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Beyond catalysis: N-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications

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This *tutorial review* compiles the advances that have been achieved in using transition metal complexes containing *N*-heterocyclic carbene ligands as components for materials. Applications of metal carbene complexes in fields different from catalysis are remarkably scarce. During the last few years, promising results have been accomplished in particular by utilizing such complexes as antimicrobial and cytotoxic agents, as photoactive sites in luminescent materials, for self-assembly into liquid crystalline materials and metallasupramolecular structures, and as synthons for molecular switches and conducting polymeric materials. These initial achievements clearly underline the great potential of N-heterocyclic carbene complexes in various fields of materials science.

Introduction

Within less than a decade, N-heterocyclic carbenes (NHCs) have transformed from niche compounds to some of the most popular ligands for catalysis.[1] Despite this rapid evolution and the widespread attention these ligands have received, application of NHCs in other areas has been scarce. This is particularly remarkable since NHCs combine a number of properties[2] of potential interest for the fabrication of materials (Fig. 1). Specifically, the metal-carbene bond comprises a substantially larger covalent portion than typical coordination bonds, which should be beneficial for addressing stability issues. In addition, M=C π bonding, deduced both experimentally and theoretically, presets metal-carbene complexes as active sites for mediating electron transfer processes. Finally, variation of the periphery of NHCs, in particular the substituents at the nitrogen (the wingtip groups), is vast and ensues a high synthetic flexibility. Here, we aim at compiling the advances that have been achieved by using metal-NHC complexes in the broad domain of materials beyond catalysis, with a special emphasis on their use for biomedical application, as luminescent components, in self-assembled structures, and as electronically active polymeric materials.

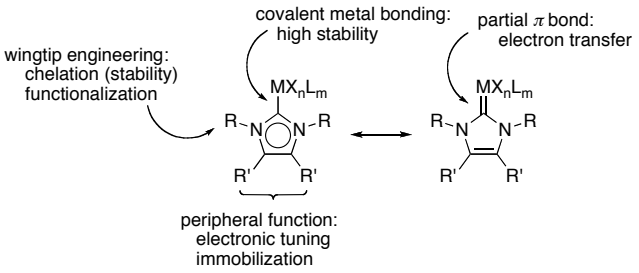


Fig. 1 Principles in the organometallic chemistry of *N*-heterocyclic carbenes relevant to materials properties.

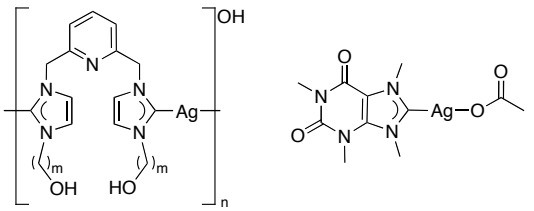
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N-heterocyclic carbene complexes for medical applications

Antimicrobial agents

Silver(I) NHC complexes offer promising solutions to overcome the problems displayed by conventional silver antibiotics such as fast loss of activity or sulfonamide resistance of pathogens. These complexes are readily available from imidazolium salts and Ag_2O, Ag_2CO_3 or AgOAc and contain relatively strong silver–carbon bonds.[3] The increased stability of the complexes is expected to be beneficial for antimicrobial activity, since silver release is retarded as compared to ionic silver complexes such as $AgNO_3$. The topic, pioneered to a large extent by Cannon and Youngs, has been reviewed recently,[4] and only a brief summary is given here. Complexes **1** have been the first water soluble silver NHC complexes that show antimicrobial activity superior to $AgNO_3$ (Fig. 2).[5] Additionally, the complex solutions with lower minimum inhibitory concentration (MIC) values inhibit the growth of microorganisms for a longer period than $AgNO_3$. The higher activity may be rationalized by the partially covalent character of the Ag–C_{NHC} bond, which provides enhanced stability and decelerates silver dissociation. Hence silver NHC complexes constitute a source of biologically active silver ions that is available for an extended period of time. Stimulated by these results, a number of silver NHC complexes have been prepared and evaluated on their antimicrobial activity.[6]

Further improvement of the bacteriostatic and antifungal activity has been achieved by encapsulating silver NHC complexes into polymers by electrospinning.[5] The modified

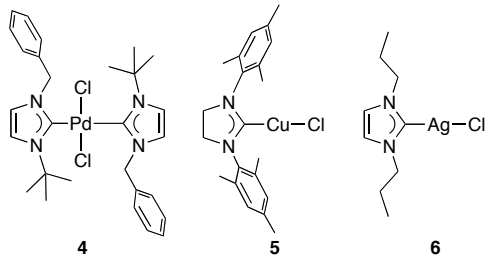


1 (m = 2, 3) **2**

Fig. 2 Antimicrobial complexes **1** and caffeine-derived NHC complex **2**.

polymer mats show bactericidal activities that are higher than the currently commercialized 1% silver sulfadiazine ointment and are similarly effective as 0.5% (w/w) $AgNO_3$, albeit already at eight times lower Ag^+ concentration. Apparently, integration of Ag–NHC complexes into polymer mats further regulates the release of silver ions. In addition and in contrast to $AgNO_3$, the discoloration of the culture medium is effectively suppressed.

