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ARTICLE TYPE

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

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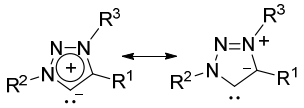
Three bis(1,2,3-triazolylidene) silver(I) complexes were synthesized, and the ruthenium complexes ([$RCH_2N_2(NMe)C_2Ph$)]$RuCl_2$(*p*-cymene) (R = $C_6H_2Me_3$ **4a$_1$**, $C_6H_2iPr_3$ **4b$_1$**) were isolated as major products with the minor C(sp^2)-H activated products ([$RCH_2N_2(NMe)C_2C_6H_4$)]RuCl(*p*-cymene) (R = $C_6H_2Me_3$ **4a$_2$**, $C_6H_2iPr_3$ **4b$_2$**). In the related case where R = Ph, the species ([$PhCH_2N_2(NMe)C_2Ph$)]$RuCl_2$(*p*-cymene) **4c$_1$** was obtained with two C(sp^2)-H activated products [$PhCH_2N_2(NMe)C_2C_6H_4$)]RuCl(*p*-cymene) **4c$_2$** and [$(C_6H_4)CH_2N_2(NMe)C_2Ph$)]RuCl(*p*-cymene) **4c$_3$** derived from metallation of the N and C-bound arene rings. Heating a solution of **4a$_1$** at 45 °C over three weeks resulted in a ruthenium(II)(1,2,3-triazolylidene) complex [$(C_6H_2Me_3)CH_2N_2(NMe)C_2Ph$)]$RuCl_2$ **5a**, where the pendant mesityl group on the triazolylidene moiety displaced the *p*-cymene ligand. The complexes **4a$_1$**, **4b$_1$**, **4c$_1$** and **5a** displayed moderate catalytic activities in base-free oxidation of benzyl alcohols to benzyldehydes 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.[1-2] This 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_2O 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.[3-11] In general, while free 1,2,3-triazolydenes (Fig. 1) are sensitive and decompose rapidly under the mild conditions,[12] Bertrand *et al.* synthesized the free 1,3,4-trisubstituted-1,2,3-triazol-5-ylidenes by the deprotonation of the 1,2,3-triazolium salt using $KN(SiMe_3)_2$ or KO*t*Bu.[13-14] The ν_{CO} stretching frequencies of the iridium dicarbonyl complex with triazolylidene ligand suggested that these ligands are slightly better donor than the normal imidazole-2-ylidene.[14]

Metal complexes with triazolylidenes have been exploited as catalysts in a wide variety of reactions including ring-opening metathesis,[14] ring-closing metathesis,[14] Suzuki coupling,[15-16] oxidative coupling and oxidation of water,[17] alcohols[18] and amines.[18]



R^1, R^2 = alkyl, benzyl or aryl; R^3 = alkyl or benzyl

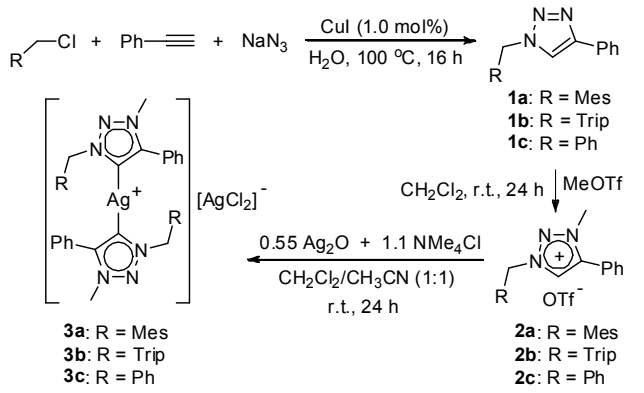
Fig. 1 1,2,3-triazole species.

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)]$_2$. 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 [$RCH_2N_3C_2HPh$] (R = $C_6H_2Me_3$ **1a,** $C_6H_2iPr_3$ **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 CuI (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-possition by using methyl triflate generating [$RCH_2N_2(NMe)C_2Ph$)][OTf] (R = $C_6H_2Me_3$ **2a,** $C_6H_2iPr_3$ **2b**, Ph **2c**). Attempts to prepare the free 1,2,3-triazol-5-ylidenes 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_2O yielded the corresponding

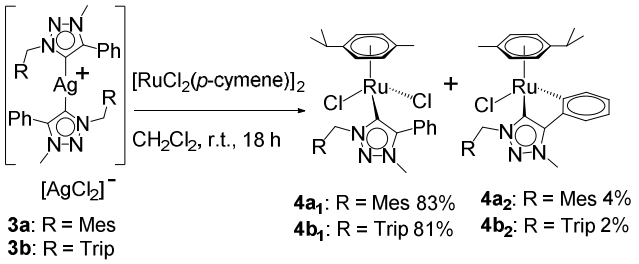
silver(I) triazolylidenes species **3a**, **3b** and **3c**, respectively. These species proved stable for months in the solid state under nitrogen at ambient temperature. While several attempts were made, structural characterization of these silver(I) triazolylidenes by single crystal X-ray analysis were unsuccessful. Mass spectrometry data suggested Schlenk equilibria result in **3a**, **3b** and **3c** being bis-triazolylidenes silver(I) salts of the general form $[L_2Ag][AgCl_2]$. 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*.[12]



Scheme 1 Synthesis of **3a**, **3b** and **3c**.

