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1,2,3-Triazolylidene Ruthenium(II)(\(\eta^6\)-arene) Complexes: Synthesis, Metallation and Reactivity

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Three bis(1,2,3-triazolylidene) silver(I) complexes were synthesized, and the ruthenium complexes ([RCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_5\)]RuCl\(_2\)(p-cymene) (R = C\(_6\)H\(_5\)Me, 4a, C\(_6\)H\(_5\)Pr, 4b) were isolated as major products with the minor C(sp\(^2\))-H activated products ([RCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_4\)iPr]RuCl(p-cymene) (R = C\(_6\)H\(_5\)Me, 4a, C\(_6\)H\(_5\)Pr, 4b)). In the related case where R = Ph, the species [PhCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_5\)]RuCl(p-cymene) 4c was obtained with two C(sp\(^2\))-H activated products [PhCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_4\)iPr]RuCl(p-cymene) 4\(\delta\)_2 and [([C\(_6\)H\(_4\)]CH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_4\)iPr]RuCl(p-cymene) 4\(\delta\)_3 derived from metallation of the N and C-bound arene rings. Heating a solution of 4a at 45 °C over three weeks resulted in a ruthenium(II)(1,2,3-triazolylidene) complex ([C\(_6\)H\(_4\)Me]CH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_5\)]RuCl\(_2\)) 5a, where the pendant mesityl group on the triazolylidene moiety displaced the p-cymene ligand. The complexes 4a, 4b, 4c, and 5a displayed moderate catalytic activities in base-free oxidation of benzyl alcohols to benzaldehydes and oxidative homocoupling of benzyl amines to imines using oxygen as oxidant.

Introduction

In 2002, Sharpless and Meldal et al. independently introduced Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC), commonly known as the “click” reaction, as a versatile, high-yielding and selective reaction which works under mild reaction conditions with little or no byproduct.\(^1\) The milestone discovery in synthetic organic chemistry was subsequently exploited to access triazolium salts via alkylation of triazoles selectively at the N3-position. Metallation of triazolium salts using Ag\(_2\)O has been successfully performed and the resulting silver(I)-triazolylidene complexes can be exploited for transmetallation reactions, thus offering a route to a variety of transition metal complexes. Such ligands represent a new family of mesoionic N-heterocyclic carbenes (NHCs). These ligands and their complexes have attracted considerable attention in recent years.\(^2\) In general, while free 1,2,3-triazolylidene (Fig. 1) are sensitive and decompose rapidly under the mild conditions,\(^3\) Bertrand et al. \(^4\) synthesized the free 1,3,4-trisubstituted-1,2,3-triazol-5-ylidene by the deprotonation of the 1,2,3-triazolium salt using K\(_2\)SiMe\(_3\) or KOrBu.\(^5\) The v\(_{\text{C=O}}\) stretching frequencies of the iridium dicarbonyl complex with triazolylidene ligand suggested that these ligands are slightly better donor than the normal imidazole-2-ylidene.\(^6\)

Metal complexes with triazolylidene have been exploited as catalysts in a wide variety of reactions including ring-opening metathesis,\(^7\) ring-closing metathesis,\(^8\) Suzuki coupling,\(^9\) oxidative coupling and oxidation of water,\(^10\) alcohols\(^11\) and amines.\(^12\)

Our on-going interest in Ru-carbene complexes and their applications in catalysis prompted the examination of the utility of Ru-triazolylidene complexes. Herein, we describe a series of reactions of bis(triazolylidene) silver(I) salts with [RuCl\(_2\)(p-cymene)]. The nature of the resulting species is discussed and the use of these species in the catalytic, aerobic oxidation of alcohols and oxidative coupling of benzyl amines is explored.

