

Strongly electron-donating triazolylidene ligands: cationic metal carbonyl complexes of 1-methyl-1,2,3- triazole as triazolium surrogates

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ABSTRACT

A new strategy for tuning the electronic properties of 1,2,3-triazol-5-ylidene metal complexes is reported using $\{\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2\}$ or $\{\text{Re}(\text{bipy})(\text{CO})_3\}$ fragments as substituents at the triazole N3 atom. Reaction of cationic Mo(II) and Re(I) 1-methyl-1,2,3-triazole compounds with the strong base $\text{KN}(\text{SiMe}_3)_2$ in the presence of electrophilic metal fragments, such as AgOTf (OTf= trifluoromethanesulfonate) or $[\text{CuCl}(\text{IPr})]$ (IPr= 2,6-(diisopropyl)phenylimidazol-2-ylidene) affords a new type of 1,2,3-triazol-5-ylidene complexes. For Ag(I) cationic bis(triazolylidene) complexes $[\text{Ag}(\text{tzNHC}^{\text{M}})_2]\text{OTf}$ (M= [Mo], **2**; [Re], **4**) are obtained, whereas in the case of Cu(I) mixed

normal/mesoionic NHC complexes $[\text{Cu}(\text{IPr})(\text{tzNHC}^{\text{M}})]\text{OTf}$ ($\text{M} = [\text{Mo}]$, **7**; $[\text{Re}]$, **8**) are formed. This special type of mesoionic N-heterocyclic carbenes bear a metal fragment at the N3 atom of the 1,2,3-triazole moiety, showing a notable enhancement of the carbene electron donor ability compared to conventional alkyl-substituted analogs. Transmetalation from cationic silver bis(triazolylidene) complexes **2** and **4**, prepared using this methodology, has proved to be very efficient towards $[\text{M}'\text{Cl}(\text{cod})]_2$ ($\text{M}' = \text{Rh}, \text{Ir}$; $\text{cod} = \text{cyclooctadiene}$), affording the corresponding cationic bis(triazolylidene) $[\text{M}'(\text{cod})(\text{tzNHC}^{\text{M}})_2]\text{OTf}$ (**9-12**) complexes. The subsequent reaction with $\text{CO}(\text{g})$ produces easily the substitution of the diene ligand, affording the corresponding *cis*-dicarbonyl $[\text{M}'(\text{CO})_2(\text{tzNHC}^{\text{M}})_2]\text{OTf}$ (**13-16**) compounds.

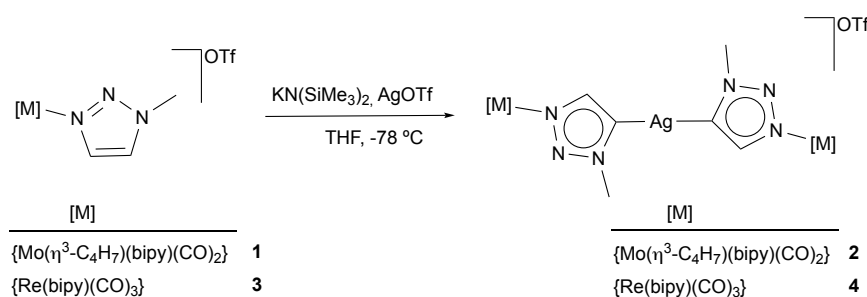
Since the isolation and characterization of the first free diaminocarbene, an imidazol-2-ylidene,¹ N-heterocyclic carbenes (NHCs) have emerged as a powerful type of compound, and as ubiquitous ligands in transition metal chemistry and catalysis.² A great number of variations of the first NHCs have been made in the last decades, modifying the substituents at the nitrogen atoms, the ring backbone nature, or the employment of different heterocyclic moieties, some of which provided less heteroatom stabilized carbenes (such as pyridylidenes or pyrazolylidenes).³ Within NHCs, the presence of only one heteroatom in a position α to the carbene carbon atom led to so termed mesoionic carbenes (MICs),⁴ for which there are no canonical resonance forms showing a carbene without additional formal charges on some nuclei, displaying a notable enhancement of the carbene electron donor properties.⁵ Belonging to this particular type of carbenes, mesoionic 1,2,3-triazol-5-ylidenes (tzNHCs)⁶ have been the subject of growing interest during the last decade, particularly their transition metal complexes because of their structural diversity and catalytic applications.⁷ One of the most common methods used to synthesize 1,2,3-triazol-5-ylidene metal complexes consists of the deprotonation of a 1,3-disubstituted-1,2,3-triazolium salt in the presence, or either followed by the addition, of the appropriate metal precursor.