These *bis*(1,2,3-triazolylidene) silver(I) complexes were utilized as efficient carbene transfer agents as transmetalation was successfully performed with $[RuCl_2(p\text{-cymene})]_2$. The reaction of **3a** with $[RuCl_2(p\text{-cymene})]_2$ formed ruthenium(II)(η^6-arene) complex with 1,2,3-triazolylidene $[(C_6H_2Me_3)CH_2N_2(NMe)C_2Ph)]RuCl_2(p\text{-cymene})$ (**4a$_1$**) almost quantitatively as evidenced by the ^{1}H NMR spectrum of the crude reaction mixture (Scheme 2). However, a second set of signals in the ^{1}H 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(sp^2)-H activated product $[(C_6H_2Me_3)CH_2N_2(NMe)C_2C_6H_4)]RuCl(p\text{-cymene})$ **4a$_2$** (4 %), whereas, the second band was the expected ruthenium(II) triazolylidene complex **4a$_1$** (83 %). Similarly, the reaction of **3b** with $[RuCl_2(p\text{-cymene})]_2$ yielded the complex $[(C_6H_2iPr_3)CH_2N_2(NMe)C_2Ph)]RuCl_2(p\text{-cymene})$ **4b$_1$** in 81 % yield together with the C(sp^2)-H activated product $[(C_6H_2iPr_3)CH_2N_2(NMe)C_2C_6H_4)]RuCl(p\text{-cymene})$ **4b$_2$** in 2 % yield (Scheme 2). These products (**4a$_1$**, **4a$_2$**, **4b$_1$**, **4b$_2$**) are formally 18-electron species and consequently air stable. The presence of the triazolylidene moiety and the spectator arene ligand was consistent with the ^{1}H and ^{13}C NMR spectra. As expected, NMR spectra of **4a$_1$** and **4b$_1$** are consistent with C_s symmetry. The benzylic-CH_2 resonances for **4a$_1$** and **4b$_1$** appeared as singlets (**4a$_1$**: 6.02 ppm, **4b$_1$**: 6.04 ppm) as the resonances for the N-CH_3 fragments (**4a$_1$**: 3.51 ppm; **4b$_1$**: 3.53 ppm). Two doublets (**4a$_1$**: 4.85 and 5.18 ppm; **4b$_1$**: 4.89 and 5.22 ppm) were observed for four aromatic hydrogen atoms of the arene moiety. Down-field resonances in the ^{13}C NMR spectra of **4a$_1$** (160.32 ppm) and **4b$_1$** (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 **4a$_2$** and **4b$_2$** displayed distinctively different NMR spectra consistent with C_1 symmetry. Two doublets (**4a$_2$**: 5.61 and 5.94 ppm; **4b$_2$**: 5.69 and 5.99 ppm) for the benzylic-CH_2 were observed in the ^{1}H NMR spectra of **4a$_2$** and **4b$_2$**. Similarly, four aromatic hydrogen atoms of the arene moiety gave rise to four doublets (**4a$_2$**: 5.23, 5.27, 5.52 and 5.57 ppm; **4b$_2$**: 5.19, 5.24, 5.55 and 5.63 ppm). In the ^{13}C NMR spectra of **4a$_2$** and **4b$_2$**, the resonances for Ru-C(imidazolylidene) and Ru-C(C_6H_4) (**4a$_2$**: 176.09 and 180.83 ppm; **4b$_2$**: 175.95 and 180.91 ppm) were observed downfield of the corresponding Ru-C(imidazolylidene) resonances for **4a$_2$** (160.32 ppm) and **4b$_2$** (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 **4a$_2$** and **4b$_2$**, respectively.



Scheme 2 Synthesis of **4a$_1$**, **4a$_2$**, **4b$_1$**, **4b$_2$**.

The crystal structures of complex **4a$_1$** (Figure 3a), **4a$_2$** (Figure 3b) and **4b$_2$** (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 **4a$_1$** are consistent with analogous species reported previously; for example the Ru-C(triazolylidene) and Ru-Cl bond distances in $[EtCH_2N_2(NMe)C_2Ph)]RuCl_2(p\text{-cymene})$ are 2.061 Å and 2.4183(11), 2.466(12) Å, respectively.[20] In the cyclometalated species **4a$_2$** the coordination sphere of **4a$_2$** is completed by two carbon [C(triazolylidene) and C(C_6H_4)] and a chlorine atom. In **4a$_2$** a five membered ring is formed by coordination of C(triazolylidene) and C(C_6H_4). In **4a$_2$** the Ru-C(C_6H_4) 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 $[(C_6H_3Me_2)N_2(NMe)C_2C_6H_4)]RuCl(p\text{-cymene})]$. [19] In both **4a$_1$** and **4a$_2$**, the pendant mesityl group on the triazolylidene moiety is oriented away from the metal center. As expected, the molecular structure of the cyclometalated complex **4b$_2$** is very similar to that of **4a$_2$**. 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.[5, 19]

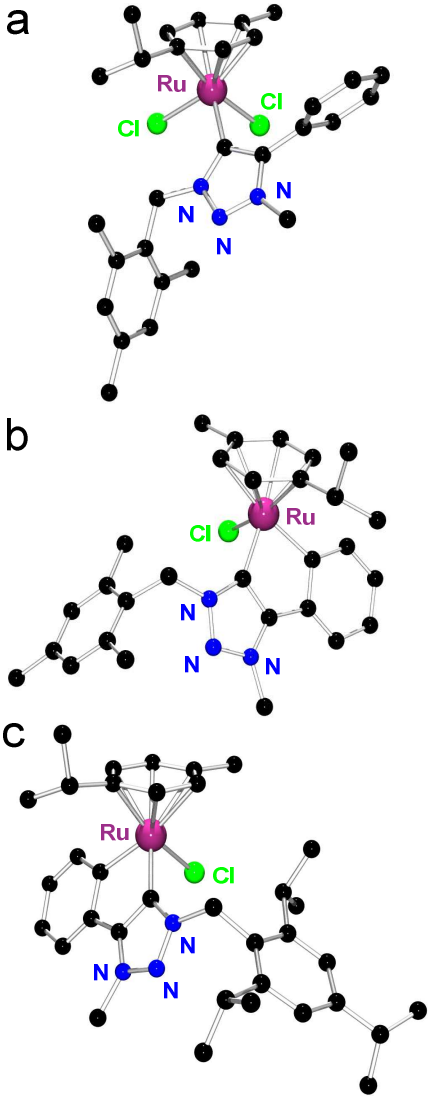
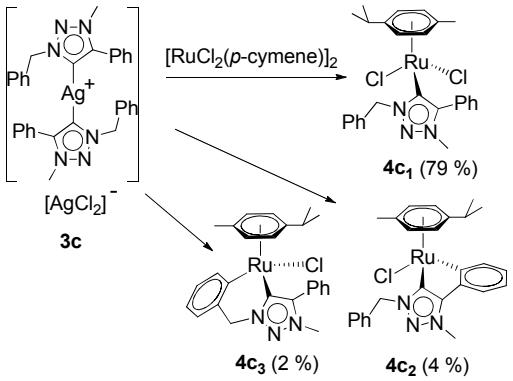


