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PERSPECTIVE

The Diverse Functions of Isocyanides in Phosphorescent Metal Complexes

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In this Perspective, we highlight many examples of photoluminescent metal complexes supported by isocyanides, with an emphasis on recent developments including several from our own group. Work in this field has shown that the isocyanide can play important structural roles, both as a terminal ligand and as a bridging ligand for polynuclear structures, and can influence the excited-state character and excited-state dynamics. In addition, there are many examples of isocyanide-supported complexes where the isocyanide serves as a chromophoric ligand, meaning the low-energy excited states that are important in the photochemistry are partially or completely localized on the isocyanide. Finally, an emerging trend in the design of luminescent compounds is to use the isocyanide as an electrophilic precursor, converted to an acyclic carbene by nucleophilic addition which imparts certain photophysical advantages. This Perspective aims to show the diverse roles played by isocyanides in the design of luminescent compounds, showcasing the recent developments that have led to a substantial growth in fundamental knowledge, function, and applications related to photoluminescence.

Background and Introduction

Isocyanides are versatile synthons in organic synthesis,[1,2] and in the field of inorganic coordination chemistry have become a prominent class of neutral supporting ligands. Though not as ubiquitous as some other monodentate "L" ligands like phosphines, carbonyl (CO) or *N*-heterocyclic carbenes (NHCs), there are nonetheless many examples of isocyanide coordination compounds across a variety of transition metals. The general structure of an isocyanide is shown in Fig. 1. In analogy to isoelectronic CO, isocyanides have a σ HOMO that can be formulated as a carbon-centered lone pair and a π* LUMO, making them both good sigma donors (through carbon) and good π-acceptors. Given their π-acidic nature, isocyanides are particularly prominent as supporting ligands for low-valent, mid-to-late transition metal complexes, i.e., compounds with 6 or more valence *d* electrons.

The linear C≡N moiety in isocyanides makes it more difficult to situate ligand steric bulk near the metal center, which is likely one reason isocyanides are less frequently used than phosphines and NHCs in homogeneous catalysis and small-molecule activation applications. That said, there are some notable examples of sterically encumbered isocyanides that can support low-coordinate, reactive metal complexes and have been used in bond activation and homogeneous catalysis.[3,4] One advantage of isocyanides is their ease of synthesis, allowing a variety of alkyl and aryl substituents to be installed. The most common synthetic strategy starts from a primary aryl amine. Addition of formic acid or formic anhydride generates the formamide, Ar–NHC(O)H. A variety of reagents, e.g. $POCl_3$, *p*-$TolSO_2Cl$, and the Burgess reagent, can be used to dehydrate the formamide and generate the isocyanide.

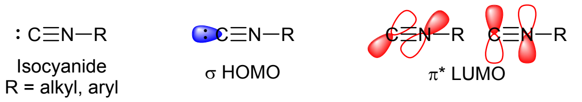

Fig. 1. General structure and frontier orbitals of isocyanides.

Acknowledging the plethora of research on isocyanide coordination chemistry and the minor roles they have played as supporting ligands for metal-mediated transformations, in this Perspective we focus on the varied roles isocyanides play as supporting ligands for photoluminescent transition metal complexes, with a particular emphasis on our own group's contributions in this area. A detailed introduction on photoluminescent transition metal complexes and their applications is beyond the scope of this article, but some important context is needed. Most luminescent transition metal complexes consist of closed-shell, 4*d* or 5*d* metal centers surrounded by a set of conjugated organic ligands. For the purposes of this article and in the field as a whole the most prominent category of luminescent compounds are bis-cyclometalated iridium complexes, which feature a six-coordinate $5d^6$ iridium center chelated by two cyclometalating ligands, with one chelating or two monodentate ancillary ligands occupying the remaining sites.[5] Complexes of this type luminesce via phosphorescence, originating from a triplet excited state with the energy of the excited state and corresponding phosphorescence spectral profile determined primarily by the cyclometalating ligands.[6] The most prominent application of cyclometalated iridium compounds is in organic light-emitting diodes (OLEDs), where they have emerged in both

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academic and commercial settings as the most successful emissive dopant for these devices.[5,7]

This review is organized by the several distinct functions isocyanides can play in supporting phosphorescent transition metal complexes. We identify and elaborate four different roles isocyanides can play:

- Ancillary or "spectator" ligands: In the first part we introduce a variety of works where the photoluminescent compound includes one or more isocyanides, but the isocyanide's frontier orbitals are not directly involved in the luminescent excited state. That said, the isocyanide has indirect but important electronic consequences, influencing the energy, character, and dynamics of the excited state. Moreover, the isocyanide can help stabilize reactive synthons that enable facile assembly of complex multi-component architectures.
- Bridging ligands for self-assembly: We highlight recent developments where linear bidentate isocyanides have been used as bridging ligands for luminescent, self-assembled polynuclear complexes.
- Chromophoric ligands and triplet acceptors: In some compounds, both mononuclear complexes and self-assembled metallacycles, the lowest-energy triplet state involves or is directly localized on the conjugated aryl isocyanide. In these cases, the phosphorescence and other triplet excited-state processes involve frontier orbitals localized on the substituted isocyanide.
- Electrophilic precursors for non-traditional carbene structures: There are some recent examples of phosphorescent transition metal complexes prepared by nucleophilic addition to coordinated isocyanides. In this case the coordinated isocyanide serves as the electrophile, and the acyclic carbene structure thus formed can be beneficial to the photoluminescence, in particular for blue-phosphorescent compounds.

Isocyanides as Ancillary Ligands

In this first part of the review, we highlight a variety of mononuclear photoluminescent complexes that include one or more isocyanide ancillary ligands.

Electronic Effects of Isocyanides

To understand the consequences of isocyanides on the excited states of photoluminescent complexes, in particular from the bis-cyclometalated iridium family, it is important to first consider the electronic consequences of isocyanides. As described in the general background above, isocyanides are strong-field ligands and therefore normally result in large HOMO-LUMO gaps relative to complexes supported by more conventional ancillary ligands, e.g. acetylacetonate (acac), ubiquitous in cyclometalated iridium chemistry. This large HOMO-LUMO gap leads to electrochemical stability in cyclometalated Ir(III) aryl isocyanide complexes. Fig. 2 demonstrates the effect of incorporating π-acidic isocyanides, shown in the context of cyclometalated iridium complexes but relevant to many other classes of compounds. In a simplified sense there are four relevant frontier orbital levels to consider: the π and π* orbitals on the C^N ligands, and the 5*d*π (i.e. t_{2g}) and 5*d*σ* (i.e. e_g) orbitals on iridium. The π-acidity of the isocyanide stabilizes the Ir dπ HOMO, leading to a larger HOMO–LUMO gap and larger ligand-field splitting. Electrochemically, this has the consequence of shifting the formal Ir^{IV}/Ir^{III} redox couple to more positive potentials, imparting better redox stability both in the ground and excited states.

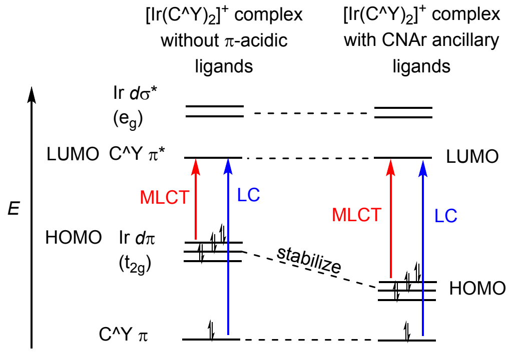


Fig. 2. Partial frontier molecular orbital diagram depicting the stabilization of the dπ HOMO in complexes with isocyanide ancillary ligands.

