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Application of 1,2,3-triazolylidenes as versatile NHC-type ligands: Synthesis, properties, and application in catalysis and beyond

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Triazolylidenes have rapidly emerged as a powerful subclass of N-heterocyclic carbene ligands for transition metals. They are readily available through regioselective [2+3] cycloaddition of alkynes and azides and subsequent metallation according to procedures established for related carbenes. Due to their mesoionic character, triazolylidenes are stronger donors than Arduengo-type imidazol-2-ylidenes.

10 Spurred by these attractive attributes and despite their only recent emergence, triazolylidenes have shown major implications in catalysis. This feature article summarises the synthetic accessibility of triazolylidene metal complexes and their electronic and structural characteristics, and it compiles their applications, in particular, as catalyst precursors for various bond forming and redox reactions, as well as first approaches into photophysical and biochemical domains.

Introduction

Carbenes have long been considered as fleeting intermediates, with reactivity properties that are hard to control. Successful strategies for taming this reactive species have concentrated on matrix isolation,[1] and on the electronic stabilisation of carbenes
20 through substituent control.[2] Expansion of this latter concept has furnished the first crystalline carbene through deprotonation of an imidazolium salt.[3] The resulting imidazol-2-ylidene is remarkably robust towards air, moisture, and thermal decomposition, in large part due to the extensive stabilisation by two adjacent nitrogen
25 substituents (**A**, Fig. 1). This discovery has induced an almost explosive investigation into the synthesis and application of these so-called Arduengo-type N-heterocyclic carbenes (NHCs) and variations thereof (**B–E**, Fig. 1), in particular as organocatalysts,[4] as stabilisers of highly reactive intermediates,[5] and as ligands for
30 transition metals.[6]
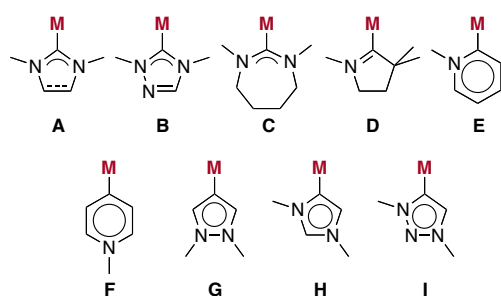
Fig. 1 Generic representation of *N*-heterocyclic carbene metal complexes featuring normal NHCs (**A–E**), remote NHCs (**F**, **G**), and abnormal/mesoionic NHCs (**H**, **I**).

35 The success of NHCs in organometallic chemistry has been attributed by and large to two key properties: *i)* the relatively high covalent contribution to the M–NHC bond, and *ii)* their strong donor ability. The latter aspect is obviously compromised to some extent by the inductive effect of the two nitrogen atoms adjacent
40 to the carbene.[7] Efforts have thus been directed towards the development of carbene systems which feature the stabilising heteroatoms in more remote positions in order to further increase the donor properties of NHCs, leading to so-called remote carbenes (rNHCs; no heteroatom adjacent to the carbene, *e.g.* **F**,
45 **G**),[8] and to abnormal/mesoionic carbenes (aNHCs, MICs; carbenes for which no uncharged resonance structure can be drawn, *e.g.* **H, I**).[9] The chemistry of these abnormal/mesoionic carbenes has predominantly focused on imidazol-4-ylidenes (**H**) and has led to new reactivity patterns.[10] A recent addition to this
50 subclass of NHC ligands are 1,2,3-triazolylidenes (**I**),[11] which result from formal substitution of the C(2)–R unit in imidazolylidenes by nitrogen. The triazolium precursors are readily available and convert smoothly to the abnormal/mesoionic carbene complexes upon metallation
55 procedures similar to those established for Arduengo-type NHCs. Due to the distinctly different properties of triazolylidenes, applications in catalysis and beyond have evolved very rapidly. Following an early review by Crowley *et al.*,[12] this feature article compiles the organometallic chemistry of triazolylidenes since
60 their first appearance in the literature in 2008, including synthetic strategies, donor properties, structural aspects, and reactivity patterns, as well as applications, especially in catalysis.

Synthesis of (functionalised) ligand precursors

In all but two cases the precursor to the triazolylidene complexes
65 is the triazolium salt. These exceptions include the synthesis from an ammonia adduct and post-modification of a metal-bound triazolyl ligand. The latter will be discussed in the next section, as the direct precursor to the ligand is a metal complex.

Synthesis of 1,3,4-substituted 1,2,3- triazolium salts

The most widely used method for triazolium salt synthesis has been to initially form the triazole via the readily accessible copper(I) catalysed 'click' cycloaddition of an alkyne and azide (CuAAC).[13] The CuAAC processs is chemoselective and has been shown to proceed in good to excellent yields.[14–16] The issue of handling highly unstable aryl and alkyl azides has been circumvented in many cases by forming the azide *in situ* and reacting it without isolation. One-pot syntheses of triazoles from an aniline starting material have been reported,[17,18] along with syntheses utilizing alkyl azide where these azides are not isolated prior to the CuAAC process.[11,19–24] Subsequent alkylation of the triazole with a suitable alkylating agent is generally selective and yields the 1,3,4-substituted triazolium salt (Scheme 1).
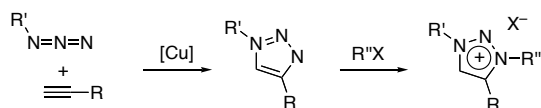
Scheme 1 Triazolium synthesis via [2+3] cycloaddition.

Although triazolylidenes are a new class of NHC ligands, the variety of ligands that have been synthesised via the CuACC reaction is substantial. Thus far, dicarbene ligand systems and other potentially multidentate ligands bearing phosphine,[24] alcohol,[25] amine,[21,25–28] thioether[29] and chiral substituents[30] have been reported (**1–12**, Fig. 2), demonstrating the broad scope of the CuAAC process. Selective alkylation of the triazole nitrogen can be an issue when intrinsically nucleophilic donor groups are also present in the triazole species. In order to avoid such selectivity issues, protecting groups have been used where possible. For example, the pyrrolidine in **4**, and the amine in **5**, have been BOC-protected prior to alkylation, similarly, the TBDMS group has been used to protect the alcohol substituent in **6**.[25,30] To obtain the mono-methylated triazolium salt, **8**, a preparative TLC after alkylation is necessary due to unselective methylation of the triazole and pyridine heterocycle.[21] The pincer ligand, **12**, is metallated prior to alkylation, thus illustrating another approach to avoid selectivity issues.[24]

The CuAAC sequence is not suitable if alkylation at N3 is not desirable, and functionalisation of the 1,4-triazole is not trivial. Bertrand and co-workers have discovered that free triazolylidenes bearing alkyl groups at the N3 position undergo decomposition by N3-alkyl bond cleavage.[17]Arylation of N3 increases stability, but triazole arylation cannot be carried out via a similar route as triazole alkylation. Therefore, formation of N3-arylated triazolium salts has been accomplished by cycloadditon of 1,3-
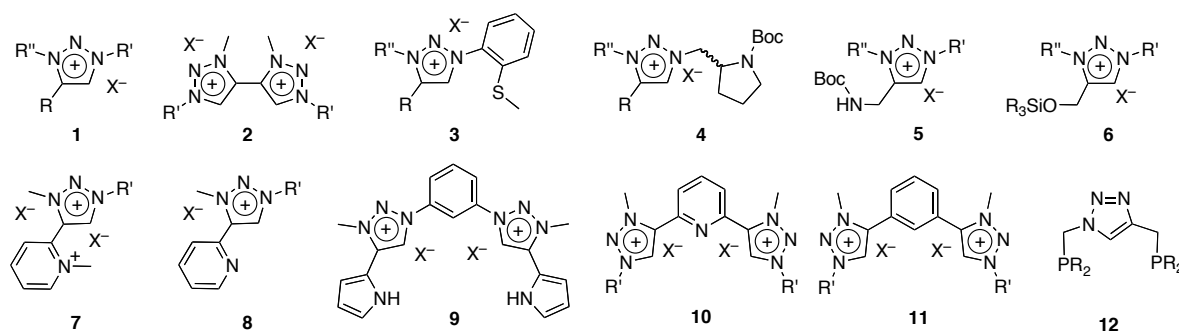
diaryl-2-azoniaallene salts and alkynes (Scheme 2).[31] Suitable triazenes are added to an alkyne (A) or synthetic alkyne equivalent (B) in the presence of *tert*-butyl hypochlorite and KPF$_6$. The hypochlorite is required to oxidise the triazene, and the potassium salt provides a suitable counterion. The salts formed by this process have been used as precursors to the free triazolylidene.
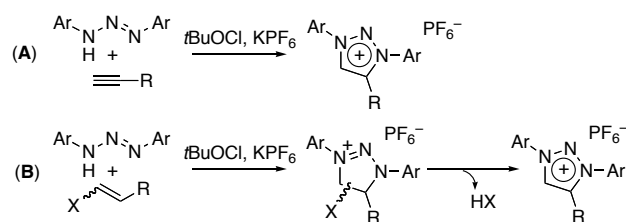
Scheme 2 Synthesis of aryl-substituted triazolium salts.

Synthesis of 1,2,4-substituted 1,2,3-triazolylidene precursors

The synthesis of precursors to 'normal' 1,2,3-triazolylidenes has been reported by Kühn and co-workers.[32] The CuAAC method would not be an effective means of ligand synthesis, since alkylation of a 1,4-substituted triazole generally occurs regioselectively and would not yield the desired substitution pattern. The 1,2,4-functionalised 1,2,3-triazolium salt **13** is prepared via the cycloaddtion of diarylnitrilimine in the presence of a base (Scheme 3).[32a] Upon addition of NaH to a solution of the salt in THF/NH$_3$, *i.e.* conditions that generate the free imidazolylidene from imidazolium salts,[32b] the 1,2,4-triazolium salt converts to the ammonia adduct. It has been suggested that the reaction proceeds via the free 1,2,3-triazolylidene species, which then reacts with ammonia, yielding **14**. In support of this mechanism pathway the computed energy barrier for the deprotonation of the salt is 7 kcal mol^{-1} lower than that for the amide addition. The formation ammonia adduct of 1,2,3-triazolylidene is unique thus far.
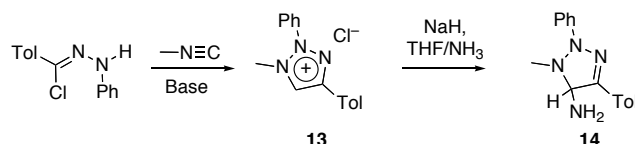
Scheme 3 Synthesis of 1,2,4-substituted triazolylidene precursors.

