

Mechanochemical Synthesis of Tripodal Tris[4-(1,2,3-triazol-5-ylidene)methyl]amine Mesoionic Carbene Ligands and Their Complexation With Silver(I)

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ABSTRACT. The conjugate acids of 1,2,3-triazolylidene mesoionic carbenes can be prepared in a straightforward fashion by alkylation of 1-substituted 1,2,3-triazoles. However, this becomes a much more challenging proposition when other nucleophilic centres are present, which has curtailed development of ligands containing multiple 1,2,3-triazolylidene donors. Herein, methylation of a series of tris[(1-aryl-1,2,3-triazol-4-yl)methyl]amines possessing both electron rich and electron deficient aromatic substituents, using Me₃OBF₄, is shown to proceed with much higher chemoselectivity under mechanochemical conditions than when conducted in solution. This provides a means to reliably access a series of tricationic tris[4-(1,2,3-triazolium)methyl]amines in good yields. DFT calculations suggest that a potential reason for this change in regioselectivity is the difference between the background dielectric of DCM solution versus the solid state, which is predicted to have a large impact on the relative

thermodynamic driving force for alkylation of the tertiary amine centre versus the triazole rings. Homoleptic silver complexes of the triazolylidene ligands derived therefrom, of formulae $[\text{Ag}_3(\mathbf{1a} - \mathbf{d})_2](\text{X})_3$ ($\text{X}^- = \text{BF}_4^-$ and TfO^-), have been isolated and fully characterized. In the case of the ligand bearing the smallest aryl substituents, **1b**, argentophilic interactions yield a triangular Ag_3 core. The $[\text{Ag}_3(\mathbf{1a} - \mathbf{d})_2](\text{X})_3$ silver salts are viable agents for transmetallation to other transition metals, demonstrated here for cobalt. In the case of **1a**, the complex $[\text{Co}^{\text{II}}(\mathbf{1a})(\text{NCMe})](\text{OTf})_2$ was obtained. Therein, the bulky mesityl substituents enforce a tetrahedral geometry, in which only the triazolylidene donors of **1a** coordinate (i.e., it acts as tridentate ligand). Transmetallation of the less sterically encumbered ligand **1b** yields 6-coordinate cobalt(III) complexes, $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{Cl})(\text{NCMe})](\text{OTf})_2$ and $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{NCMe})_2](\text{OTf})_3$, in which the ligand coordinates in a tetradentate fashion. These are the first examples of tris(1,2,3-triazolylidene) ligands containing an additional coordinating heteroatom and, more generally, of tetradentate 1,2,3-triazolylidene ligands. Crucially, we believe that the divergent chemoselectivity under mechanochemical conditions (vs conventional solution-based chemistry) demonstrated herein offers a pathway by which other challenging synthetic targets, including further multidentate carbene ligands, can be prepared in superior yields.

Introduction

N-heterocyclic carbenes (NHCs, Figure 1) are a hugely important class of spectator ligands for transition metal chemistry.¹ Their high utility can be tracked not only to their structural flexibility, which is associated with the ease of variation of their ‘wingtip’ substituents and backbone, but also to their high basicity and minimal π -acceptor character. It was later discovered by Crabtree and co-workers that NHCs can bind in an ‘abnormal’ fashion via their C-3 carbon atom (aNHC, Figure 1).² This binding mode differs from that of traditional NHCs because all resonance forms that can be reasonably

drawn for an aNHC, including that of a carbene, all possess charges. Consequently, they are referred to as mesoionic carbenes (MICs). As can be inferred from the prominence of resonance forms with negative charge at the donor carbon atom (Scheme S1), MICs display greater donor strength than NHCs.³ This makes them appealing.

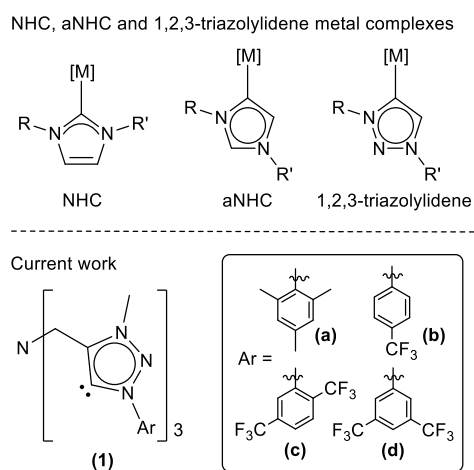


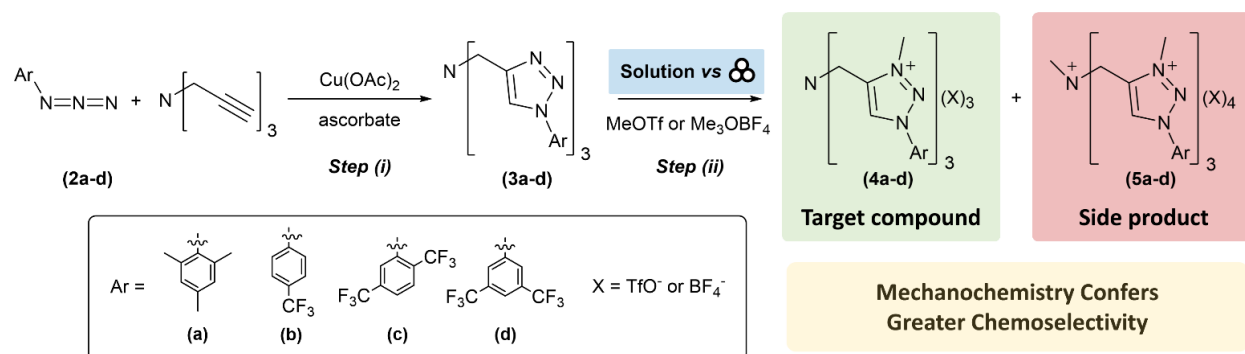
Figure 1. Top: generalized structures of metal coordinated NHC, aNHC, and 1,2,3-triazolylidene ligands. Bottom: the target tris[4-(1,2,3-triazol-5-ylidene)methyl]amine ligands **1a – d**.