Results and discussion

The 1,2,3-triazoles [RCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_5\)] (R = C\(_6\)H\(_5\)Me, 1a, C\(_6\)H\(_5\)Pr, 1b, Ph 1c) were synthesized in excellent yield by heating a mixture of appropriate chloro-derivatives, phenylacetylene and sodium azide in distilled water in presence of catalytic amount of Cul (1 mol%) (Scheme 1). The reaction is regioselective as it produced only 1,4-disubstituted 1,2,3-triazoles. Thereafter, 1a, 1b and 1c were selectively methylated at N3-position by using methyl triflate generating [RCH\(_2\)N\(_2\)(NMe)C\(_6\)H\(_5\)]OTf \((R = C\(_6\)H\(_5\)Me, 2a, C\(_6\)H\(_5\)Pr, 2b, Ph 2c). Attempts to prepare the free 1,2,3-triazol-5-ylidene was attempted by reacting triazolium salts 2a, 2b and 2c with potassium bis(trimethylsilyl)amide were unsuccessful. However, reaction of 2a, 2b and 2c with Ag\(_2\)O yielded the corresponding...
silver(I) triazolylidenes species 3a, 3b and 3c, respectively. These species proved stable for months in the solid state under nitrogen at ambient temperature. While several attempts were made, structural characterization of these silver(I) triazolylidenes by single crystal X-ray analysis was unsuccessful. Mass spectrometry data suggested Schlenk equilibria result in 3a, 3b and 3c being bis-triazolylidene silver(I) salts of the general form [L₂Ag][AgCl₂]. This was supported by the observation of the major m/z peaks at 689.25, 857.44 and 605.16 in the mass spectra of 3a, 3b and 3c, respectively (Scheme 1). A similar result for a related triazolylidene has been described by Albrecht et al.1,2

These bis(1,2,3-triazolylidene) silver(I) complexes were utilized as efficient carbene transfer agents as transmetallation was successfully performed with [RuCl₂(p-cymene)]. The reaction of 3a with [RuCl₂(p-cymene)] formed ruthenium(II)(p²-arene) complex with 1,2,3-triazolylidene with C(sp²)H₃Me₂CH₂N₂(NMe)C₂Ph)RuCl₂(p-cymene) (4a₁) almost quantitatively as evidenced by the ¹H NMR spectrum of the crude reaction mixture (Scheme 2). However, a second set of signals in the ¹H NMR spectrum was also observed, which suggested the presence of a minor byproduct. Attempt to isolate this species from the crude solid by column chromatography using silica gel as stationary phase and a mixture of dichloromethane/acetone (9/1) as eluent was undertaken. A yellow band separated quickly in the column followed by a dark orange band. The first yellow band was found to be a C(sp³)-H activated product [C₂H₅Me₂CH₂N₂(NMe)C₂Ph]RuCl₂(p-cymene) (4a₂) (4 %), whereas, the second band was the expected ruthenium(II) triazolylidene complex 4a₁ (83 %). Similarly, the reaction of 3b with [RuCl₂(p-cymene)] yielded the complex [C₂H₅Me₂CH₂N₂(NMe)C₂Ph]RuCl₂(p-cymene) (4b₁) in 81 % yield together with the C(sp³)-H activated product [C₂H₅Me₂CH₂N₂(NMe)C₂Ph]RuCl₂(p-cymene) (4b₂) in 2 % yield (Scheme 2). These products (4a₁, 4a₂, 4b₁, 4b₂) are formally 18-electron species and consequently air stable. The presence of the triazolylidene moiety and the spectator arene ligand was consistent with the ¹H and ¹³C NMR spectra. As expected, NMR spectra of 4a₁ and 4b₁ are consistent with C₄ symmetry. The benzylidene-CH₂ resonances for 4a₁ and 4b₁ appeared as singlets (4a₁: 6.02 ppm, 4b₁: 6.04 ppm) as the resonances for the N-CH₃ fragments (4a₁: 3.51 ppm, 4b₁: 3.53 ppm). Two doublets (4a₁: 4.85 and 5.18 ppm; 4b₁: 4.89 and 5.22 ppm) were observed for four aromatic hydrogen atoms of the arene moiety. Down-field resonances in the ¹³C NMR spectra of 4a₁ (160.32 ppm) and 4b₁ (160.57 ppm) were attributable to the Ru-bound carbene carbon and suggested very similar donor abilities for the two triazolylidene ligands.