An important aspect of using silver NHC complexes as sources for antimicrobial silver(I) ions consists of the acute toxicity of the corresponding imidazolium salt that is formed upon release of silver (LD_{50} ~100 mg kg^{-1} of rat).[7] This issue has been successfully resolved by using biologically relevant imidazole-containing molecules as NHC sources. An outstanding candidate is caffeine, a prevalent xanthine that is readily available, cheap, and of lower toxicity even when alkylated (LD_{50} ~1.0 g kg^{-1}). The silver(I) NHC complex **2** hence combines biological compatibility and antimicrobial activity.[8] More recent efforts aimed at improving the modest water solubility of complex **2**. For this purpose, theobromine rather than caffeine has been introduced as a basic structural motif,[9] since the unsubstituted nitrogen N1 in theobromine allows for incorporating functional groups that increase the solubility of the silver complex in water. Insertion of an ethanol residue in theobromine, followed by nitrogen N9 alkylation and subsequent metalation affords the silver NHC complex **3**. Its solubility is increased by one order of magnitude from 11 mg mL^{-1} (complex **2**) to 123 mg mL^{-1}. The modification does not affect the antimicrobial activity significantly, indicating that the N1 position is appropriate for engineering the physical properties of the complex. Moreover, recognition sites may be incorporated in order to entail selective docking of the silver carbene to specific tissues or receptor sites. Complex **3** is active against a variety of fungi



4 **5** **6**

IC_{50} (MCF-7) 0.25 μM 0.075 μM 0.03 μM

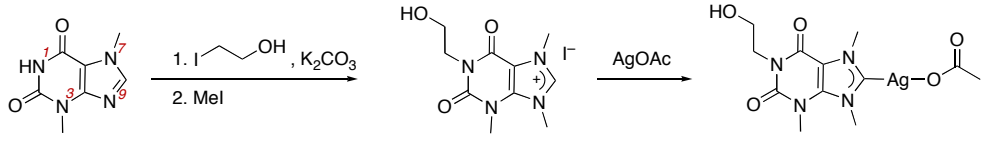
Fig. 3 NHC complexes of palladium(II), copper(I), and silver(I) that exhibit significantly lower IC_{50} values on MCF-7 cell lines than cisplatin (IC_{50} = 10.4 μM).

and several resistant respiratory pathogens, with MIC values typically around 1–2 μg mL^{-1}.

Specific tests of a variety of silver NHC complexes, including chloro-substituted imidazolylidenes and N7-functionalized caffeine derivatives indicate remarkable *in vitro* efficacy against bacteria of the *Burkholderia* family, which are listed as pathogens for warefare.[10] The MIC values are consistently in the single-digit μg mL^{-1} range, exhibiting activities that surpass those of currently used clinical antibiotics. While the antimicrobial activity is essentially independent of the substitution pattern at the NHC ligand in these *in vitro* studies, appropriate ligand functionalization may be highly relevant *in vivo* for introducing carrier function and molecular recognition sites.

Antitumor agents

The anti-cancer potential of metal-NHC complexes has recently been reviewed.[11] A number of metals have shown cytotoxicity when bound to an NHC ligand. Specifically, palladium, copper, silver, and gold complexes have been developed that display antitumor activities that largely surpass that of cisplatin (Fig. 3). Mechanistically, these metals interfere at different stages and along various pathways. Palladium-NHC complexes such as complex **4** seem to follow pathways analogous to cisplatin. In contrast, copper-NHC complexes such as complex **5** cause metal-induced apoptosis. Evaluation of their cytotoxicity on various cell lines indicates submicromolar half inhibitory concentration (IC_{50}) values, a range similar to the most active silver carbene complexes like **6**.



theobromine **3**

Scheme 1 Synthesis of the theobromine-derived silver NHC complex **3** featuring high antimicrobial activity, enhanced water solubility and providing biocompatible degradation products.

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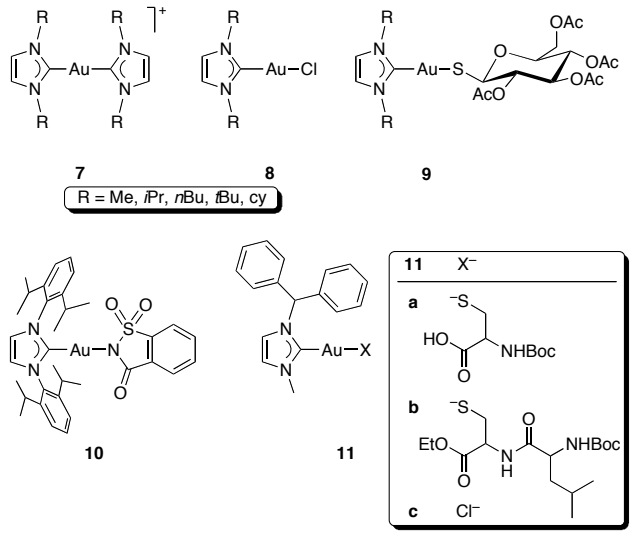


Fig. 4 Gold(I) NHC complexes with anticancer activity.

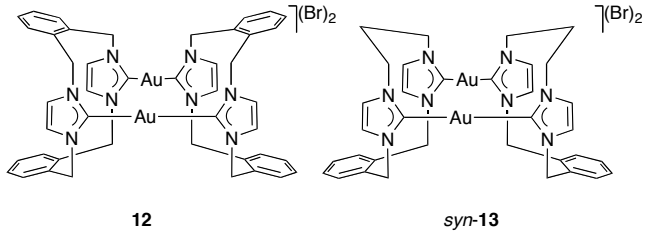


Fig. 5 Dimetallic gold(I) NHC complexes pairing antitumor activity with luminescence (complex **13** as mixture of *syn* and *anti* isomers).

Much effort has been directed towards the application of gold complexes for targeting mitochondrial cell death pathways. Following the successful application of gold phosphine complexes as antitumor agents, Berners-Price and coworkers have synthesized a variety of cationic mononuclear gold(I) biscarbene complexes **7** as potential chemotherapeutic agents (Fig. 4).[12] The wingtip groups have been modified in order to adjust the lipophilic character of the complexes, a critical factor for targeting malignant cells. The assays carried out on these gold compounds have demonstrated that ionic $[Au(NHC)_2]^+$ complexes selectively induce apoptosis in cancer cells but not in normal cell lines.[13]

Similarly, the gold(I) monocarbene complexes **8** and **9** have been considered as NHC-based mimics of the potent antitumor drugs $(Et_3P)AuCl$ and Auranofin, respectively (Fig. 4).[14] Auranofin is a tetraacetylthioglucose gold(I) phosphine complex that is currently commercialized under the trademark Ridaura. While appreciable activity has been observed for the NHC mimics, Auranofin appeared to be a more potent drug.