Fig. 3 POV-ray depiction of molecular structure of (a) $\mathbf{4a_1}$, (b) $\mathbf{4a_2}$ and (c) $\mathbf{4b_2}$. All hydrogen atoms are omitted for clarity. C, black; Cl, green; N, blue; Ru, purple. Selected bond lengths (Å) and angles (deg): $\mathbf{4a_1}$: Ru-Cl = 2.4522(9), Ru-Cl = 2.4163(9), Ru-C(triazolylidene) = 2.084(4); Cl-Ru-C(triazolylidene) = 97.0(1), Cl-Ru-C(triazolylidene) = 83.66(9), Cl-Ru-Cl = 85.12(9), $\mathbf{4a_2}$: Ru-Cl = 2.4398(6), Ru-C(C_6H_4) = 2.103(2), Ru-C(triazolylidene) = 2.0431(4); C(triazolylidene)-Ru-C(C_6H_4) = 77.22(8), C(triazolylidene)-Ru-Cl = 88.72(6), C(C_6H_4)-Ru-Cl = 84.64(6), $\mathbf{4b_2}$: Ru-C(centroid) = 1.735, Ru-Cl = 2.4212(9), Ru-C(C_6H_4) = 2.101(3), Ru-C(triazolylidene) = 2.045(3); C(triazolylidene)-Ru-C(C_6H_4) = 77.0(1), C(triazolylidene)-Ru-Cl = 87.41(9), C(C_6H_4)-Ru-Cl = 83.8(1).

The reaction of **3c** with $[RuCl_2(p\text{-cymene})]_2$ was monitored by NMR spectroscopy revealing the presence of the major product was the analog of $\mathbf{4a_1}$ and $\mathbf{4b_1}$; however, two minor byproducts were also seen. Column chromatography (stationary phase: silica gel, eluent: 9/1 mixture of CH_2Cl_2/acetone) was performed to separate these products. Two yellow bands separated quickly in the column followed by a dark orange band. These species were subsequently isolated and identified. The first yellow band was found to be a C(sp^2)-H activated product $\mathbf{4c_3}$ (2 %), the second band was another C(sp^2)-H activated product $\mathbf{4c_2}$ (4 %) and the third band was the expected ruthenium(II) triazolylidene complex $\mathbf{4c_1}$ (79 %) (Scheme 3). ^{1}H and ^{13}C NMR spectroscopy were consistent with the C_s symmetry of $\mathbf{4c_1}$ and the C_1 symmetry of $\mathbf{4c_2}$ and $\mathbf{4c_3}$. While the ^{1}H NMR resonances were consistent with formulations, it is noteworthy that a singlet (6.11 ppm) was observed for the benzylic-CH_2 of $\mathbf{4c_1}$ whereas $\mathbf{4c_2}$ and $\mathbf{4c_3}$ displayed two doublets ($\mathbf{4c_2}$: 5.73 and 5.93 ppm; $\mathbf{4c_3}$: 5.03 and 5.28 ppm) for the benzylic-CH_2 fragments. Similarly the ^{13}C NMR resonances for the the triazolylidene-C of $\mathbf{4c_1}$, appeared at 162.17 ppm, while the corresponding Ru-C signals were seen at 177.85 and 180.87 ppm for $\mathbf{4c_2}$ and 167.33 and 168.32 ppm for ; $\mathbf{4c_3}$.



Scheme 3 Synthesis of $\mathbf{4c_1}$, $\mathbf{4c_2}$ and $\mathbf{4c_3}$.

The formulations of $\mathbf{4c_2}$ and $\mathbf{4c_3}$ were further confirmed cyrystallographically (Figure 4). In the case of $\mathbf{4c_2}$ there are two molecules in asymmetric unit. The structure of complex $\mathbf{4c_2}$ is very similar to that of $\mathbf{4a_2}$ and $\mathbf{4b_2}$, whereas in complex $\mathbf{4c_3}$, the triazolylidene moiety is connected to the metal centre by two Ru-C bonds [Ru-C(triazolylidene): 2.033(6) Å, Ru-C(C_6H_4): 2.098(7) Å] thus forming a six membered metallocyclic ring which adopts a boat conformation. Both Ru-C [Ru-C(triazolylidene) and Ru-C(C_6H_4)] bonds in $\mathbf{4c_2}$ are slightly longer than those in $\mathbf{4c_3}$, 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 $\mathbf{4c_1}$[19] in 97% yield from the reaction of the in situ generated silver(I)-carbene complex with $[RuCl_2(p\text{-cymene})]_2$. In addition, Kilpin and Dyson *et al.* obtained $\mathbf{4c_1}$ in a similar procedure in 56 % yield.[21] In either of these previous publications the metallated species were not described. Conceptually similar metallated NHC products have been observed for Fe,[22-23] Co,[24] Rh,[25] Ir,[26-27] Ni,[28] Pd,[29] Pt[30-31] and Ru.[32-36] In the case of triazolylidene complexes, such species are less common. Nonetheless the groups of Abrecht,[17, 37] Fukuzawa[19, 38] and others[39] have described related metallated-triazolylidene of Ir, Pd and Ru complexes.

It is interesting to note that complexes $\mathbf{4a_2}$, $\mathbf{4b_2}$ and $\mathbf{4c_2}$ and $\mathbf{4c_3}$ proved stable to hydrogen (4 atm) at 45 °C for several days. Similarly, all attempts to convert $\mathbf{4a_1}$ to $\mathbf{4a_2}$ 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 $\mathbf{4a_1}$ was completely converted to a new species **5a**. ^{1}H and ^{13}C NMR spectra were consistent with the displacement of the *p*-cymene ligand by the pendant mesityl group of the triazolylidene moiety. The metal-bound mesityl group in **5a** gives rise to an upfield ^{1}H NMR resonance at 5.25 ppm for the aromatic mesityl hydrogens. Similarly the benzylic-CH_2 fragment is shifted upfield

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 η^6-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 $\mathbf{4a_1}$ (1.668 Å). The Ru-Cl [2.419(2) and 2.424(2) Å] 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 an angle of 71.63° with respect to each other. The displacement of coordinated *p*-cymene moiety is well precedented in the literature.[40-47] Certainly *p*-cymene fragments has been displaced by phosphines, bis-phosphines 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.