MIC is not a classification that is limited to aNHCs and it now encompasses a broad range of heterocyclic ring-containing systems.³⁻⁴ Of these, the most common are 1,2,3-triazol-5-ylidenes (Figure 1). This is largely because their conjugate acids can be prepared in a straightforward fashion by alkylation of 1-substituted 1,2,3-triazoles, which are themselves constructed using the copper-catalyzed Huisgen [1,3]-dipolar cycloaddition of alkynes to aryl or alkyl azides.⁵ In principle, the aforementioned synthetic pathway allows incorporation of a wide range of substituents. This includes aryl rings with strongly electron withdrawing substituents, which is challenging for NHCs because their construction relies upon the nucleophilic reactivity of amines. However, the aforementioned alkylation step complicates synthesis of 1,2,3-

triazolylidene ligands containing additional nucleophilic centres (*i.e.*, heteroatoms). This appears to have inhibited preparation of multidentate ligands incorporating these donors. Indeed, although there are several trinucleating ligands comprised of three 1,2,3-triazolylidene donors appended to aromatic spacers,⁶ there are only a few chelating ligand systems containing more than two of them.⁷ Thus far, strategies used to circumvent this chemoselectivity problem have included the employment of protecting groups,⁸ alkylation after complexation,⁹ and synthesis of 1,3-diaryl-1,2,3-triazol-5-ylidenes either *via* [3+2]-cycloaddition of 1,3-diaza-2-azoniaallene salts and alkynes¹⁰ or by N3 arylation using diaryliodonium salts.¹¹ Mechanochemistry may also provide a solution to this problem (in some circumstances), via modulation of the chemoselectivity of the alkylation step, so we set out to investigate this possibility.

Mechanochemistry, which involves high frequency grinding of solid reagents together under solvent-free (or low solvent) conditions, is an emergent technique that has been shown in many cases to yield reaction outcomes that diverge significantly from solution state chemistry.¹² For instance, it has displayed the ability to alter product selectivity and reactivity,¹³ enable access to previously unattainable products,¹⁴ provide a means to rapidly and efficiently synthesize a range of metal complexes,¹⁵ and has been used to promote efficient solvent-free transition metal catalyzed processes.¹⁶ To test whether it might also allow for chemoselective alkylation of 1,2,3-triazole rings in the presence of other nucleophilic centres, we targeted the previously unreported tripodal tris[4-(1-aryl-3-methyl-1,2,3-triazol-5-ylidene)methyl]amine ligand framework (**1**, Figure 1). This is structurally similar to Meyer's tripodal "nitrogen-anchored" tris(NHC) ligands,¹⁷ but **1** would be expected to offer different donor properties and the possibility of smaller (5- vs 6-membered) chelate rings.

The most straightforward pathway to the conjugate acids of **1** is delineated in Scheme 1 and involves (i) synthesis of tris[4-(1-aryl-1,2,3-triazol-5-yl)methyl]amines (**3a – d**), a number of which have been reported;¹⁸ followed by (ii) methylation of the 3-position of the triazolyl rings to give the corresponding tricationic tris[4-(1,2,3-triazolium)methyl]-amines, [**4a – d**]³⁺, which has not been reported. Although step (ii) is conceptually simple, the potential for unwanted alkylation of the tertiary amine centres in **3a – d** makes it a challenging chemical transformation. Herein, we describe our efforts to achieve this reaction chemoselectively, both in solution and using mechanochemical means. The salts [**4a – d**](X)₃ (X⁻ = BF₄⁻ and TfO⁻) thereby obtained were used to form homoleptic silver(I) complexes of the corresponding triazolylidene ligands **1a – 1d**, which displayed argentophilic interactions in one case. The feasibility of transmetallation was illustrated for cobalt, with both tridentate and tetradentate coordination of the tripodal ligands being observed.



Results and discussion

As anticipated, synthesis of **3a – d** via copper-catalyzed Huisgen [1,3]-dipolar cycloaddition of aryl azides to tripropargylamine was high yielding ($\geq 79\%$), with both electron-rich mesityl azide (**2a**) and aryl azides bearing electron withdrawing trifluoromethyl-substituents (**2b – d**). Methylation of **3a – d** was attempted using the alkylating agents Meerwein's salt (Me₃OBF₄),

methyl triflate (MeOTf), and iodomethane (MeI). Reaction of **3a** with 4.5 equiv of MeI, both at room temperature and upon heating at 50 °C (in sealed tubes), resulted in methylation of only the tertiary amine centre. In other words, the C_3 symmetric species [**6a**]⁺ (Figure 2) was obtained as the sole product. As a consequence, subsequent studies concentrated only upon the methylating agents Me₃OBF₄ and MeOTf.

Methylation using Meerwein's Salt

Reaction of **3a** with 3.3 equiv of Me₃OBF₄, in DCM solution, yielded a mixture of the target compound [**4a**](BF₄)₃ and the over-methylated compound [**5a**](BF₄)₄ (Scheme 1) in a ratio of 1.00:1.16, plus under-methylated species (Figure S74). It proved very difficult to separate these mixtures *via* recrystallization. To simplify matters, we used excess (4.5 equiv) Me₃OBF₄. This eliminated formation of the under-alkylated species, and gave [**4a**](BF₄)₃ and [**5a**](BF₄)₄ in an essentially identical ratio of 1.00:1.17 (Figure S74). Separation of these two salts was possible by recrystallization. However, yields of the target compound obtained by this means of purification were poor and highly variable (7 – 34 %). Reaction of **3b** – **d** with 4.5 equiv Me₃OBF₄ in DCM solution (Figures S76 – S78) resulted in a similar (or worse) outcome to **3a**, inasmuch as extensive overalkylation was observed in all cases but it was more severe in the cases of **3b** and **3d**. More specifically, ratios of *ca.* 1.00:1.66, 1.00:1.01 and 1.00:1.47 were observed for [**4b**]³⁺: [**5b**]⁴⁺, [**4c**]³⁺: [**5c**]⁴⁺ and [**4d**]³⁺: [**5d**]⁴⁺, respectively. Regardless, purification by recrystallization afforded these compounds in similarly poor and unreliable yields as those obtained for [**4a**]³⁺.