Most recent efforts in anti-proliferative gold(I) NHC chemistry has focused on increasing the biocompatibility. For example, complex **10** comprising a saccharin spectator ligand has recently been prepared by Nolan and coworkers (Fig. 4),[15] though its chemotherapeutic activity is still unknown. Similarly, Metzler-Nolte and colleagues have evaluated gold(I) complexes that contain either a sulfur-bound cysteine

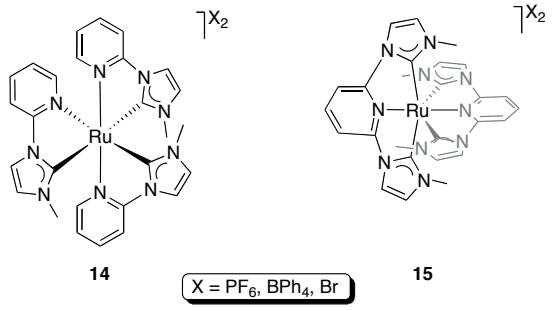


Fig. 6 Photoinactive bpy-related complex **14** and luminescent terpy-like Ru(II)–NHC complex **15**.

(**11a**) or a Cys-Leu dipeptide (**11b**) as anionic ligand *trans* to the NHC ligand.[16] Rather surprisingly, the highest cytotoxicity has been noted, however, for the chloride complex **11c**. Worth noting, cisplatin is slightly more active, whereas the analogous gold(III) complex is 3-10 times less active according to the pertinent IC_{50} values on different cell lines (HeLa, HT-29, HepG2).

A number of dinuclear gold(I) carbene complexes with a cyclophane-type carbene skeleton show good activity in the selective induction of mitochondrial permeability transition,[17] which is considered to be the primary mechanism leading to mitochondria-induced apoptosis. In addition, complex **12** comprising an *ortho*-substituted xylylene scaffold (Fig. 5) is luminescent, which has been assumed to result from short Au···Au contacts induced by the cyclophane ligand framework (*vide infra*). Luminescence properties of active substances is particularly attractive for monitoring the intracellular distribution of the complex, *e.g.* for targeting specific cell organs. While the absorption energies of complex **12** overlap significantly with those of other cellular components, modification of the cyclophane skeleton allows for adjusting the photochemical properties. In complex **13** featuring a propylene rather than an *ortho* xylylene-linker and obtained as a mixture of *syn* and *anti* isomers (only *syn* isomer shown in Fig. 5), the Au···Au separation is significantly shorter than in **12** and the aurophilic interactions are stronger.[18] As a consequence, the absorbance and emission wavelengths are both red-shifted and hence suitable for monitoring intracellular complex distributions.

Photoluminescent *N*-heterocyclic carbene complexes

Inspired by the attractive photochemical properties of ruthenium polypyridine complexes, Chung and coworkers have prepared complexes **14** and **15** (Fig. 6).[19] These NHC complexes represent structural analogues of $[Ru(bpy)_3]^{2+}$ and $[Ru(terpy)_2]^{2+}$, respectively (bpy = 2,2'-bipyridine, terpy = 2,2':6',2"-terpyridine). The synthesis involves the reductive complexation of $RuCl_3{\cdot}xH_2O$ with the carbene precursor imidazolium salt in refluxing ethylene glycol. Remarkably, this reaction protocol affords the *mer*-isomer exclusively. Based on the high *trans* influence of the carbene ligand, a facial ligand arrangement would seem thermodynamically

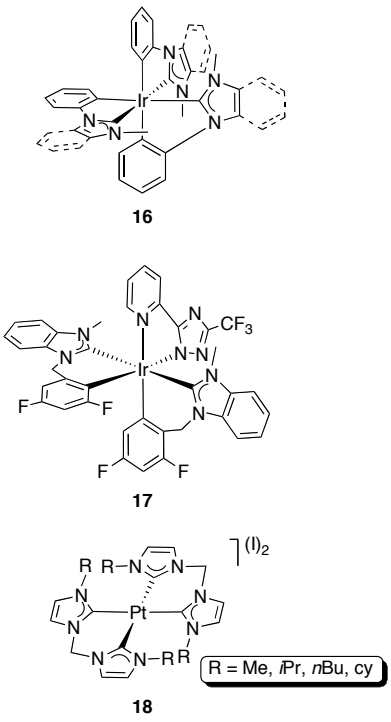
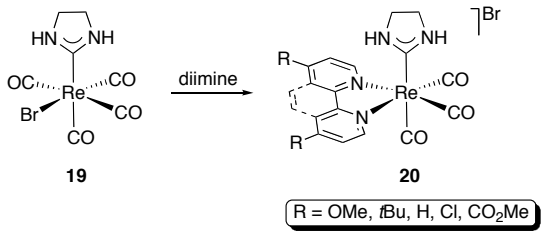


Fig. 7 Blue phosphorescent Ir(III) and Pt(II)–NHC complexes.

more favored. The prevalence of the *mer*-isomer has been attributed to the steric requirements of the NHC wingtip group.[20] While complex **14** is photochemically inactive, the terpy-like complex **15** displays long-lifetime emission at RT (820 ns in MeCN, 3100 ns in H_2O). The lifetimes are dependent on the counterion and typically about four orders of magnitude larger than that of $[Ru(terpy)_2]^{2+}$. Long lifetimes in H_2O are strongly desired for constructing artificial photosynthesis models.