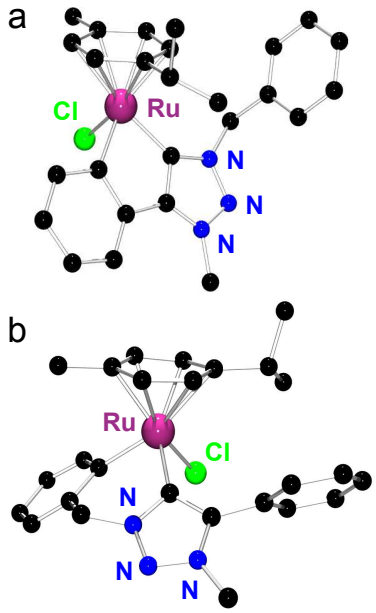
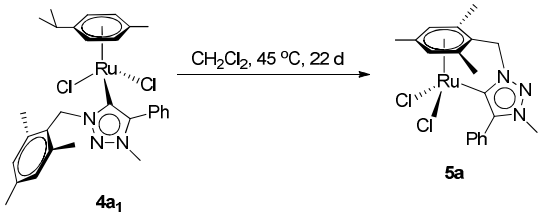


Fig. 4 POV-ray depiction of molecular structure of (a) $\mathbf{4c_2}$ and (b) $\mathbf{4c_3}$. All hydrogen atoms are omitted for clarity. C, black; Cl, green; N, blue; Ru, purple. Selected bond lengths (Å) and angles (deg): $\mathbf{4c_2}$: Ru-Cl = 2.421(1) and 2.424(1), Ru-C(C_6H_4) = 2.087(5) and 2.099(2), Ru-C(triazolylidene) = 2.041(5) and 2.035(5); C(triazolylidene)-Ru-C(C_6H_4) = 76.6(2) and 77.0(2), C(triazolylidene)-Ru-Cl = 85.0(1) and 84.4(2), C(C_6H_4)-Ru-Cl = 87.4(1) and 86.5(1), $\mathbf{4c_3}$: Ru-Cl = 2.428(5), Ru-C(C_6H_4) = 2.098(7), Ru-C(triazolylidene) = 2.033(6); C(triazolylidene)-Ru-C(C_6H_4) = 85.2(3), C(triazolylidene)-Ru-Cl = 89.0(2), C(C_6H_4)-Ru-Cl = 85.8(2).



Scheme 4 Synthesis of **5a**.

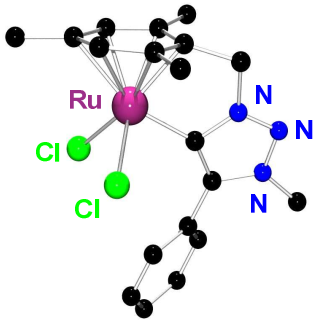


Fig. 5 POV-ray depiction of molecular structure of **5a**. All hydrogen atoms are omitted for clarity. C, black; Cl, green; N, blue; Ru, purple. Selected bond lengths (Å) and angles (deg): Ru-C(centroid) = 1.679, Ru-Cl = 2.419(2), Ru-Cl = 2.424(2), Ru-C(triazolylidene) = 2.0701(88); Cl-Ru-C(triazolylidene) = 89.8(2), Cl-Ru-C(triazolylidene) = 92.9(2), Cl-Ru-Cl = 89.5(1), C(centroid)-Ru-C(triazolylidene) = 121.32, C(centroid)-Ru-Cl = 125.87, C(centroid)-Ru-Cl = 126.90.

Catalytic Oxidations The catalytic oxidation of amine to imine using molecular oxygen as primary oxidant has attracted considerable attention.[18, 48-50] Indeed, Ru-NHC half-sandwich complexes have been previously shown to be effective for the oxidative homocoupling of primary amines.[20] The ability of the complex $\mathbf{4a_1}$, $\mathbf{4b_1}$, $\mathbf{4c_1}$ and **5a** to act as similar catalysts for the oxidative homocoupling of benzyl 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-benzylidenebenzylamine 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.

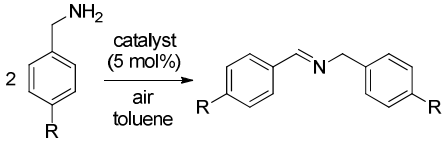


Table 1 Catalytic Oxidative Homocoupling of Benzylic Amines to Imines[a]

R	cat	Conv. (%)	cat	Conv. (%)	cat	Conv. (%)	cat	Conv. (%)
H	$\mathbf{4a_1}$	78	$\mathbf{4b_1}$	72	$\mathbf{4c_1}$	79	**5a**	83
Me	$\mathbf{4a_1}$	82	$\mathbf{4b_1}$	82	$\mathbf{4c_1}$	83	**5a**	93
OMe	$\mathbf{4a_1}$	88	$\mathbf{4b_1}$	90	$\mathbf{4c_1}$	87	**5a**	95
Br	$\mathbf{4a_1}$	73	$\mathbf{4b_1}$	71	$\mathbf{4c_1}$	72	**5a**	75
Cl	$\mathbf{4a_1}$	64	$\mathbf{4b_1}$	66	$\mathbf{4c_1}$	64	**5a**	70

[a]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 $\mathbf{4a_1}$, $\mathbf{4b_1}$ and $\mathbf{4c_1}$ 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

ligand.

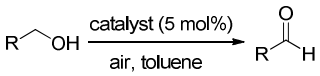


Table 2 Catalytic Oxidation of Benzylic Alcohols to Benzaldehydes[a]

R	cat	Conv. (%)	cat	Conv. (%)	cat	Conv. (%)	cat	Conv. (%)
C_6H_5	**4a$_1$**	59	**4b$_1$**	54	**4c$_1$**	44	**5a**	63
4-Br(C_6H_4)	**4a$_1$**	48	**4b$_1$**	45	**4c$_1$**	34	**5a**	54
4-Cl(C_6H_4)	**4a$_1$**	35	**4b$_1$**	32	**4c$_1$**	27	**5a**	40
4-OMe(C_6H_4)	**4a$_1$**	63	**4b$_1$**	65	**4c$_1$**	54	**5a**	66
$BrCH_2(CH_2)_9$	**4a$_1$**	34	**4b$_1$**	29	**4c$_1$**	21	**5a**	37

[a]Conditions: 0.20 mmol of substrate and 5 mol% of catalyst in toluene-D_8 (2 mL) at 110 °C for 24 h. Yields were determined by ^{1}H NMR spectroscopy.

