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Beyond click chemistry: spontaneous C-triazolyl transfer from copper to rhenium and transformation into mesoionic C-triazolylidene carbene†

Celedonio M. Álvarez, Luis A. García-Escudero, Raúl García-Rodríguez and Daniel Miguel*

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The exceptional versatility of the 1,2,3-triazole ring in tridentate carbonyl rhenium complexes has been explored starting from a "click chemistry" unexpected product obtained from the spontaneous copper to rhenium transmetalation, which opens the way to successive transformation to C-triazolyl and triazolylidene mesoionic carbene.

Copper catalyzed azide–alkyne cycloaddition (CuAAC) has become ubiquitous in nearly all areas of chemistry. The reaction was first reported independently by the groups of Meldal[1] and Sharpless[2] in 2002, and it has been applied successfully in many fields.[3]

There has been increasing interest in the use of CuAAC for the derivatization of ligands.[4,5] In most cases the triazole ring is coordinated through one of the nitrogen atoms, with there being only a few examples of complexes containing C-bonded triazolyl.[6] Triazolyl copper(I) intermediates have been used recently as transmetalation reagents for iridium complexes.[7]

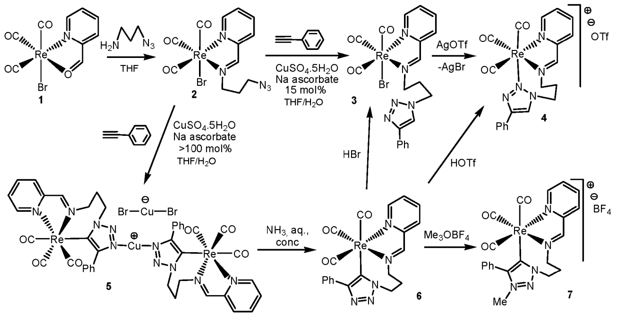
Albrecht and co-workers have recently reported that the methylation of the triazole ring and subsequent treatment with Ag_2O in the presence of a metal-halide complex can introduce the 1,2,3,-triazolyl-4,5-ylidene bonded through C-5 to the metal,[8] thus acting as a mesoionic carbene (MIC) pertaining to the class of *abnormal*-N-Heterocyclic Carbenes (*a*-NHCs).[9] The interest in triazolylidene ligands has expanded quickly in the last three years and a variety of complexes with different metals have been reported, some of which have been used in catalysis.[10] Bertrand *et al.* reported the preparation of stable bis-1,2,3-triazolyl-5-ylidene (i-bitz) ligands.[11] In most cases the ligands are introduced following original Albrecht's method, *i.e.* alkylation of the triazole ring followed by treatment with Ag_2O. However, Gandelman *et al.* have used an alternative route, by alkylation of a C-triazolyl ring of a pincer ligand, previously introduced by deprotonation with a base.[12]

In contrast to the well-known NHCs derived from imidazolium rings,[13] the mesoionic carbenes derived from 1,2,3-triazolylidene rings exhibit better donor properties.[11] Some interesting NHCs complexes of group 7 metals have been reported recently[14] but, as far as we know, there is no previous report of complexes of group 7 metals with 1,2,3-triazolylidene MICs.

We are currently interested in the use of complexes containing pyridine-2-carboxaldehyde as k^2(N,O) ligands in metal complexes[15] as convenient precursors for iminopyridine complexes *via* Schiff base condensation with primary amines,[16] with the aim of developing a methodology for the application of this reaction in the functionalization of amino acids and amino esters.[17] In the context of these studies it was expected that successive use of Schiff reaction and CuAAC could be a convenient method for preparation of triazolyl-substituted iminopyridines.

Herein we wish to report the use of CuAAC for the derivatization of metal carbonyl compounds to afford a new complex in which the triazolyl group acts as a bridge between Re and Cu after transmetalation. This is, as far as we know, the first example of a triazole ring acting as a ligand both through C and N. Additionally, the copper can be easily removed to give a Re triazolyl which can be converted into a mesoionic C-triazolylidene carbene.