With this diagram in mind, it is also possible to consider the effects of the isocyanide on the triplet excited state. Fig. 2 includes the one-electron transitions responsible for the relevant triplet excited states, and Fig. 3 further elaborates the effects of the isocyanide on these excited states. The HOMO–LUMO transition results in a metal-to-ligand charge transfer (MLCT) excited state and the π→π* transition on the cyclometalating ligand (C^Y) gives rise to a ligand-centered (LC) state. The iridium-centered *d*–*d* transition generates a metal-centered (MC) excited state, which need not be considered in this discussion but can be an important deactivating nonradiative state in some blue-phosphorescent iridium complexes (see below). The emissive triplet state, i.e. T_1, normally involves configuration interaction between ^{3}MLCT and ^{3}LC states, as shown in Fig. 3. At parity of C^Y ligand the

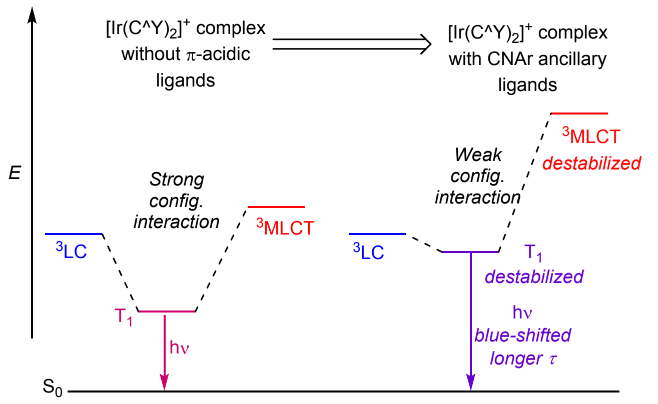
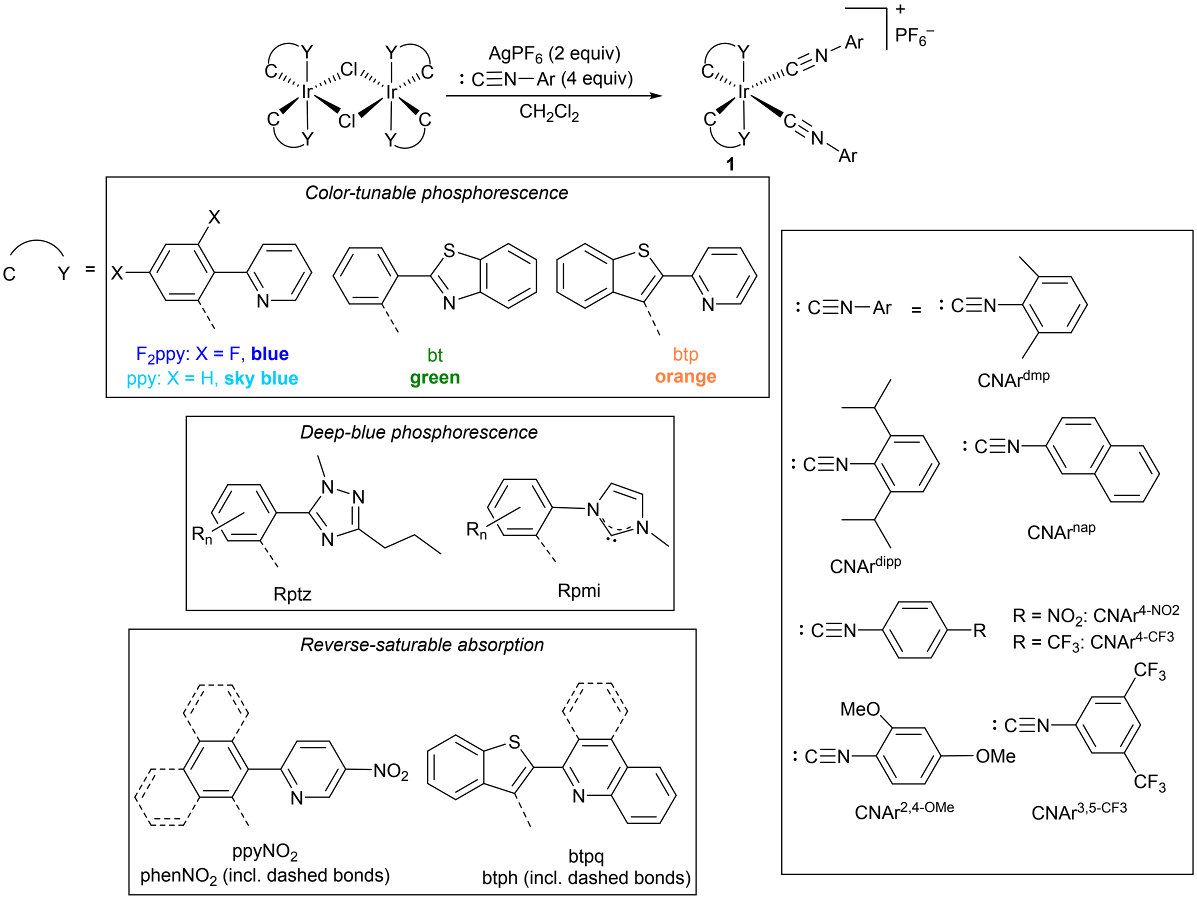


Fig. 3. Qualitative excited-state energy-level diagram showing the effects of isocyanides on configuration interaction, T_1 energy, and phosphorescence.



Scheme 1. Synthetic scheme and summary of a variety of bis-cyclometalated iridium bis-isocyanide complexes from our group.

isocyanide has minimal effect on the ^{3}LC state, but the ^{3}MLCT state is destabilized. Thus, in complexes with less π-acidic ancillary ligands there is strong configuration interaction between ^{3}MLCT and ^{3}LC, and the T_1 state has considerable ^{3}MLCT character. In complexes with isocyanides, the larger separation between ^{3}MLCT and ^{3}LC leads to weak configuration interaction and predominantly ^{3}LC character in T_1. These effects have two major consequences on the phosphorescence. In isocyanide-supported complexes the weaker configuration interaction with ^{3}MLCT leads to a measurable blue-shift in the spectrum. In addition, the more predominant ^{3}LC character in isocyanide complexes reduces spin-orbit coupling in T_1, as all of the spin-orbit coupling derives from the MLCT states.[6] This results in longer PL lifetimes for complexes with isocyanide ancillary ligands, compared to compounds with less π-acidic ancillary ligands.

Bis-isocyanide Complexes

Many luminescent coordination complexes with two isocyanide ancillary ligands, normally *cis*-oriented, have been prepared.[8,9] Most luminescent bis-isocyanide compounds, however, are centered around bis-cyclometalated iridium complexes with the general formula $[Ir(C^\wedge Y)_2(CNR)_2]^+$. Prior to our work in this area, most of the limited examples of these complexes included *tert*-butyl isocyanide as the ancillary ligand. These studies elucidated fundamental aspects of the nature and dynamics of cyclometalated iridium excited states,[10,11] and showed that *tert*-butylisocyanide was particularly useful for supporting complexes with efficient green[12] and blue phosphorescence.[13,14] In more applied settings, complexes of this type have been studied in the contexts of oxygen sensing and sensitization,[15,16] as well as organic light emitting diodes.[17]

Our group has extensively studied complexes of the type $[Ir(C^\wedge Y)_2(CNAr)_2]^+$ (**1**), where CNAr is an *aryl* isocyanide. Scheme 1 summarizes the synthesis of bis-cyclometalated iridium bis(aryl isocyanide) complexes and catalogues a large subset of the complexes we have studied. In our earliest work we varied the cyclometalating ligands (C^Y) to produce compounds which phosphoresce in the blue to orange regions.[18] In a closely related work we looked more extensively at the effects of substituents on the isocyanide, introducing electron-withdrawing or electron-donating groups at different positions.[19] Both of these initial efforts have provided insight into the consequences of the aryl isocyanide ligands on the triplet excited state and photoluminescence of these compounds, providing experimental validation for the concepts outlined in Fig. 2 and 3. Fig. 4 shows photoluminescence data for a representative set of bis(aryl isocyanide) complexes with C^Y = 2-phenylbenzothiazole (bt), which clearly shows the photophysical consequences of isocyanide ancillary ligands in comparison to the ubiquitous acetylacetonate (acac) ancillary