We have demonstrated that the addition of a strong base to a special type of triazolium salts, which display a transition metal fragment as the substituent at N3, afforded the deprotonation of the triazole C5-H moiety as would be expected for conventional 1,2,3-triazolium cations. The high reactivity of the so-formed species triggered an intermolecular nucleophilic attack onto an *ortho* CH group of a 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) ligand (coordinated to the transition metal atom) affording cyclic, dearomatized C-C coupling products (see Scheme S1 in the Supporting Information).⁸ The reaction described above can be considered as an *in situ* generation of a strong nucleophile that attacks an electrophile present in the reaction medium, which is a bipy or phen ligand. Taking into account that transition metal coordinated bipy or phen in the vast majority of the known complexes do not act as electrophiles,⁹ and the intermolecular character of the reaction, we reasoned that the presence of a better electrophile counterpart in the reaction medium, such as a metal fragment, would lead to a completely different reactivity pattern.

Herein we report the results obtained from the deprotonation of cationic transition metal complexes bearing a 1-methyl-1,2,3-triazole (Metz) ligand in the presence of metal precursors, to afford a new type of 1,2,3-triazol-5-ylidene compounds.

We started our studies by reacting equimolar amounts of compound [Mo(η^3 -C₄H₇)(bipy)(CO)₂(Metz)]OTf (**1**) (OTf= trifluoromethanesulfonate), AgOTf and the strong base KN(SiMe₃)₂ in THF at low temperature (-78 °C). IR ν_{CO} monitoring the reaction course clearly showed that the outcome was different (ν_{CO} bands at 1952, 1871 cm⁻¹) from that resulting from the same reaction in the absence of AgOTf (ν_{CO} bands at 1936, 1846 cm⁻¹),⁸ and compound **2** was obtained as a dark red microcrystalline solid in good yield (see Scheme 1). NMR spectra of **2** in CD₂Cl₂ at 213 K are fully consistent with the formation of a silver (I) 1,2,3-triazolylidene complex, as the ¹H NMR shows the signal of only one triazole CH group (at 6.80 ppm), and even more significantly, the ¹³C NMR shows the metal-carbene signal as a low intensity doublet at 158.7 ppm ($J_{\text{Ag-C}} = 156.2$ Hz). To test the generality of the reaction pathway described above, we deprotonated in the presence of AgOTf compound [Re(bipy)(CO)₃(Metz)]OTf (**3**), for which only unidentified decomposition products are obtained when

reacted only with $\text{KN}(\text{SiMe}_3)_2$. Bis(1,2,3-triazol-5-ylidene) silver compound **4** was obtained almost immediately, at low temperature, as the only organometallic product of the reaction (Scheme 1).

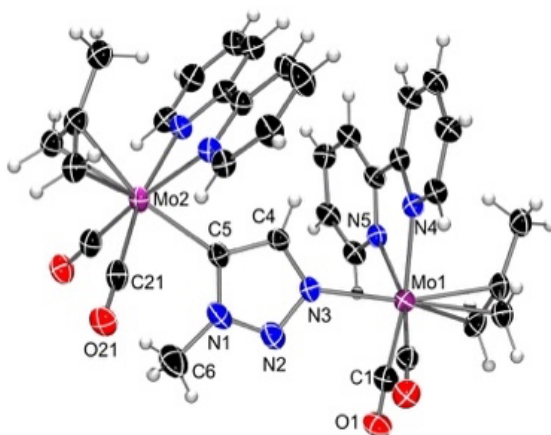


Scheme 1. Synthesis of bis(1,2,3-triazol-5-ylidene) complexes **2** and **4**.

