N-Heterocyclic carbene–carbodiimide (NHC–CDI) betaine adducts: synthesis, characterization, properties, and applications

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N-Heterocyclic carbones (NHCs) are an important class of reactive organic molecules used as ligands, organocatalysts, and σ-donors in a variety of electroneutral ylide or betaine adducts with main-group compounds. An emerging class of betaine adducts made from the reaction of NHCs with carbodiimides (CDIs) form zwitterionic amidinate-like structures with tunable properties based on the highly modular NHC and CDI scaffolds. The adduct stability is controlled by the substituents on the CDI nitrogens, while the NHC substituents greatly affect the conformation of the adduct in the solid state. This Perspective is intended as a primer to these adducts, touching on their history, synthesis, characterization, and general properties. Despite the infancy of the field, NHC–CDI adducts have been applied as amidinate-type ligands for transition metals and nanoparticles, as junctions in zwitterionic polymers, and to stabilize distonic radical cations. These applications and potential future directions are discussed.

1. Introduction

Since the first demonstrations of persistent carbenes, N-heterocyclic carbones (NHCs) have been used extensively in transition metal and main group chemistries, as organo-catalysts, and σ-donors in a variety of electroneutral ylide or betaine adducts with main-group compounds. An emerging class of betaine adducts made from the reaction of NHCs with carbodiimides (CDIs) form zwitterionic amidinate-like structures with tunable properties based on the highly modular NHC and CDI scaffolds. The adduct stability is controlled by the substituents on the CDI nitrogens, while the NHC substituents greatly affect the conformation of the adduct in the solid state. This Perspective is intended as a primer to these adducts, touching on their history, synthesis, characterization, and general properties. Despite the infancy of the field, NHC–CDI adducts have been applied as amidinate-type ligands for transition metals and nanoparticles, as junctions in zwitterionic polymers, and to stabilize distonic radical cations. These applications and potential future directions are discussed.

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Christopher Brown received his MChem degree from Newcastle University in 2011, where he synthesized air-stable primary phosphines under the supervision of Dr Lee Higham. He then moved to the University of British Columbia where he obtained his PhD in 2018 working in the group of Prof. Michael Wolf. His doctoral research focussed on using sulfur oxidation state to tune the electronic and photophysical properties of coordination complexes. Chris started as a Postdoctoral Associate in the group of Prof. Jeremiah Johnson at MIT in 2019, where he is studying N-heterocyclic materials and polymer metal–organic cages.
NHCs are extremely modular, allowing facile tuning of their electronic and steric properties. Perhaps the most well-studied are the five-membered imidazolium- and imidazolidinium-based NHCs (Fig. 1B). Variations can be made at the nitrogen substituents (i.e., the wingtip positions) to make either symmetric \( (R^1 = R^2) \) or asymmetric \( (R^1 \neq R^2) \) species, and likewise the 4- and 5-positions \( (R^3 \text{ and } R^4) \) can be modified, though with typically a lesser effect on the electronics of the system. Consequently, chemists have access to a huge synthetic library of cationic heterocycles to use as NHC precursors.

Beyond their traditional applications as ligands and organocatalysts, NHCs can add to or insert themselves into a variety of organic species to form stable, neutral adducts, and if a suitable electrophile is used, zwitterionic adducts can be formed. Halogens or boranes lead to the formation of ylides, while reactions with allenes, ketenes, or heteroallenes give betaine adducts, which can only be represented by resonance forms with formal charges (Fig. 2). To date, many stable, crystalline NHC–betaine adducts with \( \text{CS}_2, \text{CO}_2, \text{isothiocyanates}, \) and isocyanates have been reported and reviewed elsewhere.

In this Perspective, we focus on betaine adducts made from NHCs and carbodiimides (CDIs), i.e., zwitterionic amidinates (NHC–CDIs, Fig. 2 X and Y = NR). Amidinates are considered the nitrogen analogues of carboxylates. They act as coordinating ligands and feature a wide range of coordination modes; many amidinate complexes of transition metals, lanthanides, actinides, and main group elements have been reported. One important difference compared to carboxylate ligands is that the nitrogen atoms in amidinates nearly always carry an additional substituent, which allows for fine-tuning of the electronic and steric properties of the ligand system. Combined with the similarly modular NHC framework, this feature presents a unique opportunity for tailoring NHC–CDI adducts for specific applications. NHCs and amidinates are also typically both air- and moisture-sensitive, whereas NHC–CDI adducts made from \( N,N' \)-diaryl CDIs result in net neutral compounds that are more tolerant to ambient conditions while retaining a strongly Lewis basic character at the amidinyl nitrogens. This Perspective will introduce the history, common synthetic and characterization methods, and a summary of the structure–property relationships of the currently known NHC–CDI adducts. Finally, applications to coordination chemistry, nanoparticle functionalization, supramolecular polymers, and distonic radical cation stabilization will be summarized along with future directions of the field.

2. History

To our knowledge, the first zwitterionic NHC–CDI adduct was proposed by Takamizawa and co-workers in 1974. These authors found that the addition of a thiazolium iodide species to an \( N,N' \)-diaryl CDI in the presence of triethylamine (NEt\(_3\)) yields a mixture containing a cationic thiazolium–CDI adduct and a spirocycle made via cycloaddition with a second equivalent of CDI. It was proposed that deprotonation of the thiazolium adduct leads to a zwitterionic NHC–CDI intermediate, which can then react with another CDI to give the cycloadduct. While the zwitterionic intermediate could not be isolated, it was noted that analogous zwitterionic adducts formed from the reaction of a phosphorus ylide with an \( N,N' \)-diaryl CDI had been previously isolated.

It was not until 25 years later that the first stable, isolable NHC–CDI was reported by Kuhn and co-workers. 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidine was allowed to react with diisopropylcarbodiimide, yielding a zwitterionic adduct which was characterized by NMR spectroscopy and X-ray crystallography. The strong Bronsted basicity of the amidinate nitrogen atoms caused decomposition of the adduct upon exposure to moisture, but also indicated the potential for NHC–CDIs as ligands for metallic systems or as organic bases, while remaining electroneutral. Despite this promise, the next report

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![Fig. 1](image1.png)

**(A)** Ground-state electronic structure of imidazol-2-ylidenes with numbering at the heterocycle shown. **(B)** NHCs of the imidazolidine and imidazolidinium-based classes, with unsaturated and saturated backbones, respectively.

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**Fig. 2** Zwitterionic betaine adducts made from \( N \)-heterocyclic carbones with allenes, ketenes, or heteroallenes.

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on isolated NHC–CDI adducts did not come, to our knowledge, until bench-stable variants utilizing \(N,N\)-dialkyl CDIs were discovered simultaneously by the Johnson and C´ampora groups in 2015.\textsuperscript{23,27} Since then, the facile synthesis, air- and moisture-stability, and interesting properties of these betaine adducts have spurred new interest in the field.