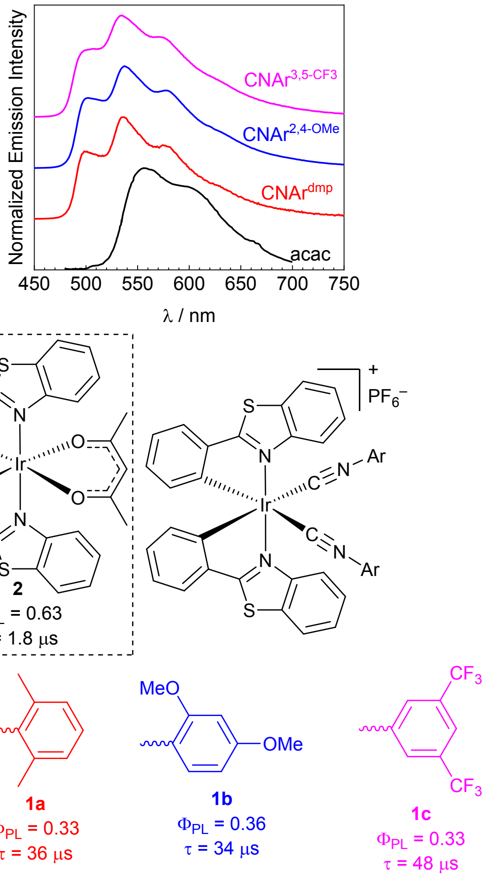


Fig. 4. Summary of photoluminescence data for Ir(bt)$_2$(acac) (**2**) and three bis(aryl isocyanide) analogues (**1a–c**). The spectrum of complex **2** is adapted with permission from reference [20]. Copyright 2001 American Chemical Society.

ligand in **2**.[20] The spectra of the bis-isocyanide complexes are substantially blue-shifted, with a ca. 2000 cm^{-1} hypsochromic shift in the E_{0-0} peaks (see Fig. 3). The more pronounced vibronic structure and ca. 20-fold increase in lifetime in the isocyanide complexes are also evidence of more ^{3}LC character in the emissive T$_1$ state. Also evident in Fig. 4, the substitution pattern on the aryl isocyanide has minimal consequences on the photophysics, with the spectra, quantum yields, and lifetimes all very similar for complexes with either electron-donating (CNAr$^{\mathrm{dmp}}$ and CNAr$^{2,4\text{-OMe}}$, **1a** and **1b**) or electron-withdrawing (CNAr$^{3,5\text{-CF3}}$, **1c**) substituents on the isocyanide. Of the substituted aryl isocyanides shown in Scheme 1, CNAr$^{4\text{-NO2}}$ is the only one that has a generalizable and substantial effect on the photophysics, greatly reducing or completely quenching phosphorescence.

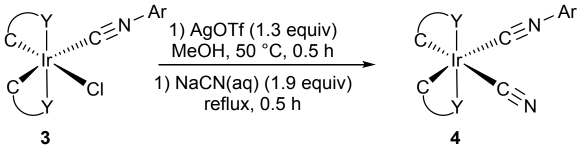
Following our initial studies on bis-cyclometalated iridium bis-isocyanide complexes, we have investigated two other directions with this structure type. Recognizing that strong-field ligands are critical design elements for blue-phosphorescent compounds, we have prepared a series of bis-isocyanide complexes with deep-blue phosphorescence (see Scheme 1).[21] Complexes with substituted 5-aryl-1,2,4-triazole (Rptz) and 1-methyl-3-aryl-imidazol-2-ylidine (Rpmi) cyclometalating ligands luminesce in the blue region, the latter giving deep-blue emission. In all cases the phosphorescence is weak in solution, but moderate to good quantum yields (Φ_{PL} = 0.13–0.50) are observed when the complexes are immobilized in transparent polymer films. We have also investigated applications of bis-isocyanide complexes in reverse-saturable absorption (RSA), using cyclometalating ligands that are highly conjugated and/or nitro-substituted.[22] In these compounds broad excited-state absorption is observed following visible excitation, with the isocyanides improving the lifetimes and redox stability relative to other related RSA compounds.

Cyano-Isocyanide Iridium Complexes

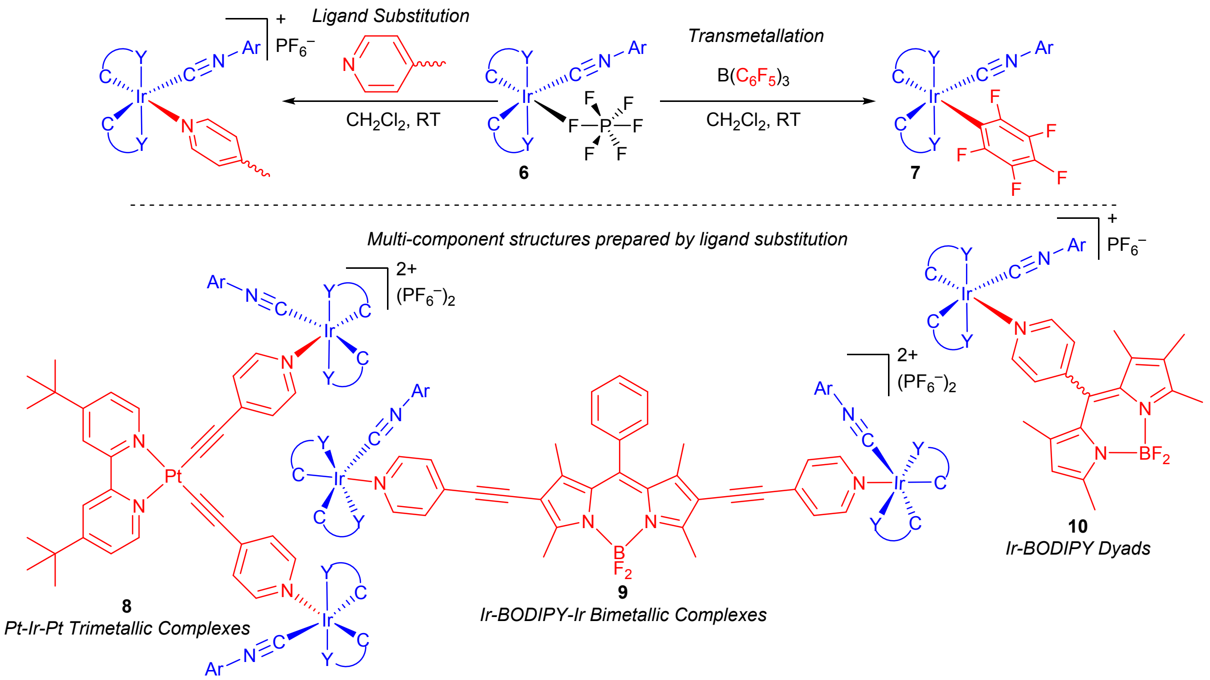
There are also many luminescent isocyanide compounds with mixed ancillary ligand sets, most often with one isocyanide combined with an anionic X$^-$ ligand. There are examples of platinum[23–27] and ruthenium[28] complexes that fall into this structure type, but our work in this area has again focused on cyclometalated iridium complexes. Previous work had established that cyclometalated iridium complexes of the type Ir(C^Y)$_2$(CN^{t}Bu)(CN) with substituted 2-phenylpyridine cyclometalating ligands display efficient sky blue to blue-green phosphorescence.[29] In our more recent work, we again targeted complexes with deep-blue phosphorescence, preparing complexes of the general type shown in Scheme 2, with 1,2,4-triazole and NHC-derived C^Y ligands to engender deep blue phosphorescence.[30] The complexes are prepared via a simple ligand substitution route, treating the Ir(C^Y)$_2$(CNAr)(Cl) (**3**) precursor complex with silver triflate and sodium cyanide. Whereas the chloride complexes are non-luminescent or very weakly luminescent (Φ_{PL} < 0.013), the corresponding cyano complexes have Φ_{PL} values at least a factor of 10 larger. These experimental results, supported by DFT calculations, support the important role that strong-field ligands play in supporting efficient blue phosphorescence. The photophysical properties of the Ir(C^Y)$_2$(CNAr)(CN) complexes (**4**) are largely similar to the cationic [Ir(C^Y)$_2$(CNAr)$_2$]$^+$ complexes (**1**) described in the previous section,[21] suggesting that the excited-state consequences of cyanide and isocyanide ligands are comparable.