The molecular structure of **4**, elucidated by a single crystal X-ray analysis, confirmed the connectivity pattern consisting of a $[\text{Ag}(\text{MetzNHC}^{\text{Re}})_2]\text{OTf}$ salt. The silver atom is in a linear arrangement with two coordinated 1,2,3-triazol-5-ylidene ligands, which contain a $\{\text{Re}(\text{bipy})(\text{CO})_3\}$ fragment coordinated to the imidazole N3 atom (N3 and N23 in Figure S1 in the Supporting Information). Unfortunately, the low quality of the crystals precludes further discussion of bond distances and angles.

NMR monitoring (^1H , COSY, HSQC, HMBC and ^1H DOSY) of the evolution of compound **4** in CD_2Cl_2 solution at room temperature shows formation of the neutral silver triazolylidene $[\text{Ag}(\text{MetzNHC}^{\text{Re}})(\text{OTf})](\mathbf{5})$, and the $[\text{Re}(\text{bipy})(\text{CO})_3(\text{Metz})]^+$ complex (in a 1:0.8:0.2 ratio of **5**:**4**: $[\text{Re}(\text{Metz})]^+$ in three days).^{10,11} In contrast, the silver-molybdenum compound $[\text{Ag}(\text{MetzNHC}^{\text{Mo}})_2]\text{OTf}$ (**2**) evolve at room temperature to the formation of the binuclear triazolylidene complex $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\text{MetzNHC}^{\text{Mo}})]\text{OTf}$ (**6**). The molecular structure of compound **6** was determined by X-ray diffraction, revealing the presence of a $\{\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2\}$ fragment bearing a 1,2,3-triazol-5-ylidene ligand which contains an identical $\{\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2\}$ fragment as substituent at nitrogen N3 of the triazole moiety (Figure 1a).

a)



b)

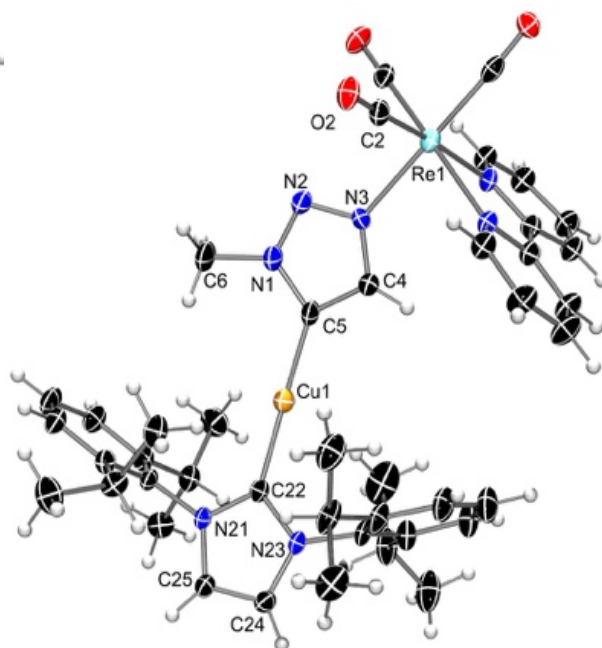


Figure 1. Molecular structures of the cations of **6** (a) and **8** (b), showing thermal ellipsoids at the 30% probability level.

