Towards new coordination modes of 1,2,3-triazolylidene: controlled by the nature of the 1st metala
tion in a heteroditopic bis-NHC ligand†

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An unusual effect of the first metal coordination of a heteroditopic N-heterocyclic carbene ligand (L2) towards the coordination behavior of 1,2,3-tzNHC is explored. The first metal coordination at the ImNHC site (complexes 3 and 4) was noted to substantially influence the electronics of the 1,2,3-triazolium moiety leading to an unprecedented chemistry of this MIC donor. Along this line, the RhIII/IrIII-orthometalation in complexes 4 makes the triazolium C4–H more downfield shifted than C5–H, whereas a reverse trend, although to a lesser extent, is observed in the case of the non-chelated PdII-coordination. This difference in behavior assisted us to achieve the selective activation of triazole C4/C5 positions, not observed before, as supported by the isolation of the homo- and hetero-bimetallic complexes, 5, 6 and 7–9 via C5– and C4-metalation, respectively. Furthermore, the %ννυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυνυ
unsubstituted triazolium salts, are rarely studied (Fig. 1).12,13 This might be due to the availability of two backbone carbons (C4 and C5), which could, in principle, be deprotonated to yield either C4− or C5− derivatives, which could be the driving force for such metalation at the C5− position.

Based on these literature reports, we engaged ourselves in developing strategies for selective activation of the backbone protons (C4− and C5−H) of the unsubstituted 1,2,3-triazolium salt as this will open up a new family of metal-NHC complexes for various applications including catalysis (activities of these regioisomeric metal complexes are expected to be different). We

Fig. 1 Comparison of previous reports on 1,2,3-triazolylidene complexes with the present work.
hypothesized that either some electronic or steric modulation could help in achieving this. In this line, along with our interest towards hetero-bimetallic complexes,\textsuperscript{10,11}b we have now designed an unsymmetrical bis-azolium salt \([\text{L2-H}_2\text{Br}_2]\) which possesses a triazolium group substituted with an \(N\)-phenyl-para-imidazolium moiety. The first metalation occurs at the imidazolium end as its \(C_2\)-H acidity is more compared to that of the triazolium backbone protons and thus, provides us the unique opportunity to control the subsequent metalation either at the \(C_4\)- or \(C_5\)-position of the triazolium group. Accordingly, mono- and orthometalation of \([\text{L2-H}_2\text{Br}_2]\) with \(\text{Pd}^{\text{II}}, \text{Au}^{\text{I}}\) and \(\text{Pd}^{\text{II}}, \text{Rhl}^{\text{II}}\) precursors yielded non-orthometalated (3) and orthometalated (4a and b) analogues, respectively which were detected to impart an unprecedented influence on the triazolium \(C_4/C_5\)-H chemical shifts and thus, essentially on their reactivities. This effect was utilized for the synthesis of their bimetallic counterparts \(\text{5, 6 from 3 and 7–9 from 4} \) \textit{via} selective activation of either the \(C_4\)- or \(C_5\)-H which was unequivocally supported by detailed NMR analyses along with the X-ray crystallographic studies.

**Results and discussion**

Previous reports on unsubstituted 1,2,3-triazolium salts with \(\text{Ir}^{\text{III}}\)- and \(\text{Pt}^{\text{II}}\)-centers\textsuperscript{12,13} suggest that metalation occurs at the \(C_5\)-position of the triazole ring. However, it should be noted that these complexes are of the cyclometalated type which might have some influence on the metalation behavior. To understand this in detail, at the outset, we intended to study the chemistry of simple \(C_4/C_5\)-backbone unsubstituted mesoionic carbene precursors such as the click derived \([\text{L1-H}]\text{Br}\) with \(\text{Pd}^{\text{II}}\) and \(\text{Au}^{\text{I}}\) centers (Scheme 1a) as they do not generally prefer the chelate complex formation \textit{via} orthometalation. After synthesis, the NMR analyses of \([\text{L1-H}]\text{Br}\) reveal that the \(C_7\)- and \(C_8\)-H resonances have very close chemical shift values (\(\delta = 10.05\) and 10.16 ppm, respectively), which might pose difficulties to its selective deprotonation cum metalation.