Rhenium Isocyanide Complexes

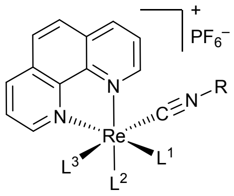
Luminescent rhenium(I) isocyanide complexes (**5** in Fig. 5) have been studied by a few groups, where the isocyanide is either *tert*-butyl isocyanide or a substituted aryl isocyanide.[31–33] In most examples of these complexes (excepting compounds with oligoaryl isocyanides, see Fig. 9 and accompanying discussion) emission originates from a ^{3}MLCT state involving the 1,10-phenanthroline and becomes further red-shifted as the number of isocyanide supporting ligands increases. This occurs because the Re 5$d\pi$ orbitals (cf. t_{2g}) are less stabilized with isocyanides compared to carbonyl, leading to smaller HOMO–LUMO gaps



Scheme 2. Synthesis of bis-cyclometalated iridium cyano-isocyanide complexes.



Scheme 3. Reactivity of Ir(C^Y)$_2$(CNAr)(FPF$_5$) complexes and their application in the preparation of complexes with multiple photoactive building blocks.



5a: $L^1 = L^2 = L^3 = CO$
5b: $L^1 = CNR$, $L^2 = CO$
5c: $L^1 = L^2 = CNR$, $L^3 = CO$
5d: $L^1 = L^2 = L^3 = CNR$

R = ^{t}Bu *or* 2,6-(^{i}Pr)$_2$C$_6$H$_3$

Fig. 5. Structures of luminescent rhenium(I) complexes with ancillary isocyanide ligands.

and red-shifted phosphorescence. Notably, Re(I) complex **5c** has a similar structure to tricarbonyl complex **5a**, with the number of isocyanides and carbonyls inverted. The phosphorescence occurs at 505 nm in **5a**[33] and shifts substantially to 668 nm in **5c**.[32]

Multi-Component Structures

Isocyanide ancillary ligands have also enabled the preparation of more complex, multi-component structures featuring cyclometalated iridium. In these compounds the isocyanide primarily serves as a spectator ligand with subtle influences on the photophysics, but it does present some synthetic advantages that allow facile construction of structures with multiple photoactive units. More specifically, we have found that treating Ir(C^Y)$_2$(CNAr)(Cl) with AgPF$_6$ in noncoordinating solvent generates an intermediate of the type Ir(C^Y)$_2$(CNAr)(FPF$_5$) (**6**), where the PF$_6^-$ anion is loosely coordinated to iridium.[34] In some cases this intermediate is stable enough to isolate and characterize crystallographically, but for reasons that remain unclear we have only succeeded in preparing this type of intermediate with isocyanide ancillary ligands, having failed to access phosphine-terminated analogues. Scheme 3 summarizes the reactivity of this synthon and how it has been used to prepare more complex structure types. The first reactivity we studied with this complex is transmetallation with B(C$_6$F$_5$)$_3$, preparing compounds of the type Ir(C^Y)$_2$(CNAr)(C$_6$F$_5$) (**7**) which are moderately phosphorescent.[34]

The Ir(C^Y)$_2$(CNAr)(FPF$_5$) synthon has proven to be a versatile precursor for the synthesis of larger structures with multiple photoactive building blocks. The labile PF$_6^-$ ion is readily displaced by other coordinating units, and in our earliest work on these compounds we have used pyridine-substituted chromophores to assemble complex structures, also summarized in Scheme 3. Our first demonstration of this approach used a pyridine-substituted platinum acetylide building block, allowing the assembly of bent trimetallic Ir-Pt-Ir structures (**8**).[35] Photophysical studies on these compounds showed efficient bidirectional energy transfer between the platinum and iridium chromophores, with the direction of energy transfer dependent on the relative excited-state energies of the two building blocks, controlled by the choice of C^Y ligand on iridium. A related structure type with a fluorescent BODIPY bridging unit between two bis-cyclometalated iridium complexes (**9**) has also been prepared.[36] In this case the photoluminescence is dominated by the bridging ligand, with strong BODIPY-centered fluorescence observed when the BODIPY is excited. Excitation of the iridium sites presumably populates the iridium-centered T$_1$ state, which funnels through a nonradiative pathway that we propose involves the dark BODIPY T$_1$ state. The simpler 1:1 Ir-BODIPY dyads (**10**) shown in Scheme 3, linked through the BODIPY meso position, exhibit dual luminescence with simultaneous BODIPY fluorescence and [Ir(C^Y)$_2$]$^+$ phosphorescence observed.[37] The phosphorescence is particularly pronounced when C^Y = 1-phenylisoquinoline (piq), which places the phosphorescence further into the red region compared to the green BODIPY fluorescence. These compounds function as effective ratiometric sensors for O_2, sensitive to oxygen partial pressure that span ca. 0–140 mmHg.

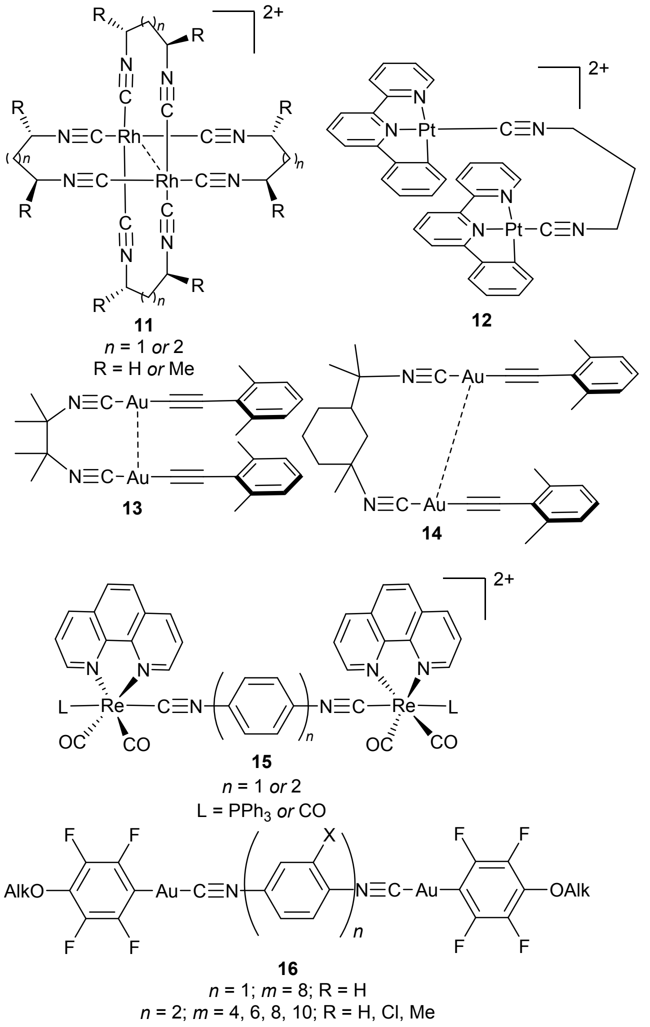


Fig. 6. Structures of dinuclear isocyanide-bridged luminescent complexes.