3. Synthesis and structure

3.1 Methods for NHC–CDI synthesis

3.1.1 Imidazol-2-ylidene and imidazolidin-2-ylidene. A variety of free NHCs and NHC precursors are available commercially as well as through robust synthetic methods,\textsuperscript{14,28} which have been reviewed elsewhere.\textsuperscript{14} Thus far, NHC–CDI adducts have utilized imidazol-2-ylidene and imidazolidin-2-ylidene NHCs (Fig. 1B). The free carbenes are most typically synthesized \textit{via} deprotonation of the corresponding imidazolium or imidazolidinium salt by a strong base, such as sodium hydride,\textsuperscript{29} potassium tert-butoxide (KO\textsubscript{Bu}),\textsuperscript{30} n-butyl lithium ("BuLi),\textsuperscript{31} potassium metal,\textsuperscript{32} or potassium hexamethyldisilazide (KHMD)\textsuperscript{31,33} (Fig. 3i). The salt byproduct is often, but not always, removed from the free NHC by filtration before subsequent reactions to avoid complications that arise from the presence of residual base or their conjugate acid.

To avoid the use of very strong bases, light-triggered deprotonation has been achieved using isopropylthioxanthone (ITX) with an azolium salt precursor containing a tetraphenylborate (BPh\textsubscript{4}\textsuperscript{−}) counteranion.\textsuperscript{34} Photoexcitation of ITX results in a triplet excited state that can accept a single electron from BPh\textsubscript{4}\textsuperscript{−} to form ITX\textsuperscript{−} which abstracts a proton from the azolium cation to generate the free carbene and ITX–H\textsuperscript{−}. Heat-sensitive progenitors can also produce free NHCs without the use of a strong base. This strategy is common for latent organocatalysis\textsuperscript{35} and has been utilized for the synthesis of NHC–CDI adducts by Johnson and co-workers, who first used carboxylate and diphenylphosphine adducts of SIMes\textsuperscript{23} and later synthesized C\textsubscript{6}F\textsubscript{5}-masked NHCs by exposing the corresponding diamines to pentafluorobenzaldehyde in acetic acid at room temperature.\textsuperscript{33}

3.1.2 Carbodiimides. Commercially available CDIs are most commonly used as amide coupling reagents or precursors to a variety of nitrogen-containing heterocycles.\textsuperscript{36} With the exception of commercial di[(para-tolyl)carbodiimide (CDI\textsubscript{Tol}) and dicyclohexylcarbodiimide (CDI\textsubscript{Cy}), CDIs used to make NHC–CDI adducts have been most commonly synthesized from the corresponding (thio)urea compounds, which in turn can be made from nucleophilic attack of an amine on an iso(thio) cyanate.\textsuperscript{35,37} Desulfurization of thioureas is accomplished with thiophilic iodine and a base, such as triethylamine\textsuperscript{48} or dimethylaminopyridine (DMAP)\textsuperscript{37} (Fig. 3ii). Triphenylphosphine can be added to increase the efficiency of this reaction\textsuperscript{35} through its complexion with iodine.\textsuperscript{39,40} Ureas can be converted to carbodiimides in a similar fashion upon the addition of triethylamine, carbon tetrabromide, and triphenylphosphine.\textsuperscript{33}

3.1.3 NHC–CDIs. Johnson and co-workers serendipitously discovered that \(N,N\)-dialkyl CDIs form stable adducts with NHCs upon heating SIMes or its derivatives for extended periods of time in toluene or dichlorobenzene at >100 °C.\textsuperscript{23} Mechanistically, they proposed a concerted \([3 + 2]\) cycloelimination of the NHC to generate ethylene and the corresponding \(N,N\)-dialkyl CDI followed by trapping with another equivalent of NHC. Though this method led to the discovery of stable NHC–CDI adducts, it is limited by the need for long reaction times and the necessity that the NHC and CDI substituents must be the same.

The most common method for the preparation of NHC–CDI adducts involves directly adding a free carbene to a free CDI in an appropriate solvent (Fig. 3iii).\textsuperscript{23,27,30,31,41,42} The often brightly-colored products form quickly at room temperature and can in many cases be readily purified by washing with, e.g., cold hexanes. If a thermally-labile NHC precursor is used instead of a free carbene, the masked NHC and free CDI can be heated in an appropriate solvent to form the NHC–CDI adduct.\textsuperscript{33} It is important to emphasize that the method of preparation is largely personal preference, as any method for releasing a free NHC in the presence of a free CDI will likely result in the formation of the same adduct.

The highly modular nature of both the NHC and the CDI fragments have led to the synthesis of a wide range of NHC–CDI adducts. Previously synthesized imidazol-2-ylidene-based adducts are shown in Fig. 4 and imidazolidin-2-ylidene-based adducts are shown in Fig. 5. The naming convention consists of the NHC backbone (I for imidazol-2-ylidene, \(\text{MeI}\) for 4,5-dimethylimidazol-2-ylidene, or \(\text{SiI}\) for saturated imidazolidin-2-ylidene) followed by the NHC wingtip substituents, “CDI”, and the amidine substituents as superscripts.

C´ampora and co-workers synthesized a variety of imidazol-2-ylidene-based adducts with alkyl substituents (methylethoxys) in the wingtip positions.\textsuperscript{27,30,41} Nembenna and co-workers expanded the library utilizing both \(N,N\)‘-dialkyl and \(N,N\)‘-diamine NHCs along with \(N,N\)‘-dialkyl CDIs with either the same or different substituents.\textsuperscript{43} Variants using saturated NHCs have been made by Johnson and co-workers with \(N,N\)‘-dialkyl, \(N\)‘-aryl-\(N\)‘-alkyl, and \(N,N\)‘-dialkyl CDIs, with variable stability (see Section 3.3.1 for more details).\textsuperscript{23,13,44} Additional adducts were made as repeat units of zwitterionic polymers, which will be discussed further in Section 4.2.

3.2 Characterization of NHC–CDIs

3.2.1 Nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy offers a convenient tool to monitor NHC–CDI formation. For example, the \(^1\text{H NMR resonances of the CDI}

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Chem. Sci., 2021, 12, 2699–2715 | 2701
substituents typically shift upward upon addition of a free NHC and NHC–CDI formation due to the increased shielding imparted by the negatively charged amidinate region. The $^{13}$C (1H) NMR resonance of the carbenic carbon has been shown to be a good indicator of NHC–CDI formation. For unsaturated (imidazol-2-ylidene) NHCs, the carbenic carbon peak shifts from 205–220 ppm in the free NHC to 140–152 ppm in the NHC–CDI adduct. For saturated (imidazolidin-2-ylidene) NHCs, the carbenic carbon is more deshielded with the free carbene and NHC–CDI resonances appearing around 241–245 ppm and 164–166 ppm, respectively.