Blue emitters are particularly sought for the fabrication of organic light emitting diodes (OLEDs). For this purpose, Thompson and coworkers have developed the iridium(III) NHC complexes **16**, which display luminescence in the blue region (Fig. 7).[21] In these complexes the strong-field carbene ligands have been postulated to destabilize thermally accessible non-emissive states. The complexes exhibit higher luminescent quantum yields than related pyrazolyl-based systems. Furthermore, they show long lifetimes in polystyrene films, demonstrating their efficiency as dopants in OLEDs. In an attempt to fabricate a prototypical device, both *fac*- and *mer*-**16** have been doped into *p-bis*(triphenylsilyl)benzene (UGH2) as a wide energy gap host.[22] Such a device avoids the use of unstable fluorine-containing components and features pure deep blue color emission, which has not been accessible with previously explored blue phosphors. Additionally, promising external quantum efficiencies have been measured (>5%). This approach has recently been extended to heteroleptic iridium complexes such as **17** containing benzyl-substituted NHCs and a 2-pyridyl triazolate chelating ligand (Fig. 7).[23] An external quantum efficiency as high as 6% has been achieved with this complex as blue emitter in multilayer OLEDs.



Scheme 2 Formation of Re(I)–NHC complexes **20** with tunable luminescence properties.

Strassner and coworkers have synthesized a series of homo- and heteroleptic platinum(II) bis(dicarbene) complexes **18** (Fig. 7).[24] These compounds emit in the deep blue region (λ = 386 nm) and have quantum yields up to 45% with a photostability exceeding 180 min at an excitation wavelength of 325 nm. Unlike the emission wavelength, the quantum yields are considerably influenced upon variation of the wingtip substituents at nitrogen. Smaller wingtip groups typically induce higher quantum yields.

The rhenium(I) NHC complexes **20** comprising a phenanthroline or functionalized bipyridine ligand have been prepared via ligand exchange from the carbene complex **19** (Scheme 2).[25] These complexes are emissive at room temperature with a maximum emission in the 550–620 nm range. The exact wavelength is directly correlated with the electron-withdrawing nature of the substituents R at the diimine ligand. Calculations indicate that the lowest energy absorption comprises a HOMO–LUMO transition that involves a filled non-bonding metal d orbital and a π^* orbital localized predominantly on the diimine ligand.

A variety of gold(I) carbene complexes exhibit luminescent properties. The monometallic complexes [AuCl(NHC)], **21a**, obtained from the *N*-methylated benzimidazolium salt and subsequent transmetalation, displays a high-energy emission band (λ_{max}^{em} ~ 400 nm). In addition, a low-energy band around 580 nm has been detected with a lifetime around 25 μs (Fig. 8, *cf.* also Fig. 4 above).[26] In the solid state, short intermolecular π –π and aurophilic interactions have been identified (Au···Au < 3.2 Å), which may account for the observed luminescent behavior. Consistent with this model, the low-energy emission is suppressed upon substitution of the methyl wingtips with ethyl groups (**21b**), probably as a consequence of the longer metal-metal distances. Similarly, cationic complexes $[Au(NHC)(pyr)]^+$ (**22**) and $[Au(NHC)_2]^+$ (**23**) lack any emission at higher wavelength, which has been ascribed to disfavored intermolecular interactions due to the mutually twisted orientation of the two heterocyclic ligands. Close contact analyses have indicated that the solid state structures of the pyridine-containing complexes **22** generally feature intermolecular Au···Au or Au···π interactions. Calculations on complex **22a** (R = NMe_2) predict[27] that emission is a consequence of an electronic transition from the HOMO–3 to the LUMO. The former is mainly associated with the pyridine ligand, while the LUMO is largely aurophilic. In

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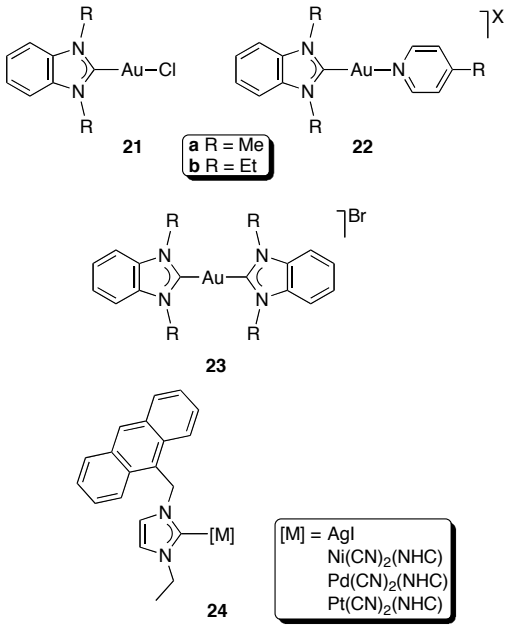


Fig. 8 Metal–NHC complexes with ligand-centered luminescent properties.

line with these calculations, the emission wavelength has been shown to sweep over *ca*. 70 nm upon variation of the pyridine ligand.

Luminescent properties have also been observed with cluster-like oligometallic gold(I) and silver(I) carbene complexes with topologies that are decidedly influenced by the pyridine and pyrazol functionalities attached to the carbene ligand.[28] The emission wavelength does not show a direct correlation with the ligand-induced metal-metal separation, and in most cases, luminescence has been attributed to an intraligand rather than a metal-centered process. Similar ligand-centered fluorescence has been evoked by decorating imidazolium salts with photochemically active anthracenyl groups (**24**, Fig. 8).[29] Metal coordination to the carbene increases the fluorescence intensity as compared to the corresponding imidazolium salt precursor, probably due to the electron-withdrawing effect associated with metal binding. Consistent with the proposed electronic control, the fluorescence intensity of group 10 metal complexes increases with increasing electrophilicity of the metal center, $Ni^{II} < Pt^{II} < Pd^{II}$. Fluorescence is quenched, however, in the presence of C_{60}, which has allowed for the construction of a silver-carbene based metallomacrocyclic receptor for C_{60} detection.[30]

N-Heterocyclic Carbene Complexes in Self-Assembly

Liquid crystalline materials

The self-assembly of amphiphilic metal NHC complexes into birefringent materials provides a suitable approach for preparing metal-containing liquid crystals. The covalent M–C_{NHC} bond increases the stability of the complexes towards air and moisture. In addition, covalent metal bonding is expected