Despite the large scope of the CuAAC reaction, the vast majority of the ligands reported to date are monodentate and bear alkyl or aryl wingtip groups. Whilst some work has been carried out in increasing the functionality of the ligands, this area is still

Fig. 2 Triazolylidene precursors with different degrees of functionality.
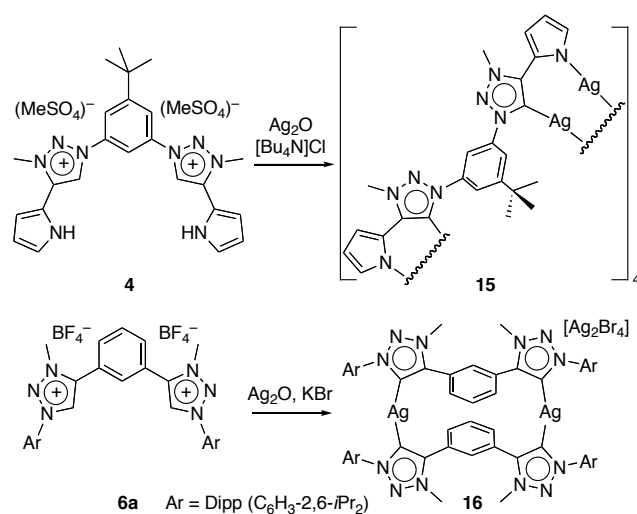
underdeveloped and will likely advance rapidly in the near future, especially when considering the huge variety of triazoles available via the copper(I)-catalysed cycloaddition.[13] Further opportunities may arise from ruthenium-catalysed azide-alkyne
5 cycloaddition yielding 1,5-triazoles,[33] which may give access to novel functionalisation patterns.

Synthetic Strategies towards Metal Triazolylidene Complexes

Transmetallation from Silver

10 Up to this point the most widely used and well-established method for the synthesis of triazolylidene metal complexes is to transmetallate from the silver triazolylidene complex. The silver carbene is prepared by the direct metallation of the triazolium salt with Ag$_2$O. Most attempts to isolate and purify the complexes
15 have been thwarted by the instability of the silver NHC complexes. Only two silver triazolylidene complexes have been isolated and X-ray structures of the complexes have been obtained (Scheme 4).[28,34] The successful isolation of these complexes are most likely aided by the steric effects of the more
20 bulky ditriazolylidene ligands. In one complex, derived from the pyrrol-functionalised ditriazolium salt, **15** (Scheme 4), each silver cation is bound to one triazolylidene and one deprotonated pyrrolyl ligand in a trans configuration.[28] Due to the four bonding sites of each ligand precursor, a macrocyclic structure is obtained,
25 comprised of four ligands, eight Ag(I) centres, and, various weak interactions, including Ag-Ag contact pairs. In contrast to this formally neutral complex, the silver carbene, **16**, is cationic and features two [Ag(trz)$_2$] moieties.[34] This complex is derived from a related ditriazolium salt that lacks stabilising pyrrol substituents,
30 suggesting that donor substituents may play an important role.

In most cases the formation of the silver carbene is surmised, using NMR spectroscopy, by the disappearance of the low field

35 H5 signal and by the downfield shift of the C5 resonance in the ^{13}C NMR spectrum. The silver carbene is treated *in situ* with an appropriate metal precursor to induce carbene transfer. Successfully used metal precursors include dimeric species that can undergo bridge-cleavage, e.g. [Rh(cod)Cl]$_2$, [IrCl$_2$(Cp*)]$_2$, or
40 [RuCl$_2$(cym)]$_2$, [PdCl$_2$]$_n$, or metal species bearing labile ligands. Halide ligands tend to be labile enough, due to the formation of the thermodynamically stable AgX (where X = halide) as a side-product e.g. [PdCl$_2$(MeCN)$_2$], [PtCl$_2$(cod)], or [CuCl]. In a number of cases an extraneous ion source is utilised to induce the
45 formation of metal complexes bearing only one type of anion.

The choice of metal precursor and metallation procedure has shown to be of utmost importance in determining the selectivity of product formation. For example, transpalladation of the silver carbene **17** with a dimeric palladium chloride source, such as
50 [Pd(allyl)Cl]$_2$ or [PdCl$_2$]$_n$, in the presence of another coordinating ligand affords the monocarbene triazolylidene complexes, **18** and **19** (Scheme 5).[22,35] Addition of Pd(OAc)$_2$ to the silver carbene complex selectively affords the dimeric palladium species, **20**.[36] It is notable that cyclopalladation of the ligand occurs in this case.
55 In contrast, [Pd(RCN)$_2$Cl$_2$] favours the formation of the biscarbene species, *trans*–**21** and *cis*–**21** (Scheme 5), with the *trans* isomer as the major species.[19,36,37] Both forms exist as syn and anti conformers.[36] However, performing the carbene transfer in the presence of NaI selectively yields the dimeric palladium
60 species, **22**, with bridging iodide groups.[19]

**Scheme 4** Octa- and dinuclear silver triazolylidene complexes.
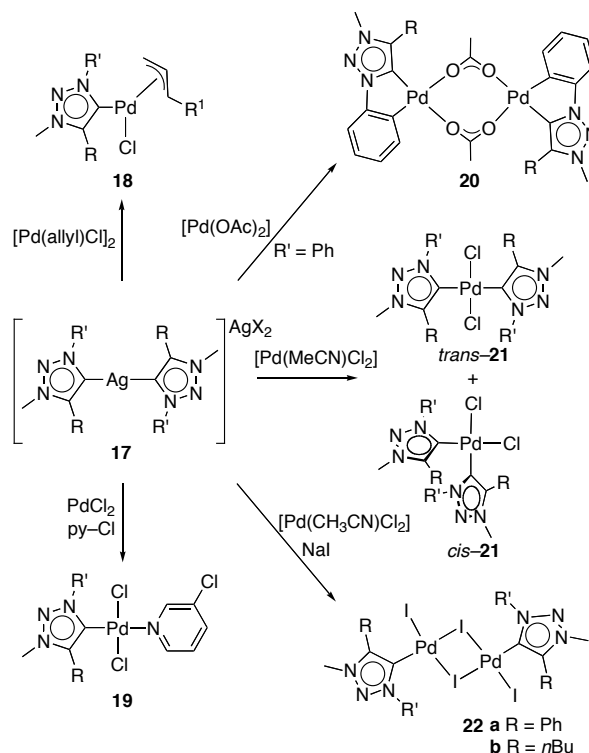
Scheme 5 Diversity in transpalladation of silver triazolylidene complexes.

Direct Metallation

Direct C-H bond activation of triazolium salts is poorly investigated. However, thermally induced direct metallation with Pd(OAc)₂ has been demonstrated.[19] A mixture of products is obtained comprising mono- and dicarbene products **22** and **21**, respectively (*cf* Scheme 5), the latter as *cis/trans* and *syn/anti* isomers. The process is much less selective than the transmetallation method.

Coordination to the Free Carbene

Bertrand and co-workers have synthesised the free 1,2,3-triazolylidenes, **23**, by deprotonation of triazolium salts using KN(SiMe₃)₂ or KO*t*Bu as a strong non-nucleophilic base (Scheme 6).[17,18] The N3-arylated carbene species, **23c-k**, are formed by deprotonation using KO*t*Bu (pKₐ = 22), whereas **23a** and **b** are obtained only with the stronger base KN(SiMe₃)₂ (pKₐ = 26). An attempt to use the weaker base to deprotonate the di-alkylated triazolium salt, **26**, does not yield the desired free carbene, instead the de-benzylated triazole is observed (Scheme 7). In full agreement, recent work has revealed a pKa ~24 for N3-alkylated triazolium salts, which is 1-3 units higher that the C2-imidazolium salts.[38,39] The N3-arylated triazolylidenes display higher stability than their N3-alkylated counterparts and can be metallated to ruthenium and iridium via ligand substitution to
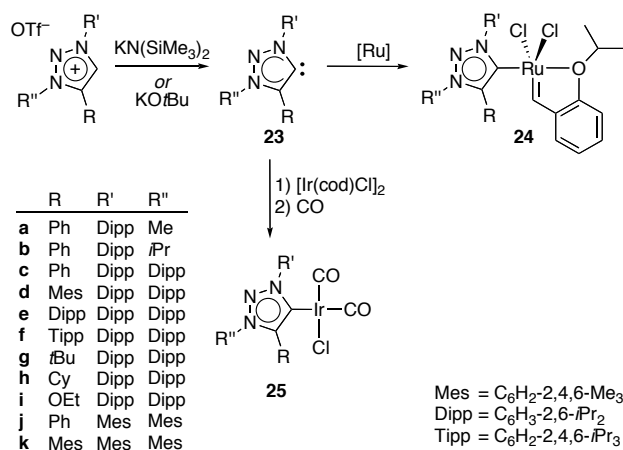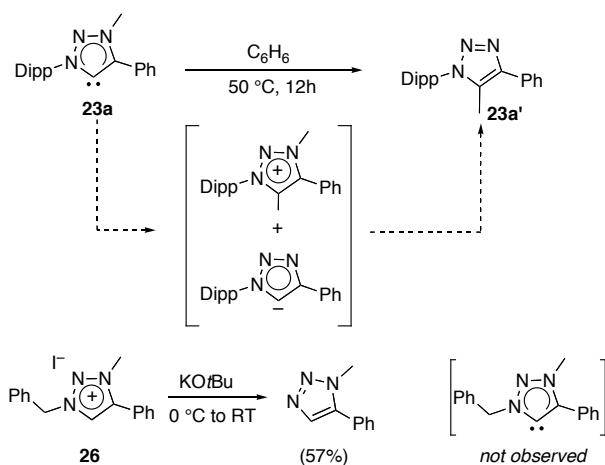
afford complexes **24** and **25**, respectively. The N3-methylated free triazolylidene, **23a**, undergoes decomposition at 50 °C to give **23a'** (Scheme 6). When an isopropyl substituent is present at N3, as for **23b**, the rearrangement process and decomposition pathway does not occur, therefore suggesting that the less electrophilic isopropyl group may increase stability of the free triazolylidene. However, attempted ruthenation of **23b** by ligand substitution does not yield the desired complex. It is apparent that the presence of aryl substituents on N1 and N3 enhances the stability of the free triazolylidenes, which will have implications if free 1,2,3-triazolylidenes are employed as organocatalysts.