Because of the delocalized double bond character, there is restricted rotation about both amidinate C=N bonds of NHC–CDI adducts, orienting the geometry of each bond as transoid (E) or cisoid (Z) with respect to the other amidinate nitrogen (Fig. 6A). $^{15}$N cross polarization magic-angle spinning (CP-MAS) solid-state NMR spectroscopy of ICyCDIPh with one $^{15}$N-labeled amidinate nitrogen exhibited two signals at 211 and 218 ppm with approximately equal intensity. Density functional theory (DFT) calculations support that these signals correspond to the two non-equivalent nitrogen atoms of the E/Z configuration. Many $^{13}$C CP-MAS NMR signals are also duplicated due to the non-equivalent phenyl substituents in the E/Z configuration. In contrast, solution-state $^1$H and $^{13}$C (1H) NMR spectra show a single set of aromatic resonances, indicating fast exchange between the E/Z and Z/E configurations in solution.

Fig. 6 (A) Priorities for assigning the geometry of amidinate C= N bonds and (B) overall adduct geometry for NHC–CDI adducts.
DFT calculations have suggested that the $E/E'$ geometry is less stable than the $E/Z$ configuration by 10.2 kcal mol$^{-1}$, ruling out facile observation of the $E/E'$ isomer.\textsuperscript{29}

Rotation of the amidinate substituents is highly dependent on the steric bulk of the NHC wingtip substituents. For example, the diastereotopic methyl groups of 2,6-diisopropylphenyl (DiIPP) moieties are well-resolved in both the $^1$H and $^{13}$C ($^1$H) NMR spectra for ICyCDIP$_2$P$^+$. Thus, fixing a lock on the rotation of the amidinate substituents is essential. For saturated imidazolidin-2-ylidene derivatives, CDIMes and IDiPP, syntheses by Kuhn and coworkers led to yellow/orange solvents from CDI-Mes and IDiPP syntheses.

3.2.2 Single crystal X-ray diffraction (XRD). Single crystal XRD has been used to study the structures of NHCDI adducts in the solid state. The NHCDI adducts studied in this way were very soluble in dichloromethane (DCM) and partially soluble in toluene, THF, and hydrocarbons. Therefore, single crystals were generally grown from mixtures of DCM and solvent.\textsuperscript{42}

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3.2.3 UV-vis absorption spectroscopy. Perhaps the most obvious indicator of NHCDI formation is the color change to bright yellow/orange that is characteristic for NHCDI adducts with $N,N'$-diaryl amidinates. UV-vis absorption spectroscopy captures this change via a trailing absorbance into the visible region ($\lambda > 400$ nm).\textsuperscript{33} Notably, the $N,N',N''$-tetraalkyl NHCDI MeIiPrCDI$iPr$ synthesized by Kuhn and co-workers is colorless,\textsuperscript{26} suggesting that aryl substituents on the amide play a key role in determining the absorption spectrum. TD-DFT calculations suggested that the color corresponds to a HOMO–LUMO transition, where the highest occupied molecular orbital (HOMO) consists of a π-orbital mainly on the anionic amidinate moiety and the lowest unoccupied molecular orbital (LUMO) is mainly centered on the cationic heterocyclic fragment.\textsuperscript{41} The energy of this transition is lower (and therefore in the visible region) because the HOMO is destabilized by nonbonding interactions with filled π-orbitals of the aryl substituents.

3.2.4 Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy can be used to monitor the disappearance of the characteristic CDI vibration at 2110–2140 cm$^{-1}$ or the appearance of the amidinate stretching band, which has been reported at 1500–1550 cm$^{-1}$ for imidazolium-based adducts\textsuperscript{41} and slightly higher at 1540–1560 cm$^{-1}$ for imidazolidinium-based adducts.\textsuperscript{33} The NHC C–N stretching modes and C–H flexion modes also overlap near 1500 cm$^{-1}$. An additional asymmetric amidinate N=C=N stretch can be detected in some systems as a medium-intensity band at ~1600 cm$^{-1}$.\textsuperscript{41}

3.2.5 Other characterization methods. Elemental analysis (EA) and electrospray ionization mass spectrometry (ESI-MS) have also been used to confirm the composition of various NHCDI adducts.\textsuperscript{33,41} Fluorescence has been detected in the violet region (389–422 nm) for $N,N',N''$-tetraaryl NHCDI adducts due to conjugation between the amide and NHCC components, which is supported by DFT calculations of the HOMO and LUMO of an $N,N',N''$-tetraaryl NHCDI.\textsuperscript{24}

3.3 Properties

3.3.1 Bonding. The carbon–carbon bond between the NH and the CDI fragments of NHCDI adducts is best described as a dative covalent bond in which the NH lone pair is donated to the central carbon of the CDI. Therefore, these bonds can be viewed as an organic analog to a dative ligand–metal bond and the adduct formation can be described by an equilibrium constant ($K_{eq}$).\textsuperscript{13} $K_{eq}$ values for NHCDI adduct formation reported so far are mostly dictated by the electronic and steric properties of the amide fragment, as seen by the fact that

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concomitant evolution of free adducts can be leveraged for the formation of (see Section 4.1) alkyl and Ar-N-bearing amidinate adducts produced from -aryl-CDIs to form air-stable adducts with both -aryl-CDIs. Monitoring this process by 1H NMR spectroscopy revealed a small amount of free NHC is present at room temperature for some adducts, while N,N'-diaryl CDIs gave robustly stable adducts. N,N'-diaryl alkyl CDIs were predicted to form adducts that strike a balance between these two extremes. While the 1H NMR analysis showed quantitative adduct formation (K_{eq} \gg 550 M^{-1}) similar to N,N'-diaryl CDIs, competitive binding experiments revealed that N-aryl-N'-alkyl amine CDIs are indeed more dynamic than their N,N'-diaryl counterparts. N-Aryl-N'-alkyl amine CDIs could be quantitatively displaced by N,N'-diaryl CDIs to form N,N',N,N''-tetraaryl NHC-CDIs, with concomitant evolution of free N-aryl-N'-alkyl CDI (Fig. 7B). Monitoring this process by 1H NMR spectroscopy revealed a first-order rate constant for this transformation as k_{2} (50 °C) = (4.0 ± 0.4) \times 10^{-4} s^{-1}. N,N,N',N''-Tetraaryl NHC-CDI adducts do not undergo such CDI exchange, even in the presence of a different N,N'-diaryl CDI (Fig. 7C), indicating that the adduct bond with N-aryl-N'-alkyl amine is dynamic at 50 °C, while the bond with N,N'-diaryl amine is not.