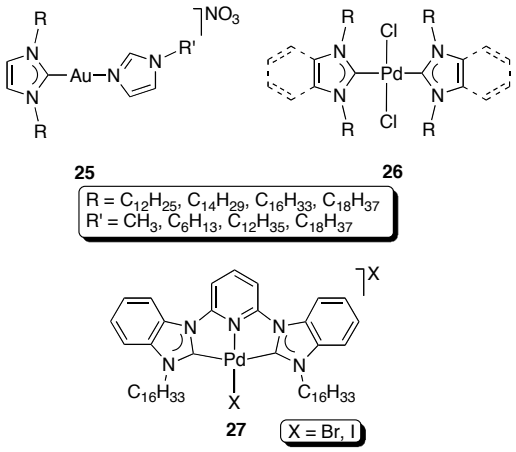


Fig. 9 Introduction of long alkyl wingtip groups for evoking liquid crystalline behavior (**25** and **26**, see also **23** in Fig. 8) and gelating properties (**27**).

to increase the thermal stability and hence to prevent decomposition at the clearing point as often observed with liquid-crystalline coordination compounds.[31] Lin and coworkers have prepared the gold(I) biscarbene complexes **23** from benzimidazolium salts functionalized with long alkyl chain (*cf*. Fig. 8, $R \geq C_{12}H_{25}$).[32] They are thermally stable up to 240 °C and liquid crystalline in the 90–160 °C temperature range, depending on the wingtip chain length. X-ray diffraction analyses indicate the formation of lamellar β mesophases as a result of π–π and hydrophobic interactions in combination with hydrogen bonding.

A decrease of the number of alkyl chains combined with a different anion as in complexes **25** reduces the tendency to form mesophases.[33] For example, the dodecyl-substituted complex **23** ($R = C_{12}H_{25}$) is liquid crystalline over a 60 K window (between 92 °C and 152 °C), whereas complex **25** with identical substituents ($R, R' = C_{12}H_{25}$) exhibits a smectic A phase in a much narrower temperature range (78–87 °C). Stronger Coulombic and hydrogen bonding interactions between the cationic headgroup and the anionic NO_3^- in **25** have been suggested to account for such different behavior of these metallomesogens. In line with this hypothesis, the introduction of hydroxyl groups in the R' substituent of the imidazole ligand further quenches birefringence.

In related liquid-crystalline palladium(II) biscarbene complexes **26** (Fig. 9),[34] the alkyl chains are not interdigitating as in the gold(I) analogs **23** and are arranged nearly perpendicular to the palladium coordination plane. These compounds display smectic mesophases that start to form as low as 55 °C. Remarkably, the imidazolylidene complexes have lower melting temperatures (54.3–79.4 °C *vs*. 90.0–103.8 °C) and higher clearing points (155.1–187.7 °C *vs*. 121.2–138.5 °C) than their benzimidazolylidene analogs, which has been attributed to enhanced core-core interactions in the latter species.

Structurally diverse silver(I) carbene complexes have been tested for liquid crystalline behavior. The pure complexes do

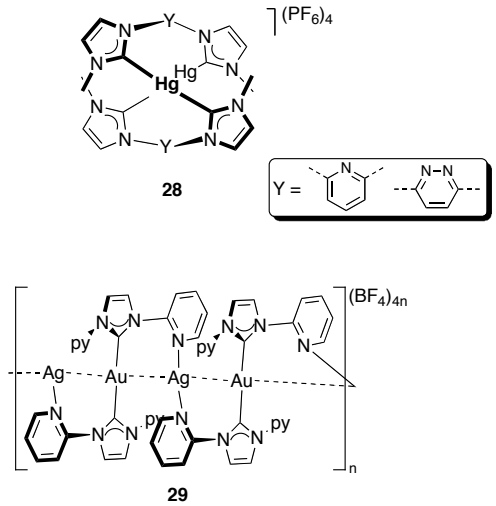


Fig. 10 Helical Hg(II)–NHC complexes and bimetallic helical polymer based on Au(I)–NHC entities.

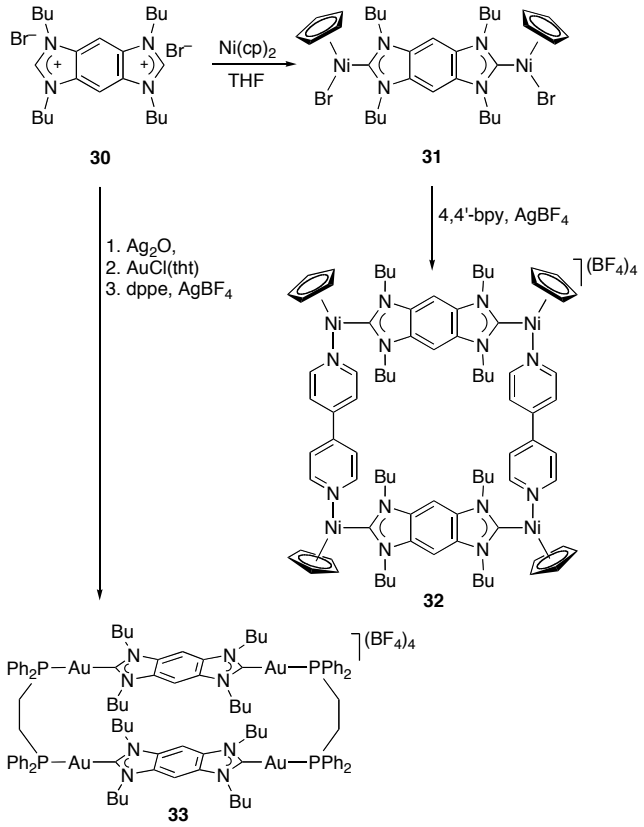
not display any birefringence, but are liquid crystalline when mixed with their corresponding imidazolium salts.[35]

Related to this topic, pincer-type cyclometalated palladium(II) dicarbene complexes **27** have shown to be efficient gelators when decorated with long alkyl chains (Fig. 9).[36] Notably, the metallic core of this complex is fully planar and the planes of all heterocycles coincide with the palladium coordination plane. Remarkably, complexes **27** not only gelate various protic and aprotic organic solvents but also several ionic liquids such as pyridinium and imidazolium.