Base-Mediated proton abstraction/C-H activation

In some cases metallation has been accomplished in the presence of KO*t*Bu (Scheme 8).[29,40] Sarkar *et al* have utilised this method in the formation of triazolylidene copper(I) complexes **27**,[29] and Bertrand and co-workers have reported a base-mediated metallation of a ditriazolium salt to yield the cationic ditriazolylidene rhodium complex **28**.[40] This reactivity is distinctly different from related 1,2,4-ditriazolylidenes, which do not form related chelating rhodium(I) complexes.[41]

The mechanism of these base-mediated metallations cannot be clearly determined. It is not possible to safely distinguish between a C-H activation by an *in situ*-generated M(O*t*Bu) intermediate, similar to [Pd(OAc)₂] induced metallation, or, a metallation via generation of the free triazolylidene as a transient intermediate from deprotonation by KO*t*Bu. Previous work has however indicated that KO*t*Bu is not strong enough to deprotonate the N3-alkylated triazolium salts prior to metallation, and KN(SiMe₃)₂ is required to form the free dicarbene **29** (Scheme 8).

Scheme 6 Preparation of a series of free triazolylidenes and coordination to ruthenium(II) and iridium(I).

	R	R'	R''
a	Ph	Dipp	Me
b	Ph	Dipp	*i*Pr
c	Ph	Dipp	Dipp
d	Mes	Dipp	Dipp
e	Dipp	Dipp	Dipp
f	Tipp	Dipp	Dipp
g	*t*Bu	Dipp	Dipp
h	Cy	Dipp	Dipp
i	OEt	Dipp	Dipp
j	Ph	Mes	Mes
k	Mes	Mes	Mes

Mes = C₆H₂-2,4,6-Me₃
Dipp = C₆H₃-2,6-*i*Pr₂
Tipp = C₆H₂-2,4,6-*i*Pr₃

Scheme 7 *N*-dealkylation of triazolium salts with strong bases.


Scheme 8 Rh and Cu triazolylidene preparation in the presence of a base.

Other Methods

The ammonia adduct of the 1,2,4-substituted triazolylidene, **14**, undergoes metallation reactions with Ir(I), Rh(I), Cu(I) and Au(I), resulting in normal 1,2,3-triazolylidene complexes **30** (Scheme 9).[32] The ammonia adduct is susceptible to retro-cycloaddition processes at elevated temperatures. Hence the metallation reactions must be carried out at low temperatures to obtain maximum yields.

Gandelman and co-workers have demonstrated that platinum and palladium complexes bearing cyclometallated triazolyl ligands can be modified after metallation to yield analogous triazolylidene complexes.[24] Alkylation of the neutral complexes **31**, obtained by cyclometallation of the triazole precursor **12**,
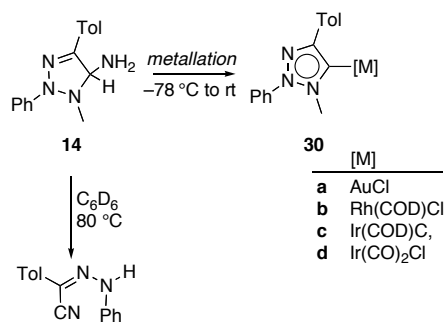
Scheme 9 Triazolylidene complexes from metal-induced ammonia elimination

M	X	X	R''
a	Pd	I	I	Me
b	Pt	Cl	Br	CH$_2$C$_6$H$_4$-4-CF$_3$
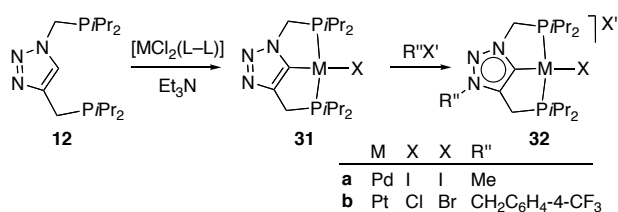
Scheme 10 Triazolylidene metal complexes from alkylation of triazolyl precursors.

affords the triazolyldidene metal complexes **32** (Scheme 10). A similar post-modification procedure allows for the formation of a rhenium triazolylidene complex.[42]

Donor Properties of 1,2,3-Triazolylidenes

By far the most widely used method to evaluate donor properties has been to measure the CO stretching frequencies of carbonyl metal complexes by IR spectroscopy. The CO stretch vibrations of iridium complexes of the form [(NHC)Ir(CO)$_2$Cl] provide a direct probe for the donor properties of the ligand, as a linear correlation between the average CO stretch frequency, ν_{av}(CO) and the Tolman electronic parameter (TEP) has been established by Crabtree and co-workers.[43] The 1,2,3-triazolylidene iridium complexes, **25a-f** exhibit ν_{av}(CO) stretch frequencies between 2018 cm^{-1} and 2021 cm^{-1} (Table 1), just slightly higher than the normal triazolylidene complex **30d** (ν_{av}(CO) = 2017 cm^{-1}), thus suggesting that the normal/abnormal nomenclature overemphasises the difference in this case. According to the measured data, the donor ability of 1,2,3-triazolylidenes is stronger than the most donating normal 2-imidazolylidenes, **33**, yet weaker than abnormal 4-imidazolylidenes, **34**. The presence of three nitrogens in 1,2,3-triazolylidenes reduces the electron density of the ligand and may thus explain their lower donor ability relative to 4-imidazolylidenes.

In line with these conclusions, the bidentate chelating ligand **29** (*cf* Scheme 8) is a stronger donor to a Rh(CO)$_2$ fragment than the 1,2,4-ditriazolylidene analogue and also than basic diphosphine ligands such as bis(diclohexylphosphinoethane).[44]

Various studies have shown that the CO stretching energies are not unambiguous probes for characterising ligand donor properties. For example, stereoelectronic effects can affect one or both CO ligands and thus impact the stretching frequencies without modifying the actual donor properties of the carbene ligand.[47] In triazolylidene chemistry, the donor ability has been confirmed by various orthogonal techniques.

Table 1 IR stretch vibrations and Tolman Electronic Parameter (TEP) for a series of carbene iridium complexes

Complex	R	R'	R''	R'''	ν_{av}(CO) cm^{-1}	TEP ^{a} cm^{-1}	Ref
25a	Dipp	Dipp	Me	---	2019	2046	35
25b	Mes	Mes	Me	---	2019	2046	35
25c	Et	Ph	Me	---	2021	2047	11
25d	Ph	Dipp	Me	---	2019	2046	17
25e	OEt	Dipp	Dipp	---	2018	2045	18
25f	Dipp	Dipp	Dipp	---	2020	2046	18
30d	Tol	Me	---	Ph	2017	2044	32
33a	Dipp	Dipp	H	H	2024	2050	35
33b	Mes	Mes	H	H	2023	2049	35
33c	Cy	Cy	H	H	2023	2049	45
33d	Ad	Ad	H	H	2021	2048	45
34	*i*Pr	Me	Ph	Ph	2003	2033	46

^{a} TEP calculated according to ref 45, TEP = 0.847[ν_{av}(CO)] + 336 cm^{-1}.

Fukuzawa and co-workers have evaluated the ligand properties in the carbene palladium complex **35** by X-ray photoelectron spectroscopy (XPS; Fig. 3).[35] The electron binding energy of the 3d electrons is 335.7 eV and hence 0.5 eV lower than in the analogue featuring an isostructural 2-imidazolylidene. These results reveal a higher electron density on the metal centre bearing a 1,2,3-triazolylidene than for a metal bearing a normal imidazolylidene, further corroborating the TEP analyses (*cf* **25a** vs **33a**) for these ligands.

Huynh *et al* have evaluated the donor properties of 1,2,3-triazolylidenes by synthesizing palladium complexes, **36**, bearing an *i*Pr$_2$-bimy ligand as the reporter ligand (*i*Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene).[48] The ^{13}C NMR spectroscopic shift of the palladium-bound C$_{bimy}$ is sensitive to the ligand in *trans* position and has been used as a diagnostic signal. Accordingly, the 1,2,3-triazolylidenes have been determined to fall between 2-imidazolylidenes and the stronger mesoionic NHCs in terms of donor strength. Subtle shifts have been proposed to reflect the inductive effect of the substituents on the triazolylidene ligand. In support of this proposal, the NMR characteristics of the CO ligand *trans* to the carbene in rhodium complexes **37** are weakly dependent on the electronic properties of the wingtip groups.[19] An increase of the coupling constant ($^1J_{RhC}$) is observed when less electron-donating aryl wingtip groups are present, whereas alkyl substituents result in smaller coupling constants.
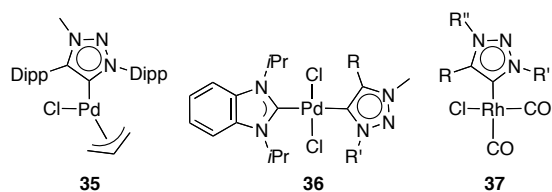

Fig. 3 Complexes used to evaluate the donor properties of triazolylidenes by X-ray photoelectron spectroscopy (**35**), by ^{13}C NMR chemical shifts (**36**) and by Rh–C coupling constants (**37**) as orthogonal techniques to the Tolman electronic parameter.