3.3.2 Basicity and stability. The basicity of NHC-CDI adducts can be leveraged for the formation of (see Section 4.1) cationic amine species via protonation with HCl; however, adducts with N,N'-diaryl amine substituents – such as Me_4PrCDI - decompose over the course of 12 h on exposure to moisture, presumably due to sufficient basicity to deprotonate water. The strong basicity of these adducts was also supported by a 1974 report on the thiazolium iodide reaction with a N,N'-diaryl CDI to form a spiro-heterocycle via cycloaddition. The authors’ inability to isolate the proposed betaine adduct intermediate was most likely a direct result of using the weak base triethylamine to deprotonate the [HNEt_3][I]^- in solution, even in the presence of excess triethylamine.

The dynamics of the central NHC-CDI bond also play a role in stability. While stable under inert atmospheres, NHC-CDI adducts with N-aryl-N'-alkyl amine CDIs are less stable to moisture compared to their N,N'-diaryl amine counterparts due to a more dynamic central C-C bond (see Section 3.3.1). Upon exposure to ambient conditions, the bis-adduct SIMesCDI \( \rightarrow \) SIMesCDI^+Ph^+ decomposes over 15 h as measured by changes in its 1H NMR spectra over time. Liquid chromatography mass spectrometry (LCMS) analysis of the resulting solution suggested a complex mixture of degradation products. These data indicate that while there is complete adduct formation according to 1H NMR spectroscopy, a small amount of free NHC is present at equilibrium, which reacts with moisture in the air, similar to M_4PrCDI^+. Notably, no such degradation was observed for the N,N'-diaryl amine CDI analogues SIMesCDІMes,Ph^2 and SIMesCDІMesBuPh,Ph^2.

4. Applications

4.1 NHC-CDIs as ligands

Amidinates are π-electron rich chelating ligands, whose coordination chemistry has been extensively studied across the periodic table. These complexes have seen applications in homogeneous catalysis, in particular, olefin polymerization. Amidinates are the nitrogen-analogues of carboxylates, containing two nitrogen atoms that can coordinate to metals as monodentate, bidentate, or bridging ligands (Fig. 8). As bridging ligands, amidinates can generate...
bimetallic “paddlewheel” complexes in both trigonal and tetragonal modes. It is well known that tuning the amidinyl substituents can have a profound effect on the binding modes of these ligands.

NHC–CDI adducts can act as analogues to amidinate ligands but with an electronically neutral character due to their quinardfier structure. This neutrality imparts bench-stability to NHC–CDIs which sets them apart from monoaonic amidinate, guanidinate, or carboxylate ligand systems that can be moisture-sensitive. Similar to amidinate ligands, the substituents at the nitrogen atoms of the N₂C⁺ moiety can also be altered, a feature which sets them apart from monoanionic amidinate ligands. To a solution of Al₂O₃ MeCDI at the CDI fragment (Fig. 9). In this work they did not first isolate the NHC–CDI adduct to act as the ligand, but instead used CDICy to probe the non-innocent bonding of group 13 atoms with NHCs. To a solution of Al₂O₃ NHC species 1 in THF was added CDICy, which resulted in the formation of 2. The solid-state structure of 2 revealed the insertion of the carbodiimide into the Al-carbene bond, yielding a zwitterion that contains aluminat and imidazolium. Measured bond distances and angles were consistent with electronic delocalization of the NHC ring. CDICy was then reacted with boron-terminated CDIs which sets them apart from monoanionic amidinate ligands. An equimolar mixture of Cu(I) acetate and either DiPP or CDIDiPP as the CDI fragment and formation of a bis-NHC Cu(I) complex. (A) Mono- and bimetallic complexes. (B) Heating complexes to 90 °C causes ejection of CDIDiPP and formation of a bis-NHC Cu(I) complex.

Fig. 9 Carbodiimides such as CDICy can be used to probe the non-innocent bonding of NHCs to group 13 atoms.

Fig. 10 Copper complexes of NHC–CDIs. (A) Mono- and bimetallic complexes. (B) Heating complexes to 90 °C causes ejection of CDIDiPP and formation of a bis-NHC Cu(I) complex.
used, a mononuclear \([\text{CuL}_2][\text{BPh}_4]\) species was isolated (6), which contained two terminally-bound NHC–CDI ligands. Interestingly, upon heating a solution of the complex to 90 °C, the CDI fragments were ejected as free carbodiimide, and a bis-NHC Cu(Ⅰ) complex (7) was formed quantitatively. This thermal decomposition also occurred for the other species discussed, with varying degrees of selectivity.

Expanding on this work, in 2017 Nembenna and co-workers isolated the first \(\text{N}_2\text{N}′\)-chelated NHC–CDI adducts as magnesium and zinc complexes.\(^{24}\) Five new complexes were isolated (Fig. 11) based on previously-reported,\(^{27}\) moisture-stable NHC–CDI adducts utilizing \(\text{MeIEt}\) and either \(4\)-tert-butylphenyl or \(4\)-isopropylphenyl substituents on the CDI. Initially, coordination with group 1 metals (where \(M = \text{Li, Na, and K}\)) was explored. While complexation was detected by \(^1\text{H}\) NMR spectroscopy, the desired products could not be isolated.

Complexes 8–11 were formed by exposure of the appropriate NHC–CDI to \(M[\text{N}([\text{SiMe}_3]_2)_2]_2\) (\(M = \text{Mg or Zn}\)) in toluene at room temperature. Species 12 was prepared through the reaction of \(\text{MeIEtCDIPPP}\) with \(\text{ZnEt}_2\). The complexes were characterized using multinuclear NMR experiments (\(^1\text{H}, ^{13}\text{C}, \text{and } ^{29}\text{Si}\)) and single crystal XRD analysis, which all indicated \(\text{N}_2\text{N}′\)-chelating binding modes for the NHC–CDIs to form four-membered rings with the metal. Ligand displacement reactions of compounds 8 and 9 were probed using neutral-type ligands (NHCs and isocyanides). No displacement of the NHC–CDI was seen, indicating a greater stability of the zwitterionic \(\text{N}_2\text{N}′\)-chelate compared to neutral monodentate ligands.

Complex 8 was then tested for its utility as a carbonyl hydroboration catalyst; main-group metal amidinate complexes are known to catalyze this reaction.\(^{24}\) An equimolar ratio of 2-chlorobenzaldehyde and pinacolborane was exposed to 5 mol% of 8 in benzene-\(d_6\) at room temperature. Quantitative conversion of the aldehyde to the boronate ester was seen in 2 h, signifying, to our knowledge, the first use of an NHC–CDI metal complex as a catalyst.