Isocyanides as Bridging Ligands for Polynuclear Luminescent Complexes

In the preceding section, all the compounds featured terminal, monodentate isocyanide ligands. Although not nearly as prevalent as polypyridyl-derived bridging ligands,[38,39] there are some recent developments in using directionally oriented polyisocyanide (usually diisocyanide) bridging ligands to assemble multimetallic structures, some of which have intriguing photophysical properties. This section will describe some of these developments, with a focus on the advances that have come from our own group.

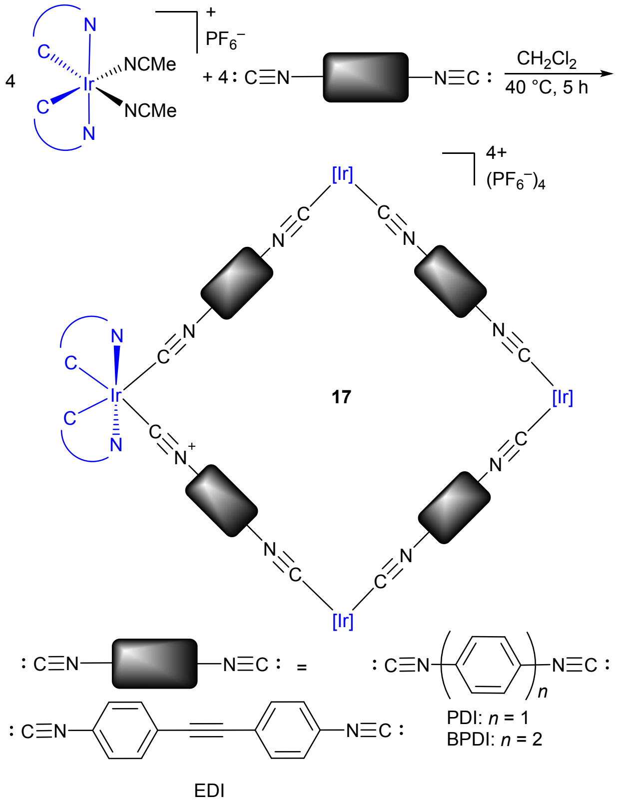
Isocyanide-Bridged Dinuclear Complexes

Prior to our work in this area, there were a few scattered examples in the literature of luminescent dinuclear structures bridged by isocyanides, summarized in Fig. 6. Many of these used bent, alkyl-spaced diisocyanides to assemble dinuclear complexes. Some of the earliest and best-known examples, introduced and extensively studied by Harry Gray and co-workers, are paddlewheel complexes of the type $[Rh_2L_4]^{2+}$ (**11**), where "L" is an alkyl-spaced diisocyanide bridging ligand.[40–42] In these complexes the isocyanides serve as supporting ligands but are not intimately involved in the photophysics. The close metal-metal interaction between the two rhodium centers enables low-energy absorption and photoluminescence from a *d*σ*→pσ excited state. Using the same type of bridging ligand, a luminescent diplatinum complex (**12**) has been obtained.[43] The complex exists in two conformations with differential Pt···Pt interactions, which effects the photophysics of the complex. The emission of the complex is still largely dominated by the C^N^C pincer ligands, however the lifetime and quantum yields of the diplatinum complexes ($\Phi_{PL} = 5 \times 10^{-3}$, $\tau = 3.27$ μs, respectively) are markedly increased relative to mononuclear counterparts. At 77 K the complex exhibits a low energy emission at 744 nm that arises from a stacking of the metals, leading to a metal-metal ligand charge transfer state (^{3}MMLCT). Related bent diisocyanides have also been used to span gold(I) acetylide complexes (**13** and **14**).[44] As is typical for Au(I), supported aurophilic interactions are observed. These complexes are weakly luminescent in the blue region from primarily acetylide-centered ^{3}LC states.

More relevant to our own work, linear aromatic diisocyanide bridging ligands have been also used to assemble dinuclear complexes. Phenylene (PDI) and biphenylene (BPDI) diisocyanides can support dincuclear rhenium phenanthroline complexes.[45] Phosphorescence arises from the expected dπ(Re)→π*(phen) ^{3}MLCT state, and there are no major effects of dinuclear organization on the emission when compared to mononuclear analogues. The broad featureless emission profiles in **15** have λ_{max} at 564 and 566 nm with Φ_{PL} of 0.17 and 0.13, for the PDI and BPDI spaced complexes, respectively. PDI, BPDI, and substituted analogues have been used as bridging ligands in bimetallic Au(I) aryl complexes (**16**).[46] In these complexes the emission arises from a triplet state centered on the biphenylene core, meaning the isocyanide is intimately involved in the photophysics, a phenomenon that will be described in more detail in the following section.

Self-Assembled Isocyanide-Bridged Metallacycles

Our group has used linear aromatic diisocyanides as bridging ligands for the [4 + 4] coordination-driven self-assembly of M_4L_4 squares, with bis-cyclometalated iridium units as the corner nodes.[47] Unlike the above examples (**15** and **16**) where the linear diisocyanides are terminated by two metal centers, in our work we achieved the synthesis of closed metallacycle structures. There are only a few previous examples of self-assembled cyclometalated iridium metallacyles, which used cyanide,[48] 1,3,5-tricyanobenzene,[49] or pyridine-terminated cyclotriguaiacylene[50] bridging ligands. Scheme 4 depicts the general synthetic strategy for the preparation of the cyclometalated iridium squares (**17**) with variable C^Y ligands and bridging ligand lengths. The strongly-coordinating



Scheme 4. Synthesis of M_4L_4 cyclometalated iridium squares.

diisocyanide bridging ligands allow assembly under mild conditions, and mass spectrometry confirms that the M_4L_4 products are formed. For the complexes with C^Y = bt and piq, the photoluminescence strongly resembles related mononuclear $[Ir(C^{\wedge}Y)_2(CNAr)_2]^+$ complexes, e.g. **1a** in Fig. 4, indicating that the excited state is the typical ^{3}LC/^{3}MLCT state localized on the cyclometalated iridium nodes. However, in complexes with C^Y = 2-phenylpyridine (ppy), the phosphorescence is dependent on the bridging ligand, as will be discussed further in the proceeding section.

Isocyanides as Chromophoric Ligands

In the examples described above the aryl isocyanide ligand(s) played important structural roles, and their π-accepting nature perturbed the metal dπ orbitals that are involved in the MLCT excited states. However, the π* LUMO was always localized on a different ligand, the C^Y ligand in the many examples of cyclometalated iridium complexes given above, and the T_1 state only involved the π system of the C^Y ligands, not the isocyanide. In contrast, the examples described in this section all luminesce from excited states directly involving orbitals from the isocyanide ligands.

Isocyanide MLCT States

The best-known examples of complexes with MLCT excited states, where the "L" in the excited state is an isocyanide, are group 6, M(0) homoleptic isocyanide complexes. Two major structural classes have been studied, and both are summarized in Fig. 7. The first of these classes (**18**) is made up of monodentate isocyanide ligands; Harry Gray and co-workers have long studied homoleptic $M(CNAr)_6$ complexes, where M is Cr, Mo, or W. In some of the earliest work on these compounds, using CNPh or CNAr^{dipp} (see Scheme 1) as the isocyanide, photoluminescence from the Mo and W analogues was observed, and it was attributed to a ^{3}MLCT state.[51] Much more recent studies on the tungsten series, which include analogues with more extended oligoaryl isocyanides, revealed strategies for increasing the ^{3}MLCT PL lifetime and quantum yield, and showed that these compounds are powerful visible-light photoreductants.[52,53]

The second class (**19**–**21**) contains polydentate isocyanide ligands wherein Wenger and co-workers popularized related designs featuring terphenyl-derived chelating isocyanides. These ligands have enabled the design of a few examples of luminescent first-row transition metal complexes which are highlighted here. A more comprehensive review on luminescent first-row transition metals supported by several different ligand