Reactivity and stability

Cyclometallation

Triazolylidene complexes that contain an aryl wingtip group can undergo cyclometallation. This process strongly depends on the location of the aryl group (N- *vs* C-bound) within the ring and has been observed in several metal complexes. For example, complex **22** cyclopalladates in the presence of acetate as promoter and base (Scheme 11).[19] The palladacycle **38** is formed exclusively, demonstrating a strong preference for activating the N-bound phenyl group over the C-bound substituent. Similarly, Sankararaman *et al*. have prepared the related acetate-bridged palladacycle **20** by transmetallation of the corresponding silver complex with $Pd(OAc)_2$ and concomitant C–H activation of the N-bound phenyl ring (*cf* Scheme 5).[36] Cyclopalladation is base-dependent and does not occur in the presence of NEt_3. Formation of **38** is fully reversible and complex **22** is regenerated upon exposure of complex **38** to excess HI.
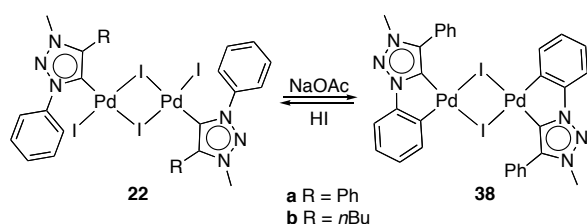
Scheme 11 Reversible cyclopalladation on a triazolylidene platform.

Cyclometallation is not restricted to palladium and has been observed also in ruthenium(II), rhodium(III) and iridium(III) complexes (**39–41**, Fig. 4).[49] The N-bound phenyl group cyclometallates preferentially and spontaneously during transmetallation involving the triazolium salt and Ag_2O. Considering the beneficial role of NaOAc, the electron-deficient nature of the metal centres, and the resistance of more electron-rich metals such as rhodium(I) or platinum(II) to cyclometallate, an electrophilic C–H bond activation has been concluded, which prefers high electron-density in the aromatic ring. Consequently, the inductive effect of N1 surpasses the electron-withdrawing properties of the triazolylidene fragment.
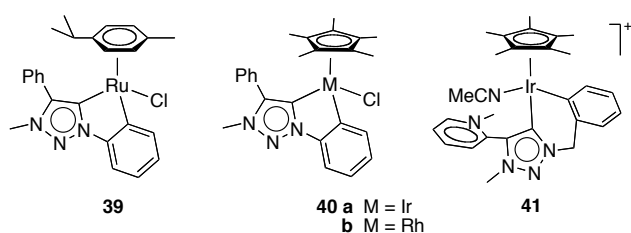

Fig. 4 Cyclometallated complexes **39–41** obtained by activation of the *N*-bound wingtip group.

When the N1-bound substituent is a benzyl rather than a phenyl group, cycloiridation is transient and the six-membered metallacyclic product **41** has been characterised only in solution and has not been isolated thus far. If cyclometallation of the N1-bound substituent is prevented (*e.g.* for R' = alkyl), the C-bound phenyl group can be activated, though harsher conditions are required. For instance, treatment of complex **42** with NaOAc (12 h, 60° C) induces cyclometallation and formation of complex **43**

(Scheme 12).[23] Again the C–H bond activation is reversible and addition of HCl restores the monodentate bonding mode and complex **42** already at RT. When DCl in D_2O is used, the monodeuterated complex **42**–d_1 featuring a single deuterium in the phenyl *ortho* position is obtained exclusively, implying that the C–Ir bond cleavage is irreversible under these conditions.

A different type of cyclometallation has been identified upon reaction of the pyridinium-functionalised triazolium salt **10** with $[IrCp*Cl_2]_2$ (Scheme 13).[50] In the presence of Ag_2O, the two complexes **44** and **45** are formed. The bidentate coordination in
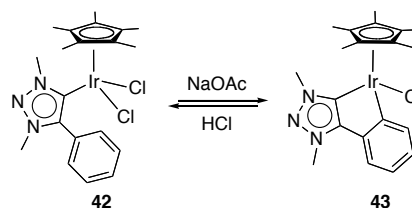
Scheme 12 Iridium-mediated C–H activation at a C-bound phenyl group.

44 originates from aromatic C–H bond cleavage affording a pyridylidene ligand site, whereas formation of **45** involves the activation of the N-bound methyl group of the pyridinium fragment. The latter pathway is suppressed if the substituent at N1 is a methyl or a pentafluorobenzyl group, $CH_2C_6F_5$. This outcome points to an intermediate akin to **41** that is relevant for inducing $C(sp^3)$–H bond activation and formation of **45**. Notably, iridation of the triazolium salt **7** in the presence of AcO^- changes the reaction pathway considerably and leads to unusual N_{pyr}–CH_3 bond cleavage.
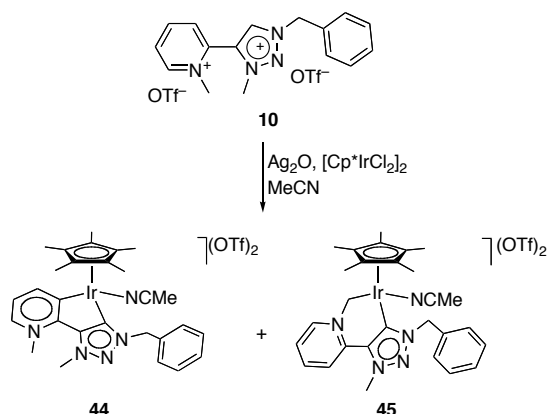
Scheme 13 Intramolecular $C(sp^2)$–H *vs* $C(sp^3)$-H bond activation mediated by a triazolylidene iridium species.

Acidolysis

In contrast to the phenyl group in the metallacycles (*cf* Schemes 11, 12), the triazolylidene–metal bonds M–C_{trz} are generally stable under acidic conditions. For example, the iridium complexes **42** and **44** tolerate aqueous 1 M HCl for several days.[23,50] Under these conditions, no traces of triazolium salt are observed, demonstrating the high resistance of the M-C_{trz} bond towards acidolysis. Hence, the C_{trz}–Ir bond and also the iridium–pyridylidene bond are substantially more robust towards protonation than the C_{aryl}–Ir bond.

Similarly, the palladium complex **22** is stable in acidic conditions and exposure to HI for several days does not induce

any degradation.[19] Both the stability of the Pd-C_{trz} bond toward acids and bases and the sensitivity of N-bound phenyl groups toward cyclopalladation under basic conditions have obvious implications when using this type of complexes in catalysis.

In contrast, Bertrand and Grubbs have established acidolysis of the ruthenium triazolylidene complex **46** in the presence of excess HCl or TFA (Scheme 14).[51] This reactivity has been successfully exploited to develop an olefin metathesis system that utilises acids as initiators for the formation of the active catalyst **47**. The unsubstituted nitrogen (N2) has been proposed to act as a proton acceptor followed by heterocycle dissociation with concomitant 1,3 proton-shift to form the triazolium salt. Not unlikely, the absence of a shielding substituent at the C5 position further enhances the acid-sensitivity of the triazolylidene in **46** and may provide a rationale for the different stability of this ligand as compared to those discussed previously. These reactivity patterns highlight that the triazolylidene ring may not be innocent and can act as a proton acceptor either by undergoing reversible activation of the wingtip substituents or by capturing a proton within the heterocycle.
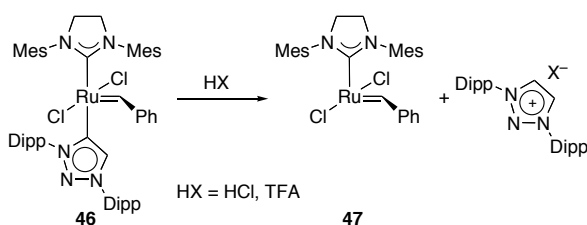
Scheme 14 Acid-mediated activation of a latent olefin metathesis catalyst.

Oxidative M–C bond cleavage

The triazolylidene copper(I) complexes **48** react with CsOH to afford the mesoionic oxides **49** exclusively (Scheme 15).[52] This demetallation pathway is distinctly different from the reactivity of 2-imidazolylidenes, and also differs from decomposition of the complexes in the presence of air and moisture, which produces predominantly the protonated triazolium salt and only minor quantities of **49**.
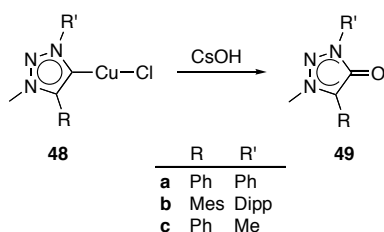
Scheme 15 Mesoionic oxides from oxidative Cu–C_{trz} bond cleavage.

Additionally, these mesoionic oxides have been synthesised directly from the triazolium salts with CsOH, or with Ag_2O, though the reactions are generally less clean and proceed with lower yield. The reaction with Ag_2O is highy solvent-dependent. In CH_2Cl_2, the corresponding silver carbene is formed, which is sufficiently stable for being used for triazolylidene transfer (*cf* section on synthesis). In THF, however, an unstable intermediate, presumably an [Ag(carbene)(OH)] species, is generated, which demetallates to yield the mesoionic oxide **49**.

Structural features

All crystallographically analysed triazolylidene complexes have been collated to evaluate their bond lengths and angles. This analysis includes complexes that have been published, that are currently in press, or are not yet published but have been structurally resolved (the latter predominantly from the authors' labs). Average M–C bond lengths of these complexes are compiled in Table 2. They are not markedly different from other NHC complexes, though some values may need to be adapted once a more substantial data set is available (*e.g.* rhenium, silver, and copper triazolylidenes).