The Mo-C_{carbene} bond distance, 2.240(7) Å, is very close to that of the only Mo(II) 1,2,3-triazolylidene reported complex 2.221(4) Å, which is a rare case of a ‘normal’ 1,2,4-trisubstituted-1,2,3-triazol-5-ylidene,¹¹ and in the general range from 2.143(2) Å to 2.285(9) Å established for Mo(II) NHC complexes.¹² The most remarkable difference is observed in the ¹³C NMR signal of the carbene carbon atom, which is significantly highfield shifted (at 166.1 ppm in CD₂Cl₂) compared to that of the above mentioned ‘normal’ 1,2,3-triazol-5-ylidene Mo(II) complex at 185.8 ppm,¹¹ and to those found in the range from 188.2 to 184.6 ppm for imidazol-2-ylidenes of the same {Mo(η³-C₄H₇)(bipy)(CO)₂} fragment.¹³ This fact points to a higher σ-donor ability of the MIC 1,2,3-triazol-5-ylidene compared to the ‘normal’ analog, or to imidazol-2-ylidenes which are stabilized by the two adjacent nitrogen atoms.

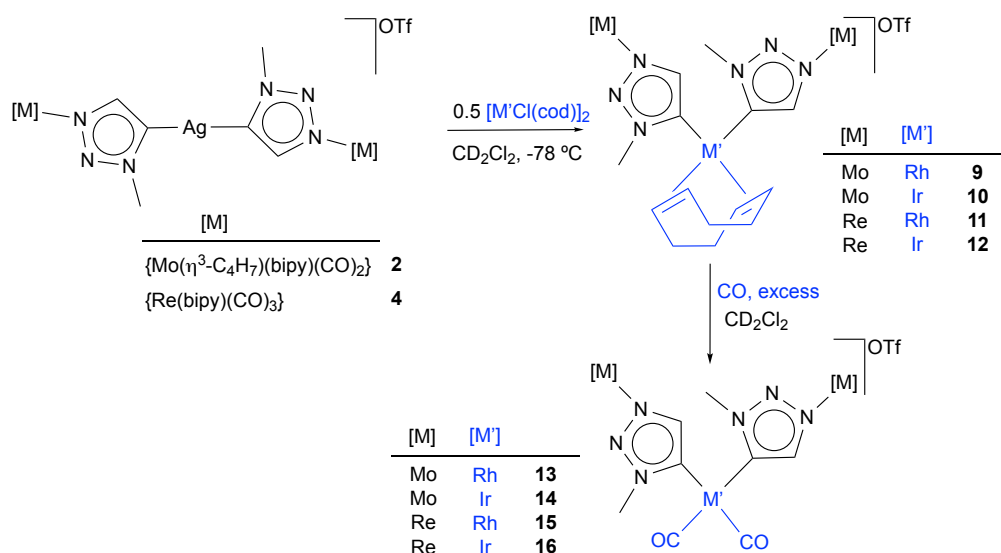
The reactions described above, in the presence of AgOTf, as well as those previously reported consisting of the deprotonation of cationic Mo(II) triazole complexes,⁸ suggest a significant difference in the acidity

of C4-H and C5-H groups of the 1-methyl-1,2,3-triazole ligand. An NBO analysis of the non-hydrogen atoms of the Metz ligand of the cation of Mo(II) in compound **1** reveals that the most favorable CH group for being deprotonated is C5, as it displays a lower negative NBO charge than C4 (-0.046 vs. -0.060), and also this position is less hindered than the C4 for being attacked by the base. In the same way, the relative energies of the C4- and C5-deprotonated species show that the latter is 8.3 kcal/mol more stable, reflecting a more effective electron delocalization.¹⁰