Nevertheless, \([\text{L1-H}]\text{Br}\) was first reacted with \([\text{Pd(CH}_3\text{CN})_2\text{Cl}_2]\) under suitable conditions (Scheme 1a) and the \(^1\text{H}\) NMR spectrum with only one triazolylidene backbone proton along with a \(\text{Pd}^{\text{II}}\)-MIC \(^{13}\text{C}\)(\(\text{H}\)) signal at \(\delta = 139.5\) ppm suggest the formation of a monopalladium complex. The X-ray crystallographic analysis disclosed the structure of complex 1 (Scheme 1b) in which the non-cyclometalated \(\text{Pd}^{\text{II}}\)-center is attached at the \(C_5\)-position of MIC ligand \(\text{L1}\). To ascertain whether this is the preferred coordination mode of the ligand under consideration (\(\text{L1}\)) or not, we then attempted the synthesis of an analogous \(\text{Au}^{\text{I}}\)-complex (Scheme 1a). We first proceeded with the most common transmetalation strategy \textit{via} \(\text{Ag}^{\text{I}}\)-NHC complex formation using \(\text{Ag}_2\text{O}\). To our surprise, formation of a mixture of \(C_4\)- and \(C_5\)-ylidene coordinated \(\text{Au}^{\text{I}}\)-complexes\textsuperscript{15} was observed even at room temperature, which could be due to the formation of both \(C_4\)- and \(C_5\)-ylidene coordinated \(\text{Ag}^{\text{I}}\) complexes having similar stability and/or comparable carbene transfer efficiency.\textsuperscript{12} This observation clearly suggests that both the backbone protons \((C_4/C_5\text{-H})\) are susceptible towards deprotonation. However, a \(C_5\)-ylidene coordinated \(\text{Au}^{\text{I}}\)-complex 2 was exclusively obtained in good yield (80%) \textit{via} a \(\text{Cs}_2\text{CO}_3\) assisted metalation strategy and the multinuclear NMR data along with the \(^1\text{H}\)-\(^1\text{H}\) NOESY spectrum (Fig. S10†) confirmed the coordination of \(\text{Au}^{\text{I}}\) at the \(C_7\)-position of \(\text{L1}\). This conclusion was established by the molecular structure determination \textit{via} X-ray crystallography (Scheme 1b).

After studying the coordination behavior of the simple MIC ligand \(\text{L1}\), we started investigating the possibilities of selective triazolium backbone activation. In this direction, as per our postulated electronic modulation, we designed an unsymmetrical bis-azolium salt \([\text{L2-H}_2\text{Br}_2]\), containing an imidazolium group along with a 1,2,3-triazolium moiety, the precursor for a bissarcarbene ligand. \([\text{L2-H}_2\text{Br}_2]\) was synthesized as an air stable white powder in excellent yield (94%) following the multistep procedure as detailed in Scheme 2. The \(^1\text{H}\) NMR analysis reveals the most downfield shifted imidazolium \(N\)-CH–N proton resonance at \(\delta = 10.20\) ppm, whereas the two triazolium backbone \(N\text{-CH}\) protons were observed at \(\delta = 9.79\) \((C_5\text{-H})\) and 9.37 \((C_4\text{-H})\) ppm (confirmed by 2D NMR spectroscopy).

![Scheme 1](image1.png)

**Scheme 1**: (a) Synthesis of \([\text{L1-H}]\text{Br}\) and its palladium (1) and gold (2) complexes: (i) \(\text{NaNO}_2, \text{HCl/H}_2\text{O}\) (10% solution), 0 °C, 1 h; (ii) \(\text{NaNO}_2, 0^\circ \text{C-RT, 12 h}\); (iii) \(\text{vinyl acetate, reflux, 24 h}\); (iv) \(\text{EtBr, CH}_3\text{CN, reflux, 24 h}\); (v) \(\text{Pd(CH}_3\text{CN})_2\text{Cl}_2\), \(\text{Cs}_2\text{CO}_3\), \(\text{KBr, CH}_3\text{CN/pyridine, 70 °C, 24 h}\); (vi) \(\text{[Au(SMe}_2\text{)]Cl, C}_5\text{C}_5\text{CO}_2\), \(\text{CH}_3\text{CN, 70 °C, 24 h}\). (b) Molecular structures of 1 and 2 with ellipsoids at a 50% probability level. Hydrogen atoms except \(H_8\) and \(Me\) moieties of the \(N\)-\(Et\) groups are omitted for clarity. Pyridine is shown in capped stick.