Table 2. Overview of M–C bond lengths (Å) in triazolylidene complexes

M	average M–C_{trz}	shortest M–C_{trz}	longest M–C_{trz}	#[a]	references
Re	2.174	n.a.	n.a.	1	42
Ru	2.030	1.991	2.098	14	18,20,21,27,28,51
Rh	2.048	2.023	2.071	9	11,40,52
Ir	2.037	2.010	2.081	14	11,18,23,26,50,66
Pd	1.986	1.901	2.049	21	11,19,22,24,35,36,48
Cu	1.889	1.879	1.898	3	29,54
Ag	2.071	2.065	2.076	2	28,34
Au	1.999	1.963	2.029	8	25,55

[a] # = number of complexes considered

Metallation (E = M) induces slight, yet diagnostic, structural changes in the triazole heterocycle compared to the triazolium salt precursor (E = H, Table 3). In particular, the C4–C5 bond becomes longer. Elongation is less significant for the C5–N1 and the N1–N2 bonds, while the C4–N3 and the N2–N3 bonds are essentially unaffected. This result may hint to a strong electrostatic contribution to the metal bonding, with only marginal π-conjugated contributions. Most characteristically, the C4–C5–N1 bond angle becomes more acute by about 3°. The same structural changes, yet more pronounced, are observed upon deprotonation and formation of the free triazolylidene (E = lone pair). For example, the carbene bond angle (vertex C5) decreases from 105.9° to 99.7°. The decrease of the bond angle as well as the C4–C5 bond elongation may be related to an increase of the p character at the carbenoid carbon.[56] While in 2-imidazolylidene chemistry, these structural modulations have been proposed as an indicator for quantifying metal-carbon π back-bonding,[57] such a

N1–C5–C4   101.3(1)°   102.3(5)°
C5–C4   1.408(2) Å   1.394(7) Å
C5–N1   1.379(2) Å   1.358(7) Å
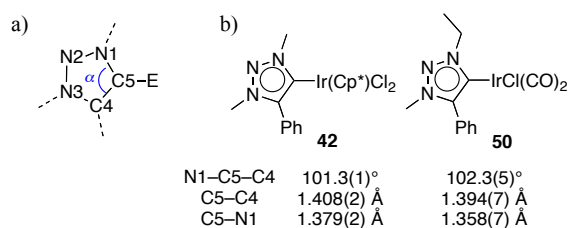
Fig. 5 a) Labelling scheme used in Table 3; b) complexes **42** and **50** featuring opposite geometrical parameters than expected for the higher backbonding propensity of iridium(I) compared to iridium(III).

Table 3. Bond lengths and angle α in triazolium salts, triazolylidene complexes, and free triazolylidenes (*cf* Fig. 5).[a]

E	N1–N2	N2–N3	N3–C4	C5–N1	C4–C5	α
H	1.320(5)	1.319(6)	1.362(11)	1.351(5)	1.367(11)	105.9(3)
M	1.337(10)	1.320(13)	1.361(11)	1.367(10)	1.389(12)	102.3(9)
:	1.344(2)	1.323(5)	1.375(5)	1.372(7)	1.401(5)	99.7(4)

[a] Bond lengths in Å, angle a (N1–C5–C4) in °

trend is not confirmed in triazolylidene complexes. For example, the iridium(I) complex **50** features a more acute C4–C5–N1 angle (102.3 *vs*. 101.3 °) and shorter C5–C4 and C5–N1 bond distances (by 0.014 and 0.021 Å, respectively) than the supposedly less electron-rich iridium(III) complex **42** (Fig. 5).[11,23] These data are contrary to the trend expected from the propensity of these metal centres to π backbond and demonstrate subtle differences between imidazolylidenes and triazolylidenes.

Catalysis

The use of triazolylidene complexes in catalysis has experienced a rapid growth in recent years. In parts, this development may be rationalised by the specific donor properties of triazolylidenes. These ligands feature two extreme bonding situations comprising either a formally neutral carbenoid carbon or an anionic carbon bound to the metal centre. This suggests electronic flexibility, *e.g.* for stabilizing transition states or critical intermediates, and is also reflected in the mesoionic *vs* abnormal nomenclature used for these ligands. Triazolylidene metal complexes have been reported to be active catalyst precursors for a variety of processes including [3+2] cycloaddition, cross coupling, olefin metathesis, cyclisation and oxidation processes.

Triazolylidene copper-catalysed alkyne-azide coupling

Complexes **48** are versatile catalysts for the copper-catalysed [3+2] cycloaddition of a wide range of alkynes and azides (Scheme 16).[29,54] Very low catalyst loadings (0.05 mol%) are sufficient for reaching high conversions. Electron-poor phenylacetylenes are converted faster than electron-rich analogues or alkyl-substituted alkynes. Functional groups such as alcohols, esters, and pyridines are well tolerated, while primary amines-containing alkynes are not coupled efficiently and produce mixtures. The best of the series, complex **48a** is more active than 2-imidazolylidene copper analogues.[54] This complex performs well in reactions where classical catalysts tend to fail. For example, the coupling of sterically bulky alkynes with bulky azides such as Dipp-CCH with Dipp-N$_3$ proceeds with high conversion, albeit after longer reaction times. This reactivity is obviously attractive for preparing new triazolylidene ligands.

	R	R'
a	Ph	Ph
d	Mes	Mes
e	Xyl	Dipp
f	Ph	Bn
g	Ph	2-C$_6$H$_4$-SMe
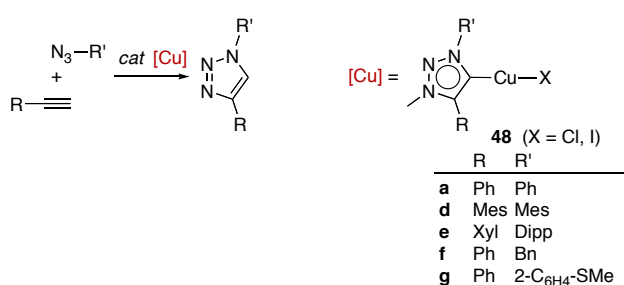
Scheme 16 Cu(trz)-catalysed cycloaddition of alkynes and azides.

The potential of the 1,2,3-triazole product to act as a ligand for copper and to participate in the catalytic cycle has been addressed by preparing a representative N3-bound triazole copper complex (R = Ph, R' = Bn).[29] This complex is indeed a catalyst precursor, however its activity (67% after 7 h) is two orders of magnitude lower than that of complexes **48** and is thus not competitive. In line with this conclusion, deliberate addition of triazole as auxiliary to complex **48a** has no catalysis-accelerating effect. In

this context, it is interesting to note that complex **48a** displays activity similar to a mixture of CuCl and the mesoionic oxide **49a** (*cf* Scheme 15) in the coupling of benzyl azide and phenylacetylene.[23] The mesoionic oxide/CuCl mixture may be generated directly from **48a**, a process that is not unlikely to occur under catalytic conditions.

Triazolylidene palladium-catalysed C–C cross coupling reactions

Considering the popularity of palladium in cross-coupling reactions, and of aryl-aryl cross-coupling in particular, it is not surprising that many triazolylidene palladium complexes have been investigated as catalyst precursors for Suzuki-Miyaura cross-coupling. Specifically, the enhanced donor properties of triazolylidenes compared to phosphines and C2-bound imidazolylidenes, is expected to promote the oxidative arylhalide addition to the palladium(0) intermediate, often a limiting factor in arylchloride conversion. Sankararaman *et al* have observed diaryl formation when using the chiral triazolylidene palladium complex **51** for the coupling of different arylbromides with arylboronic acids.[30] At moderately elevated temperatures (75 °C) and with 2-5 mol% **51**, activated arylbromides are converted in high yield over several hours (Scheme 17). Sterically more demanding substrates, *e.g.* naphthylbromides are poorly converted with phenylboronic acid (3-9 TONs) and are not cross-coupled to naphthylboronic acid because of a relatively fast deboronation process. Hence, evaluation of a potential asymmetric induction of the chiral ligand in **51** is prevented. Addition of elemental mercury decelerates the reaction but does not stop conversion.

	R = R'	R^3
a	Ph	H
b	Mes	H
c	Dipp	H
d	Dipp	Me
e	Dipp	Ph

	R	R'
a	Ph	Me
b	Ph	Et
c	*n*Bu	*n*Bu
d	Ph	Mes
e	Mes	Mes
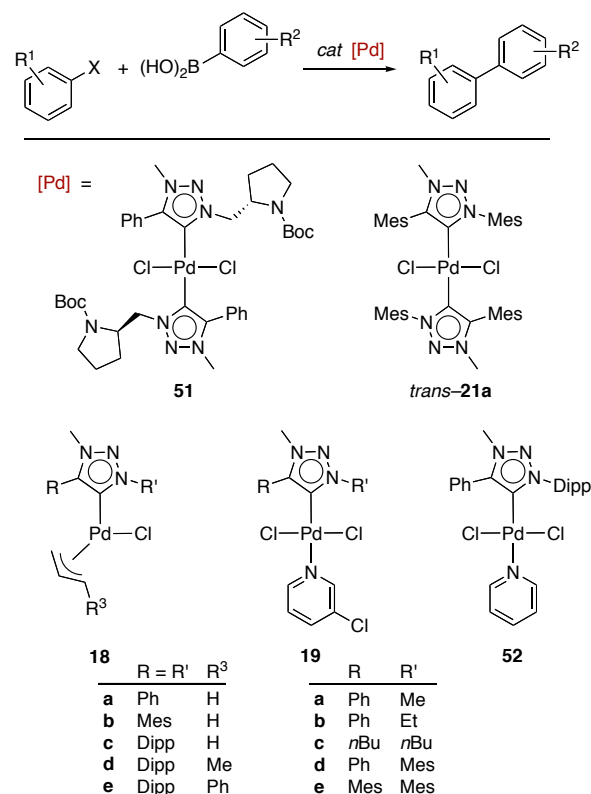
Scheme 17 Pd(trz)-catalysed Suzuki-Miyaura cross-coupling.

Adaptation of the wingtip groups of the triazolylidene ligand to

mesityl substituents (complex *trans*–**21a**) increases the catalytic activity and allows less reactive arylchlorides to be cross-coupled.[37] Under optimised conditions deactivated *p*-chloroanisol is converted quantitatively, while the analogous complex with IMes ligands gives only 60% conversion (IMes = *N,N'*-bismesityl-2-imidazolylidene). Heteroaromatic chlorides as well as *ortho*-substituted arylchlorides including naphthylchloride are efficiently arylated.

As most Suzuki catalyst precursors require only one carbene ligand,[35,36] the monotriazolylidene palladium complexes **18** and **19** bearing a 'throw-away' ligand have been investigated in Suzuki-Miyaura catalysis. A series of (substituted) allyl complexes **18** have been reported by Fukuzawa *et al* to catalyse arylation of arylchlorides at room temperature.[35] Complex **18e** containing Dipp wingtip groups and featuring a cinnamallyl ligand yields the most active catalytic system of the series of allyl complexes **18**. Interestingly, and in contrast to complex **21a**, 3-chloropyridine is not converted at all.