In 2018, C´ampora, Mosquera, and co-workers reported the remarkable case of DCM activation when investigating the coordination chemistry of ICyCDI\(^{\text{Bol}}\) with \(\text{ZnCl}_2\) (Fig. 12).\(^{58}\) Initially, the complexation reaction progressed very slowly at room temperature despite the strong basicity of the NHC–CDI adduct. After four days, the \(^1\text{H}\) NMR spectrum of the solution showed a large decrease in ICyCDI\(^{\text{Bol}}\), accompanied by the growth of two new species. Some crystalline material was seen; however, the crystal quality was not good enough to produce a solid-state structure. In a case of serendipity while setting up an NMR experiment, \(\text{ZnCl}_2\) was added to a week-old \(\text{CD}_2\text{Cl}_2\) solution of ICyCDI\(^{\text{Bol}}\). The \(^1\text{H}\) NMR spectrum indicated that one of the new species was more prevalent, and crystals were grown from this solution. Single crystal XRD revealed the structure to be a methylene-bridged aminal \(\text{ZnCl}_2\) (13), while the free NHC–CDI adduct prefers an \(E,Z\)-geometry. This unusual geometry is due to intramolecular \(\text{CH} \cdots \text{N}\) hydrogen bonds between the bridging methylene and CDI nitrogen atoms. In order to determine the second species seen in the \(^1\text{H}\) NMR spectrum, ICyCDI\(^{\text{Bol}}\) was exposed to \(\text{ZnCl}_2\) in a 3 : 2 ratio in bromobenzene, a solvent that is less susceptible to nucleophilic attack. Through NMR and XRD studies, the species was determined to

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**Fig. 11** NHC–CDI complexes with Mg and Zn reported by Nembenna and co-workers.\(^{24}\)

**Fig. 12** (A) Single crystal structure of methylene-bridged aminal 13. Hydrogen bonds shown in dotted lines. Ellipsoids plotted at 30% probability. Reproduced from ref. 60 with permission from The Royal Society of Chemistry. (B) Reaction of NHC–CDI ICyCDI\(^{\text{Bol}}\) with \(\text{ZnCl}_2\) in DCM, as reported by C´ampora and Mosquera.\(^{62}\) (Cy = cyclohexyl, \(p\)-Tol = 4-methylphenyl, DCM = dichloromethane).
be a \([\text{ZnL}_3]^{2+}\) dication counterbalanced by a \([\text{ZnCl}_4]^{-}\) dianion (14, Fig. 12A).

It was initially thought that the Lewis acidic ZnCl\(_2\) was assisting ICyCDITol in the nucleophilic activation of dichloromethane; however, the preferential formation of 13 from "aged" solutions of ICyCDITol suggested that the ZnCl\(_2\) merely acts to trap the formed cation. Monitoring a solution of ICyCDITol in CD\(_2\)Cl\(_2\) over the course of a week showed slow formation of the methylene-bridged product with no observed intermediates. Additionally, ICyCDITol was shown to react with other polychloroalkane solvents, such as chloroform and 1,2-dichloroethane, eliminating HCl and generating ICyCDITolH\(^+\)Cl\(^-\), with protonation occurring at one of the amidinyl nitrogen atoms.

Due to the unusual nature of this reaction, a DFT model was built using a simplified version of the NHC–CDI adduct, using Me instead of Cy in the wingtip position. The rate-determining step was ascribed to be the initial S\(_\text{N}2\) attack of the adduct on dichloromethane, with a 3 kcal mol\(^{-1}\) reduction of the energy barrier if ICyCDITol rearranges from the \(E,Z\) to \(E,E\) configuration. The calculated energy barrier (28.0 kcal mol\(^{-1}\)) to the first transition state was found to be in very good agreement with the experimental barrier (27.8 kcal mol\(^{-1}\)). The \([\text{NHC–CDI–CH}_2\text{Cl}]^+\) intermediate then undergoes a second S\(_\text{N}2\) reaction with another NHC–CDI to give the bridged species. This work sets the stage for future work involving NHC–CDI adducts as nucleophiles.

4.1.2 Functional nanoparticle surfaces. The synthesis of metallic nanoparticles (NPs) with controlled sizes and functional ligands has enabled numerous technological innovations in fields such as green catalysis,\(^{63,64}\) energy conversion,\(^{63,64}\) electronics,\(^{65,66}\) and biomedicine.\(^{67,68}\) Small NP size is crucial for these applications, but bare surfaces often lead to aggregation.\(^{69}\)

Surface functionalization stabilizes these NPs and enables further control of the optical, electronic, and catalytic properties of the metallic core.\(^{70,71}\) NHCs have been used for the stabilization of metallic surfaces including NPs due to their ability to coordinate at the surface.\(^{8,9,72-81}\) NHC–CDIs have more recently been targeted as surface ligands; their basic nitrogen atoms may coordinate to transition metals more strongly than typical electronically neutral ligands, and their modular syntheses could open new avenues for tuning surface properties.

In 2015, Càmpora, Philippot, Chaudret, and co-workers explored the stabilization of ruthenium NPs (RuNPs) using NHC–CDIs as stabilizing ligands with different Ru:ligand ratios.\(^{27}\) It is difficult to control the size of RuNPs in the range of 1 nm, with the vast majority of NPs reported in the 1.5–1.8 nm range, depending on the stabilizer used.\(^{82}\) Metal-to-ligand ratio is commonly used to control NP size, with increased ligand density typically leading to smaller NPs. Thus, the authors hypothesized that the large steric protection afforded by NHC–CDIs could lead to smaller NPs.

Toward this end, ICyCDITol was added to THF solutions of Ru(COD)(COT) (COD = 1,5-cyclooctadiene, COT = 1,3,5-cyclooctatriene) at room temperature under 3 bar H\(_2\) (Fig. 13A) with ligand:Ru ratios of 0.1, 0.2 and 0.5. L\(_1\)(0.1)@Ru, L\(_1\)(0.2)@Ru, and L\(_1\)(0.5)@Ru had mean particle diameters of 1.3 nm, 1.0 nm, and 1.0 nm, respectively, as determined by transmission electron microscopy (TEM) and radial distribution function (RDF) analysis. Increasing the ligand from 0.1 to 0.2 equiv. resulted in the expected NP size reduction, but a further increase to 0.5 equiv. had no effect on the RuNP diameter due to steric hindrance.\(^{83}\)

To test the coordination stability of the NHC–CDI ligands, L\(_1\)(0.1)@Ru was exposed to 10 equiv. of octanethiol and the mixture was heated at 65 °C in C\(_6\)D\(_6\) for 24 h. \(^1\)H and \(^{13}\)C\(^{1}\)H\(^{-}\) NMR spectroscopy did not show the presence of free NHC–CDI in the solution, indicating that, assuming free NHC–CDI would be stable under the reactions conditions, the strongly coordinating thiol was unable to displace the ligand to a discernible amount on the NMR timescale. Di-n-octyl disulfide, however, was observed, due to the catalytic oxidation of the octanethiol at the metal surface, suggesting that free Ru sites are still accessible as further confirmed by CO binding experiments.