In contrast, species 4a₂ and 4b₂ displayed significantly different NMR spectra consistent with C₄ symmetry. Two doublets (4a₂: 5.61 and 5.94 ppm; 4b₂: 5.69 and 5.99 ppm) for the benzylidene-CH₂ were observed in the ¹H NMR spectra of 4a₂ and 4b₂. Similarly, four aromatic hydrogen atoms of the arene moiety gave rise to four doublets (4a₂: 5.23, 5.27, 5.52 and 5.57 ppm; 4b₂: 5.19, 5.24, 5.55 and 5.63 ppm). In the ¹³C NMR spectra of 4a₂ and 4b₂, the resonances for Ru-(imidazolylidene) and Ru-(C₆H₄) (4a₂: 176.09 and 180.83 ppm; 4b₂: 175.95 and 180.91 ppm) were observed downfield of the corresponding Ru-(imidazolylidene) resonances for 4a₂ (160.32 ppm) and 4b₂ (160.57 ppm). These data while similar to other triazolium-Ru complexes,18,19,21 further indicated metallation of the C₄-bound phenyl ring in 4a₂ and 4b₂, respectively.

The crystal structures of complex 4a₁ (Figure 3a), 4a₂ (Figure 3b) and 4b₁ (Figure 3c) confirmed the connectivity. The geometry around the ruthenium metal centre in these half-sandwich complexes is pseudo-tetrahedral and are best described as three-legged “piano-stool” with the p-cymene being the “seat” and the carbon [C(triazolylidene)] and two chlorine atoms, constituting the “legs”. The Ru-C(triazolylidene) [2.084(4) Å] and Ru-Cl [2.4522(9) Å, 2.4163(9) Å] bond distances in 4a₁ are consistent with analogous species reported previously; for example the Ru-C(triazolylidene) and Ru-Cl bond distances in [Et(CH₂)₆(NMe)C₂Ph]RuCl₂(p-cymene) are 2.061 Å and 2.4183(11), 2.466(12) Å, respectively.10 In the cyclometalated species 4a, the coordination sphere of 4a₁ is completed by two carbon [C(triazolylidene)] and C(C₆H₄) and a chlorine atom. In 4a₂ a five membered ring is formed by coordination of C(triazolylidene) and C(C₆H₄). In 4a₂ the Ru-C(C₆H₄) bond of 2.103(2) Å is longer than the Ru-C(triazolylidene) bond which is 2.0431(4) Å. A similar trend was observed in the analogous cyclometalated species [(C₂H₅Me)₆(NMe)C₂H₄]RuCl₂(p-cymene).19 In both 4a₁ and 4a₂, the pendant mesityl group on the triazolylidene moiety is oriented away from the metal center. As expected, the molecular structure of the cyclometalated complex 4b₁ is very similar to that of 4a₁. To best of our knowledge, three analogous cyclometalated-triazolylidene ruthenium complexes have been reported; one which is metallated at the phenyl ring on C4 of the triazolylidene,19 and two others metallated at the phenyl ring on the corresponding N1.19
The reaction of the in situ generated silver(I)-carbene complex with \( \text{FeCl}_2 \) activated product \( 3c \) was unsuccessful. However, on heating to 45 °C for three days, a new species was beginning to emerge. After 22 days, complex \( 3c \) was completely converted to a new species which proved stable to hydrogen (4 atm) at 45 °C for several days. In the case of triazolylidene complexes, such species are very similar to that of \( 3b \) reported by Fukuzawa et al. in a recent publication. 