Conducting the reaction in a different solvent could potentially impact chemoselectivity and, thereby, provide the products in improved yields. However, the high reactivity of Me₃OBF₄ greatly limits the range of solvents that can be used. In response, we turned to mechanochemistry. Pleasingly, grinding a mixture of **3a** and 3.3 equiv Me₃OBF₄ in a ball miller at 25 Hz for 30 – 120 minutes, with longer times required for larger scale reactions (as judged

by ^1H NMR spectroscopy), afforded $[\mathbf{4a}](\text{BF}_4)_3$ with much greater selectivity. It was obtained in a 1.00:0.20 ratio relative to $[\mathbf{5a}](\text{BF}_4)_4$ (**Table 1** and Figure S75) and no under-alkylated species were observed. Washing the crude product with copious amounts of hot ($70 - 80^\circ\text{C}$) water removed the overalkylated product $[\mathbf{5a}](\text{BF}_4)_4$ and reliably gave $[\mathbf{4a}](\text{BF}_4)_3$ in isolated yields of $\sim 60\%$. Thus, unlike in solution, use of excess Me_3OBF_4 was not required. Furthermore, reaction with 4.5 and 6.0 equiv of Me_3OBF_4 did not elicit a significant increase in the yield of $[\mathbf{5a}](\text{BF}_4)_4$ (Figure S75). Similarly, prolonged milling of $\mathbf{3a}$ and 4.5 equiv Me_3OBF_4 for 6 hrs did not cause an increase in the amount of $[\mathbf{5a}](\text{BF}_4)_4$ generated relative to 1 hr of milling (Figure S74), at which point reaction was already complete. In other words, the ratio of $[\mathbf{4a}]^{3+}$ to $[\mathbf{5a}]^{4+}$ does not approach the solution limit with time or in the presence of excess Me_3OBF_4 .

Application of the mechanochemical reaction protocol to $\mathbf{3b} - \mathbf{d}$ (using 3.3 equiv Me_3OBF_4) also yielded greatly improved outcomes, with respective ratios of *ca.* 1.00:0.28, 1.00:0.28 and 1.00:0.10 obtained for $[\mathbf{4b}]^{3+}:[\mathbf{5b}]^{4+}$, $[\mathbf{4c}]^{3+}:[\mathbf{5c}]^{4+}$ and $[\mathbf{4d}]^{3+}:[\mathbf{5d}]^{4+}$ (Figures S76 – S78). After purification, isolated yields of 50 – 60 % could be reliably obtained for $[\mathbf{4b}](\text{BF}_4)_3$, $[\mathbf{4c}](\text{BF}_4)_3$ and $[\mathbf{4d}](\text{BF}_4)_3$. Thus, although slightly poorer chemoselectivity was obtained for $\mathbf{3b}$ and $\mathbf{3c}$ (compared with $\mathbf{3a}$), greatly improved selectivity for methylation of the triazolyl rings was observed in all cases under mechanochemical conditions, relative to reaction in solution.

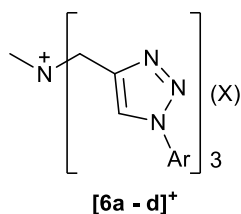


Figure 2. Side-product from methylation of the tertiary amine centre in $\mathbf{3a} - \mathbf{d}$.

Table 1. Ratios of desired to overalkylated products, $[\mathbf{4}]^{3+}:[\mathbf{5}]^{4+}$, obtained from methylation of $\mathbf{3a} - \mathbf{3d}$ by Me_3OBF_4 .^a

Reactant	[4] ³⁺ : [5] ⁴⁺	
	Mechanochemistry	DCM Solution
3a	1.00: 0.20	1.00: 1.17
3b	1.00: 0.28	1.00: 1.66
3c	1.00: 0.28	1.00: 1.01
3d	1.00: 0.10	1.00: 1.47

^aValues from ¹H NMR spectra of crude products.

The observation of remarkably high selectivity for alkylation of the 3-position of the triazole rings under mechanochemical conditions is counterintuitive, as the basicity of trialkylamine centres is, generally speaking, much higher than 1,2,3-triazoles. For instance, the pK_A of the conjugate acid of 1-methyl-1,2,3-triazole is ~1.25,¹⁹ whereas that of triethylammonium is > 10. To provide further insight into the inherent chemoselectivity favoured under both regimes, we examined the outcome of reacting **3a** with only 1 equiv of Me₃OBF₄. When performed in DCM solution, almost exclusive formation of [6a]⁺ was observed. In contrast, grinding **3a** with 1 equiv Me₃OBF₄ yielded a mixture of species, including a significant amount of [6a]⁺. Not only do these results conclusively demonstrate that methylation of the tertiary amine centre is more strongly preferred in solution, but it also implies that in both cases methyl group transfer from the tertiary amine centre to triazole must occur during formation of compound [4a]³⁺. Otherwise, [5a]⁴⁺ would be a more prominent product in the solid state and the sole product in solution. In support of possibility of methyl group transfer, we found that treating mixtures of [4a]³⁺ and [5a]⁴⁺ (obtained from reaction with 4.5 equiv Me₃OBF₄ in DCM solution) with triethylamine led to a decrease in the relative amount of [5a]⁴⁺. However, it also led to formation of other, presumably under-alkylated, species and was, therefore, not synthetically useful.