![Scheme 2](image2.png)

**Scheme 2**: (a) Synthesis of bisazolium salt, \([\text{L2-H}_2\text{Br}_2]\): (i) \(\text{NaNO}_2, \text{HCl/H}_2\text{O}\) (10% solution), 0 °C, 1 h; (ii) \(\text{NaNO}_2, 0^\circ \text{C-RT, 12 h}\); (iii) \(\text{vinyl acetate, reflux, 24 h}\); (iv) \(\text{imidazole, K}_2\text{CO}_3, \text{CuO, DMSO, 150 °C, 48 h}\); (v) \(\text{EtBr, DMF, reflux, 24 h}\). (b) Molecular structure of \([\text{L2-H}_2\text{Br}_2]\) with ellipsoids at a 50% probability level. Hydrogen atoms except \(H_5, H_{12},\) and \(H_{13}\) countorniers, solvent of crystallization and Me moieties of the \(N\)-\(Et\) groups are omitted for clarity.
It is worth mentioning that the difference in chemical shifts of the triazolium backbone protons became more prominent after the installation of the imidazolium moiety in [L2-H2]Br2 as compared to that in [L1-H]Br. This indicates some electronic influence of the installed imidazolium moiety on the triazolium unit, which would probably be beneficial for the selective activation of its backbone protons. Moreover, the relatively higher acidity of the imidazolium N–CH–N proton than that of the triazolium ones implies that the first metalation should happen preferably at the imidazolylidene site, which would provide us with a unique opportunity to fine tune the electronics of the triazolium moiety via first metalation. Similar behavior was observed previously with a related unsymmetrical bis-azolium salt and was attributed to the difference in acidities of the azolium moieties. Finally, the structure of [L2-H2]Br2 was confirmed by X-ray crystallographic analysis (Scheme 2b).

With the well characterized bis-azolium salt [L2-H2]Br2 in hand, we proceeded to study its metalation behavior. Initially [L2-H2]Br2 was treated with [Pd(CH3CN)2Cl2] in the presence of Cs2CO3 under the conditions shown in Scheme 3a. The NMR analyses confirmed the formation of complex 3 via coordination of a PdII-center to the imidazolylidene moiety, suggested by the absence of the most downfield shifted proton in the 1H NMR spectrum as well as the PdII-bound ImNHC 13C{1H} NMR signal at δ = 150.2 ppm. The chemical shift values of the backbone protons (δ = 9.92 (C4-H) and 10.24 (C5-H) ppm) were assigned from the NOESY spectrum (Fig. S15). Finally, the X-ray crystallographic analysis confirmed the coordination of PdII to the imidazolylidene donor (Scheme 3b). Before proceeding towards the synthesis of bimetallic complexes from 3, we also synthesized the IrIII-complex of [L2-H2]Br2, 4a/a' in good yields of 78–80%. The absence of the imidazolium proton of [L2-H2]Br2 and the observed integration of 3 instead of 4 aryl protons in the 1H NMR spectrum along with the 13C{1H} NMR signal for the IrIII, ImNHC at δ = 165.8 ppm suggest the attachment of IrIII to the imidazolylidene donor and the phenyl ring in an orthometalated fashion in complex 4a. This is further substantiated by the diastereotopic nature of the imidazolium N–CH2 protons (two multiplets of one proton intensity at δ = 4.24 and 4.40 ppm).

The X-ray crystallographic analysis of a single crystal of 4a' establishes the structure of the monoiridium complex (Scheme 3b) as concluded from NMR analyses. Interestingly, the 2D-NOESY (Fig. 2) spectrum of 4a reveals that the triazolium C4-H is significantly downfield shifted (δ = 9.86 ppm) compared to C5-H (δ = 9.05 ppm).

In order to confirm this switching of triazolium backbone proton chemical shifts upon orthometalation, we also synthesized the analogous RhIII-complex, 4b (Scheme 3). The NMR analysis confirmed that the RhIII-center also coordinates to the ImNHC in a similar way to IrIII and importantly, has a comparable influence on the triazolium proton chemical shifts (δ = 9.83 and 9.09 ppm for C4-H and C5-H, respectively), in sharp contrast to that observed in the case of the non-orthometalated PdII-complex 3. This may be attributed to the planar orthometalated RhIII/IrIII-center, which possibly attracts some electron density from the triazolium ring making the C4-H more acidic than C5-H.

All the above findings from the 1st metalation of ligand [L2-H2]Br2 ascertain that the nature of metal coordination offers substantial electronic influence on the triazolium moiety and thus, governs the chemical shifts, which would essentially control the activity of its backbone protons. It is in line with previous observations by several research groups that the coordination mode of a metal centre and its orientation after metatation strongly influence the site-selective C–H activation due to some electronic effect in the resulting system.