The formulations of \( 4c_1 \) and \( 4c_3 \) were further confirmed crycrystallographically (Figure 4). In the case of \( 4c_1 \) there are two molecules in asymmetric unit. The structure of complex \( 4c_1 \) is very similar to that of \( 4a_2 \) and \( 4b_3 \), whereas in complex \( 4c_3 \), the triazolylidene moiety is connected to the metal centre by two Ru-C bonds thus forming a six membered metallocyclic ring which adopts a boat conformation. Both Ru-C bonds in \( 4c_2 \) are slightly longer than those in \( 4c_3 \), whereas the reverse is observed for Ru-Cl bonds. In both cases, the uncoordinated phenyl ring is oriented away from the metal centre. It is noteworthy that in a recent publication, Fukuzawa et al. have described the synthesis of \( 4c_1 \) in 97% yield from the reaction of the in situ generated silver(I)-carbene complex with \( \text{RuCl}_2(\text{p-cymene})_2 \). In addition, Kilpin and Dyson et al. obtained \( 4c_1 \) in a similar procedure in 56% yield. In either of these previous publications the metallated species were not described. Conceptually similar metallated NHC products have been observed for \( \text{FeCl}_2 \), \( \text{CoCl}_2 \), \( \text{RhCl}_3 \), \( \text{IrCl}_3 \), \( \text{NiCl}_2 \), \( \text{PdCl}_2 \) and Ru complexes. In the case of triazolylidene complexes, such species are less common. Nonetheless the groups of Abrecht, et al. and others have described related metallated-triazolylidene of Ir, Pd and Ru complexes.

It is interesting to note that complexes \( 4a_2 \), \( 4b_2 \) and \( 4c_2 \) and \( 4c_3 \) proved stable to hydrogen (4 atm) at 45 °C for several days. Similarly, all attempts to convert \( 4a_1 \) to \( 4a_2 \) with various bases were unsuccessful. However, on heating to 45 °C for three days, a new species was beginning to emerge. After 22 days, complex \( 4a_1 \) was completely converted to a new species \( 5a \). \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra were consistent with the \( C_1 \) symmetry of \( 4c_1 \) and the \( C_1 \) symmetry of \( 4c_3 \) and \( 4c_5 \). While the \(^1\text{H} \) NMR resonances were consistent with formulations, it is noteworthy that a singlet (6.11 ppm) was observed for the benzyl-CH\(_2\) of \( 4c_5 \) whereas \( 4c_3 \) and \( 4c_5 \) displayed two doublets (4.57 and 5.93 ppm; 4.53 and 5.28 ppm) for the benzyl-CH\(_2\) fragments. Similarly the \(^{13}\text{C} \) NMR resonances for the the triazolylidene-C of \( 4c_1 \) appeared at 162.17 ppm, while the corresponding Ru-C signals were seen at 177.85 and 180.87 ppm for \( 4c_2 \) and 167.33 and 168.32 ppm for \( 4c_3 \).
to 5.33 ppm. The $^{13}$C NMR resonance observed at 165.41 ppm is attributable to the Ru-bound triazolylidene carbon. Single crystal X-ray analysis of 5a (Figure 5) confirms that the mesityl group of the triazolylidene moiety is indeed bound to the ruthenium center in an $\eta^5$-fashion. The distance from the Ru to the centroid of the arene ring is 1.679 Å, similar to that seen for the $p$-cymene-Ru distance in the precursor 4a$_1$ (1.668 Å). The Ru-Cl [2.419(2) and 2.424(2)] and Ru-C [2.070(9) Å] bond distances fall in the expected range. The planes of the five-membered triazolylidene ring and six-membered mesityl ring are oriented at an angle of 71.63° with respect to each other. The displacement of the triazolylidene moiety is indeed bound to the ruthenium center by phosphines, bisphosphines or donor solvent such as acetonitrile but in addition, intramolecular displacement of $p$-cymene moiety by the pendant arene rings attached to the already coordinated ligands has also been previously observed.