In order to study the electronic properties of these new type of N-metalated 1,2,3-triazol-5-ylidene species, copper(I) complexes bearing also an imidazol-2-ylidene ligand were synthesized. Deprotonation of cationic molybdenum or rhenium triazole complexes, **1** or **3** respectively, with a slight excess of KN(SiMe₃)₂ in THF at -78 °C, in presence of [CuCl(IPr)] (IPr= 2,6-(diisopropyl)phenylimidazol-2-ylidene) afforded cationic bis(carbene) complexes [Cu(IPr)(MetzNHC^M)]OTf (M= {Mo(η^3 -C₄H₇)(bipy)(CO)₂} **7**, {Re(bipy)(CO)₃} **8**; see Scheme S2 in the Supporting Information). The ¹H NMR spectra of the new compounds **7** and **8** in CD₂Cl₂ indicate the presence of one {Cu(IPr)} fragment per each {M(bipy)} moiety, and clearly show the disappearance of a 1,2,3-triazole CH group, while the remaining CH occurs at 6.94 ppm and 6.68 ppm for molybdenum and rhenium complexes, respectively. The different electronic nature of the two NHCs is clearly appreciated in the ¹³C NMR spectra of **7** and **8**, which show the signal of the 1,2,3-triazol-5-ylidene carbene atom about 25 ppm highfield shifted from the one corresponding to the imidazol-2-ylidene carbon (*i. e.* for complex **7** these signals are observed at 155.0 and 181.6 ppm, respectively).¹⁴ Whereas the chemical shifts corresponding to the latter (Cu-IPr) are very close to those of similar complexes (for example $\delta_{\text{C(NHC)}}$ in [CuCl(IPr)] is 180.6 ppm in CDCl₃),¹⁵ the signals of the new triazolylidene carbon atoms appear at higher fields than those reported for copper(I) 1,2,3-triazol-5-ylidene complexes (in the range from 162 to 167 ppm).^{4b,16} The molecular structure of the rhenium derivative **8**, determined by X-ray diffraction, shows the Cu atom bonded to the triazol-5-ylidene and imidazol-2-ylidene ligands in a linear disposition (Figure 1b). Both Cu-C bond distances are equivalent (Cu1-C22 1.906(6) Å and Cu1-C5 1.888(7) Å), but shorter than those found in normal

imidazol-2-ylidene complexes such as [CuCl(IMes)] and [CuCl(IPr)] (1.956(10) Å and 1.953(8) Å, respectively), and fitting well with those reported for Cu(MIC) complexes.^{4b,16}

Finally, we decided to test the ability of the silver bis(triazolylydene) complexes **2** and **4** to transfer the N-metalated MIC ligands to other metal fragments. Transmetalation was easily achieved with Rh(I) and Ir(I) metal precursors, affording immediately, at low temperature, cationic bis(triazolylydene) complexes **9-12** (Scheme 2). Formation of the neutral monocarbene derivatives [MCl(cod)(MetzNHC)] (cod= 1,5-cyclooctadiene; M= Rh, Ir) was not observed, a fact that can be attributed to the high donor strength of the new type of 1,2,3-triazol-5-ylidene ligands. ¹³C NMR spectra of **9-12** showed the metal-bound C5 carbon signal in the range from 164.4 ppm to 162.3 ppm, *i.e.* remarkably highfield shifted compared to similar Rh(I) bis(triazol-5-ylidene),¹⁷ and neutral [MCl(cod)(MIC)] complexes previously reported.^{6,18,19}



Scheme 2. Transmetalation reactions from silver bis(triazolylydene) complexes **2** and **4** to [MCl(cod)]₂ (M= Rh, Ir), followed by reaction with CO(g).

To further assess the donor properties of the molybdenum and rhenium MICs, compounds **9-12** were reacted with an excess of CO for 10 min, leading to the corresponding *cis*-dicarbonyl derivatives **13-16** by substitution of the diene ligand, as evidenced by the signals at 5.55 and 2.35 ppm in the ¹H NMR

(CD₂Cl₂) corresponding to the free cod (Scheme 2). The IR CO vibration frequencies corresponding to the new M(CO)₂ (M= Rh, Ir) fragments are shifted to remarkably lower values in comparison with analogous complexes bearing conventional 1,2,3-triazol-5-ylidene ligands.^{4b} In fact, average wavenumber values, $\nu_{\text{av}(\text{CO})}$, for Rh(I) **13** and **15** (2025 cm⁻¹ and 2027 cm⁻¹, respectively) and for Ir(I) **14** and **16** complexes (2010 cm⁻¹ for both) are close to those values found for the same Rh and Ir fragments bearing an anionic 1,2,3-triazol-4,5-diylidene ligand,²⁰ which is clearly indicative of the strong donation ability of the new neutral 1,2,3-triazol-5-ylidene metalloligands. Accordingly, the signal of the carbene carbon atom in the ¹³C NMR spectra of compounds **13-16** is found at even higher field shifts than the corresponding cod precursors **9-12** (in the range from 154.4 ppm to 155.6 ppm in CD₂Cl₂). The molecular structure of compounds **15**¹⁰ and **16** (Figure 2) were determined by X-ray diffraction, showing the square planar coordination of the Rh(I) or Ir(I) atom, with a mutually cis-disposition of both the carbonyls and the Metz-NHC^{Re} ligands.