Complex **1** containing pyridine-2-carboxaldehyde (pyca) as a chelate k^2(N,O) ligand reacts with 3-azido-1-propylamine in refluxing MeOH to give, after workup, orange microcrystals of **2** (Scheme 1), which was characterized by analytical and spectroscopic methods (see ESI† for experimental details and spectroscopic data). An X-ray determination on a crystal of **2** (see Fig. S1, ESI†) confirmed the formation of the iminopyridine ligand arising from the Schiff base condensation of the amine



Scheme 1 Reaction schemes for the preparation of new complexes.

GIR-MIOMeT-IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena, s/n 47005, Valladolid, Spain. E-mail: dmsj@qi.uva.es; Fax: +34 983423013; Tel: +34 983184096

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group with the coordinated aldehyde, and the presence of the azide group in the pendant arm of the iminopyridine.

Treatment of **2** with phenyl acetylene in the presence of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate under catalytic conditions (15–20 mol%) in THF:water produced the expected complex **3** bearing a triazole ring from the [3 + 2] cycloaddition of the azide and acetylene groups. Spectroscopic data for complex **3** are in agreement with the structure depicted in Scheme 1. The coordination ability of the pendant triazole ring in **3** can be exploited to obtain cationic complexes *via* bromide abstraction with silver triflate, to afford complex **4**.[18]

In the course of the CuAAC reaction to give **3** from **2**, IR monitoring in solution revealed the presence of a small amount of an unexpected product **5** with bands at 2017 vs. 1921 s, 1904 vs. cm^{-1} (*cf.* 2026 vs. 1927 s, 1903 s, cm^{-1} for **2**). It was also observed that the addition of increasing amounts of a copper reagent led to the presence of larger amounts of **5**. Indeed when a stoichiometric amount of copper and ascorbate was added at the beginning, the reaction afforded **5** as the only product, which could be isolated as orange-red microcrystals. Better yield and shorter reaction times are obtained by using a slight excess (1.2 : 1) of Cu/ascorbate. An X-ray determination showed that the structure of **5** consists of a $CuBr_2^-$ anion and a cation in which one copper atom is bonded to two *N*-triazolyl-$(CH_2CH_2CH_2N{=}CPy)Re(CO)_3$ fragments. Both anion and cation are centrosymmetric, with the copper atoms Cu(1) and Cu(2) placed in the centres of symmetry of the anion and cation, respectively. The connectivity sequences propyl–N(3)–N(4)–N(5) and phenyl–C(4)–C(5) confirm unambiguously that the triazole ring is C-bonded to Re and N-bonded to Cu. This situation is quite unexpected since, as far as we know, there is no precedent of a triazole ring acting simultaneously as C- and N-donor.

A rationale for the process is presented in Scheme 2: the copper triazolyl resulting from the cycloaddition (**A**) transfers the triazolyl to rhenium in exchange for Br to give **B**, in which the copper atom remains bonded to the triazole ring through one N atom, followed by recombination to give the final product **5**. Similar transmetalations from Cu carbenes have been reported by Cazin and Albrecht.[19]

As shown in Fig. 1, the cation of **5** can be regarded as a copper(I) complex having two neutral N-donor ligands. To test whether the Re moiety would be stable on its own, it was deemed to be of interest to liberate the ligands. A CH_2Cl_2 solution of **5** was stirred with aqueous concentrated ammonia for 1 h. IR monitoring showed a slight change in the *ν*(CO) stretching. Subsequent workup afforded **6** as pale yellow microcrystals. An X-ray determination (Fig. 2) confirmed that **6** is the expected mononuclear rhenium tricarbonyl complex with the tridentate (N,N,C) triazolylpropyliminopyridine. The ^{13}C NMR spectrum shows the signal for the carbon bonded to rhenium at 153.5 ppm, slightly shifted from that of the parent **5** (153.8 ppm).

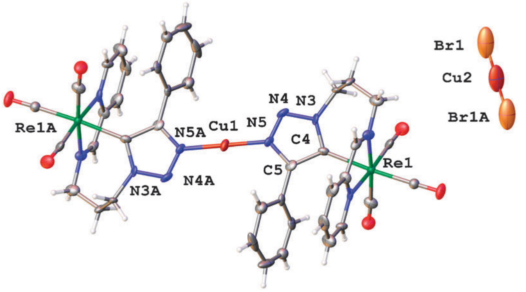


Fig. 1 Structure of **5** showing the atom numbering. Both anion and cation are centrosymmetric, with only one-half of each contained in the asymmetric unit.