The catalytic oxidation of amine to imine using molecular oxygen as primary oxidant has attracted considerable attention. Indeed, Ru-NHC half-sandwich complexes have been previously shown to be effective for the oxidative homocoupling of primary amines. The ability of the complex 4a$_1$, 4b$_1$, 4c$_1$ and 5a to act as similar catalysts for the oxidative homocoupling of benzylic amines in the presence of molecular oxygen was evaluated. To this end, reactions were performed in toluene-d$_8$ at 150 °C and using a catalyst loading of 5 mol%. After 24 h, the reaction mixtures were cooled to 25 °C and the products analyzed by NMR spectroscopy (Table 1).

Using benzyl amine as the substrate, conversions to N-alkylated benzylamine were achieved in 72-83% yields. The catalytic activity of all of these catalysts was increased when electron donating substituents such as Me and OMe were incorporated on the aryl group of the amines.

### Table 1 Catalytic Oxidative Homocoupling of Benzylic Amines to Imines

<table>
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<tr>
<th>R</th>
<th>cat</th>
<th>Conv. (%)</th>
<th>cat</th>
<th>Conv. (%)</th>
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<th>Conv. (%)</th>
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<td>4c$_1$</td>
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<td>4b$_2$</td>
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<td>4b$_3$</td>
<td>90</td>
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<td>95</td>
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<td>72</td>
<td>5a</td>
<td>75</td>
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<tr>
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<td>4b$_5$</td>
<td>66</td>
<td>4c$_5$</td>
<td>64</td>
<td>5a</td>
<td>70</td>
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</tbody>
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*Conditions: 0.20 mmol of substrate and 5 mol% of catalyst in toluene-D$_8$ (2 mL) at 150 °C for 24 h. Yields were determined by $^1$H NMR spectroscopy.*

Conversely, the electron withdrawing substituents, Br and Cl reduced the catalytic activity. Complex 4a$_6$, 4b$_6$ and 4c$_6$ displayed very similar reactivity, whereas complex 5a gave slightly better conversions. This infers that altering the aryl substituents on the imidazolylidene moiety has little impact on the catalytic activity. The small increase in activity seen with 5a is attributed to the lesser steric congestion about the ruthenium centre resulting from the constrained nature of the chelating...
The catalysis of similar oxidation of benzyl alcohols have been previously described by related Ru-complexes incorporating the NH, iBu ligand and by triazolyl complexes R’N₂(C₃R’C₅R’RuCl₂(p-cymene) (R = Me, Et). In the latter case, the reactivity of these catalysts showed a correlation with the nature of the substituents on N1 and C4 position of the triazolylidene moiety. More recently, cationic Ru(η⁴-arene)

complexes have been shown to be highly effective catalysts for aerobic oxidation of a variety of alcohols. In a similar fashion the complexes 4a, 4b, 4c and 5a were also evaluated for aerobic oxidation of alcohols (Table 2). Using a benzyl alcohol as substrate these catalysts effect moderate conversions to benzaldehyde in yields ranging from 44 to 63%. As with the amine oxidation, electron donating groups on the aryl ring of the aldehyde resulted in increased conversion, while electron withdrawing substituents reduced the activity.

**Experimental section**

**General Procedures.** Syntheses were carried out partly under an atmosphere of dry, oxygen free nitrogen atmosphere employing an Innovative Technology glove box and a Schlenk vacuum-line and partly in an air atmosphere. Dry solvents were used for some reactions and purification, while solvents used for other reactions and purifications were used as received from suppliers. Dry solvents (hexanes and CH₂Cl₂) were obtained from a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-value stopcocks and stored over molecular sieves. CH₂CN was stored over CaH₂, distilled and degassed before use. Deuterated solvents (CDCl₃, CD₂Cl₂ and toluene-D₈) were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly. ¹H and ¹³C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to SiMe₃ and referenced to the residual solvent signals. Chemical shifts are reported in ppm. Mass spectra were measured on an AB Sciex APIStar and were reported in the form m/z (%) [M⁺] where “m/z2” is the mass observed, the intensities of the most intense peaks are reported, and “M⁺” is the molecular ion peak. Combustion analyses were performed in house, employing a Perkin-Elmer CHN Analyzer. All reagents were purchased from Aldrich and were used as received. 1c, 2c and 4c were previously reported and were synthesized using slight modifications of the literature methods. As repeated elemental analysis of 3a, 3b and 3c failed to produce acceptable results, HRMS was performed as a further characterization.