Metal nanoparticles are attractive for catalysis because the facile tuning of both the electronic configuration and surface area of the particle combine the advantages of homogenous and heterogeneous catalysts.\(^{84}\) They frequently display high catalytic activities and can often be reclaimed at the end of the reaction. RuNPs are known to catalyze hydrogenation of alkenes and arenes under mild conditions; thus, L\(_1\)(0.1)@Ru and L\(_1\)(0.2)@Ru were tested for their performance in styrene hydrogenation to probe the selectivity between vinyl and aromatic moieties. With L\(_1\)(0.1)@Ru, full hydrogenation to ethylcyclohexane was
observed after 24 h, while L1(0.2)@Ru gave a mixture of 26:74 ethylbenzene and ethylcyclohexane over the same time period. Therefore, L1(0.2)@Ru has greater selectively for vinyl hydrogenation over L1(0.1)@Ru, attributed to fewer faces present in L1(0.2)@Ru compared to L1(0.1)@Ru.

In 2020, Martinez-Prieto, van Leeuwen, and co-workers prepared nickel nanoparticles (NiNPs) stabilized by three different NHC–CDI ligands featuring ICy and para-substituted phenyl groups at the amidinyl nitrogens (R = Me, OMe, Cl for L1, L2 and L3, respectively). NiNPs were formed by exposing Ni(COD)2 to 0.2 equiv. of the appropriate ligand in toluene at 70 °C under H2 at 3 bar (Fig. 13B). The resultant spherical L1@Ni and L2@Ni NPs had sizes of ~2.8 nm, while L3@Ni NPs were larger (3.4 nm) and considerably more disperse. Structural characterizations were performed using high-resolution TEM, wide-angle X-ray scattering (WAXS), powder X-ray diffraction (pXRD), and X-ray photoelectron spectroscopy (XPS).

In order to screen the catalytic properties of the NiNPs, L1@Ni was tested in the hydrogenation of 8 substrates containing different functional groups (alkenes, alkenes, and carbonyl groups). The hydrogenation reactions proceeded in toluene at room temperature and utilized 3 mol% Ni. Double and triple carbon–carbon bonds both underwent hydrogenation, with 3-hexyne and diphenylacetylene displaying high selectivities for the [Z]-alkenes and only traces of the (E)-alkenes and corresponding alkanes. Carbonyls were not hydrogenated to a significant extent under the same conditions.

Electronic variations at the amidinate moiety (R = Me, OMe, Cl) were tested in the context of 3-hexyne hydrogenation in toluene. At long reaction times (8 h), all three species showed >99% conversion, with selectivity (78–90%) to produce the (Z)-olefin. At shorter reaction times (2–6 h), lower conversions were seen, with the more electron-withdrawing species L3@Ni (R = Cl) displaying the lowest activity. L3@Ni was, however, found to have a slightly higher selectivity towards the formation of (Z)-3-hexene, possibly due to its lower activity. The catalytic activity of these NiNPs are higher than those of other Ni-based systems previously reported. Notably, the NiNPs could be easily removed from solution with a magnet and recycled up to 3 times while maintaining good activity.

In 2020, C´amora, van Leeuwen, and co-workers utilized the modularity of NHC–CDIs to synthesize Pt nanoparticles (PtNPs) of varying diameters in order to experimentally probe the effect of NP size on the Knight shift, which is a feature in the NMR frequency of a paramagnetic species caused by an interaction between nuclear spins and the spins of conduction electrons. Knight shifts occur for metal NPs due to the presence of free electrons on the surface; they can complicate the NMR chemical shifts of both the metallic isotope and the ligands bound to the surface. “Ultra-small” (<1 nm) Pt nanoparticles, however, do not exhibit a Knight shift due to the absence of free electrons on the surface and, thus, behave similarly to molecular species.

The PtNPs were stabilized using similar NHC–CDI adducts, consisting of ICy as the NHC fragment and para-substituted phenyl groups on the CDI nitrogens (R = Me, OMe, Cl, H for L1, L2, L3 and L4, respectively). PtNPs were formed by reaction of Pt(NBE)3 (NBE = 2-norbornene) in THF under 3 bar H2 with the appropriate NHC–CDI adduct (Fig. 13C). Pt(NBE)3 is advantageous over typical precursors, such as Pt2(DBA)3 (DBA = dibenzylideneacetone) or Pt(CH3)3(COD), due to faster reaction times and the ability to remove norbornene under vacuum. The PtNPs were synthesized with differing L1 : Pt ratios of 0.1, 0.2 and 0.5 molar equiv. (L1(0.1)@Pt, L1(0.2)@Pt, and L1(0.5)@Pt), giving particle diameters of 2.3 nm, 2.1 nm, and 1.9 nm, respectively, as determined by TEM. Crystallinity was confirmed using WAXS. As expected, elemental analysis (EA) indicated that the NHC–CDI adducts remained intact on the NP surface. FTIR studies comparing the strong stretching C=C=N bands of the free adduct L1 at 1530 and 1495 cm−1 and the particle L1(0.5)@Pt at 1630 and 1598 cm−1 suggested that the ligand binds through the amidinate moiety.

Surface properties of the PtNPs were probed using solid state NMR spectroscopy by exposing the nanoparticles to 13C and then obtaining the 13C MAS NMR spectrum to monitor the Knight shift. The paramagnetic effect caused by surface electrons of the NP cause the 13C signals of the CO to be shifted downfield and broadened considerably (the Knight shift). As the size of the NP is decreased from 2.3 nm to 1.9 nm, a small decrease in the magnitude of the Knight shift was observed. Regardless, in all cases, the large, broad Knight-shifted CO signals (~100–600 ppm, centered ~400 ppm) obscure any other resonances in the spectrum. As a correlation was seen between NP size and the magnitude of the Knight shift on the CO band, the authors prepared PtNPs of average ~1.2 nm diameter using Pt2(DBA)3 as the platinum source in a ligand : Pt ratio of 0.2 molar equiv. in order to suppress the Knight-shifted signal. Following exposure to 13CO, the 13C MAS NMR showed three clear CO resonances between 190–230 ppm. The Knight-shifted CO resonance is heavily suppressed, though still present due to CO coordinated to larger PtNPs present in the sample. Additional FTIR studies showed that CO is adsorbed to the Pt surface in both bridging and terminal coordination modes.

It is important to note here the similarities in NP synthesis between the three reports discussed (Fig. 13). All NHC–CDI adducts were synthesized using methods discussed in 3.1.3 and differ only in the substituent at the para-position of the phenyl groups attached to the CDI nitrogens. Irrespective of the metal precursor used, all NPs were formed by reacting the metal complex with the NHC–CDI in THF under 3 bar H2 and purified by precipitation with pentane. This straightforward methodology, coupled with the subtle structural and electronic effects afforded by NHC–CDIs, allows for fine-tuning of NP size and catalytic activity and may find utility in metal nanoparticle and metal nanocluster applications at the frontier of molecular and solid-state chemistry.