The catalysis of similar oxidation of benzyl alcohols have been previously described by related Ru-complexes incorporating the NHC, IBu ligand[18] and by triazolium complexes R"N_2(NR)C_2R′)RuCl_2(*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.[20] More recently, cationic Ru(η^6-arene) complexes have been shown to be highly effective catalysts for aerobic oxidation of a variety of alcohols.[51] In a similar fashion the complexes **4a$_1$**, **4b$_1$**, **4c$_1$** 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 CH_2Cl_2) were obtained from a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks and stored over molecular sieves. CH_3CN was stored over CaH_2, distilled and degassed before use. Deuterated solvents ($CDCl_3$, CD_2Cl_2 and toluene-D_8) were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to $SiMe_3$ and referenced to the residual solvent signals. Chemical shifts are reported in ppm. Mass spectra were measured on a AB Sciex QStar and were reported in the form *m/z* (%) [M^+] where "*m/z*" 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$_1$** were previously reported and were synthesized use slight modifications of the literature methods.[19, 21] As repeated elemental analysis of **3a**, **3b** and **3c** failed to produce acceptable results, HRMS was performed as a further characterization.

Synthesis of [R$CH_2N_3C_2$HPh] (R = $C_6H_2Me_3$ 1a, $C_6H_2iPr_3$ 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 NaN_3 (60.0 mmol) with CuI (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 CH_2Cl_2 (200 mL) resulting in a pale yellow solution, which was washed with dilute NH_4OH (5 x 30 mL) and distilled water (3 x 50 mL). After the solution was dried over $MgSO_4$, all volatiles were removed under high vacuum yielding an off-white solid. The solid was dissolved in minimum amount of CH_2Cl_2. 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), NaN_3 (3.903 g, 60.0 mmol) and CuI (0.113 g, 0.60 mmol) yielded **1a** (14.48 g, 87%). ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 5.57 (s, 2H, CH_2), 6.94 (s, 2H, Ar-H), 7.23-7.38 (m, 4H, Ar-H), 7.74 (s, 1H, Ar-H), 7.76 (s, 1H, triazole-H). ^{13}C NMR ($CDCl_3$): δ 20.59 (CH_3), 21.95 (CH_3), 49.19 (CH_2), 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 $C_{18}H_{19}N_3$ (277.36): C, 77.95; H, 6.90; N, 15.15. Found: C, 77.70; H, 7.01; N, 15.09.

1b: A mixture of 2,4,6-triisopropylbenzyl chloride (15.171 g, 60.0 mmol), phenylacetylene (6.130 g, 60.0 mmol), NaN_3 (3.902 g, 60.0 mmol) and CuI (0.114 g, 0.60 mmol) yielded **1b** (19.09 g, 88%). ^{1}H NMR ($CDCl_3$): δ 1.10 (d, ^{3}J = 7 Hz, 12H, CH_3 of *i*Pr), 1.19 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 2.84 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.08 (sept, ^{3}J = 7 Hz, 2H, CH of *i*Pr), 5.58 (s, 2H, CH_2), 7.02 (s, 2H, Ar-H), 7.12-7.29 (m, 4H, Ar-H), 7.64 (s, 1H, Ar-H), 7.66 (s, 1H, triazole-H). ^{13}C NMR ($CDCl_3$): δ 24.82 (CH_3 of *i*Pr), 25.16 (CH_3 of *i*Pr), 30.53 (CH of *i*Pr), 35.23 (CH of *i*Pr), 47.32 (CH_2), 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 $C_{24}H_{31}N_3$ (361.52): C, 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), NaN_3 (3.903 g, 60.0 mmol) and CuI (0.115 g, 0.60 mmol) yielded **1a** (12.82 g, 91%). ^{1}H NMR ($CDCl_3$): δ 5.57 (s, 2H, CH_2), 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 [RCH_2N_2(NMe)C_2Ph)][OTf] R = $C_6H_2Me_3$ 2a, $C_6H_2iPr_3$ 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 CH_2Cl_2 (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%). ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 2.36 (s, 6H, CH_3), 4.21 (s, 3H, N-CH_3), 5.81 (s, 2H, CH_2), 6.94 (s, 2H, Ar-H), 7.47-7.65 (m, 5H, Ar-H), 8.39 (s, 1H, triazolium-H). ^{13}C NMR ($CDCl_3$): δ 20.63 (CH_3), 21.92 (CH_3), 39.60 (N-CH_3), 53.12 (CH_2), 122.75, 125.48, 128.74, 130.36, 130.47, 130.70, 132.69, 139.60, 141.19, 144.24 (Ar-C and triazolium-C). Anal. Calcd for $C_{20}H_{22}F_3N_3O_3S$ (441.47): 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%). ^{1}H NMR ($CDCl_3$): δ 1.22 (d, ^{3}J = 7 Hz, 12H, CH_3 of *i*Pr), 1.27 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 2.92 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.22 (sept, ^{3}J = 7 Hz, 2H, CH of *i*Pr), 4.24 (s, 3H, N-CH_3), 5.93 (s, 2H, CH_2), 7.12 (s, 2H, Ar-H), 7.49–7.65 (m, 5H, Ar-H), 8.40 (s, 1H, triazolium-H). ^{13}C NMR ($CDCl_3$): δ 24.70 (CH_3 of *i*Pr), 25.12 (CH_3 of *i*Pr), 30.69 (CH of *i*Pr), 35.25 (CH of *i*Pr), 39.66 (N-CH_3), 51.29 (CH_2), 122.57, 122.75, 123.01, 128.64, 130.39, 130.57, 132.79, 144.29, 150.18, 152.46 (Ar-C, triazolium-C). Anal. Calcd for $C_{26}H_{34}F_3N_3O_3S$ (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%). ^{1}H NMR ($CDCl_3$): δ 4.22 (s, 3H, N-CH_3), 5.76 (s, 2H, CH_2), 7.35-7.61 (m, 10H, Ar-H), 8.66 (s, 1H, triazolium-H). ^{13}C NMR ($CDCl_3$): δ 39.56 (N-CH_3), 58.45 (CH_2), 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. Calcd for $C_{17}H_{16}F_3N_3O_3S$ (399.39): C, 51.12; H, 4.04; N, 10.52. Found: C, 50.98; H, 4.16; N, 10.60.