Topologies

Coordination of heteroarene-linked dicarbenes to mercury(II) centers gives dinuclear complexes **28** with helical topology (Fig. 10).[37] This approach has been further expanded to carbenes containing two pyridyl wingtip groups. When coordinated to gold(I), mononuclear biscarbene complexes similar to **7** are formed. Upon addition of Ag^+ ions, the wingtip pyridine coordination sites interlink these complexes via formation of $Ag(pyridine)_2$ entities, thus affording the helical polymer **29**.[28b] Such compounds may become useful models for biologically relevant helical macromolecules reminiscent to polypeptide α-helices and doublestranded DNA. Introduction of a bidentate coordinating carboxylate anion rather than using non-coordinating BF_4^- allows for the incorporation of a second Ag^+ ion, thus expanding the Ag:Au ratio from 1:1 in **29** to 2:1.[38]

The tetrametallic molecular square **32** has been synthesized by Hahn and coworkers *via* reaction of nickelocene with the benzdiimidazolium salt **30** and subsequent coupling of the bimetallic Ni_2(dicarbene) complex **31** with 4,4'-bipyridine as connecting ligand (Scheme 3).[39] Crystallographic analysis of the remarkably air- and water-stable molecular square indicates an essentially coplanar arrangement of the nickel atoms and virtually identical Ni···Ni separation along the dicarbene and the bipyridine axes. The synthetic approach is very versatile and has recently been extended to the

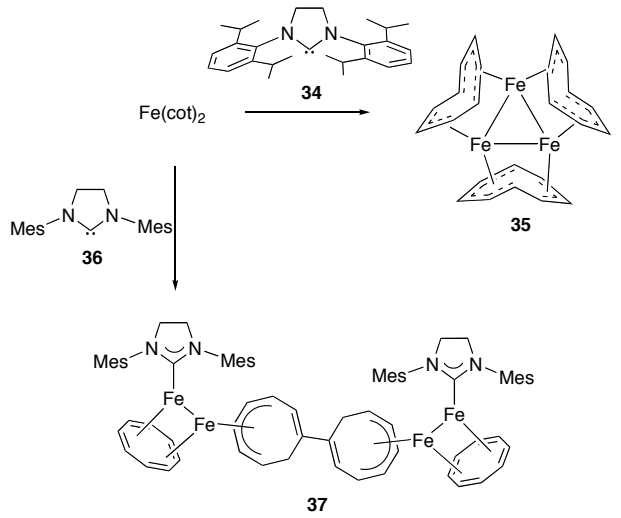


Scheme 3 Synthesis of a metallasupramolecular structures **32** and **33** comprising four nickel(II) and gold(I) centers, respectively.

fabrication of the molecular rectangle **33** comprising four gold(I) centers (Scheme 3).[40] Such organometallic building blocks may find wide application for metallosupramolecular structures due to the enhanced stability of the metal-carbon bond as opposed to kinetically more labile heteroatom coordination of the metal center. Clearly, though, irreversible M–C bond formation lacks thermodynamic control and requires a careful design of self-assembling procedures.

A different application of NHC ligands for the synthesis of new topologies has been reported by Lavallo and Grubbs. Reaction of the free carbene **34** with $Fe(cot)_2$ (cot = cyclooctatetraene) affords the star-like tri-iron system **35** (Scheme 4).[41] Crystallographic analysis suggests close Fe···Fe contacts, which may become appealing when constructing electronically active devices. For this purpose, it may be interesting to assess the metal-metal bond order as well as the metal oxidation state. In the synthesis of complex **35**, the NHC ligand acts catalytically, thus implying the reversible making and breaking of $Fe–C_{NHC}$ bonds. While these results may cast some doubt on the stability of the metal-carbon bond, it is worth noting that using the less bulky carbene **36** (Mes = mesityl) yields the tetranuclear bis(carbene) species **37**, resulting from reductive C–C bond formation. Unlike during the formation of the trimetallic complex **35**, the $Fe–C_{NHC}$ bond in **37** seems to have been formed irreversibly.

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Scheme 4 NHC-mediated assembly of the trinuclear structure **35** and NHC-assisted reductive C–C coupling to build up the tetranuclear synthon **37**.

Organometallic Polymers Comprising *N*-Heterocyclic Carbene Complexes

The incorporation of metal NHC synthons into polymeric materials has been studied predominantly through the functionalization of polymer side chains.[42] Main-chain metal–NHC polymers have received much less attention, even though organometallic polymer main-chains may effectively combine the advantageous properties of organic polymers and organometallic complexes, thus providing access to multifunctional materials.

The availability of ditopic NHC ligands constitutes an essential prerequisite for fabricating main-chain metal NHC polymers. The shortest interconnection of metal centers by a ditopic NHC ligand has been realized by Bertrand and coworkers upon metalation of the triazol-diylidene precursor **38**, affording the linear silver carbene polymer **39** (Scheme 5).[43] The carbene linker has been expanded by Bielawski and coworkers to benzannelated dicarbenes, oxobridged dibenzimidazolylidenes, bibenzimidazolylidenes, and ferrocene-bridged dicarbene complexes (**40–43**, Scheme 5).[44]

