds of this type are reported on.

MIIs in catalysis

The first report on MIIs already suggested their possible application in catalysis. Hydrogen-atom transfer (HAT) of heteroatom-containing substrates with organic molecules is a powerful tool for converting C-H bonds into precious C-C bonds.[91, 92] Such processes can be mediated by catalysts such as secondary amides, as they provide a sufficiently high bond dissociation enthalpy (BDE). As sensitive amidyl-radicals are involved in these steps, a rational molecular design, which allows for modularity to further gauge the scope of substrates is notoriously difficult.[93–95] Ooi and co-workers could harness in

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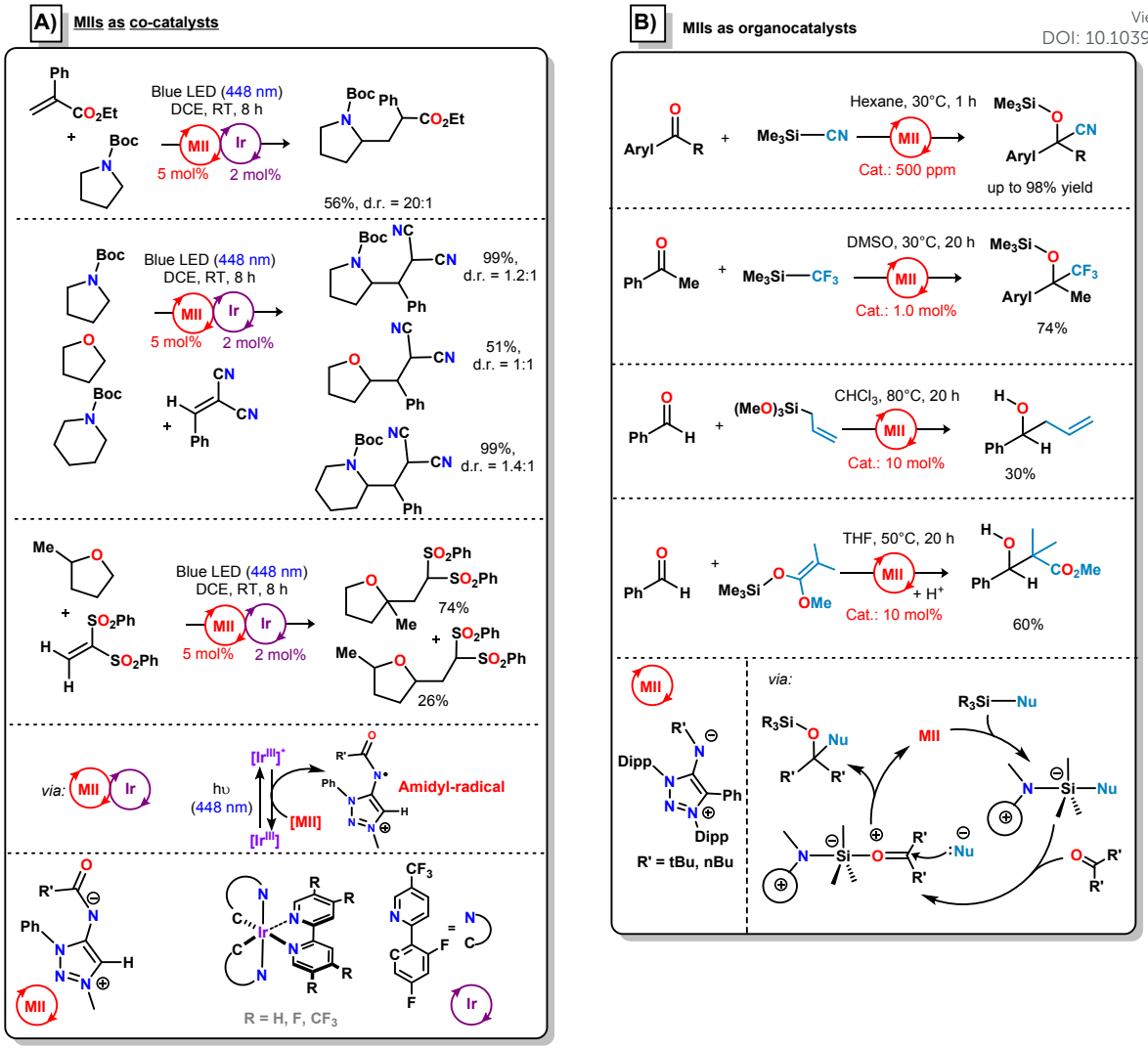

Scheme 9 Application of MIIs. A) As Co-catalyst in light-driven HAT with IrIII-complexes. B) Addition of silyl-based nucleophiles on aromatic carbonyls under MII-catalysis.

that regard the well balanced stability of MII-based amidates with sufficient BDE-values (~ 100 kcal/mol) as catalysts for HAT.[69] In these systems, the MII-scaffold provides a modular, synthetic platform. Additionally, the amidyl-radical can be generated under mild conditions (~ 1.2 V vs. SCE) and is efficiently stabilised by the cationic triazolium core. Together with Ir^{III}-based complexes as the photoredox catalysts with a blue light emitting diode as the photon source, this system could not only couple quite a large library of alkenes to the *α*-position of O- and N-containing heterocycles *via* HAT after 8 hours under relatively low catalyst loadings (amidate 5 mol-% and Ir-complex 2 mol-%) (Scheme 9 A)). The reactions were also under regio- and stereoselective control dependent on the substitution pattern on the MII-catalyst. The authors state in that regard that this conceptual approach provides a new rational approach for the design of HAT-catalyst systems especially if zwitterionic amidates based on the modular MII-scaffold are further investigated.