Concomitantly and inspired by the PEPPSI concept (pyridine enhanced precatalyst preparation, stabilisation and initiation), our group has investigated complexes **19** containing an easily cleavable 3-chloropyridine ligand.[22] Moderate catalytic activities for arylbromide conversion have been established (TOF$_{50}$ ~ 53 h^{-1}) at 50 °C.[22] At higher temperatures, significant decomposition of **19** occurs. Activated arylchlorides are arylated, though conversions do not exceed 60%, thus suggesting the active species has a limited life-time. Variation of the wingtip groups on the triazolylidene ligand indicates a reverse trend to that of 2-imidazolylidene PEPPSI catalysts, as the smallest substituents (**19a**, **b**) induce the highest activity. Under slightly modified conditions, substantially better conversions can be achieved.[35]

Mechanistic studies using mass spectrometry (MS) and transmission electron microscopy (TEM) have revealed the formation of ligand-free clusters and particles in the 3–5 nm range under catalytic conditions.[22] These results paired with the poisoning effect of mercury suggest a heterogeneous process in which nanoparticles of palladium are generated, constituting the catalyst resting state.[58] The nanoparticles formed may be stabilised by triazolylidenes, or by triazolium cations.[59] Leaching of palladium atoms from these nanoparticles, with or without bound triazolylidene, generates the molecular and catalytically active species responsible for the conversion of arylchlorides under relatively mild conditions. Similar conclusions have been drawn in independent work by Crudden and coworkers using complex **52** and a related bimetallic system derived from **11** as catalyst precursors.[60] Hence, these triazolylidene complexes have a distinctly different mode of action than the corresponding imidazolylidene derivatives, in part because of the weaker Pd–C$_{trz}$ bond.

The mixed triazolylidene benzimidazolylidene complexes **53** are precatalysts for the arylation of pentafluorobenzene by direct C–H bond activation (Scheme 18). The catalytic activity is higher at low catalysts loading (1-0.5%) than with higher concentrations of **53**. This behaviour, together with the rather high operation temperature (120 °C) and the incidental observation of palladium black point to a possibly heterogeneous mechanism as established for the PEPPSI-type triazolylidene complexes **19** and **52**.
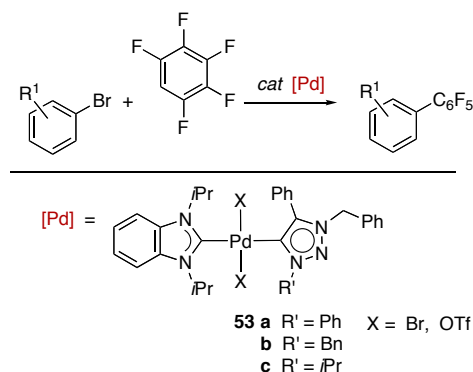
Scheme 18 Pd(trz)-catalysed arylation of pentafluorobenzene.

Leibscher and coworkers have developed a Suzuki cross-coupling protocol based on triazolium salts, Pd$_2$(dba)$_3$, and Cs$_2$CO$_3$ as a base.[61] This *in-situ* procedure avoids the formation of triazolylidene complexes as precatalysts, however, results are the same when only Pd$_2$(dba)$_3$ is used. The mixture is catalytically inactive when the triazolium salts are replaced by bis-triazolium units, the latter most likely promoting the formation of a robust dicarbene complex. Mixed imidazolium-triazolium precursors give better yields, perhaps because of the higher stability of the Pd–C$_{imidazolylidene}$ bond compared to the M–C$_{trz}$ bond.

The triazolylidene palladium complexes **21** catalyse the arylation of olefins (Heck-Mizoroki reaction; Scheme 19).[62] Mesityl wingtip groups induce higher activity than phenyl substituents. For example, the coupling of bromobenzene with *t*-butylacrylate reaches 80% conversion after 3 h with **21a**, yet only 40% after 8 h with **21b**. though the high selectivity towards the *trans* olefin product is preserved. Arylbromides are converted well, but aryl chlorides give much lower yields and are only converted if activated by an electron-withdrawing group. Heteroatoms and *ortho* substituents constitute a further limitation to this catalyst system. While **21** performs substantially less well than the most active carbene complexes,[63] it is worth nothing that it is more active than the corresponding 2-imidazolylidene analogues, *e.g.* [PdCl$_2$(IMes)$_2$]. This higher activity has been attributed to the better donor properties of the triazolylidene compared to IMes, entailing easier ArX oxidative addition to palladium(0). Considering the harsh reaction conditions (150 °C), this activity enhancement may also be correlated with the weaker Pd–C bond stability in triazolylidene complexes.
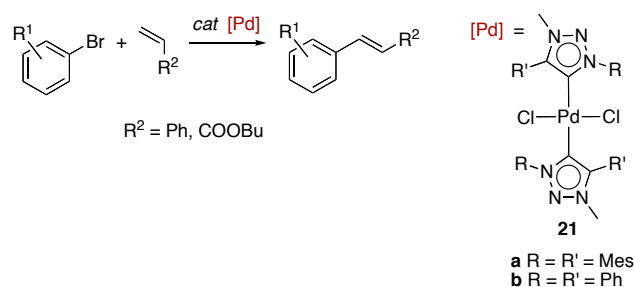
Scheme 19 Pd(trz)-catalysed Heck-Mizoroki olefination of aryl bromides.

Complex **21a** is also effective in the arylation of alkynes (Sonogashira reaction; Scheme 20). The reaction is only practical for electron-poor aryl bromides, while electron-donating

substituents on the aryl halide induce moderate to low conversion. A variety of terminal alkynes have been successfully coupled. As in the case of Mizoroki-Heck coupling, neutral and electron-rich aryl halides present lower conversions, complex **21a** outperforms the analogous normal carbene complex comprising two IMes ligands.
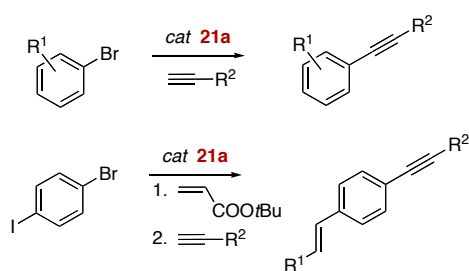

Scheme 20 Pd(trz)-catalysed Sonogashira cross-coupling and tandem Heck/Sonogashira functionalisation of iodobromobenzene.

The efficiency of complex **21a** both in the Mizoroki-Heck and the Sonogashira coupling has been exploited to perform tandem reactions (Scheme 20). Thus, a sequential Heck-arylation and subsequent Sonogashira coupling has been developed to generate the desired product in 69% yield, though formation of small amounts of the double Mizoroki-Heck reaction is observed as a minor byproduct.

## Triazolylidene complexes for catalytic hydroarylation of alkynes

Triazolylidene palladium complex **20** catalyses the hydroarylation of alkynes (Scheme 21), though less efficiently than the normal NHC Pd analogues.[36] Reaction of mesitylene with ethyl propiolate produces the corresponding vinylarene steroselectively, forming only the *Z*-isomer. Formation of the double addition product also occurs and is not suppressed when using a large excess of arene. The reaction works well for low catalyst loadings (0.5%) in the presence of excess TFA in CH_2Cl_2. In the absence of TFA only propiolate polymerisation takes place. Evaluation of the scope of catalyst **20** indicates high activity with electron-rich arenes, while 4-*tert*butylphenol produces 6-tertbutylcoumarine as the single product resulting from an intramolecular transesterification. Phenylacetylene also induces a mixture of mono- and bishydroarylation products. With phenyl- or tolylpropionate, only a single insertion is observed, though the product ester is partially hydrolysed.
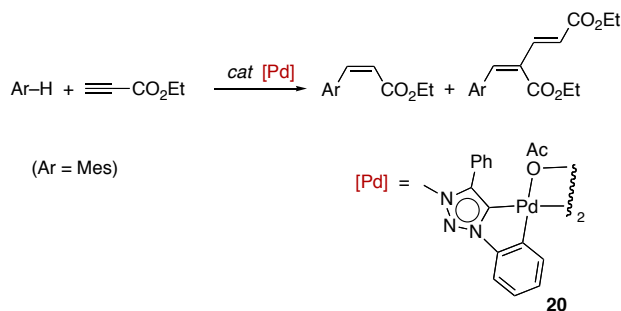
**Scheme 21** Pd(trz)-catalysed hydroarylation of alkynes.

Triazolylidene Au complexes for addition reactions

Inspired by the success of gold(I) complexes in a variety of catalytic processes,[64] Crowley and coworkers have demonstrated triazolylidene gold complexes to be highly active catalyst precursors for carbene insertion and cyclisation reactions.[55] Thus complex **54** promotes the carbene insertion into O–H bonds of primary, secondary, and tertiary alcohols (Scheme 22). Insertion into phenolic O–H bonds or into the N–H bond of aniline is less efficient. Likewise, using larger carbene precursors than ethyldiazoacetate (EDA) is not clean, though still feasible. Considering the modularity of the triazolylidene ligand, such limitations may be overcome by appropriate tailoring of the carbene substituents.
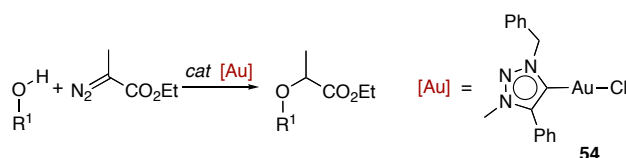
Scheme 22 Au(trz)-catalysed hydroalkoxylation of carbenes.