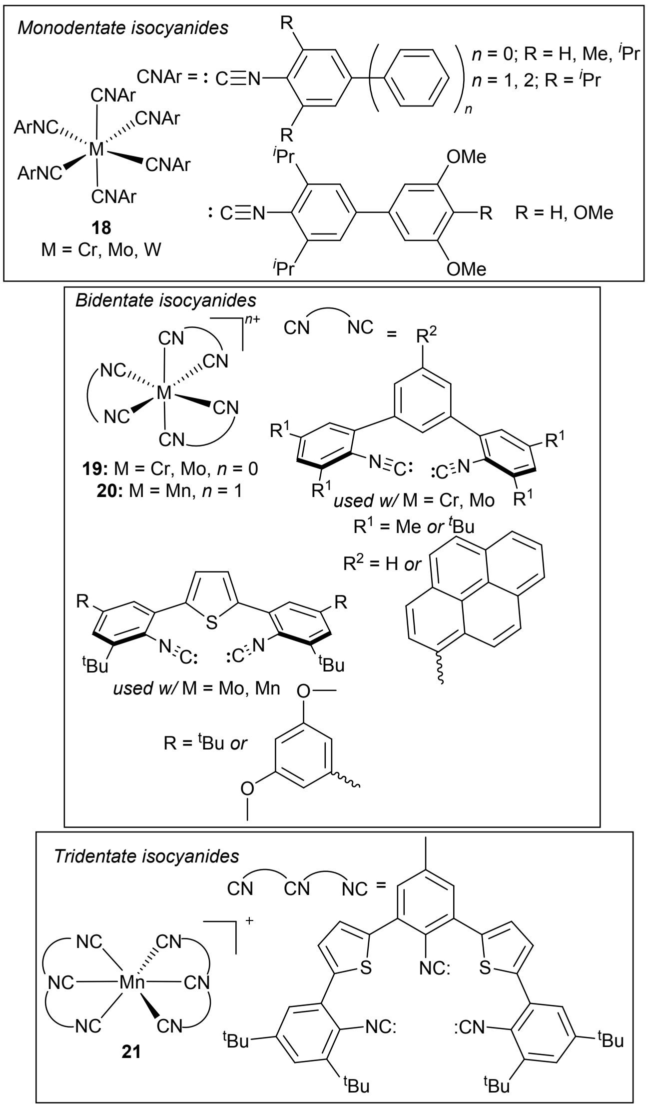


Fig. 7. Structures of homoleptic group 6 isocyanide complexes with ^{3}MLCT phosphorescence.

classes was published very recently.[54] The chelating isocyanides are most commonly used with group 6 metals, with the chromium analogues of these compounds presenting rare examples of MLCT photoluminescence from a $3d^6$ metal complex.[55,56] The molybdenum analogues are likewise powerful photoreductants with emerging applications in photoredox catalysis.[56–58] In their most recent work on this class of complexes they also showed that extending the π-conjugation of the isocyanide, in this case via appending a pyrene unit to the terphenyl backbone, can also lead to more efficient photoluminescence from the chromium analogues.[59] In these homoleptic complexes, the only ligand-centered orbitals that can participate are from the isocyanides. Excitation involves ligand-localized (^{1}LC) and ^{1}MLCT states of the isocyanides, the latter being lower in energy. The T_1 state, populated following intersystem crossing and internal conversion, is the ^{3}MLCT state involving the isocyanides. Additionally, Wenger and co-workers synthesized a related molybdenum complex containing a bidentate chelating diisocyanide ligand with a thiophene backbone.[60] Replacing the phenyl spacer in the previous complexes with a thiophene and adding two 3,5-dimethoxyphenyl substituents to the ligand further extends the π-conjugation of the complex and shifts the MLCT absorption and emission further into the red, with the emission occurring at 720 nm. This group also extended the set of $3d^6$ metals to include two Mn(I) complexes, incorporating the theme of bi- and tridentate arylisocyanide thiophene backbone ligands.[61] These complexes, labelled **20** and **21** in Fig. 7, display an emissive MLCT state at room temperature, with triplet energy transfer arising from a $^3\pi$–π^* state centered on the isocyanide ligands.

Isocyanide-Localized Triplet States

There are other compounds where the isocyanide features prominently in the photophysics, with a subtle but important distinction from the MLCT compounds described above. In contrast to the compounds described in the previous section, these compounds pair chromophoric isocyanide ligands with one or more other chromophoric chelating ligands, normally a cyclometalating ligand (C^Y) in the examples described here. In these cases, the low-energy UV-vis absorption bands typically are ^{1}LC and ^{1}MLCT bands associated with the cyclometalating ligands, with the ^{1}LC ($\pi \rightarrow \pi^*$) bands of the isocyanide occurring at higher energy. However, in the triplet manifold the lowest-energy triplet state is the ^{3}LC state of the isocyanide. Thus, the accessible ^{3}MLCT and ^{3}LC states involving the C^Y ligand may be initially populated following intersystem crossing, but intramolecular triplet-triplet energy transfer (TTET) populates the ^{3}LC state of the isocyanide. The photoluminescence in such compounds is characteristic of phosphorescence from an aromatic π-conjugated triplet state – well-resolved vibronic structure, long (> μs) lifetimes, and a progressive red-shift in $E_{0\text{–}0}$ as the conjugation is increased.

A few examples of mononuclear and polynuclear compounds described in previous sections of this review exhibit photoluminescence from an isocyanide-centered triplet state. The bridging diisocyanide in gold complexes **16** is intimately involved in the low-energy triplet state.[46] In our own work, the complex [Ir(F$_2$ppy)$_2$(CNAr^{nap})$_2$]$^+$ (see Scheme 1) phosphoresces from a naphthyl-centered triplet state,[18] substantially red-shifted from the phosphorescence in analogous compounds with alkyl or substituted phenyl isocyanides.[10,13,18,19] One series of the M$_4$L$_4$ squares that we have prepared (**17** in Scheme 4) nicely demonstrate the concept of photoluminescence from a triplet state localized on a conjugated isocyanide.[47] Fig. 8 shows the spectra of the three M$_4$L$_4$ squares where C^Y = ppy, in comparison to the mononuclear analogue [Ir(ppy)$_2$(CNAr^{dmp})$_2$]$^+$ (**1d**).[18] The spectrum of **17a**, with the shortest bridging ligand PDI, is nearly identical to **1d** albeit with a much lower quantum yield, indicating phosphorescence from the [Ir(ppy)$_2$]$^+$ nodes but suggestive of a nearby nonradiative excited state. In **17b** and **17c** where the conjugation of the bridging ligand is progressively lengthened, progressive red-shifting of the $E_{0\text{–}0}$ band is observed, along with pronounced changes in the vibronic structure. Despite the quantum yields of **17b** and **17c** being quite low the lifetimes remain longer than 10 μs. All of these photoluminescence properties are hallmarks of aromatic ligand-centered triplet states, indicating that in these latter compounds the excited-state energy migrates from the [Ir(ppy)$_2$]$^+$ nodes to the conjugated bridging ligands.