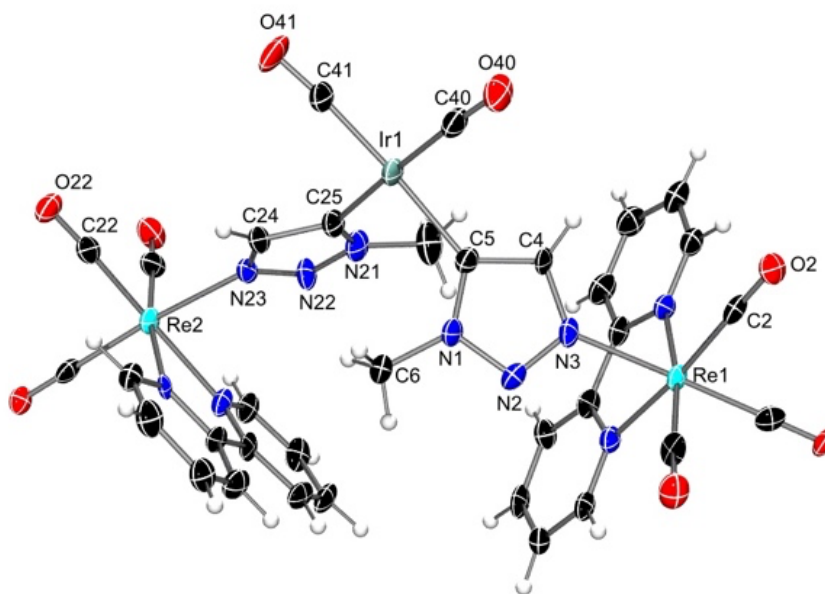


Figure 2. Molecular structure of the cation of **16**, showing thermal ellipsoids at the 30% probability level.

In summary we have found that deprotonation of the cationic triazole complexes **1** and **3** in the presence of appropriate Ag(I) or Cu(I) sources affords a new type of 1,2,3-triazol-5-ylidenes which display a carbonyl rhenium (I) or molybdenum (II) complex as substituent at the triazole N3 atom. The

spectroscopic features of the new complexes are consistent with a strong donation capability of the N-metalated MIC ligands, a characteristic that, as a general trend, has proven to be key for designing better catalysts. Furthermore, the silver 1,2,3-triazol-5-ylidene complexes act as highly efficient carbene transfer reagents under mild conditions towards Rh(I) and Ir(I) metal precursors. These results provide a radically different strategy for tuning the electronic properties of 1,2,3-triazol-5-ylidene metal complexes, a task that remains challenging through the widely employed click reaction, and consequently broadens their potential properties and applications.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge: Synthetic and computational details, including preparative procedures, spectroscopic data and NMR spectra for the characterization of compounds (PDF).

Cartesian coordinates of computed complexes (XYZ).

CCDC 2100367-2100370 (compounds **4**, **6**, **8** and **16**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Notes

The authors declare no competing financial interest.

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SYNOPSIS

Cationic rhenium(I) or molybdenum(II) carbonyl complexes bearing a 1-methyl-1,2,3-triazole ligand behave as triazolium salts, affording, after deprotonation in the presence of appropriate metal precursors, 1-methyl-1,2,3-triazol-5-ylidene metal complexes. Transmetalation from silver (I) bis(triazolyldene) species to other metals, such as Rh(I) or Ir(I) is easily achieved.