Similar insertion reactions are catalysed by complex **54** when using allenes instead of diazo precursors of carbenes. For example, allenes featuring a primary alcohol undergo an intramolecular cyclisation (Scheme 23a). Similarly, enynes cyclise to give, depending on the conditions, cyclopentenes (in CH_2Cl_2) or cyclopentanes with an exocyclic double bond if more polar solvents are used (CH_2Cl_2/MeOH 1:1, Scheme 23b). The latter method also induces the insertion of the intermediate into the MeO–H bond and affords the corresponding methoxylated product with excellent conversions.
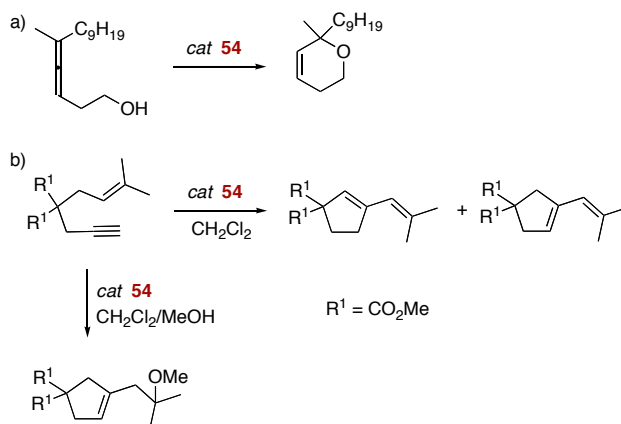

Scheme 23 Au(trz)-catalysed intra- and intermolecular hydroalkoxylation and intramolecular cycloaddition.

Triazolylidene Ru complexes for olefin metathesis

Bertrand and Grubbs have explored various triazolylidene ruthenium complexes in olefin metathesis.[18,51] Complexes with an alkyl substituent at N3 have been noted to be unstable, though complexes **24** comprised of an arylated N3 are considerably more robust. Complexes **24c**, **24d**, and **24j** display high activity in ring opening metathesis polymerisation (ROMP) of cyclooctadiene while **24f** only induces low conversions, even after several days. Comparison of these triazolylidene-derived catalysts with Grubbs' second generation catalyst (GII) indicates that **24d**

performs similarly, **24j** is slightly slower, and **24c** comparably slow. The presence of a phenyl wingtip group at the triazolylidene C4 position may be responsible for this reduced activity, as cyclometallation may deactivate olefin metathesis.[65] Kinetic and computational studies suggest an associative or a dissociative interchange initiation step, and indicate that the sterics of **24f** play a significant role in inhibiting the catalyst initiation.
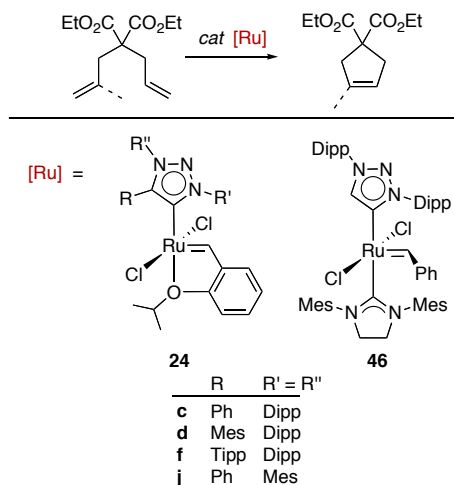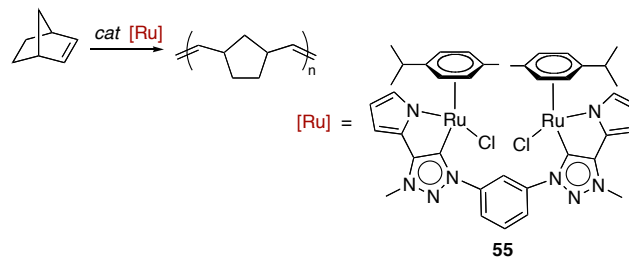

Scheme 24 Ru(trz)-catalysed ring closing metathesis.

Ring closing metathesis (RCM, Scheme 24) follows related trends. Complex **24f** is essentially inactive, while **24c**, **24d** and **24j** show conversion profiles consistent with the activation energies determined for the initiation.[18] Complex **24c** displays relatively slow initiation after an induction period. In contrast, no induction period has been noted for **24d**, presumably because of complex decomposition. In support of this hypothesis, conversion ceases before reaching completion. Complex **24j** performs best and displays fast initiation as well as catalytic activity similar to GII. Furthermore, it catalyses the formation of trisubstituted olefins.

As reported for related bis(carbene) species, the ruthenium complexes **46** featuring a normal NHC and a triazolylidene ligand is RCM and ROMP inactive (Scheme 24). High activity is induced upon addition of a strong acid such as trifluoroacetic acid (TFA) or HCl, but interestingly not with HBF$_4$. Acidolysis of the Ru–C$_{trz}$ bond has been demonstrated to yield an active Ru(NHC) species along with the corresponding triazolium salt.[51] Hence, complex **46** represents a latent catalyst precursor that can be activated at room temperature. Selective triazolium formation suggests that the ruthenium–triazolylidene bond is less stable than the Ru–NHC bond, which is in agreement with observations in triazolylidene palladium catalysis (see above). Detailed mechanistic studies indicate that protonation of the triazolylidene, presumably at N2, rather than ligand dissociation is the rate-determining step in catalyst activation. The relevance of such a protonation mechanism is further underlined by the observation that a complex analogous to **46** yet comprised of two SIMes as normal NHC ligands is considerably less active than **46**.

Complex **55** catalyses the ROMP of norbornene when activated by trimethylsilyl-diazomethane (Scheme 25), however, less strained cyclic olefins are not efficiently polymerised.[28]

Scheme 25 Ru(trz)-catalysed ring-opening metathesis polymerisation.

Triazolylidene Ru complexes for organic oxidations

Complexes **56** are catalyst precursors for the base- and oxidant-free oxidation of alcohols and amines (Scheme 26).[20] Using benzyl alcohol as a model substrate, complex **56a** displays higher activity than both **56b** and normal NHC analogues and affords benzaldehyde quantitatively within 16 h. Substitution of the metal-bound chlorides in **56** for carbonate (**57**) has diverging effects. While the activity is reduced in the cymene-containing series, a significant increase of the conversion from 55% to 85% is achieved in the hexamethylbenzene analogue **57b**. Lower temperatures (70 °C instead of 120 °C) still lead to high conversions, though increased catalyst loading (10 mol %) and reaction times are required. Primary and secondary benzylic alcohols are readily oxidised with **56a**, though electron-withdrawing substituents need longer reaction times. Aliphatic alcohols such as 2-phenylethanol and 1-octanol are poor substrates, indicating some selectivity for synthetic purposes when targeting more complex substrates.
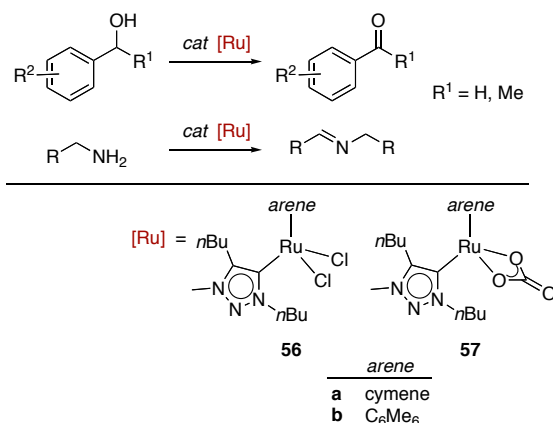

Scheme 26 Ru(trz)-catalysed dehydrogenation of alcohols and amines.

The oxidation of primary amines generates homocoupled imines due to condensation of the initially formed imine with residual amine (Scheme 26). Slightly higher reaction temperatures (150 °C) are needed than for the analogous alcohol oxidation. The harsher conditions required for amine oxidation may be a consequence of the stronger imine–Ru bond as compared to ketone binding to the metal centre, and might thus point to product release from the metal coordination sphere as the rate-limiting step. Notably, the normal NHC analogue is more active in amine oxidation than the triazolylidene complexes **56**. Complexes **57** are inactive, presumably because substitution of the chelating carbonate ligand by the amine substrate is inhibited. Aliphatic amines are also oxidised, though at lower rates.

When alcohol and amine oxidation are combined, amides are

formed if a base is added as auxiliary (Scheme 27). Thus, reaction of benzyl alcohol with benzylamine in the presence of catalytic amounts of **56a** and NaH affords the corresponding phenyl benzyl amide.
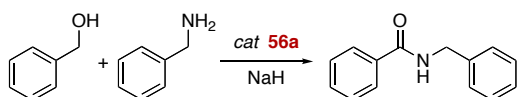
Scheme 27 Ru(trz)-catalysed oxidative coupling of alcohols and amines.

Triazolylidene Ru and Ir complexes for water oxidation

Water oxidation is the arduous half-cycle water splitting, a key technology to capture solar energy for fuel generation. Both ruthenium and iridium complexes containing triazolylidene ligands have demonstrated high activity in water oxidation. For example, complexes **42**, **44**, **45**, and **58** lead to efficient O_2 evolution from water in the presence of $(NH_4)_2[Ce(NO_3)_6]$ (CAN) as sacrificial oxidant (Scheme 28).[23,50] High turnover numbers (TONs > 10,000) have been achieved, and these turnover numbers are limited only by the availability of Ce^{IV} and not on the stability of the catalytically active species from complexes **44**, **45**, and **58**.[50]
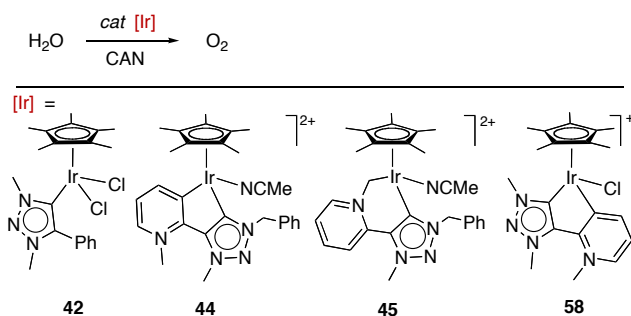
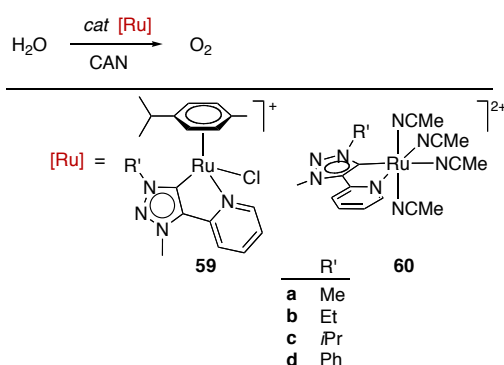**Scheme 28** Ir(trz)-catalysed water oxidation.