With this definite idea about the electronic effect of the first metal coordination, we focused on the synthesis of the corresponding bimetallic complexes from 3 and 4. First, the monopalladium complex, 3 was reacted with [Pd(CH3CN)2Cl2] (Scheme 4a) and the product was isolated in good yield (85%). The NMR spectroscopic analyses provided primary evidence for

**Scheme 3** (a) Synthesis of palladium (3), iridium (4a and a'), and rhodium (4b) complexes: (i) [Pd(CH3CN)2Cl2], Cs2CO3, KBr, CH3CN/pyridine, RT, 12 h. (ii) [M(Cp*)Cl2] (M = Ir/Rh), NaOAc, K2CO3/Cs2CO3, KBr (for 4a and b) or KI (for 4a'), CH3CN, 75 °C, 24 h. (b) Molecular structures of 3 and 4a' with ellipsoids at 50% probability level. Hydrogen atoms except H15/H16 in 3 and H20/H21 in 4a', counteiors, and the Me groups of N–Et moieties are omitted for clarity. Pyridine and Cp* moieties are shown in capped stick.

**Fig. 2** 2D-NOESY NMR spectrum of 4a showing the interaction of triazolium C4–H with the N–CH2 protons of the ethyl group.
the homobimetallic complex (5) formation. First of all, the \(^{13}\text{C} \{^1\text{H}\}\) resonances at \(\delta = 150.6\) and 140.4 ppm, concluded to be \(\text{Pd}^{II}\)-immNHC and \(\text{Pd}^{II}\)-MIC, respectively from the HMBC spectrum (Fig. S31†), confirm the attachment of two \(\text{Pd}^{III}\)-centers to ligand 1,2, which was also supported by the ESI-mass analysis. Furthermore, a resonance at \(\delta = 7.74\) ppm in the \(^1\text{H}\) NMR spectrum was assigned to the triazole backbone \(\text{C}_4\)-H based on the NOESY spectrum (Fig. S32†), indicating the \(\text{Pd}^{III}\)-coordination at the triazolylidene \(\text{C}_3\)-position. Finally, the single crystal X-ray crystallographic analysis confirmed the coordination of the second \(\text{Pd}^{IV}\)-center to the \(\text{C}_3\)-position of 1,2,3-tzNHC (Scheme 4b), which was observed to have a more downfield shifted proton in 3 as per the detailed NMR analyses. To validate this further, we also synthesized another heterobimetallic (\(\text{Pd}^{III}-\text{Au}^{I}\)) complex 6 from 3 (Scheme 4) and the \(^1\text{H}\) NMR spectrum of the obtained complex suggested the formation of the expected complex. Further support for the formation of the heterobimetallic complex, 6, was obtained from the ESI-MS analysis, exhibiting the most intense peak at \(m/z = 729.8502\) for [M–Cl–py]\(^+\) (calcd. \(m/z = 729.8540\)) with the isotopic patterns matching perfectly. Coordination of \(\text{Au}^{I}\) to the 1,2,3-tzNHC \(\text{C}_3\)-position was finally established via single crystal X-ray crystallographic analysis of 6. All the above results reinforce that the more downfield shifted triazolium complex is activated during the second metalation of a \(\text{Pd}^{III}\)-NHC complex (3) of [L2-H2]Br. Keeping this in mind, we proceeded with the second metalation of the orthometalated \(\text{Ir}^{III}\)-complex 4a with the anticipated activation of the triazolylidene \(\text{C}_4\)-H. In this direction, complex 4a was reacted with [Pd(CH\(_3\)CN)\(_2\)Cl\(_2\)] using Cs\(_2\)CO\(_3\) as the base in the CH\(_3\)CN/pyridine solvent mixture and the desired \(\text{Ir}^{III}-\text{Pd}^{II}\) bimetallic complex 7 was obtained in 64% yield (Scheme 5a). The \(^1\text{H}\) NMR spectrum of 7 unveils that one of the triazolium protons of the precursor complex 4a is missing as expected and the 2D NMR data confirmed the \(\text{Pd}^{II}\)-coordination to the \(\text{C}_3\) instead of the \(\text{C}_5\)-position. This establishes the deprotonation of carbon having a more downfield shifted proton in 4a during sequential metalation and notably, the \(\text{C}_3\)-H resonance is upfield shifted to \(\delta = 7.93\) ppm in 7 from 9.05 ppm in 4a. Furthermore, the attachment of \(\text{Pd}^{II}\) to the mesoionic carbene was supported by the \(^{13}\text{C} \{^1\text{H}\}\) NMR carbene signal at \(\delta = 136.3\) ppm, which was upfield shifted compared to the corresponding \(\text{Pd}^{II}\)-bound \(\text{C}_5\)-MIC signal at 140.4 ppm in 5. Eventually, the X-ray crystallographic studies authenticate the attachment of \(\text{Pd}^{II}\) to the triazole \(\text{C}_4\) position (Scheme 4b).