4.2 NHC–CDIs in zwitterionic materials

Zwitterionic polymers comprise macromolecules that contain both cationic and anionic groups either along the main chain or incorporated into the side chain. These polymers have gained interest across a variety of fields due to their biocompatibility, antifouling properties, high ionic conductivity, and ability to...
stabilize nanoparticles and proteins.\textsuperscript{89} Zwitterionic polymers can be prepared from mixtures of oppositely charged monomers or from zwitterionic monomers.\textsuperscript{89,90} The vast majority of the latter materials are made with pendant sulfobetaine, carbobetaine, or phosphobetaine moieties,\textsuperscript{91} though main-chain polybetaines have also been synthesized from phospholipids,\textsuperscript{92,93} polysquaraines,\textsuperscript{89} and NHC-isothiocyanate adducts.\textsuperscript{95}

In 2018, Johnson and co-workers reported a new class of polybetaines based on NHC–CDI adducts called poly(azolium amidinates) (PAzAms, Fig. 14).\textsuperscript{27} The dative-character of the NHC–CDI adduct bond (see Section 3.3.1) makes PAzAms supramolecular polymers where the equilibrium of adduct formation ($K_{eq}$) and rate of dissociation ($k_d$) will affect the material properties. NHC–CDIs are good candidates for making such supramolecular polymers due to their high modularity leading to control over $K_{eq}$, $k_d$, adduct geometry, charge delocalization, air- and moisture-stability, and the potential to use the resulting amidinate-type fragments for metal ion ligation.

Initially, two polymers were made via the step-growth polymerization of bis-imidazolidinum salts and bis-CDIs (AA + BB type monomers, poly1 and poly2 in Fig. 14). On the basis of different adduct stabilities in small molecule NHC–CDIs (see Section 3.3.1), PAzAms were synthesized from both bis-{N-N'-aryl diaryl CDI}s and bis-{N,N'-diaryl CDI}s. Number-average molar masses ($M_n$) of ~14.0 kDa for poly1 and ~6.5 kDa for poly2 were obtained by $^1$H NMR spectroscopy, which corresponds to degrees of polymerization (DP) of ~11 and ~4, respectively. Gel permeation chromatography (GPC) traces exhibited broad dispersities ($D$) expected from a step-growth polymerization. It was found that the preparative procedure for these polymers greatly affected their molar masses; filtering the salt byproduct after purification of the imidazolidinium salt resulted in low DP ($M_{n,PNMR} = 2–4$) for both polymers, perhaps due to considerable loss of the bis-NHC during filtration. Removing this filtration step resulted in higher DP for both poly1 ($M_{n,PNMR} = 11$) and poly2 ($M_{n,PNMR} = 9$), however; the GPC trace of poly2 was irregular and displayed a very broad dispersity ($D = 2.87$), likely due to aggregative effects. When bis-NHC pentafluorobenzene adducts were used as the monomer, DP = 8 poly2 was isolated and displayed a more typical GPC trace, but the polymer was not very soluble in THF. Therefore, the lower DP oligomers of poly2 formed using the filtration procedure were used for initial investigations.

The dynamics of poly1 impacted by the N-aryl-N'-alkyl CDI were probed in many ways. First, depolymerization was investigated through heating to 50 °C in the presence of a free N,N'-diaryl CDI (CDI$_\text{Tol}$). First-order kinetics suggested that this process is rate-limited by NHC–CDI adduct dissociation followed by rapid trapping of the free carbene by N,N'-diaryl CDI. Second, poly1 could be converted to poly2 in the presence of CDI$_\text{BuPh,Ph}_2$ at 50 °C for 12 h. Complete CDI exchange occurs as the thermally-labile poly1 is converted to the stable poly2. Finally, the stability of poly1 to ambient conditions was tested. While poly1 seems indefinitely stable in solution under inert atmosphere, significant decomposition upon exposure to air was documented via $^1$H NMR spectroscopy, GPC, and LCMS over the course of 18–24 hours. This was explained via degradation of the small fraction of free NHCs present at equilibrium. In contrast, poly2 was very stable to both depolymerization and ambient conditions. Depolymerization could be achieved, but only at 100 °C in molten CDI$_\text{Tol}$.

The air- and moisture-stability of poly2 prompted further exploration of N,N'-diaryl CDIs in the context of supramolecular polymers. Heat-activated pentafluorophenyl-masked NHCs were designed to obviate the need for deprotonation of imidazolidinum salts by strong base (see Section 3.1.1). Both AA + BB type and AB type monomers were synthesized, showing the power of this methodology to access both pairwise alternating ($+$ + $-$) and purely alternating ($+$) charge sequences. Monofunctional end caps were utilized to control the molecular weight of the PAzAms and/or introduce end functionality to the chains. Due to perfect 1 : 1 stoichiometry, AB monomers facilitated higher DP polymers of $\geq$25 for poly3 and ~16 for poly4. As expected, increasing the amount of chain-capping agent leads to progressively lower DPs. The DP for AA + BB oligomers could be controlled via monomer ratio, varying between 2 and 8. Generally, hydrophobic linkers led to higher DPs compared to polymers with hydrophilic linkers (poly5), possibly due to residual moisture in hydrophilic monomers leading to unwanted termination events. As expected, all N,N'-diaryl CDI-derived PAzAms displayed excellent stability under ambient conditions, which was tested by heating to 70 °C in 1,2-dichloroethane-$d_4$ under air. The solid material could be annealed at 100 °C for 24 h under N$_2$ with no significant change in $M_n$; however, in the presence of free CDI$_\text{Tol}$, depolymerization takes place under these conditions, underscoring the supramolecular nature of these polymers. Thermogravimetric analysis (TGA)
also supports high thermal stability, as mass loss was not observed until \(\sim 175-200 \, ^\circ\text{C}\).