**Synthesis of [RCH₃N₂C₅H₃Ph] (R = C₆H₅Me₂, 1a, C₆H₅Pr₂, 1b, Ph 1c).** These compounds were prepared in similar methods and thus only a general preparation is detailed. An equimolar mixture of appropriate chloro-derivative (60.0 mmol), phenylacetylene (60.0 mmol) and NaN₃ (60.0 mmol) with Cul (1 mol%) in distilled water (140 mL) was stirred at elevated temperature (65 °C for 1a and 100 °C for 1b and 1c) for 16 h resulting in grey chunks of solid. The solid was washed with distilled water (3 x 100 mL) and hexane (3 x 50 mL) and air-dried. The dry solid was dissolved in CH₂Cl₂ (200 mL) resulting in a pale yellow solution, which was washed with dilute NH₄OH (5 x 30 mL) and distilled water (3 x 50 mL). After the solution was dried over MgSO₄, all volatiles were removed under high vacuum yielding an off-white solid. The solid was dissolved in minimum amount of CH₂Cl₂. The solution was added dropwise to hexanes (1000 mL) while stirring vigorously, which resulted in white precipitate. The precipitate was filtered off and dried under high vacuum to give pure product.

1a: A mixture of 2,4,6-trimethylbenzyl chloride (10.121 g, 60.0 mmol), phenylacetylene (6.132 g, 60 mmol), NaN₃ (3.903 g, 60 mmol) and Cul (0.113 g, 0.60 mol) yielded 1a (14.48 g, 87%). ¹H NMR (CDCl₃): δ 2.30 (3H, CH₃), 3.21 (6H, CH₂), 5.57 (2H, CH), 6.94 (2H, Ar-H), 7.23-7.38 (m, 4H, Ar-H), 7.74 (s, 1H, Ar-H), 7.76 (s, 1H, triazole-H), 7.76 (s, 1H, triazole-H). ¹³C NMR (CDCl₃): δ 20.59 (CH₃), 21.95 (CH₃), 49.19 (CH₃), 119.48, 126.53, 128.28, 128.91, 129.63, 130.62, 131.59, 138.77, 139.95, 148.46 (Ar-C and triazole-C). Anal. Calcd for C₁₃H₁₀N₂: 77.70; H, 6.90; N, 15.15. Found: C, 77.70; H, 7.01; N, 15.09.

1b: A mixture of 2,4,6-trisopropylbenzyl chloride (15.171 g, 60.00 mmol), phenylacetylene (6.130 g, 60.0 mmol), NaN₃ (3.902 g, 60 mmol) and Cul (0.114 g, 0.60 mol) yielded 1b (19.09 g, 88%). ¹H NMR (CDCl₃): δ 1.10 (d, 3J = 7 Hz, 12H, CH₃ of iPr), 1.19 (d, 3J = 7 Hz, 6H, CH₃ of iPr), 2.84 (sept, 3J = 7 Hz, 1H, CH of iPr), 3.08 (sept, 3J = 7 Hz, 2H, CH of iPr), 5.58 (2H, CH₂), 7.02 (2H, Ar-H), 7.12-7.29 (m, 4H, Ar-H), 7.64 (s, 1H, Ar-H), 7.66 (s, 1H, triazole-H). ¹³C NMR (CDCl₃): δ 24.82 (CH₃ of iPr), 25.16 (CH₃ of iPr), 30.53 (CH of iPr), 35.23 (CH of iPr), 47.32 (CH₂), 119.69, 122.77, 125.31, 126.54, 128.87, 129.61, 131.62, 148.23, 149.37, 151.22 (Ar-C and triazole-C). Anal. Calcd for C₁₅H₂₀N₂: 79.73; H, 8.64; N, 11.62. Found: C, 79.68; H, 8.70; N, 11.70.