In order to affirm the activation of \(\text{C}_5\) rather than the \(\text{C}_3\)-position of the triazolium moiety during the second metalation of the monoiridium complex 4a, we further synthesized the related \(\text{Au}^{I}\) complex, 8 in 61% yield, following the transmetalation procedure (Scheme 5a). The HMBC spectrum, displaying a correlation of the \(\text{Au}^{I}\)-MIC \(^{13}\text{C} \{^1\text{H}\}\) resonance with the \(\text{Tz}–\text{N}–\text{CH}_2\) resonance (Fig. S41†), provides strong evidence for \(\text{Au}^{I}\)-coordination at the triazolylidene \(\text{C}_5\) position which was ultimately established by the X-ray diffraction analysis (Scheme 5b). Furthermore, to prove the generality of this finding, we also utilized the mono-\(\text{Rh}^{III}\)-complex, 4b for the synthesis of a \(\text{Rh}^{III}-\text{Pd}^{IV}\) bimetallic complex 9 following a similar procedure used for the synthesis of complex 7 (Scheme 5). Multinuclear NMR spectroscopic along with mass spectrometric data analyses reveal the formation of the expected heterobimetallic complex, 9. Moreover, the HMBC NMR spectrum (Fig. S45†) confirms the coordination of the \(\text{Pd}^{IV}\)-center to the triazole \(\text{C}_4\) position by exhibiting a correlation between the \(\text{Pd}^{IV}\) bound tzNHC \(^{13}\text{C} \{^1\text{H}\}\) signal at \(\delta = 136.5\) ppm and the triazole \(\text{Tz}–\text{N}–\text{CH}_2\) protons at \(\delta = 5.09\) ppm, as observed in the case of the complex 7. All of the above results establish that the orthometalated coordination of the \(\text{Ir}^{III}/\text{Rh}^{III}\)-center has a distinct electronic impact on the triazolium moiety in 4a and b which plays a crucial role in achieving the selective activation of the triazole backbone \(\text{C}_4–\text{H}\) proton during the second metalation. It is worth mentioning that the complexes 7–9 represent the first ever isolated metal complexes of a \(\text{C}_5\)-unprotected 1,2,3-triazol-4-ylidene donor.

More insight into the contrasting influence of the \(\text{Pd}^{II}\) and \(\text{Ir}^{III}\)-metal centres on the second metalation was obtained from the \%\(V_{\text{bur}}\) analysis and DFT calculations. The \%\(V_{\text{bur}}\) calculated at the triazole \(\text{C}_5\) position of the monometallic complexes, 3 and 4a′ was found to be essentially similar (50.1 vs. 50.4, calculated with a sphere radius of 3.5 \(\text{Å}\), see the ESI†). This
observation clearly suggests that the selectivity observed during the formation of complexes 5/6 from 3 and 7/8/9 from 4 is primarily controlled by electronic factors. Furthermore, the difference of DFT calculated ground state energy between the representative bimetallic systems 5 with its C4-analogue, 5’ and 7 with its C5-analogue, 7’ was noted to be significant (0.7 kcal mol⁻¹ and 1.4 kcal mol⁻¹, respectively, see the ESI†) and is in favour of the experimentally observed regioisomers. Thus, DFT calculations also endorse the isolation of C5- and C4-bound bimetallic systems (5 and 7, respectively) based on the nature of the 1st metal coordination to L2.

Conclusions

In conclusion, we have uncovered an unprecedented electronic influence of the 1st metal coordination on altering the reactivity/metalation behavior of the C4/C5-unprotected 1,2,3-triazolium moiety of a bis-azolium salt, [L2-H2]Br2. Importantly, the impact of monometalation in a non-chelated (complex 3) or chelated (complexes 4a and b) fashion on the triazole backbone (C4/C5) protons could be ascertained easily by 2D NMR analysis. Crucially, these changes in the electronic nature of triazole protons assisted us to access the first ever selective metalation at either the C4- or C5-position of 1,2,3-triazolylidene as undoubtly supported by the synthesis of bimetallic complexes 5–9. Furthermore, the %V₉₄₈ calculations suggest that the observed selectivity is primarily controlled by the electronic nature of the first metal coordination. Moreover, the DFT studies of selected complexes (5 and 7) strongly support the exclusive formation of a particular regioisomer as observed experimentally. The tandem catalytic activity studies of the synthesized complexes are underway in our laboratory.

Data availability

Experimental data including experimental procedures and characterization data (NMR, ESI-MS, and single crystal X-ray); the NMR and ESI-MS spectra of the new compounds; detailed computational studies are available in the ESI†

Author contributions

A. R. conceived and designed the project. P. M. I. and C. S. T. performed the experiments. P. M. I. and A. R. wrote the manuscript and all authors approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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