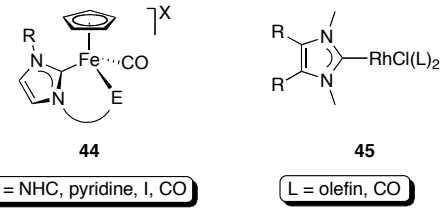
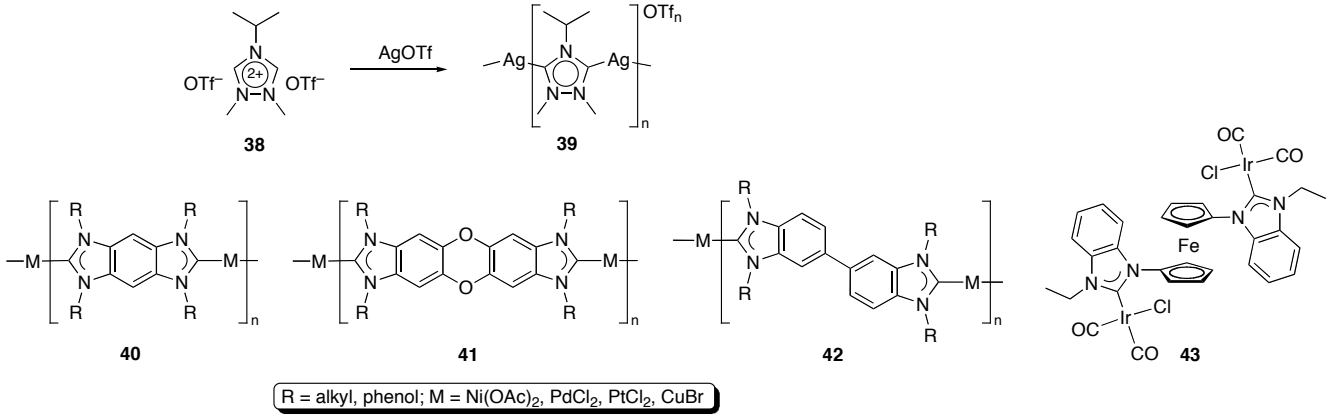


Fig. 11 Redox-active Fe^{II}–NHC complexes **44** with metal-carbon π interactions and rhodium complex **45** featuring p acceptor ligands that respond on modifications of substituents R.

Polymeric complexes are accessible either by a free carbene route or via direct metalation using C–H bond activation. The latter procedure is less sensitive towards moisture and air[45] and allows for the incorporation of a variety of metals including palladium(II), platinum(II), nickel(II), and copper(I) centers. Modification of the wingtip group R, specifically the introduction of chelating groups increases the stability of the M–C_{NHC} bond. Polymers with molecular weights of up to 2000 kDa have thus been obtained. They are thermally stable (up to 300 °C), conductive ($\sigma \sim 10^{-3}$ S cm^{-1}; *cf.* 10^{-5} S cm^{-1} for silicon), and structurally dynamic. These properties have prompted their use as self-healing, electronically active materials.[46]

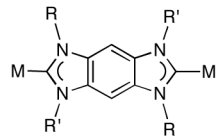
Considerable efforts have been dedicated in recent years to evaluate such ditopic carbene ligands as components for molecular electronics. Specifically, their potentially conducting properties have been suggested to enable the electronic coupling of the bound metal centers, thus giving access to mixed-valent species and eventually to conducting molecular wires. Such application has been supported by fundamental studies on complexes **44** and **45**, (Fig. 11) which provided evidence for non-negligible π contribution to the M–C_{NHC} bond, and for the tunability of these π interactions.[47]

Based on these results, Bielawski and ourselves have evaluated the electronic communication between two redox-active metal centers interlinked by ditopic carbene ligands.[48] Not surprisingly, the bibenzimidazolium-derived bimetallic complexes (*cf.* **42**, Scheme 5; M = RhCl(cod) or $RhCl(CO)_2$) lack intermetallic communication, much like 4,4'-bipyridine-linked dinuclear complexes. Much more remarkable seems,



Scheme 5 Organometallic dimetallic and polymer species with metal-containing main chains derived from different ditopic NHC ligands.

a)



46

	[M]	R,R'	$\Delta E_{1/2}$
a	Fe(cp)I(CO)	Bu, Bu	80 mV
b	$RuCl_2$(cymene)	Bu, Bu	58 mV
c	IrCl(cod)	Me, Ph	60 mV
d	Ir(2-phenylpyridine)$_2$	Me, C_6H_4	---

b)

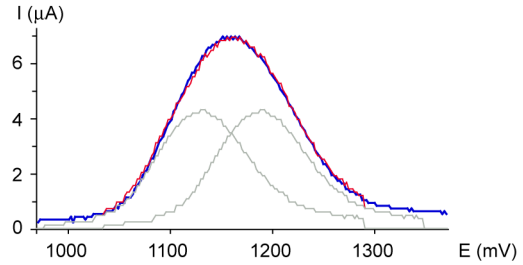
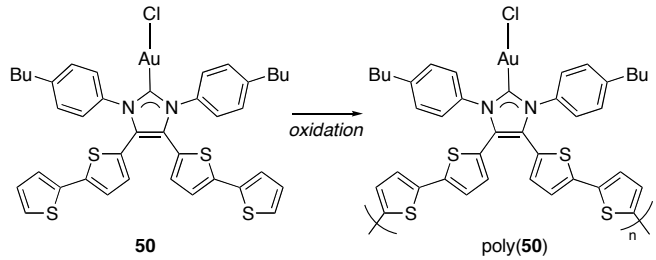


Fig. 12 Bimetallic complexes **46** and their separation of oxidation potentials $\Delta E_{1/2}$ as determined from deconvolution of the pertinent differential pulse voltammetry signals (*a*), illustrated for **46b** (*b*; blue: measured, grey: deconvolution using monometallic model complexes, red: sum of deconvoluted signals.