Alkylation of 1,2,3-triazole rings yields sp^2 hybridized C–N bonds and one might expect these to be stronger than the sp^3 hybridized C–N bonds formed upon reaction with the tertiary amine centres. DFT calculations support this notion, with geometry optimization for **[6a]⁺** yielding a solution that 11.7 kcal mol⁻¹ high in energy than its triazole methylated isomer (Figure 3). This difference becomes even more pronounced as the level of alkylation increases; the target compound **[4a]³⁺** is predicted to be 26.1 kcal mol⁻¹ higher in energy than its tertiary amine-methylated isomer. However, inclusion of a SMD continuum solvent model for DCM leads to a significant diminution of these differences. Under these conditions, **[6a]⁺** is calculated to be only 2.7 kcal mol⁻¹ higher in energy than its triazole methylated isomer, and **[4a]⁺** is 11.7 kcal mol⁻¹ more stable than its tertiary amine-methylated isomer. These results suggest that the dielectric constant of the reaction medium may be able to significantly modulate the relative thermodynamic favourability of triazole vs tertiary amine methylation and, thereby, impact the outcome of reaction. Furthermore, consistent with experimental observations (Figure S79), methylation of the tertiary amine centre of **3a** is most likely to occur in the first or second alkylation step, rather than later. Additionally, methyl transfer is likely to become more favoured (thermodynamically) as the level of alkylation increases. This is presumably due to the comparatively close proximity of the 3-position of the 1,2,3-triazole rings and the tertiary amine centres, which results in maximization of repulsive Coulombic forces when both of these centres are methylated. Inclusion of a dielectric field (i.e., solvation) stabilizes charge and mitigates these effects.

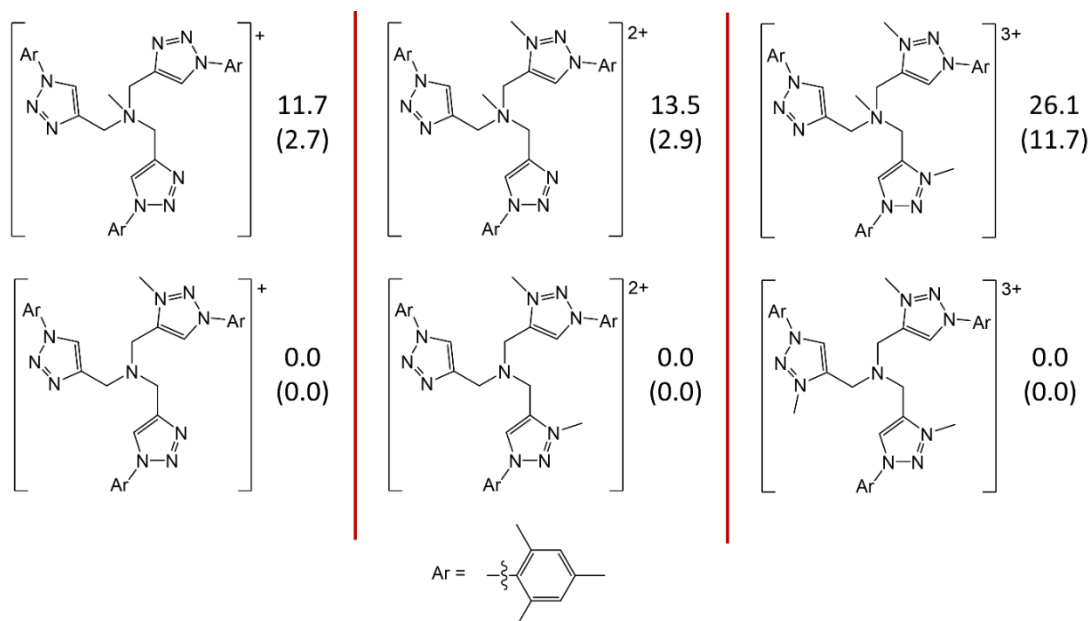


Figure 3. Structures of mono-, di- and trimethylated **3a**, plus DFT calculated free energies in both vacuum and dichloromethane. The latter are given in parentheses.

Methylation using methyl triflate

Substitution of Me_3OBF_4 by MeOTf tends to result in more complex product mixtures. For instance, although reaction of **3a** with 4.5 equiv of MeOTf in DCM solution produced the overalkylated compound $[\mathbf{5a}](\text{OTf})_4$ in small amounts, relative to the desired product $[\mathbf{4a}](\text{OTf})_3$, several other triazolium salts were formed as minor products (Figure S81). This is, presumably, due to methylation at the 2-position of the triazolyl rings, which introduces the possibility of sporadic alkylation of **3a** and, by extension, formation of a multitude of products. Layering acetonitrile solutions of the crude product routinely yielded combinations of crystals and oils. Mechanical separation of the former gave $[\mathbf{4a}](\text{OTf})_3$ in best isolated yields (~30 %) comparable to those obtained from solution-based reactions that used Me_3OBF_4 as a methylating agent. However, recrystallization did provide crystals of $[\mathbf{4a}](\text{OTf})_3$ suitable for X-ray crystallography (Figure 4 and Table S1), which confirmed our structural formulation of this compound. As was the case for Me_3OBF_4 , mechanochemical grinding of **3a** with 3.3 equiv MeOTf resulted in a cleaner reaction, with reduced amounts of side-products, than when

conducted in solution (Figure S81). As a consequence, purification was more straightforward and the desired product **[4a]**(OTf)₃ was obtained in much improved yields of > 60 %.