Favale, Castellano and co-workers have also prepared a series of compounds using oligoaryl isocyanides like those used to support the homoleptic tungsten compounds in Fig. 7. Their studies included rhenium(I) tricarbonyl complexes with a single isocyanide ancillary ligand,[33] analogues of **5a** (see Fig. 5), and bis-cyclometalated iridium bis-isocyanide complexes,[62]

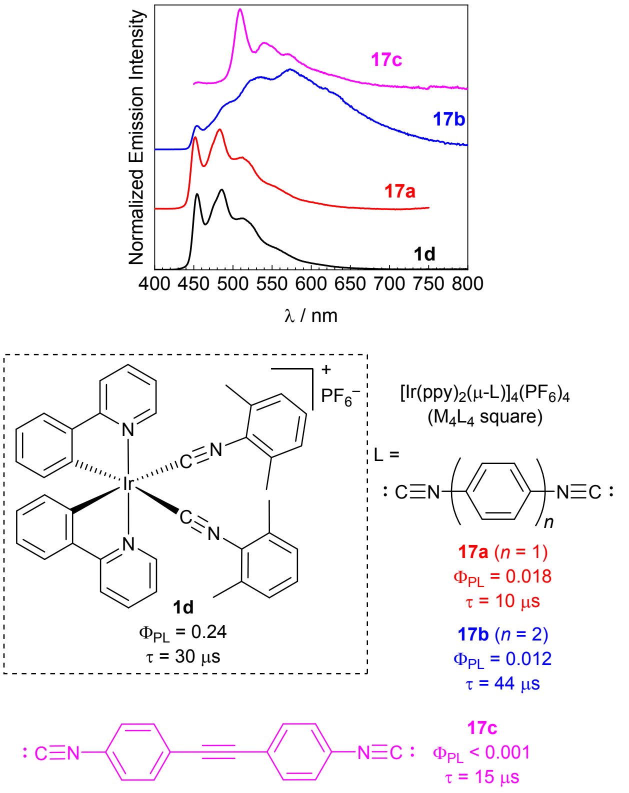
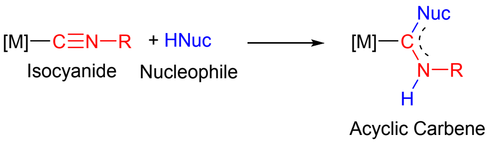


Fig. 8. PL data for a series of [Ir(ppy)$_2$(μ-L)]$_4$(PF$_6$)$_4$ squares as a function of the bridging isocyanide, in comparison to a mononuclear analogue.

analouges of **1** (Scheme 1). These structures are summarized in Fig. 9. In the complexes with CNAr^{dipp} (the iridium analogue is also shown in Scheme 1), phosphorescence originates from the phenanthroline ^{3}MLCT state (**5a**) or the C^Y ^{3}LC/^{3}MLCT state (**1**). Increasing π-conjugation stabilizes the isocyanide ligand-centered state (^{3}LC$_{CNAr}$), resulting in T_1 residing on the conjugated isocyanide instead of the other conjugated ligands.

Isocyanides as Precursors to Acyclic Carbenes

This section describes one final role of isocyanides in the design of photoluminescent organometallic complexes. Many organometallic phosphors, especially those that luminesce in the blue region, benefit from strong σ-donor ligand sets which can destabilize higher-lying metal-centered excited states and prevent nonradiative pathways involving these states.[63,64] Isocyanides are reasonably strong σ donors in their own right, but addition of nucleophiles to the electrophilic coordinated isocyanide (Scheme 5) can convert the isocyanide to an acyclic carbene, a stronger σ donor than both the precursor isocyanide and the ubiquitous *N*-heterocyclic carbenes (NHCs) that are commonly used as supporting ligands in phosphorescent metal complexes.[65–67]



Scheme 5. Nucleophilic addition to coordinated isocyanides to form acyclic carbenes.

Luminescent Acyclic Diaminocarbene (ADC) Iridium Complexes

Our group has introduced the concept that nucleophilic addition to isocyanide-bound precursors can furnish luminescent compounds supported by ADCs. The classes of compounds we have studied, along with some recent examples from other groups, are depicted in Fig. 10. Complexes **22**, supported by bis-ADC "Chugaev" ligands were prepared by nucleophilic addition of hydrazine to cationic bis-isocyanide precursors (**1**).[68] Complexes **22** can be protonated in a separate step with HBF_4, generating cationic analogues **23** which differ only with respect to the protonation state of the Chugaev carbene backbone. These compounds are moderately luminescent in solution[68] and strongly luminescent in (**23**) exhibiting a subtle luminescence blue shift relative to the transparent polymer films,[69] with the protonated analogues neutral versions (**22**). Using chloro-isocyanide precursors **2** (see Scheme 2), addition of amines furnishes cyclometalated ADC complexes **24**. The cyclometalated ADC forms via a cascade reaction involving nucleophilic addition followed by base-assisted cyclometallation. We have used this strategy to prepare sky-blue emitters with C^Y = F_2ppy, with Φ_{PL} as high as 0.79 in polymer film,[70] and deep-blue emitters supported by NHC-derived C^Y ligands.[71] The reactions used to prepare **22** and **24** require electron-withdrawing groups on the isocyanide

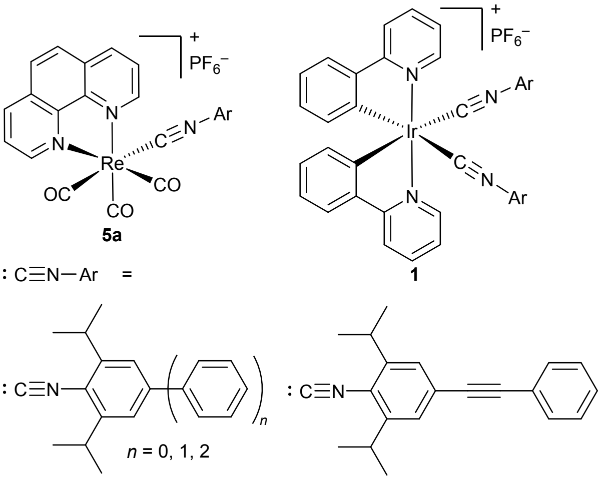


Fig. 9. Structures of Re and Ir complexes with oligoaryl isocyanides that exhibit triplet migration to the conjugated isocyanide.

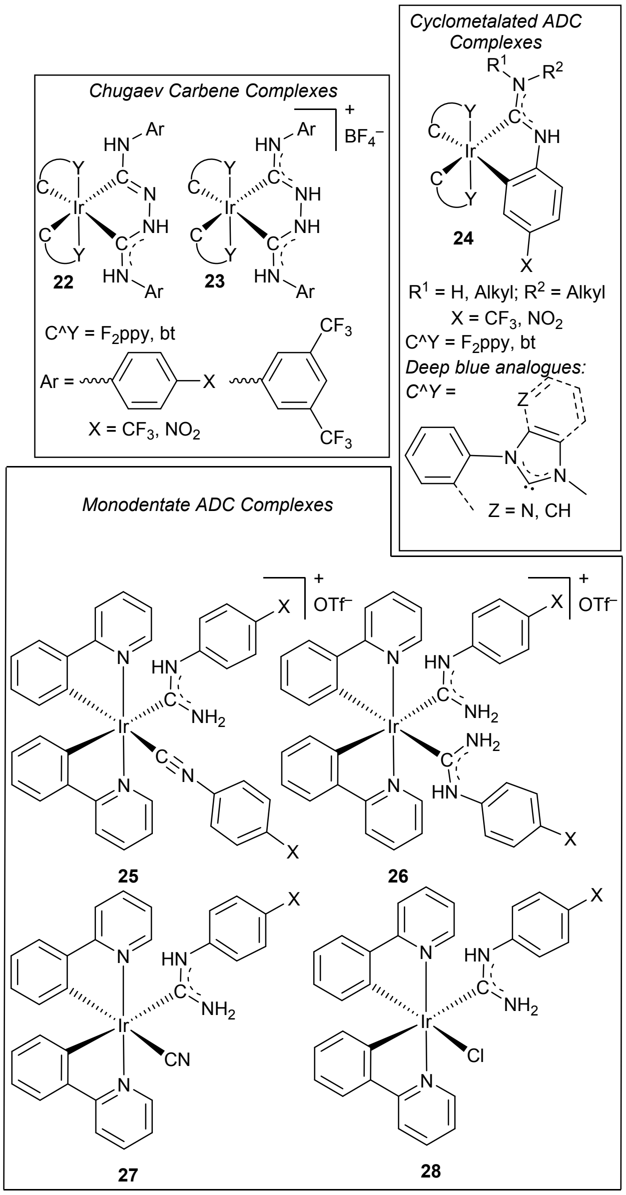


Fig. 10. Structures of cyclometalated iridium ADC complexes.