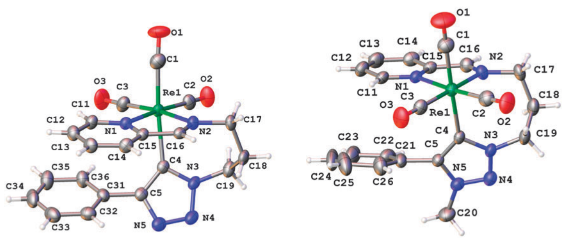
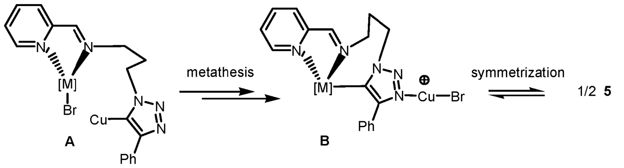


Fig. 2 Structures of **6** (left) and the cation of **7BF$_4$** (right), showing the atom numbering. Only one of the two independent molecules of 7 is shown. The geometrical parameters of the other molecule are not significantly different from the one shown.



Scheme 2 Metathesis of the intermediate copper C-triazolyl and subsequent symmetrization to give the final product.

The steps leading from **1** to **2** (Schiff base condensation) and from **2** to **5** (cycloaddition and triazolyl transfer) were performed in a sequential one-pot fashion, since the isolation of **2** is not required, as the only by-product of the Schiff reaction is a small amount of water, and the transformation of **2** into **3** or **5** is done in THF/water (see ESI†).

Upon addition of trimethyloxonium tetrafluoroborate to a solution of **6** the IR spectra show a change in the *ν*(CO) absorptions from 2012 vs. 1912 s, 1899 s, cm^{-1} to 2023 vs. 1923 s, 1905 s cm^{-1}, which is consistent with the formation of the cationic complex **7** (Scheme 1). An X-ray determination (Fig. 2) confirmed the methylation of the nitrogen in position 3, converting the triazolyl ring into a triazolylidene. This heterocyclic structure formally contains a positive and a negative charge in the same ring and can thus be regarded as a mesoionic carbene. The geometry of the triazole ring is not significantly changed upon going from **6** to **7**. The Re–C distance is shortened from 2.202(6) Å in **6** to 2.175(7) and 2.173(7) Å in **7BF$_4$**, and the NMR signal for the carbon bonded to Re changes from 153.5 ppm in **6** to 162.1 ppm in **7**, all of which are consistent with the change from an anionic triazolyl to a carbene-like triazolylidene.

Treatment of triazolyl complex **6** with acid produces instantaneous protonation of the nitrogen, which can be reverted by treatment with Na_2CO_3. When **6** was heated with a slight excess of HBr (aq.) for 2 h, it was quantitatively converted into the bromo complex **3**, according to IR and NMR data. Similarly, heating **6** with HOTf in THF (4 h) produced the triflate salt of the cation **4**.

In conclusion, the successive use of Schiff base condensation and CuAAC on the pyca complex is a convenient way to obtain triazolyl-functionalized iminopyridines, which can be used upon halide abstraction to produce cationic complexes with the triazole ligand acting as (N,N,N) tridentate. When the copper reagent used for the cycloaddition is added in a stoichiometric amount, a triazolyl transfer produces a cationic complex in which the triazolyl ring is C-bonded to Re and N-bonded to Cu. This is an unprecedented coordination mode for the triazolyl ligand. Thus, choosing stoichiometric *vs.* catalytic conditions directs the C or N coordination of the triazole ring. The copper can be extracted with aqueous ammonia, leaving a mononuclear neutral Re complex with the triazolylpropyliminopyridine acting as a (N,N,C) anionic tridentate ligand. Reaction with trimethyloxonium tetrafluoroborate yields a cationic complex in which the triazolylidene ring acts as a mesoionic carbene. To close the cycle, protonolysis of the Re–C-triazolyl produces complexes with uncoordinated or N-coordinated triazole depending on the counter anion used.

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