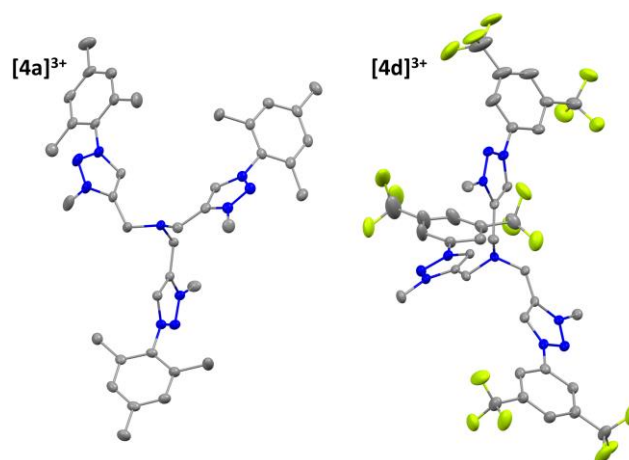


Figure 4. X-ray crystal structures of (left) **[4a]**(OTf)₃ and (right) **[4d]**(OTf)₃. Both are depicted using 50 % probability thermal ellipsoids. For clarity, hydrogen atoms, counterions and solvent molecules are omitted. White, grey, yellow-green, and blue spheroids correspond to Ag, C, F, and N atoms, respectively.

Methylation of **3b – d** using methyl triflate produced a more complicated picture. In the case of **3c**, reaction in DCM solution yielded two main products in a ratio of 1.00:1.56 (Figure S83). Based upon ¹H NMR spectroscopy (both compounds display C₃ symmetry) and mass spectrometry, the minor component corresponds to the target compound **[4c]**(OTf)₃ and the main product, **[6c]**(OTf) (Figure 2), is a consequence of methylation of *only* the tertiary amine centre (Figures S50 and S96). Although the corresponding mechanochemical reaction was found to contain a larger number of side-products, including **[5c]**⁴⁺, the relative amount of **[6c]**⁺ was greatly reduced and **[4c]**³⁺ became the main product (Figure S83). Solution-state reaction of **3b** and **3d** yielded superior outcomes in terms of ratios of **[4]**³⁺:**[5]**⁴⁺, relative to mechanochemical grinding (Figures S82 and S84). However, reaction in solution was messier, with greater numbers and larger amounts of side-products. Thus, on balance, the solid-state

reactions with **3b** and **3d** are more selective for the desired products. The relatively high solubility of triflate salts hampered separation of [**4b – d**](OTf)₃ from charged by-products. Recrystallization was the best method of purification, but it proved to be highly unreliable and low yielding. However, it did provide access to an X-ray crystal structure of [**4d**](OTf)₃ (Figure 4 and Table S1), which confirmed its identity.

Complexation by silver(I)

A number of protocols are used in generation and complexation of 1,2,3-triazolylidene ligands from their 1,2,3-triazolium conjugate acid precursors. The most direct is deprotonation to afford “free” triazolylidene, which can then be reacted with transition metal salts. However, this approach can be problematic for 1,2,3-triazol-5-ylidenes bearing 3-alkyl substituents. This is because these MICs display instability stemming from transfer of the alkyl group to the carbenic centre.²⁰ As a consequence, it is more common to first generate silver complexes of the triazolylidene ligands (by reaction with Ag₂O) and, subsequently, employ them in metathesis reactions with transition metal halide salts/ complexes. Although widely used, such silver complexes are not routinely isolated and crystallographically characterized.^{6d, 21}

Silver complexes of our MIC ligands, **1a – d**, were generated by heating mixtures of [**4a-d**](X)₃ (X = BF₄ and OTf) and Ag₂O in dimethylsulfoxide. X-ray crystallographic characterization of the products (Figures 5 and S104, Tables S2 and S4) reveals that trimetallic sandwich complexes, of formulation [Ag₃(**1a – d**)₂](X)₃, were formed in all four cases. (The structure of [Ag₃(**1c**)₂](BF₄)₃ is of poor resolution, so has been relegated to the Supporting Information.) Consistent with expectations for silver(I) coordination complexes, each Ag^I ion binds to two triazolylidene donors in a near linear fashion. These two triazolylidene donors originate from different ligands, and each tripodal ligand binds to three different Ag^I ions. As such, the tertiary amine centres remain unbound. The Ag–C bond lengths in all four complexes are typical, inasmuch as they fall in the range reported for other Ag^I complexes of 1,2,3-

triazolylidene.^{6d, 21} More complete lists of structural parameters and a more in-depth discussion of the structures of the complexes can be found in the Supporting Information.

Although the complexes of the four ligands are similar in many respects, there is one obvious difference; the Ag...Ag separations in $[\text{Ag}_3(\mathbf{1a})]^{3+}$, $[\text{Ag}_3(\mathbf{1c})]^{3+}$, and $[\text{Ag}_3(\mathbf{1d})]^{3+}$, which vary in the range 5.793(1) – 6.2809(6) Å, are significantly larger than the average value of 3.110(1) Å in $[\text{Ag}_3(\mathbf{1b})]^{3+}$. The Ag...Ag distances in the latter compound are within the van der Waals radii of Ag (3.44 Å) and are, therefore, indicative of argentophilic bonding.²² This difference can be attributed to the steric impact of the 1-aryl substituents. When sufficiently small (*i.e.*, 4-trifluoromethylphenyl), the triazolylidene donors are able to interdigitate, thereby allowing the Ag^I centres to closely approach one another. For the larger aryl substituents of **1a**, **1c** and **1d** this is not possible and the silver ions are forced apart, which prohibits argentophilic bonding.