aryl ring; complexes supported by CNAr^{dmp} are not electrophilic enough to undergo nucleophilic addition. Luzyanin and co-workers have recently reported four related classes of ADC-supported cyclometalated iridium complexes accessed by addition of NH_3 to isocyanide precursors. Diffusion of ammonia into bis-isocyanide precursors results in sequential addition to each isocyanide, forming initially the asymmetric ADC-isocyanide complex **25**, which converts to symmetric bis-ADC complex **26**.[72] Prolonged exposure to NH_3 under forcing conditions cleaves one ADC to produce ADC-cyano complex **27**. Chloro-ADC complex **28** is prepared by ammonia addition to chloro-isocyanide precursor **2**; addition of CNAr and AgOTf to **28** provides an alternate route to complex **25**.[73] Complexes **25**–**28** are moderately to strongly luminescent in the sky blue to blue-green regions, and **27** has been applied as a luminescent sensor for Hg^{2+}.[73]

Luminescent Acyclic Diaminocarbene (ADC) Platinum Complexes

Our group has also expanded the chemistry of luminescent ADC complexes to platinum, and this set of compounds even more clearly demonstrates the role the ADC plays in the photoluminescence and excited-state dynamics. Fig. 11 shows the structures of the ADC-supported platinum acetylide compounds reported by our group.[74] The isocyanide precursors **29** were prepared first and observed to exist exclusively in the *cis* geometry. Addition of diethylamine to **29** furnishes ADC complexes **30**; despite using a large excess of amine and prolonged reaction times, only one of the two isocyanides was functionalized. Fig. 12 summarizes the photoluminescence data of **29** and **30**. The T_1 state in these compounds is a ^{3}LC state localized on the acetylide ligands, and as such nucleophilic addition to convert one isocyanide into an ADC minimally perturbs the PL wavelengths and vibronic structure. However, conversion of an isocyanide into an ADC results in sizeable increases in Φ_{PL}, as high as 16-fold for the *tert*-butyl analogue. The lifetimes of the ADC complexes are also longer, in part because of a large decrease in k_{nr}. This experimental data, in combination with DFT calculations on these compounds, is consistent with the notion that the strong σ-donor ADC ligand destabilizes the higher-lying ligand-field (^{3}MC) states, preventing population of these states which would lead to nonradiative decay. Again, the role of the isocyanides in these compounds was to provide an electrophilic precursor, enabling the installation of the strongly-donating ADC that enhances blue phosphorescence.

A few other examples of ADC-supported phosphorescent platinum complexes have also recently emerged from other groups and are also shown in Fig. 11. Il'in et al. reported a chelated ADC platinum complex **32**, accessed by insertion of cyclohexyl isocyanide into an aminonitrone precursor (**31**). The preparation of **32** involves addition of the isocyanide electrophile to the coordinated nucleophile, the opposite of the examples presented above where the nucleophile was added to the coordinated isocyanide. Complex **32** is phosphorescent in the red region (λ_{max} = 600 nm) with a quantum yield of 0.23 at room temperature. Cyclometalated platinum complexes with ADC ancillary ligands have also been prepared. Isocyanide complexes **33** had previously been investigated,[24] and the emission was studied in solution, polymer film, and in the solid

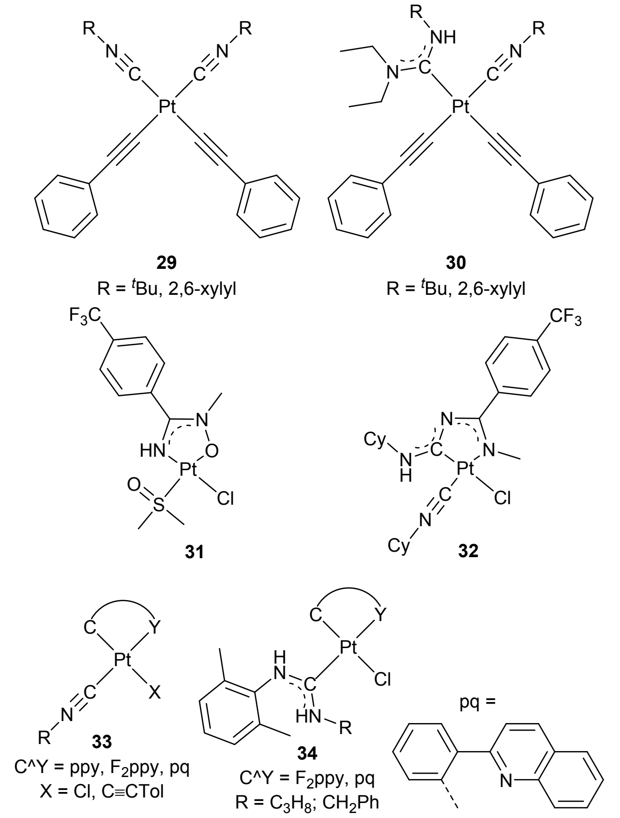


Fig. 11. Structures of luminescent platinum complexes supported by isocyanide and/or ADC ligands.

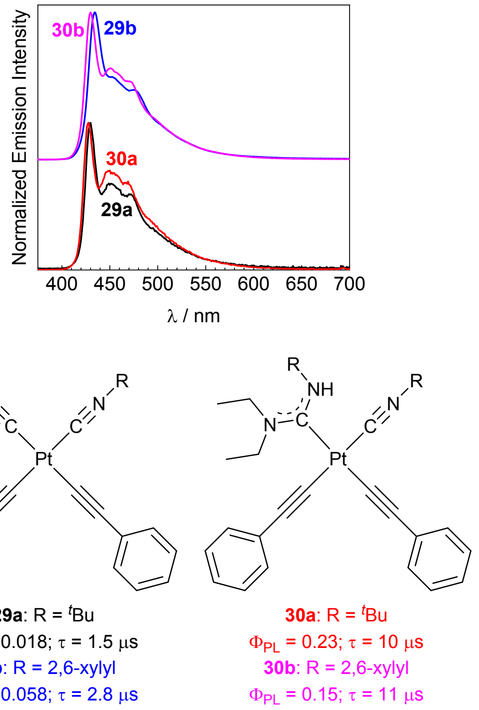


Fig. 12. Summary of photoluminescence data for isocyanide and ADC-supported platinum acetylide complexes, recorded at 2 wt% in PMMA film.

state. Addition of amine nucleophiles to **33** converts the coordinated isocyanide to an ADC, generating complexes **34**. These complexes are luminescent, with the emission color determined by the choice of cyclometalating ligand, blue-green for F_2ppy and orange for pq.

Conclusions

In this Perspective, we highlighted the many roles that isocyanides play in supporting photoluminescent organometallic compounds, focusing mostly on very recent developments. Isocyanides have been a reasonably prominent ligand in coordination chemistry, and their applications as supporting ligands for photoluminescent complexes has grown considerably in the past several years. There is a large diversity of structure types supported by isocyanides, which includes simple mononuclear structures and more complex structures with multiple combined building blocks. In many cases the isocyanide plays no direct role in the photophysics, although the strong σ-donating and π-accepting characteristics do have important consequences on the frontier orbital energies, which in turn exerts subtle effects on the emission spectra and excited-state dynamics. However, there are some examples of compounds where the isocyanide frontier orbitals are intimately involved in the low-energy excited states, which offers new avenues for controlling the photoluminescence and other excited-state pathways in these compounds. Finally, in the last section of the review we showed that nucleophilic addition to coordinated isocyanides, a long-established reaction in coordination chemistry, has recently been used to prepare new luminescent carbene-containing structures, where the acyclic carbene is often beneficial to the photoluminescence properties.

Conflicts of interest

There are no conflicts to declare.

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