Synthesis of $[RCH_2C_2N_2(NMe)Ph)_2Ag][AgCl_2]$ (R = $C_6H_2Me_3$ 3a, $C_6H_2iPr_3$ 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), Ag_2O (3.9 mmol) and NMe_4Cl (7.7 mmol) in a 1:1 mixture of CH_2Cl_2 (15 mL) and CH_3CN (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 CH_2Cl_2 (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). yelding 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 CH_2Cl_2 (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.

3a: 2a (3.115 g, 7.06 mmol), Ag_2O (0.901 g, 3.88 mmol) and NMe_4Cl (0.852 g, 7.77 mmol) yielded **3a** (2.857 g, 93%). ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 6H, CH_3), 2.25 (s, 12H, CH_3), 4.07 (s, 6H, N-CH_3), 5.49 (s, 4H, CH_2), 6.83 (s, 4H, Ar-H), 7.41-7.54 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 20.36 (CH_3), 21.02 (CH_3), 37.63 (N-CH_3), 53.91 (CH_2), 127.36, 127.46, 129.17, 129.40, 129.56, 130.16, 138.16, 139.14 (Ar-C), 148.72 (Ag-C). MS (70 eV, ESI): m/z (rel intens) 689 (100) $[C_{38}H_{42}N_6Ag^+]$. HRMS (ESI; m/z): calcd for $C_{38}H_{42}N_6Ag$, 689.2516; found, 689.2539.

3b: **2b** (3.680 g, 7.00 mmol), Ag_2O (0.893 g, 3.85 mmol) and NMe_4Cl (0.844 g, 7.70 mmol) yielded **3b** (3.088 g, 85%). ^{1}H NMR ($CDCl_3$): δ 1.10 (d, ^{3}J = 7 Hz, 24H, CH_3 of *i*Pr), 1.22 (d, ^{3}J = 7 Hz, 12H, CH_3 of *i*Pr), 2.88 (sept, ^{3}J = 7 Hz, 2H, CH of *i*Pr), 3.23 (sept, ^{3}J = 7 Hz, 4H, CH of *i*Pr), 4.07 (s, 6H, Me), 5.61 (s, 4H, CH_2), 7.04 (s, 4H, Ar-H), 7.41–7.60 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 23.80 (CH_3 of *i*Pr), 24.12 (CH_3 of *i*Pr), 30.13 (CH of *i*Pr), 34.29 (CH of *i*Pr), 37.64 (N-CH_3), 52.14 (CH_2), 121.71, 124.60, 127.38, 129.23, 129.37, 130.30, 148.64 (Ar-C), 150.38 (Ag-C). MS (70 eV, ESI): m/z (rel intens) 857 (100) $[C_{50}H_{66}N_6Ag^+]$. HRMS (ESI; m/z): calcd for $C_{50}H_{66}N_6Ag$, 857.4394; found, 857.4402.

3c: 2c (2.796 g, 7.00 mmol), Ag_2O (0.893 g, 3.85 mmol) and NMe_4Cl (0.844 g, 7.70 mmol) yielded **3c** (2.226 g, 81%). ^{1}H NMR ($CDCl_3$): δ 4.12 (s, 6H, N-CH_3), 5.51 (s, 4H, CH_2), 7.23-7.34 (m, 10H, Ar-H), 7.38-7.53 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 37.50 (N-CH_3), 59.57 (CH_2), 127.27, 128.44, 129.02, 129.07, 129.17, 129.39, 130.18, 134.19 (Ar-C), 149.15 (Ag-C). MS (70 eV, ESI): m/z (rel intens) 605 (100) $[C_{32}H_{30}N_6Ag^+]$. HRMS (ESI; m/z): calcd for $C_{32}H_{30}N_6Ag$, 605.1577; found, 605.1581.

Synthesis of $[RCH_2N_2(NMe)C_2Ph)]RuCl_2$(*p*-cymene) R = $C_6H_2Me_3$ 4a$_1$, $C_6H_2iPr_3$ 4b$_1$, Ph 4c$_1$), $[RCH_2N_2(NMe)C_2C_6H_4)]RuCl$(*p*-cymene) (R = $C_6H_2Me_3$ 4a$_2$, $C_6H_2iPr_3$ 4b$_2$, Ph 4c$_2$), and $[(C_6H_4)CH_2N_2(NMe)C_2Ph)]RuCl$(*p*-cymene) 4c$_3$. These compounds were prepared in similar methods and thus only a general preparation is detailed. **3a** (0.905 g, 1.04 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.613 g, 1.00 mmol) yielded red solid (1.166 g) as crude products mixture. Elution with a mixture of CH_2Cl_2/acetone (9/1) induced the separation of **4a$_2$** as the first yellow band and of **4a$_1$** as the second orange-red band. Removal of solvents under high vacuum yielded **4a$_2$** (0.040 g, 4%) as a yellow solid and **4a$_1$** (0.986 g, 83%) as an orange-red solid. X-ray quality crystals of **4a$_2$** (yellow needles) and **4a$_1$** (orange blocks) were obtained by slow diffusion of Et_2O into the respective solution of compound in CH_2Cl_2.