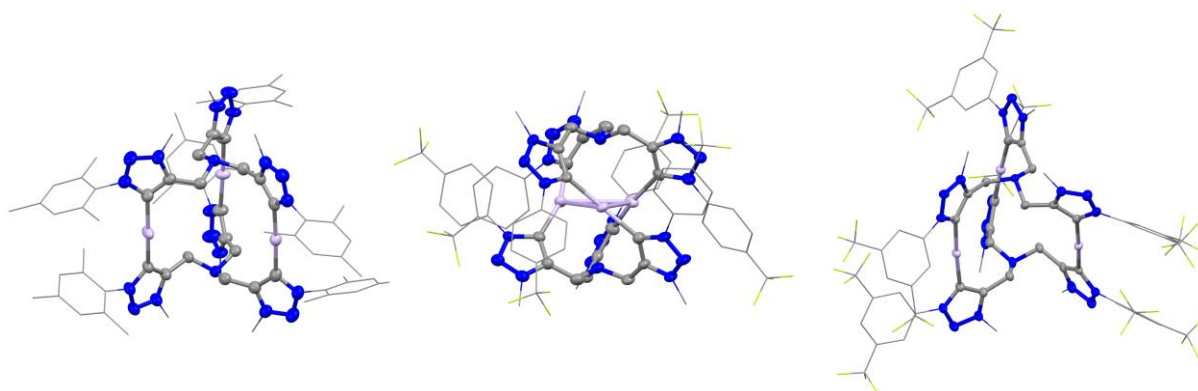


Figure 5. X-ray crystal structures of (left) $[\text{Ag}_3(\mathbf{1a})_2](\text{OTf})_3$, (middle) $[\text{Ag}_3(\mathbf{1b})_2](\text{BF}_4)_3$, and (right) $[\text{Ag}_3(\mathbf{1d})_2](\text{OTf})_3$. Whereas the methyl and aryl substituents are rendered as sticks, the remainder is depicted using 50 % probability thermal ellipsoids. For clarity, hydrogen atoms, counterions and solvent molecules are omitted. Atom colour scheme: Ag, light purple-pink; C, grey; F, yellow-green; N, blue.

To confirm the presence of argentophilic bonding in $[\text{Ag}_3(\mathbf{1b})_2]^{3+}$, DFT calculations were performed. As might be expected, this provided an electronic structure in which the highest occupied molecular orbital (HOMO) and HOMO-1 are close in energy and localized primarily

on the Ag ions, whereas the closely-spaced lowest unoccupied molecular orbital (LUMO) and LUMO+1 are triazole-based (Figure S112). More importantly, a QTAIM (Quantum Theory of Atoms in Molecules) analysis revealed clear bond critical points between the three Ag atoms, designated as blue dots in the electron density map in Figure 6, which strongly supports the presence of Ag–Ag bonding. Accordingly, geometry optimization to an “open structure” lacking argentophilic bonding, like those seen for the Ag complexes supported ligands **1a**, **1c** and **1d**, yielded a structure 31.8 kcal mol⁻¹ higher in energy than the former (Figure S113).

Conversely, we were also able to locate a “closed structure” structure, indicative of argentophilic bonding, for [Ag₃(**1a**)₂]³⁺ (Figure S114). However, it was found to be 22.3 kcal mol⁻¹ higher in energy than the crystallographically observed “open structure”. This strongly supports our previous assertion that the sterically encumbered nature of the aryl substituents in **1a**, **1c** and **1d** disfavours formation of “closed structures” (i.e., argentophilic bonding). Interestingly, solutions of [Ag₃(**1b**)₂]³⁺ contains two species that are in a solvent- and temperature-dependent equilibrium with one another (Figures S55 and S59). Given that the other silver complexes contain single species at room temperature, this is presumed to be due to a mixture of the crystallographically observed “closed” structure and a thermally accessed “open structure”.

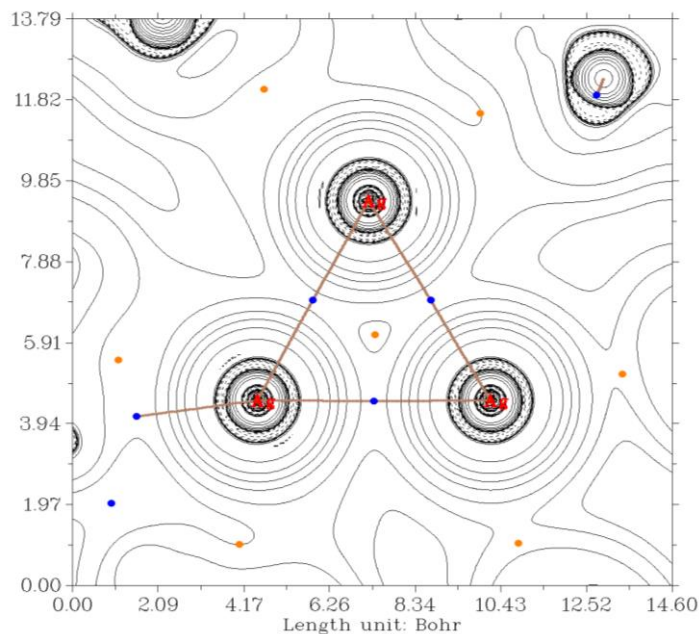


Figure 6. QTAIM map of the complex $[Ag_3(\mathbf{1b})_2]^{3+}$, which contains three Ag atoms and shows three intermetallic bond critical points (blue dots).

Illustrative examples of transmetallation

The silver salts $[Ag_3(\mathbf{1a} - \mathbf{d})_2](X)_3$ are able to perform transmetallation to other transition metals, with the steric bulk of the aryl groups impacting the mode of coordination observed. For instance, combination of $[Ag_3(\mathbf{1a})_2]^{3+}$ with two equiv of $CoCl_2$ and one equiv of $AgOTf$ in acetonitrile solution yields solely the blue cobalt(II) complex $[Co^{II}(\mathbf{1a})(NCMe)](OTf)_2$. 1H NMR spectra of this complex display five well-defined, but paramagnetically shifted and broadened peaks distributed over the chemical shift range of -2 to 80 ppm (Figure S68). This is indicative of C_3 symmetric coordination of $\mathbf{1a}$; i.e., either a tetrahedral or a trigonal bipyramidal geometry. Consistent with the presence of a high-spin cobalt(II) centre, a solution magnetic moment of 3.97 B.M. was measured.