Most of the reported PAzAms were quite hydrophobic; in order to test the stability of these polybetaines in aqueous environments, a polyethylene glycol (PEG)-containing capping agent was utilized to increase water solubility. The ratio of hydrophilic to hydrophobic blocks was controlled by the amount of capping agent added. The following samples were prepared: PEG2k-\((\text{AzAm})_b\), PEG2k-\((\text{AzAm})_b\), and PEG2k-\((\text{AzAm})_b\) \((\text{AzAm} = \text{the repeat unit of poly3})\) and all exhibited good water solubility \((5-30 \, \text{mg mL}^{-1})\). \(^1\)H NMR spectroscopy in \(\text{D}_2\text{O}\) showed evidence of aggregation-induced peak broadening as expected for amphiphilic block copolymers; however, the material could be extracted back into organic solvents without showing any significant changes compared to the native sample. These data indicate that PAzAms are stable in aqueous environments for at least several hours at room temperature. The aggregation of these materials was further investigated using dynamic light scattering (DLS) and TEM after dialysis into water from acetone. DLS showed a Gaussian size distributions and average particle diameters ranging from 66-100 nm; no correlation between particle size and hydrophobic block size was observed, perhaps due to the high dispersities \((1.47-1.85)\) of the materials. TEM revealed that most of the aggregates had spherical morphologies of similar sizes to those measured by DLS except for a small amount of elongated worm-like morphologies for PEG2k-\((\text{AzAm})_b\). This work lays the foundation for future materials and tunable surface modification based on PAzAm zwitterionic polymers. Recently, Larsen and co-workers were inspired by these dynamic bonds to develop thermal guanidine-based covalent adaptable networks.\(^{99}\)

### 4.3 Distonic radical cation stabilization

Radicals play critical roles in biological and chemical processes, and efforts to harness the reactivity of organic radicals has led to applications in organic synthesis,\(^{98-99}\) energy storage,\(^{100-101}\) biological imaging,\(^{102-103}\) and in polymerization reactions.\(^{104-105}\) It is well studied in the literature that carbenes – in particular NHCs – have been used to stabilize a wide range of main-group radicals\(^{106-107}\) due to their strong \(\sigma\)-donating and \(\pi\)-accepting properties. These species include boryl,\(^{108}\) silyl,\(^{109}\) pnictogenyl,\(^{110-111}\) and aluminium-bound adducts.\(^{112}\) Aminyl radicals that have been stabilized by NHCs\(^{113-114}\) were extensively delocalized into the empty \(p\)-orbital of the carbene. Through leveraging the unique electronic properties of neutral, zwitterionic NHC–CDIs, Johnson and co-workers investigated an alternative mode of radical stabilization that does not rely on the \(\pi\)-accepting ability of the carbene in the hopes that these stabilized radical species could be used for a range of redox-active materials.\(^{44}\)

In this work, pyrene-substituted \(\text{SIMesCDI}^{+}\) is oxidized to generate a “distonic” radical cation \((\text{SIMesCDI}^{+\ast})\), \(i.e.,\) a radical cation where the charge and spin occupy spatially distinct regions within the same molecule (Fig. 15). The positive charge resides on the NHC moiety, while the unpaired electron is stabilized across the \(N\)-pyrene substituents. As a comparison, analogous phenyl-derived amidinate species were also synthesized; however, as expected, the generated radical cations of these compounds were too reactive to be observed at room temperature due to insufficient resonance delocalization, causing the compounds to quickly degrade.

The electrochemical properties of the species were studied using cyclic voltammetry (CV). The \(\text{SIMesCDI}^{+}\) showed a reversible one-electron oxidation, corresponding to the distonic radical cation. The phenyl species, however, displayed irreversible oxidation in their CVs, suggesting a stabilizing influence of the pyrene moieties. Chemical oxidation of the \(\text{SIMesCDI}^{+\ast}\) with silver bistriflimide (AgTFSI) also formed the distonic radical cation, and the extensive delocalization of the unpaired electron across the pyrene groups was observed using electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum was simulated with the unpaired electron coupled to the two amidinyl nitrogens, which was in good agreement with experimental data and consistent with \(C_2\) symmetry in solution. Coupling to 10 protons—corresponding to the bound pyrene groups—was observed, with a significant spin density across each \(\pi\)-system. DFT calculations supported the assignment of a distonic radical cation, with the spin density and singly occupied molecular orbital (SOMO) occupying only the amidinate and pyrene groups on the adduct, with minor contributions from the cationic imidazolidinium moiety. The increased resonance stabilization afforded by the pyrene substituents allowed the distonic radical cation to exist even after exposure to air, with no significant change in the EPR spectral intensity observed. The phenyl-substituted analogues with reduced \(\pi\)-systems, however, showed dimerization after chemical oxidation.

Redox applications are a potential use for this new type of persistent, distonic radical cation. To demonstrate an example, the authors used \(\text{SIMesCDI}^{+\ast}\) as a catholyte (\(i.e.,\) the electrolyte on the cathode side of an electrochemical cell) in an organic redox-flow battery, with \(N\)-methylphthalimide (N-MPI) as the anolyte. During the first charging cycle, the distonic radical showed a flat voltage plateau around 150 mV vs. Ag/Ag\(^{+}\). The species also demonstrated a high reversibility, with an average coulombic efficiency of 94.6\% after 20 charging cycles and no performance decay for 100 cycles.

### 5. Conclusions and outlook

This Perspective is a comprehensive survey of the nascent field of NHC–CDI betaine adducts. While hypothesized as far back as
the 1970s, it has only been the recent discovery of robust, air-
and moisture-stable variants based on N,N'-diaryl CDIs that has
sparked the rapid growth in this field. The highly modular
nature of both NHCs and CDIs has enabled the synthesis of many
adducts with electronic and steric modifications that
allow the probing of structure–property relationships. Although
all currently known adducts utilize imidazol-2-ylidene and
imidazolidin-2-ylidene NHCS, other NHC classes – such as 1,2,4-
triazol-3-ylidene, thiazol-2-ylidene, and cyclic alkylamino-
carbenes – could result in even greater variety of properties and
applications in the future.

Coordination complexes containing NHC-CDIs as net-
neutral amidinate-like ligands have been synthesized with
terminal, chelating, and bridging binding modes. They can also
stabilize a variety of metal nanoparticles. A few of these examples
showed catalytic behavior, but given the breadth of reactions
that provide a desirable toolbox for exciting research for many
years to come.

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Synthesis and application of water-soluble NHCligands also contributes to their nucleophilicity,
as shown by the reaction of ICyCDI$^+$ with DCM, hinting at the
ability of appending these moieties to organic molecules.

Beyond the fields presented here, there is a remarkable
opportunity for NHC-CDIs in the field of organocatalysis. The
strong precedent of NHC betaine adducts as latent organo-
catalysts for Umpolung reactions or lactone polymerization
poise NHC–CDI adducts as a more modular alternative to the
common carboxylate adducts. It is clear that the NHC–CDI
scaffold holds a lot of promise across a variety of fields and the
positive attributes of facile synthesis, modularity, and robust-
ness provide a desirable toolbox for exciting research for many
years to come.

Conflicts of interest
The authors have no conflicts to declare.

Acknowledgements
We acknowledge the National Science Foundation (NSF CHE-
1904867) for support of this work. J. R. L. gratefully acknowl-
edges the National Institutes of Health for a postdoctoral
fellowship (1F32GM126913-01A1).

Perspective
Chemical Science

© 2021 The Author(s). Published by the Royal Society of Chemistry
Chem. Sci., 2021, 12, 2699–2715 | 2711
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