4a$_1$: ^{1}H NMR (CD_2Cl_2): δ 1.10 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 1.83 (s, 3H, Me), 2.20 (s, 6H, Me), 2.22 (s, 3H, Me), 2.55 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.51 (s, 3H, N-CH_3), 4.85 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.18 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 6.02 (s, 2H, CH_2), 6.84 (s, 2H, Ar-H), 7.35-7.45 (m, 3H, Ar-H), 7.46-7.53 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 18.87 (CH_3), 20.53 (CH_3), 21.20 (CH_3), 22.89 (CH_3), 31.18 (CH), 37.48 (N-CH_3), 54.13 (CH_2), 83.35 (Ar-C of *p*-cymene), 86.01 (Ar-C of

p-cymene), 97.30 (Ar-C of *p*-cymene), 105.50 (Ar-C of *p*-cymene), 128.19, 128.70, 129.32, 129.54, 129.96, 132.36, 138.66, 139.17, 148.82 (Ar-C), 160.32 (Ru-C). Anal. Calcd for $C_{29}H_{35}Cl_2N_3Ru$ (597.58): C, 58.29; H, 5.90; N, 7.03. Found: C, 58.43; H, 5.93; N, 6.95.

4a$_2$: ^{1}H NMR (CD_2Cl_2): δ 0.70 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 0.86 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 1.92 (s, 3H, CH_3), 2.15 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 2.23 (s, 3H, CH_3), 2.32 (s, 6H, CH_3), 4.01 (s, 3H, N-CH_3), 5.23 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.27 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.52 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.57 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.61 (d, ^{2}J = 14 Hz, 1H, CH of CH_2), 5.94 (d, ^{2}J = 14 Hz, 1H, CH of CH_2), 6.82-6.95 (m, 4H, Ar-H), 7.19-7.26 (m, 1H, Ar-H), 8.12-8.19 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 19.06 (CH_3), 20.50 (CH_3), 21.21 (CH_3), 22.06 (CH_3), 23.17 (CH_3), 31.64 (CH), 37.68 (N-CH_3), 51.57 (CH_2), 82.91 (Ar-C of *p*-cymene), 87.27 (Ar-C of *p*-cymene), 89.54 (Ar-C of *p*-cymene), 92.51 (Ar-C of *p*-cymene), 99.53 (Ar-C of *p*-cymene), 102.73 (Ar-C of *p*-cymene), 120.97, 122.07, 126.86, 128.36, 129.45, 137.53, 139.13, 142.67, 152.10 (Ar-C), 176.09 (Ru-C), 180.83 (Ru-C). Anal. Calcd for $C_{29}H_{34}ClN_3Ru$ (561.12): C, 62.07; H, 6.11; N, 7.49. Found: C, 61.91; H, 6.08; N, 7.57.

4b$_1$: ^{1}H NMR (CD_2Cl_2): δ 1.11 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 1.13 (d, ^{3}J = 7 Hz, 12H, CH_3 of *i*Pr), 1.20 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 1.80 (s, 3H, CH_3), 2.51 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 2.85 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 2.97 (sept, ^{3}J = 7 Hz, 2H, CH of *i*Pr), 3.53 (s, 3H, N-CH_3), 4.89 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.22 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 6.04 (s, 2H, CH_2), 7.02 (s, 2H, Ar-H), 7.35-7.43 (m, 3H, Ar-H), 7.45-7.52 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 18.66 (CH_3), 22.92 (CH_3), 24.14 (CH_3), 24.45 (CH_3), 30.43 (CH), 31.32 (CH), 34.71 (CH), 37.35 (N-CH_3), 52.59 (CH_2), 83.79 (Ar-C of *p*-cymene), 85.83 (Ar-C of *p*-cymene), 96.72 (Ar-C of *p*-cymene), 105.33 (Ar-C of *p*-cymene), 121.77, 126.16, 128.20, 129.54, 129.99, 132.41, 148.91, 149.55, 150.06 (Ar-C), 160.57 (Ru-C). Anal. Calcd for $C_{35}H_{47}Cl_2N_3Ru$ (681.74): C, 61.66; H, 6.95; N, 6.16. Found: C, 61.48; H, 6.94; N, 6.21.

4b$_2$: ^{1}H NMR (CD_2Cl_2): δ 0.70 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 0.87 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 1.18 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 1.21 (d, ^{3}J = 7 Hz, 12H, CH_3 of *i*Pr), 1.93 (s, 3H, CH_3), 2.15 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 2.86 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.24 (sept, ^{3}J = 7 Hz, 2H, CH of *i*Pr), 4.04 (s, 3H, N-CH_3), 5.19 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.24 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.55 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.63 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.69 (d, ^{2}J = 15 Hz, 1H, CH of CH_2), 5.99 (d, ^{2}J = 15 Hz, 1H, CH of CH_2), 6.86-6.96 (m, 2H, Ar-H), 7.05 (s, 2H, Ar-H), 7.22-7.27 (m, 1H, Ar-H), 8.14-8.19 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 19.04 (CH_3), 21.98 (CH_3), 23.21 (CH_3), 24.11 (CH_3), 24.45 (CH_3), 30.13 (CH), 31.58 (CH), 34.76 (CH), 37.66 (N-CH_3), 49.76 (CH_2), 82.31 (Ar-C of *p*-cymene), 87.15 (Ar-C of *p*-cymene), 89.62 (Ar-C of *p*-cymene), 92.90 (Ar-C of *p*-cymene), 99.53 (Ar-C of *p*-cymene), 103.00 (Ar-C of *p*-cymene), 120.99, 121.90, 122.06, 125.66, 126.89, 142.70, 150.34, 152.20 (Ar-C), 175.95 (Ru-C), 180.91 (Ru-C). Anal. Calcd for $C_{35}H_{46}ClN_3Ru$ (645.28): C, 65.15; H, 7.19; N, 6.51. Found: C, 65.21; H, 7.11; N, 6.55.

4c$_1$: ^{1}H NMR (CD_2Cl_2): δ 1.04 (d, ^{3}J = 7 Hz, 6H, CH_3 of *i*Pr), 1.60 (s, 3H, CH_3), 2.49 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.65 (s, 3H, N-CH_3), 4.64 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.05 (d, ^{3}J = 6 Hz, 2H, Ar-H of *p*-cymene), 6.11 (s, 2H, CH_2), 7.22-7.48 (m, 8H, Ar-H), 7.50-7.59 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 18.51 (CH_3), 22.67 (CH_3), 30.89 (CH), 37.62 (N-CH_3), 57.73 (CH_2), 82.76 (Ar-C of *p*-cymene), 86.11 (Ar-C of *p*-cymene), 97.41 (Ar-C of *p*-cymene), 106.42 (Ar-C of *p*-cymene), 128.26, 128.46, 128.88, 128.94, 129.40, 130.09, 132.39, 137.04, 148.72 (Ar-C), 162.47 (Ru-C). Anal. Calcd for $C_{26}H_{29}Cl_2N_3Ru$ (555.50): C, 56.22; H, 5.26; N, 7.56. Found: C, 56.05; H, 5.44; N, 7.51.