In contrast, performing the same reaction using $[Ag_3(\mathbf{1b})_2]^{3+}$, in place of $[Ag_3(\mathbf{1a})_2]^{3+}$, afforded a yellow-orange solution. From X-ray crystallographic and electrospray ionization mass spectrometry (ESI-MS) studies (Figures 7 and S101, respectively), it is clear that the major product is the cobalt(III) complex $[Co^{III}(\mathbf{1b})(Cl)(NCMe)](OTf)_2$ (i.e., oxidation by

silver(I) has taken place). However, ^1H NMR spectroscopic measurements (Figure S70) confirm the presence of multiple minor diamagnetic impurities. Thus far, attempts to remove these impurities have been unsuccessful. In an effort to overcome this problem, $[\text{Ag}_3(\mathbf{1b})_2]^{3+}$ was reacted with 2 equiv CoCl_2 and 3 equiv AgOTf , which was intended to yield a single cobalt(III) complex, $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{NCMe})_2](\text{OTf})_3$. This was ostensibly successful but, once again, the target complex could not be separated from minor diamagnetic impurities (Figure S72 and S73). Consistent with formulation of both $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{Cl})(\text{NCMe})](\text{OTf})_2$ and $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{NCMe})_2](\text{OTf})_3$ as 6-coordinate low-spin cobalt(III) complexes, their ^1H NMR spectra display resonances that are confined to the diamagnetic region (0 – 10 ppm), with well-resolved J -coupling. Additionally, the triazolylidene donors give rise to two sets of peaks in a 2:1 ratio, which implies two triazolylidene donors are *trans* to each other and the third is *trans* to an exogenous ligand.

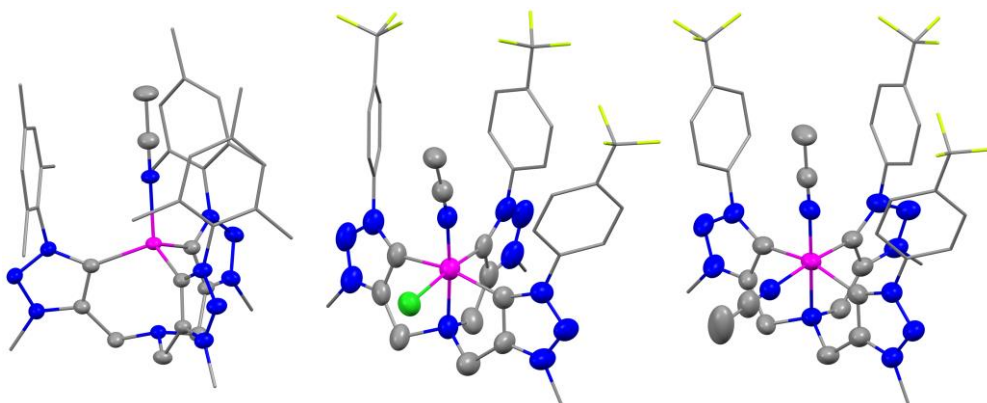


Figure 7. X-ray crystal structures of (left) $[\text{Co}^{\text{II}}(\mathbf{1a})(\text{NCMe})](\text{OTf})_2$, (middle) $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{Cl})(\text{NCMe})](\text{OTf})_2$, and (right) $[\text{Co}^{\text{III}}(\mathbf{1b})(\text{NCMe})_2](\text{OTf})_3$. Whereas the methyl and aryl substituents are rendered as sticks, the remainder is depicted using 50 % probability thermal ellipsoids. For clarity, hydrogen atoms, counterions and solvent molecules are omitted. Atom colour scheme: C, grey; Cl, green; Co, magenta; F, yellow-green; N, blue.

The origin of the differences in the coordinative behaviour of $\mathbf{1a}$ and $\mathbf{1b}$ is readily apparent from the X-ray crystal structures of the complexes $[\text{Co}^{\text{II}}(\mathbf{1a})(\text{NCMe})](\text{OTf})_2$,

[Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂, and [Co^{III}(**1b**)(NCMe)₂](OTf)₃ (Figure 7). Crystallographic data and structural parameters are listed in Tables S3 and S5, alongside other viewpoints of the structures in Figures S109 – S111. The complex [Co^{II}(**1a**)(NCMe)](OTf)₂ possesses a tetrahedral geometry ($\tau_4^{23} = 0.99$), with **1a** coordinating as a tridentate ligand via its triazolylidene donors only and a MeCN solvent ligand occupying the remaining site. As is evident from the long Co \cdots N_{amine} distance of 2.747 Å, the tertiary amine centre of **1a** remains uncoordinated. This is a similar outcome to that observed with Meyer's TIMEN^{xy1} ligand system¹⁷ and, indeed, the average Co–C and Co–NCMe bond distances of 2.016(4) and 2.066(6) Å, respectively, observed in [Co^{II}(**1a**)(NCMe)](OTf)₂ are very similar to those reported for [Co^{II}(TIMEN^{xy1})(NCMe)](BPh₄)₂ (2.036(3) and 2.035(3) Å, respectively).^{17c} Commensurate with its larger chelate ring size, the Co \cdots N_{amine} distance in [Co^{II}(TIMEN^{xy1})(NCMe)](BPh₄)₂ (3.146 Å) is significantly longer than that observed in [Co^{II}(**1a**)(NCMe)](OTf)₂.