Haraguchi and co-workers studied the activity of MIIs as organocatalysts in the addition of various silyl-based nucleophiles onto aromatic aldehydes and ketones (Scheme 9 B)).[61, 62] The cyanosilylation of acetophenone displayed unprecedented high TOFs (1500 h^{-1}) with a MII as the catalyst at extremely low loadings (500 ppm). Also, less activated nucleophiles such as (trifluoromethyl)trimethylsilane or allyltrimethoxysilane were successfully added to either acetophenone or benzaldehyde under the presence of a MII-catalyst, although the yields were unsatisfactory. The authors did not elaborate further on the mechanism of the conducted reactions. Given the references by the authors in the primary sources, we speculate that the mechanism most likely involves a pentavalent adduct of the MII and the silane.[96–99] This hypervalent, neutral silicate is then coordinated by the O-atom of the carbonyl-substrate under depletion of the nucleophile (CN, CF_3) which attacks the C-atom of the now activated carbonyl-substrate. As quite Lewis-basic compounds, MIIs will engage readily in the nucleophilic attack onto the silyl-based substrate which can explain the high catalytic activity.

These preliminary studies disclose very fascinating facettes of MIIs as catalysts besides their use as ligands.

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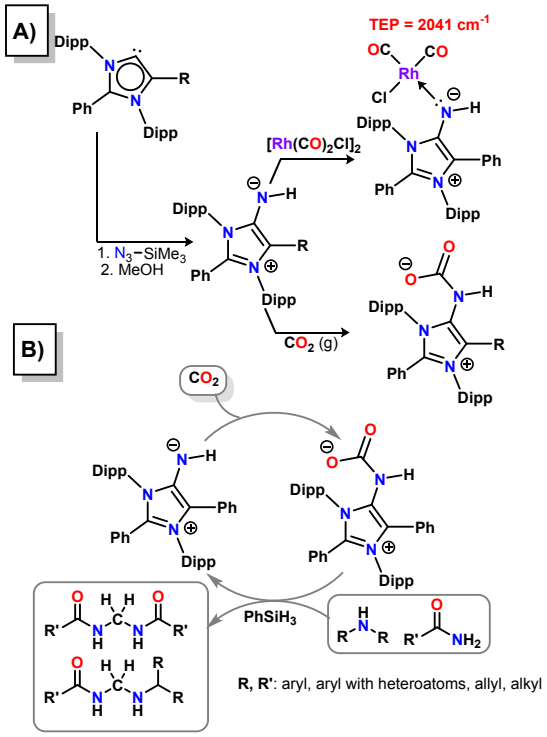
Synthesis and Applications of aNHIs

The first and *hitherto* only report on aNHIs was from *Mandal* and coworkers in 2022.[71] Similar to the synthetic methods used by *Yan et al*, the aNHIs were generated by a *Staudinger*-type reaction of a free imidazole-5-ylidene with trimethylsilyl-azide followed by methanolysis (Scheme 10 A)). Like MIIs, the aNHIs show intense orange to red colours which is the result of $n(N_{exo})\rightarrow\pi^*$(imidazole) (HOMO→LUMO) transitions.

The strongly donating nature of the obtained aNHIs were established by determination of TEP and the reaction of CO_2-gas with an aNHI under the generation of the corresponding aNHI-CO_2 adduct. The small HOMO-LUMO energy gap makes aNHIs very intruiging compounds in the activation of small molecules like CO_2. This reactivity was probed in detail in the same publication by a plethora of coupling reactions: A large variety of amides and amines were coupled by deoxygenation of CO_2-gas in the presence of aNHIs as an organocatalyst (Scheme 10 B)). Besides "simple" amides and amines, also bioactive molecules were active in such coupling reactions.



Scheme 10 A) Synthesis of aNHIs as reported by Mandal et al, the reactivity thereof with CO_2-gas and $[Rh(CO)_2Cl]_2$ and the respective TEP determined. B) Amide/amine-coupling with CO_2 catalysed by an aNHI. [71]

Conclusions

The investigations on mesoionic compounds based on 1,2,3-triazoles have delivered intriguing chemical and physical aspects, which were heavily studied during the last 10 years. Reports on 1,2,3-triazole based mesoionic imines during the last ca. five years have opened up a new sub-field within mesoionic compounds. The modular synthetic route which has been developed for MIIs make the synthesis of molecules with tailormade properties straightforward. MIIs and aNHIs not only deliver interesting photophysical properties, but they also act as powerful organocatalysts for the metal-free deoxygenative CO_2-coupling or in "classical" aldol-chemistry. As ligand for main-group element substrate but also transition metal complexes, MIIs provide a platform for the stabilisation of elusive fragments. Prominent examples for this are the isolation and structural characterisation of an elusive Ir^{III}-CO complex or the intriguing reactivity of Ir^{III}-Cp* complexes towards the activation of alkynes. The properties of MIIs can be traced back to their electronic ambivalence. As has been pointed out here, the frontier orbitals and hence the electronic ambivalence in these compounds can be engineered in a targeted way by making use of the modular synthetic route. Thus, designing molecules with predictable physical and chemical properties should be possible. Given the recent developments in this field, we are confident that the potential of MIIs will unlock intriguing facets in organometallic chemistry, photochemistry/photophysics and catalysis in the coming years.

Author contributions

We strongly encourage authors to include author contributions and recommend using CRediT for standardised contribution descriptions. Please refer to our general author guidelines for more information about authorship.

Conflicts of interest

There are no conflicts to declare.

Data availability

A data availability statement (DAS) is required to be submitted alongside all articles. Please read our full guidance on data availability statements for more details and examples of suitable statements you can use.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
§
§§
etc.

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