Complex **42** featuring a monodentate carbene ligand is less soluble in water and achieves under dilute conditions a respectable 22,800 turnovers.[23] However, this TON is substantially lower than those from bidentate complexes such as **44** or **58**, and conversion decreases markedly after consumption of about 50% of sacrificial oxidant, suggesting only limited catalyst lifetime. Therefore, chelation seems to be important for generating robust water oxidation catalysts.

Variation of the triazolylidene ligand framework has direct implications on activity and has allowed for catalyst optimisation. For example, complex **58** accomplishes about 40,000 turnovers and consumes all available Ce^{IV}. Turnover frequencies with this complex are improved to 450 h^{-1} (*cf* 280 h^{-1} for **44** and 190 h^{-1} for **45**).[66] Kinetic studies and DLS analyses, paired with the strong dependence of the catalytic activity on the ligand setup strongly suggest that the active catalyst is a well-defined molecular species.

When complex **42** is combined with hematite as photoabsorber and anode, photoelectrochemical water oxidation is indicated by an enhancement in the photocurrent by ca. 35%.[23] Further engineering of this system may lead to efficient artificial photosynthesis.

Ruthenium complexes **59** and **60** are also precursors for Ce^{IV}-mediated water oxidation (Scheme 29).[21] While turnover frequencies and numbers (max. 7,000 TON, 19 h^{-1}) are remarkable for ruthenium-based systems, they are clearly lower than when using iridium pre-catalysts such as **44** or **58**. Intriguingly, though, the catalytic activity and selectivity is directly correlated to the ligand framework, which allows both parameters to be rationally tailored. Substantial fractions of CO_2 (1–34%) are produced with all cymene complexes **59**, and the selectivity towards O_2 evolution is markedly higher with complexes **60**. Whereas **60d** still generates detectable quantities of CO_2 (ca. 1%), presumably due to cyclometallation of the phenyl substituent and subsequent ligand degradation, complexes **60a-c** are highly selective and produce O_2 exclusively. The triazolylidene ligand in these complexes is thus sufficiently stable towards oxidation. Moreover, the activity of complexes **60a-d** directly correlates with the first oxidation potential of the ruthenium centre and also with the expected impact of the wingtip group at N1. Thus, a methyl substituent entails the lowest Ru^{II}/Ru^{III} potential and the fastest water oxidation rate (19 TONs in 1000 s). This correlation is interesting when considering that the supposedly rate-limiting O–O bond formation process is typically assumed to involve higher valent ruthenium intermediates such as Ru^{IV} or Ru^{V}.

Scheme 29 Ru(trz)-catalysed water oxidation.

The excellent performance of these ruthenium and iridium complexes and, in particular, the robust catalytic cycle has been attributed in part to the specific properties of the mesoionic triazolylidene. Closely related mesoionic imidazol-4-ylidenes have been demonstrated to actively participate in bond activation processes, as the ligand can transiently bind a proton through reversible tautomerisation.[67] For the triazolylidene complexes, this tautomerisation by analogy involves the transformation of the mesoionic ligand **J** into a carbene **K** with a saturated C5 site and a positive charge at the remote N–N–N subunit (arbitrarily depicted in Scheme 30 for the first proton transfer in water oxidation). This reactivity pattern exploits the mesoionic character of triazolylidene ligands, which can serve as a transient reservoir for both positive and negative charges and may bring
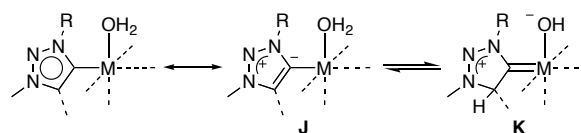
Scheme 30 Potential proton transfer from water to the triazolylidene ligand to enable proton-coupled electron transfer processes.

about synergistic effects through ligand-metal cooperativity similar to those observed in bi- and multimetallic systems. Specifically, the transient proton acceptor ability enables an intramolecular transfer of protons coupled to electron transfer (proton-coupled electron transfer, PCET), which is a key concept for facilitating multielectron processes that take place in water oxidation.[68]

Applications beyond catalysis

Much like the chemistry of Arduengo-type NHC chemistry, most efforts to disclose applications of triazolylidene complexes have been directed towards catalysis and only little is known of the utilisation of these systems in other areas.

Photophysical applications

The heteroleptic bis(tridentate) ruthenium(II) complex **61** comprised of a *C,N,C*-tridentate coordinating bis(triazolylidene)pyridine ligand as a tpy analog (tpy = 2,2':6',2''-terpyridine) displays interesting photochemical properties (Fig. 6).[27] Detailed luminescence and electrochemical studies indicate that the longest wavelength MLCT absorption involves the tpy ligand, while the [3]MLCT emission originates from the carbene ligand. The [3]MLCT states are rather high in energy due to the strongly donating triazolylidene ligands. Therefore these triplet states are barely populated thermally, which efficiently suppresses radiationless deactivation pathways.
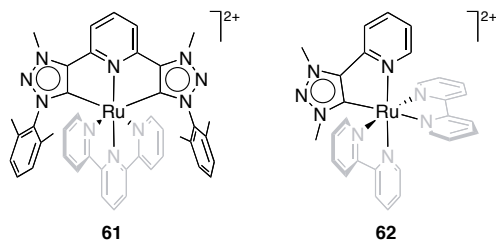

Fig. 6 Photoluminescent triazolylidene ruthenium complexes.

The triazolylidene complex **62** (Fig. 6), a close analogue of [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine), has interesting electro- and photochemical characteristics.[69] Because of the strong donor properties, the oxidation potential of the ruthenium(II) centre is lowered by some 300 mV compared to the bpy homologue, while the electron-acceptor properties remain bpy-centred and are therefore unaffected, resulting in a net decrease of the HOMO-LUMO gap by 0.3 eV. Excited state lifetimes are not significantly affected by the replacement of one pyridyl ligand by a triazolylidene, which holds promise for application of this class of compounds as photosensitisers.

Enzyme mimicry

A triazolylidene iridium scaffold constitutes a functional analogue of methyl transferases such as *S*-adenosyl methionine (SAM). SAM transfers a methyl or a methylene group from a sulfonium site to an sp^2-hybridised carbon atom, *e.g.* in cytosine to produce 5-methyl-cytosin (Scheme 31a). An analogous reactivity is observed when the pyridinium-functionalised triazolium salt **7** is metallated with [Ir(Cp*)Cl$_2$]$_2$ in the presence of acetate (Scheme 31b).[26] After formation of the triazolylidene iridium bond, a methylene group is selectively transferred from

the pyridinium fragment to the aryl unit of the *N*-bound benzyl group with concomitant activation of a solvent molecule to yield complex **63** comprising a *N,C,N*-tridentate triazolylidene chelate. Formation of **63** involves C–H and C–N bond cleavage and formation of two new C(sp^2)-C(sp^3) bonds within the iridium coordination sphere. Isotope labelling experiments have unambiguously confirmed the selective transfer of the pyridin-bound carbon. The pyridinium moiety in **7** is consequently an equally useful methyl source as the sulfonium group in SAM.
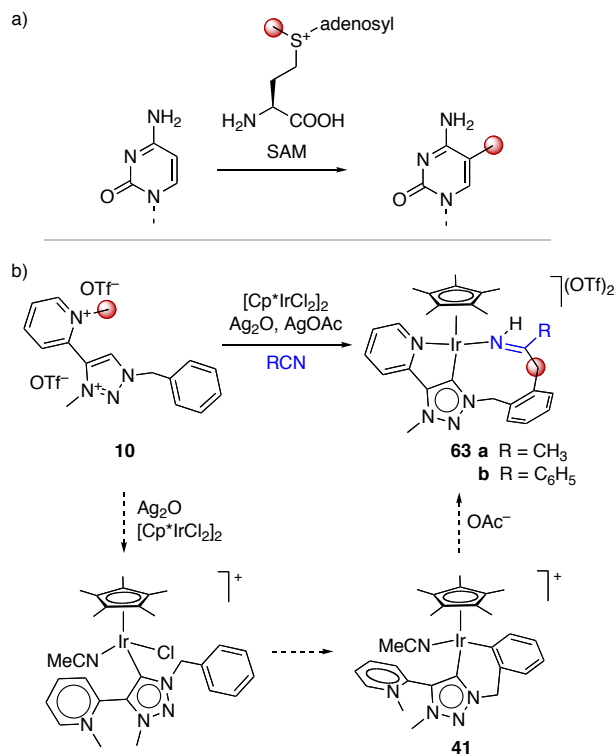
Scheme 31 Methyl transfer a) biochemically mediated by *S*-methyladenosyl methionine (SAM) and b) on a Ir(trz) platform using methylpyridinium as a CH$_2$ source.

Conclusions

Despite the short time elapsed since their first appearance as NHC-type ligands in transition metal chemistry, 1,2,3-triazolylidenes have been remarkably well investigated in their fundamental properties, and have also made substantial contributions to various areas of catalysis. The mesoionic character offers opportunities for transient proton/electron storage and increases the polarity and water solubility of the complexes. These properties provide access, for example, to reactions in aqueous media without further ligand functionalisation (*cf* water oxidation). Initial applications in materials science and in a biochemical context have appeared, and further progress is more than likely to be achieved in the next few years. In particular, the ease of accessibility of this subclass of NHC ligands, and the limitless options to introduce structural and functional diversity on the wingtips constitute attractive attributes for promoting further development in this area of carbene chemistry. Triazole chemistry has been well-established in various areas, including peptide chemistry, surface functionalisation, and self-assembly to name a few, and such triazole-containing scaffolds may be
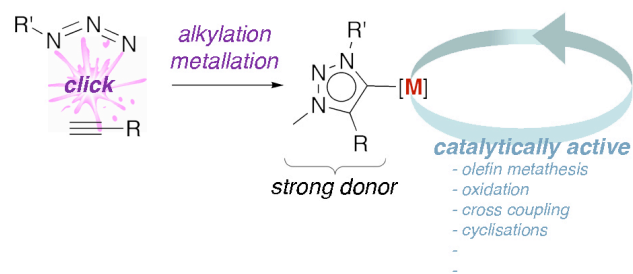
readily converted into organometallic conjugates by using a selective alkylation-metallation sequence as described here, thus providing access to multifunctional systems with exciting properties.

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