Consistent with the inferences drawn above, [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂ and [Co^{III}(**1b**)(NCMe)₂](OTf)₃ exhibit 6-coordinate geometries. In both cases, ligand **1b** binds to cobalt in a tetradentate fashion, with the three triazolylidene donors coordinated in the equatorial plane and the tertiary amine occupying an axial position. The remaining equatorial and axial sites are occupied by chloride and/or MeCN ligands. The Co–ligand bond lengths in these complexes are typical of low-spin cobalt(III) complexes and are, as expected, significantly shorter than those of the high-spin cobalt(II) complex [Co^{II}(**1a**)(NCMe)](OTf)₂. In line with the high *trans* influence of carbene donors, the Co–C bonds for the two triazolylidene donors *trans* to one another (e.g., 1.951(7) and 1.967(6) Å in [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂) are elongated relative to that of the triazolylidene donor *trans* to the chloride/ MeCN ligand (1.895(6) Å in [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂). This also manifests in the Co–NCMe bond lengths of [Co^{III}(**1b**)(NCMe)₂](OTf)₃: 1.963(8) and 1.864(7)

Å for the MeCN ligands *trans* to triazolylidene and tertiary amine donors, respectively. Although the Co–N_{amine} bonds in [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂ and [Co^{III}(**1b**)(NCMe)₂](OTf)₃ (2.094(7) and 2.116(7) Å, respectively) are significantly longer than the Co–C distances, they are clearly indicative of coordination.

Interestingly, the angles between the mean planes of triazolylidene rings and their aryl substituents are all close to 90 ° in [Co^{II}(**1a**)(NCMe)](OTf)₂ (81.75 – 88.00 °), but are on average much smaller in [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂ and [Co^{III}(**1b**)(NCMe)₂](OTf)₃, where they range from 49.34 to 76.05 ° and 47.29 to 86.82 °, respectively. In other words, the mesityl rings in **1a** orientate strictly perpendicular to the triazolylidene rings, whereas alignment of the 4-trifluoromethylphenyl substituents in **1b** with respect to the triazolylidene rings is much more flexible (Figures S109 – S111). This is a consequence of the steric impact of the ortho-substituents on the aryl rings and it imbues the donors in **1a** with greater effective cone angles, which leads to the reduced coordination number of [Co^{II}(**1a**)(NCMe)](OTf)₂ relative to [Co^{III}(**1b**)(Cl)(NCMe)](OTf)₂ and [Co^{III}(**1b**)(NCMe)₂](OTf)₃. Furthermore, it is likely that the comparative ease of oxidation of the initially formed cobalt(II) complexes of **1b** originates from them possessing low-spin ground states and 6-coordinate geometries analogous to the isolated cobalt(III) products.

Conclusions

In summary, we have used mechanochemical means to generate the first examples of tripodal tris[4-(1,2,3-triazol-5-ylidene)methyl]amine MIC ligands (**1a** – **d**) in good yields. This allowed for remarkably high chemo- and regioselectivity in methylation of the 3-position of the 1-aryl-1,2,3-triazol-5-yl rings of **3a** – **3d** over the more basic tertiary amine centres, relative to conventional solution-based methods. Based upon DFT calculations, it can be concluded that the products obtained, [**4a** – **d**](BF₄)₃, are thermodynamically favoured, with the difference in product distributions between

solution and the solid state possibly being due to differences in the dielectric constants of their respective reaction media. Complexation of ligands **1a** – **d** by reaction of their conjugate acids with Ag₂O yielded trimetallic sandwich compounds of formulation [Ag₃(**1**)₂](X)₃. Argentophilic interactions are observed for the ligand bearing the least sterically encumbered aryl substituents (i.e., **1b**), but not the other systems.

These silver salts offer an entry point for exploration of the transition metal coordination chemistry of this family of tripodal MIC ligands. For bulky mesityl substituents (i.e., **1a**), transmetallation to cobalt(II) yielded a 4-coordinate complex, in which tridentate coordination via only the triazolylidene donors was obtained. With the reduced steric bulk of the 4-trifluoromethylphenyl substituents of **1b**, tetradentate coordination of the tripodal ligand and 6-coordinate complexes are observed. These are the first examples of tris(1,2,3-triazolylidene) ligands containing an additional coordinating heteroatom and, more generally, of tetradentate 1,2,3-triazolylidene ligands. At present, we are further exploring the transition metal coordination chemistry of this class of tripodal tris(triazolylidene) ligand systems, particularly their ability to support high oxidation states, and we will report this in due course. Lastly, it is clear that mechanochemistry is able to provide divergent outcomes even for simple transformations, such as S_N2 reactions, and we are investigating the potential of this methodology for the synthesis of other multidentate triazolylidene ligands.

ASSOCIATED CONTENT

Supporting Information

Synthetic and experimental procedures, standard molecular characterization, ¹H NMR spectral comparison of solution state and ball milling reaction product mixtures, and additional X-ray crystallographic data are provided in the Supporting Information. CIF files of the crystal

structures have been deposited in the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2013469 – 2013474, and 2058781 – 2058783.

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Notes

There are no conflicts to declare.

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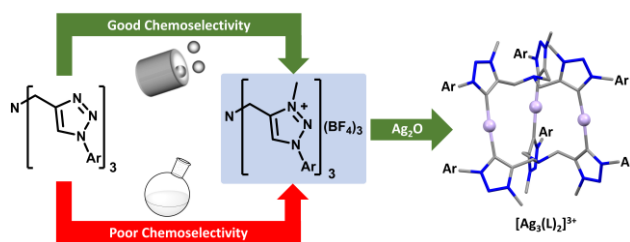
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Selective alkylation of the 1,2,3-triazolyl rings of tris[(1-aryl-1,2,3-triazol-4-yl)methyl]amines by Me_3OBF_4 , to yield a series of tricationic tris[4-(1,2,3-triazolium)methyl]amines, is complicated by the presence of the more basic tertiary amine centre. Chemoselectivity is poor when reaction is conducted using conventional solution-based methods, but greatly improved when mechanochemical techniques are employed. Based upon DFT calculations, we attribute this divergent behaviour to differences in background dielectric. Silver complexes of these tripodal mesoionic carbene ligands were synthesized and used in preparation of cobalt complexes.