however, the small electronic coupling of redox centers in complexes of type **46** comprising a supposedly π-conjugated dicarbene linker. When bound to iron (**46a**), these bimetallic complexes display only moderate intermetallic communication, as revealed by the small separation of the two half-wave potentials for metal oxidation ($\Delta E_{1/2}$ = 80 mV). When bound to ruthenium(II) or iridium(I) centers, the communication further decreases, and it is completely absent in iridium(III) complexes. Various arguments have been put forward for rationalizing these results, including (*i*) weak overlap between the central arene ring and the NCN amidinylidene fragment, (*ii*) insufficient *d*(metal)–π(ligand) orbital overlap due to an energetic mismatch of the involved orbitals, and (*iii*) unfavourably large torsion of the metal's hypothetical xy-coordination plane and the heterocyclic ring plane, which also results in weak *d*–π orbital interactions. Notably, the latter effect can be ruled out in complex **46d**, since C–H bond activation of the phenyl wingtip group provides a chelating NHC ligand that is planar and thus well aligned for interacting with metal d orbitals.[48b]

Considerably better metal-metal communication has been observed when the NHC ligands are interconnected via the nitrogen atoms rather than the backbone carbons. Electrochemical analysis of the redox properties of the bimetallic complex **47** reveals a large separation of the oxidation potentials for the two metal centers (Scheme 6). Together with the substantial comproportionation constants, a mixed-valence state at the borderline between Class II and III systems has been deduced. Based on these results, main-chain organometallic polymers have been fabricated by interlinking diiron species with different ditopic imine ligands.[49] When using 4,4'-bipyridine, the formed polymer **48** exhibits relatively sharp oxidation waves. In contrast, the pyrazine-linked polymeric structure **49** is oxidized over a broad potential range, which has been assigned to multimetallic communication and oxidation events that are strongly affected by the redox-state of neighboring metal centers. Hence, polymeric materials such as **49** hold great promise as novel molecular wires for electronic applications.

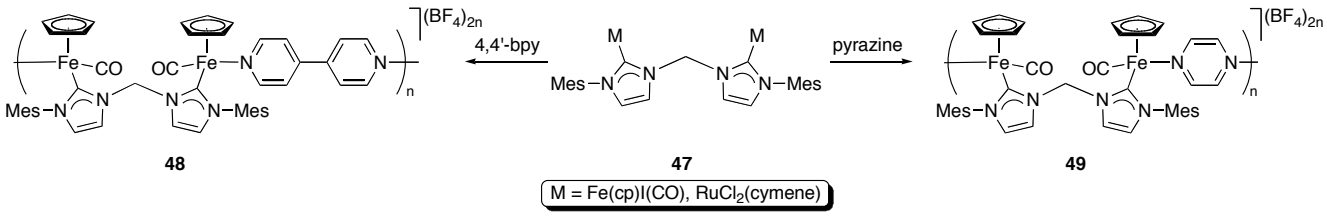


Scheme 7 Electropolymerization of the tetrathiophene **50** comprising a central gold(I) NHC unit..

A different approach towards polymeric materials containing NHC complexes as integral components of the main chain has been developed by electropolymerization of the dithiophene-substituted gold(I) NHC complex **50** (Scheme 7).[50] Polymerization onto a platinum disk or an indium tin oxide glass within –0.2 to 1.5 V affords a film of poly(**50**). The polymer film oxidation current gradually increases with the number of scans, indicating continuous film growth as well as good conductivity through the film. Such devices may become highly attractive for application in gated molecular electronics.

Conclusions and perspectives

The use of metal carbene complexes in various fields beyond catalysis has experienced substantial advances during the last decade. Based on the specific properties of *N*-heterocyclic carbene ligands, a variety of applications have been disclosed.



48 47 49

Scheme 6 Redoxactive organometallic main chain polymers featuring electronically separated iron centers (**48**) and electronically all-coupled iron centers (**49**) derived from ditopic N-interlinked dicarbene ligand precursors.

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For example, $[Au(NHC)_2]^+$ complexes with appropriately functionalized wingtip groups constitute components that combine luminescent, anti-proliferative, and mesogenic properties. While there is ample room for improvement and further refinement in most domains, *e.g.* in terms of long term stability and fatigue resistance, the results achieved up to now unambiguously demonstrate the potential of *N*-heterocyclic carbene complexes as active units for diverse applications beyond catalysis, ranging from medical to optical and electronic areas. Given the current interest in these applications and the significant rise of activities in carbene chemistry directed to materials science in the last few years, there is little doubt that further exciting results will be accomplished in this area.

Acknowledgements

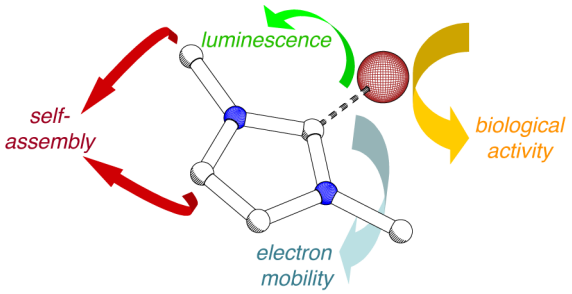
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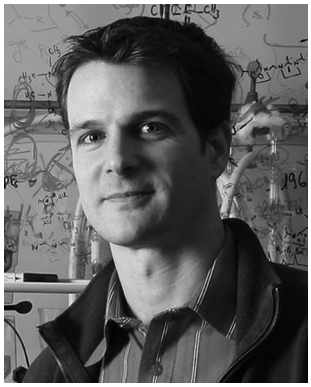
N-heterocyclic carbene complexes have much more to offer than catalytic activity — recent achievements highlight the potential of these species as versatile active sites in medicinal chemistry and materials science.

Bibliographic entry

Laszlo Mercs earned his degree in chemistry in 2003 from the University of Debrecen (Hungary) under the guidance of Prof. Tamas Patonay. After a one-year research fellowship at CNR-ISTM Milan (Italy), he joined the group of Prof. Martin Albrecht as graduate student and obtained a Ph.D in chemistry in 2009 from the University of Fribourg (Switzerland). He is currently performing postdoctoral work as a Swiss National Science Foundation fellow with Prof. Sally Brooker at the University of Otago (New Zealand).

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