4c$_2$: ^{1}H NMR (CD_2Cl_2): δ 0.57 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 0.74 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 1.83 (s, 3H, CH_3), 1.98 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 4.14 (s, 3H, N-CH_3), 4.81 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.12 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.32 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.47 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.73 (d, ^{2}J = 15 Hz, 1H, CH of CH_2), 5.93 (d, ^{2}J = 15 Hz, 1H, CH of CH_2), 6.84-6.96 (m, 2H, Ar-H), 7.23-7.39 (m, 6H, Ar-H), 8.11-8.17 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 19.01 (CH_3), 21.98 (CH_3), 22.94 (CH_3), 31.37 (CH), 37.72 (N-CH_3), 56.29 (CH_2), 83.08 (Ar-C of *p*-cymene), 87.02 (Ar-C of *p*-cymene), 89.09 (Ar-C of *p*-cymene), 92.89 (Ar-C of *p*-cymene), 98.76 (Ar-C of *p*-cymene), 103.45 (Ar-C of *p*-cymene), 121.06, 122.12, 126.95, 127.76, 128.62, 129.32, 136.47, 137.63, 142.71, 152.58 (Ar-C), 177.85 (Ru-C), 180.87 (Ru-C). Anal. Calcd for $C_{26}H_{28}ClN_3Ru$ (519.04): C, 60.16; H, 5.44; N, 8.10. Found: C, 60.20; H, 5.49; N, 7.99.

4c$_3$: ^{1}H NMR (CD_2Cl_2): δ 0.79 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 0.93 (d, ^{3}J = 7 Hz, 3H, CH_3 of *i*Pr), 1.62 (s, 3H, CH_3), 2.16 (sept, ^{3}J = 7 Hz, 1H, CH of *i*Pr), 3.79 (s, 3H, N-CH_3), 4.65 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.74 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.85 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.93 (d, ^{3}J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.03 (d, ^{2}J = 14 Hz, 1H, CH of CH_2), 5.28 (d, ^{2}J = 14 Hz, 1H, CH of CH_2), 6.72-6.79 (m, 1H, Ar-H), 6.81-6.87 (m, 1H, Ar-H), 6.88-6.92 (m, 1H, Ar-H), 7.43-7.49 (m, 3H, Ar-H), 7.75-7.81 (m, 2H, Ar-H), 7.86-7.91 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 18.95 (CH_3), 22.71 (CH_3), 22.89 (CH_3), 31.69 (CH), 37.23 (N-CH_3), 59.68 (CH_2), 86.09 (Ar-C of *p*-cymene), 87.66 (Ar-C of *p*-cymene), 87.98 (Ar-C of *p*-cymene), 97.21 (Ar-C of *p*-cymene), 105.75 (Ar-C of *p*-cymene), 121.63, 124.74, 125.55, 128.59, 129.38, 132.03, 138.46, 145.88, 148.60 (Ar-C), 167.33 (Ru-C), 168.32 (Ru-C). Anal. Calcd for $C_{26}H_{28}ClN_3Ru$ (519.04): C, 60.16; H, 5.44; N, 8.10. Found: C, 60.11; H, 5.48; N, 8.13.

Synthesis of [($C_6H_2Me_3$)CH_2N_2(NMe)C_2Ph)]$RuCl_2$ 5a. The following synthesis was performed under N_2 using dry solvents. A solution of **4a** (0.149 g, 0.25 mmol) in CH_2Cl_2 (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

(CD_2Cl_2): δ 1.97 (s, 6H, CH_3), 2.14 (s, 3H, CH_3), 3.92 (s, 3H, N-CH_3), 5.25 (s, 2H, CH_2), 5.33 (s, 2H, Ar-H), 7.22-7.34 (m, 3H, Ar-H), 7.58-7.66 (m, 2H, Ar-H). ^{13}C NMR (CD_2Cl_2): δ 16.86 (CH_3), 17.44 (CH_3), 38.06 (N-CH_3), 52.04 (CH_2), 84.88, 89.66, 97.34, 100.81, 126.57, 127.96, 129.80, 131.82, 146.72 (Ar-C), 165.41 (Ru-C). Anal. Calcd for $C_{19}H_{21}Cl_2N_3Ru$ (463.37): C, 49.25; H, 4.57; N, 9.07. Found: C, 49.29; H, 4.52; N, 9.09.

General Procedure for Alcohol Oxidations. A mixture of alcohol (0.2 mmol) and ruthenium complex (0.01 mmol) in toluene-D_8 was heated to 110 °C and stirred for 24 h. The reaction mixture was cooled down to 25 °C and analyzed by ^{1}H NMR spectroscopy.

General Procedure for Oxidative coupling of Amines. A mixture of amine (0.2 mmol) and ruthenium complex (0.01 mmol) in toluene-D_8 was heated to 150 °C and stirred for 24 h. The reaction mixture was cooled down to 25 °C and analyzed by ^{1}H 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 N_2 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 data were collected at 150(±2) K for all. Data for compound **4c$_3$** were collected with Cu radiation while the others were done with Mo radiation. The data integration and absorption corrections were performed with the Bruker Apex 2 software package.[52]

X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations.[53] The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function ω (F_o-F_c)^2 where the weight ω is defined as 4F_o^2/2σ (F_o^2) and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. For more information see Supporting Information.

Summary and conclusions

A series of bis(1,2,3-triazolylidene) silver(I) complexes **3a**, **3b** and **3c** have been shown to react with [$RuCl_2$(*p*-cymene)]$_2$ to form the ruthenium(II)(η^6-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$_2$**, **4b$_2$**, **4c$_2$** and **4c$_3$** are the newest examples of C-H activated triazolylidene ligands complexes. Despite the apparent relation, the ruthenium(II)(η^6-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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Notes and references

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