1c: A mixture of benzyl chloride (7.595 g, 60.0 mmol), phenylacetylene (6.128 g, 60.0 mmol), NaN₃ (3.903 g, 60 mmol) and Cul (0.115 g, 0.60 mol) yielded 1c (12.82 g, 91%). ¹H NMR (CDCl₃): δ 5.57 (s, 2H, CH), 7.28-7.42 (m, 8H, Ar-H), 7.66 (s, 1H, Ar-H), 7.79 (s, 1H, Ar-H), 7.81 (s, 1H, triazole-H).

**Synthesis of [RCH₃N₂(C₆H₅)(NMe)(OTf)] R = C₆H₅Me₂, 2a, C₆H₅Pr₂, 2b, Ph 2c.** These compounds were prepared in similar methods and thus only a general preparation is detailed. MeOTf
(16.5 mmol) was added dropwise to a solution of 1,2,3-triazole (15.0 mmol) in CH₂Cl₂ (30 mL) at 25 °C. The reaction mixture was stirred for 24 h resulting in a colorless solution. All volatiles were removed under high vacuum resulting in a colorless oil which solidified on standing. The solid was washed with hexane (3 x 20 mL) and dried under vacuum to give pure product.

2a: 1a (4.161 g, 15.0 mmol) and MeOTf (2,710 g, 16.5 mmol) yielded 2a (6.410 g, 96%). ¹H NMR (CDCl₃): δ 2.29 (s, 3H, CH), 2.36 (s, 6H, CH₂), 4.21 (s, 3H, N-CH₃), 5.81 (s, 2H, CH=), 6.94 (s, 2H, Ar-H), 7.47-7.55 (m, 5H, Ar-H), 8.39 (s, 1H, triazolium-H). ¹³C NMR (CDCl₃): δ 20.63 (CH₃), 21.92 (CH₂), 39.60 (N-CH₃), 53.12 (CH₂), 122.75, 125.48, 128.74, 130.36, 130.47, 130.70, 132.69, 139.60, 141.19, 144.26 (Ar-C and triazolium-C). Anal. Calc'd for C₂₀H₂₂F₂N₄O₅S: 447.47: C, 54.41; H, 5.02; N, 9.52. Found: C, 53.94; H, 5.08; N, 9.34.

2b: 1b (5.424 g, 15.0 mmol) and MeOTf (2,710 g, 16.5 mmol) yielded 2b (7.645 g, 97%). ¹H NMR (CDCl₃): δ 1.22 (d, J = 7 Hz, 3H), 1.27 (d, J = 7 Hz, 6H, CH₃ of pPr), 2.92 (sept, J = 7 Hz, 1H, CH of pPr), 3.22 (sept, J = 7 Hz, 2H, CH of pPr), 4.24 (s, 3H, N-CH₃), 5.93 (s, 2H, CH₂), 7.12 (s, 2H, Ar-H), 7.49−7.65 (m, 5H, Ar-H), 8.40 (s, 1H, triazolium-H). ¹³C NMR (CDCl₃): δ 24.07, 132.69, 139.60, 141.19, 144.26 (Ar-C and triazolium-C). Anal. Calc'd for C₂₀H₂₃F₂N₅O₅S: 525.63: C, 59.41; H, 6.52; N, 7.99. Found: C, 59.82; H, 6.35; N, 8.01.

2c: 1c (3.532 g, 15.0 mmol) and MeOTf (2,709 g, 16.5 mmol) yielded 2c (5.712 g, 95%). ¹H NMR (CDCl₃): δ 4.42 (s, 3H, N-CH₃), 5.76 (s, 2H, CH₂), 7.35−7.61 (m, 10H, Ar-H), 8.66 (s, 1H, triazolium-H). ¹³C NMR (CDCl₃): δ 39.56 (N-CH₃), 58.45 (CH₂), 122.72, 129.28, 130.29, 130.36, 130.56, 130.62, 130.86, 132.10, 132.79, 144.41 (Ar-C and triazolium-C). Anal. Calc'd for C₁₇H₁₆F₂N₅O₅S: 399.39: C, 51.12; H, 4.04; N, 10.52. Found: C, 50.98; H, 4.16; N, 10.60.

Synthesis of [RCH₂C₆H₄(NMe₂)Ph]₂Ag(III) (R = C₂H₄Me₃, 3a, C₂H₄pPr₃, 3b, Ph 3c). These compounds were prepared in similar methods and thus only a general preparation is detailed. A mixture of triazolium salt (7.00 mmol), AgO₂ (3.9 mmol) and NMe₂Cl (7.7 mmol) in a 1:1 mixture of CH₂Cl₂ (15 mL) and CH₂CN (15 mL) was stirred at 25 °C for 24 h under dark resulting in yellow solution with grey precipitate. All volatiles were removed under vacuum to give a grey solid which was extracted with CH₂Cl₂ (30 mL). The solution was concentrated to approximately one-fourth its original volume and filtered through a plug of Celite. The solution was added dropwise to well-stirred hexanes (30 mL), yielding a sticky precipitate with pale yellow solution. The solution was discarded and the solid was dried under vacuum resulted in a foamy solid. The solid was dissolved in minimum amount of CH₂Cl₂ (ca. 4-5 mL) and the solution was added dropwise to well-stirred hexanes (30 mL) to give an off-white solid with colorless solution. The liquid was removed by cannula and the solid was dried under high vacuum to give pure product.
Synthesis of \([\text{C}_5\text{H}_4\text{Me}_3]_{\text{Cl}}\text{H}_2\text{N}2(\text{NMe}_2\text{C}_6\text{Ph})\text{RuCl}_2\) 5a. The following synthesis was performed under N₂ using dry solvents.

A solution of 4a (0.149 g, 0.25 mmol) in CH₂Cl₂ (5 mL) was stirred at 45°C for 22 d. The orange-red solution turned into a red-brown solution. The solution was concentrated to ca. 1 mL and was added dropwise to hexanes while stirring vigorously, which resulted in an orange-brown precipitate with pale brown solution. The solid was filtered off and dried under high vacuum to give 5a (0.107 g, 92%) as a pure compound.

\(^1\)H NMR
which they are bonded. The H atom contributions were taken from the literature tabulations.

X-Ray Data Solution and Refinement

General Procedure for Oxidative coupling of Amines. A mixture of amine (0.2 mmol) and ruthenium complex (0.01 mmol) in toluene-D8 was heated to 150 °C and stirred for 24 h. The reaction mixture was cooled down to 25 °C and analyzed by ¹H NMR spectroscopy.

X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTeGen Micromount and placed under an N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software and optimized to provide >96.6% complete data. In The Paratone-N oil in the glovebox, mounted on a MiTeGen Micromount and placed under an N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software and optimized to provide >96.6% complete data.

Notes and references

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† Electronic Supplementary Information (ESI) available: CIF for all structural studies have been deposited. CCDC: 998715-998720

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Summary and conclusions

A series of bis(1,2,3-triazolylidene) silver(I) complexes 3a, 3b and 3c have been shown to react with [RuCl₂(p-cymene)]₂ to form the ruthenium(II)(η⁶-arene)(1,2,3-triazolylidene) complexes as well as the related cyclometalated byproducts. These compounds could be separated by column chromatography. The cyclometalated complexes 4a, 4b, 4c and 4d are the newest examples of C-H activated triazolylidene ligands complexes. Despite the apparent relation, the ruthenium(II)(η⁶-arene)(1,2,3-triazolylidene) complexes could not be thermally converted to the metalated analogs. Instead, heating for several weeks resulted in the displacement of p-cymene ligand by the pendant mesityl group (5a) of the triazolylidene moiety. These compounds exhibited modest catalytic activity for the oxidation of alcohols and oxidative coupling of benzyl amines. We are continuing to study the utility of 1,2,3-triazolylidene in catalytic applications and the results of these studies will appear in due course.

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