Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Half Sandwich Ruthenium(II) Hydrides: Hydrogenation of Terminal, Internal, Cyclic and Functionalized Olefins

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

ABSTRACT: *Bis*(1,2,3-triazolylidene) silver(I) complex **1a** was reacted with $[RuCl_2(p\text{-cymene})]_2$ to give the ruthenium complex $[PhCH_2N_2(NMe)C_2(C_6H_4CF_3)]RuCl_2(p\text{-cymene})$ (**2a**) as major product in addition to the minor C(sp^2)-H activated product $[PhCH_2N_2(NMe)C_2(C_6H_3CF_3)]RuCl(p\text{-cymene})$ (**2a'**). Similar ruthenium complexes **2b**, **2c**, **2d** and **2e** with general formula $RuCl_2(p\text{-cymene})(NHC)$ (NHC = $MesCH_2N_2(NMe)C_2Ph$ **2b**, $PhCH_2N_2(NMe)C_2Ph$ **2c**, $TripCH_2N_2(NMe)C_2Ph$ **2d**, IMes **2e**) were also synthesized. Subsequent reaction of $Me_3SiOSO_2CF_3$ with **2a** and **2b** resulted in cationic ruthenium species $[(PhCH_2N_2(NMe)C_2(C_6H_4CF_3))RuCl(p\text{-cymene})][OSO_2CF_3]$ (**3a**) and $[(MesCH_2N_2(NMe)C_2Ph)RuCl(p\text{-cymene})][OSO_2CF_3]$ (**3b**), respectively. Complexes **3a** and **3b** dissolved in CD_3CN to give $[(PhCH_2N_2(NMe)C_2(C_6H_4CF_3))RuCl(CD_3CN)(p\text{-cymene})][OSO_2CF_3]$ (**4a**) and $[(MesCH_2N_2(NMe)C_2Ph)RuCl(CD_3CN)(p\text{-cymene})][OSO_2CF_3]$ (**4b**), respectively. Cationic ruthenium species **4a** and **4b** failed to show catalytic activity towards hydrogenation of olefins. Ruthenium(II) complexes **2b-e** with the general formula $RuCl_2(p\text{-cymene})(NHC)$ were reacted with Et_3SiH to generate a series of ruthenium(II) hydrides **5b-e**. These compounds **5b-e** are effective catalysts for the hydrogenation of terminal, internal and cyclic and functionalized olefins.

INTRODUCTION

It was the discovery by Sabatier in the latter part of the nineteenth century that unveiled the utility of heterogeneous catalysis for the hydrogenation of organic unsaturates.[1] In the mid-sixties, Wilkinson et al. discovered the homogeneous hydrogenation catalyst $RhCl(PPh_3)_3$.[2] This seminal discovery inspired countless developments and academic and industrial applications.[3] Subsequent work by Osborn and Schrock,[4] Crabtreeand Morris[5] revealed the cationic hydrogenation precatalysts $[(COD)Rh(Ph_2PCH_2CH_2PPh_2)]^+$ and $[(COD)Ir(py)(PCy_3)]^+$, respectively. While since the 1970s, numerous reports have led to the modification of these precious metal systems for asymmetric catalysis,[6] more recent work in hydrogenation catalysis has focused on earth abundant metal catalysts. For example, Chirik and coworker[7] and subsequently the groups of Chirik[8] and Hanson[9] have reported highly effective Fe-based systems for olefin hydrogenation, while Beller has recently reported an iron-oxide catalyst for nitroarenes reductions to anilines.[10]

Wilkinson and co-workers also reported the Ru species $RuHCl(PPh_3)_3$ (**A**) as an olefin hydrogenation catalyst,[11] however its high air-sensitivity has precluded broad use. While Ru-based hydrogenation catalysts for asymmetric hydrogenation of ketones[12] and other polar functional groups have emerged[13], it was three decades after Wilkinson's original work that a variety of Ru hydrogenation catalysts have emerged. Yi *et al.* described $RuHCl(CO)(PCy_3)_2$ (**B**) as an effective catalyst for the hydrogenation of terminal and cyclic alkenes.[14] Yi, Nolan and Fogg *et al.* also synthesized the complex $RuHCl(CO)(NHC)(PR_3)$ (**C**)[15] while in 2009, Albrecht *et al.* reported a series of cationic

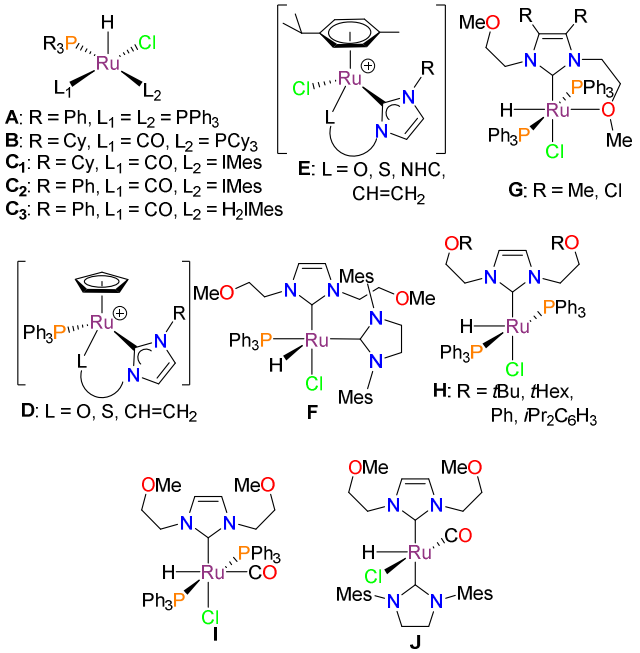


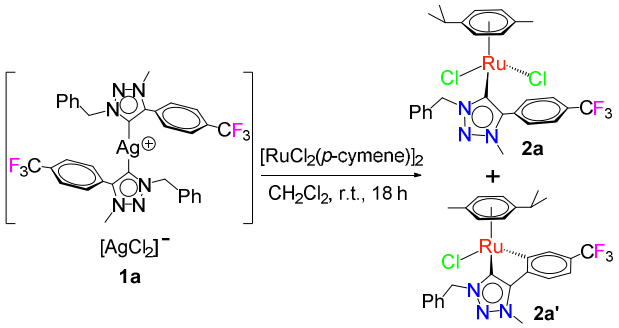
Fig. 1 Ruthenium complexes for olefin hydrogenation.

Ru-species with chelating NHC ligands (**D, E**) as robust hydrogenation catalysts for styrene,[16] and more recently described the use of Ru-NHC for the transfer hydrogenation of olefins.[17] Recently, we described a famly of *cis*-*bis*-mixed-carbene Ru-hydride species (**F-J**) which provided catalysts selective for olefin hydrogenations[18] or terminal olefins reduction.[19]

1,2,3-triazol-5-ylidenes are a recent addition to the family of NHCs, that have attracted considerable attention in recent years.[20] Ru-complexes of 1,2,3-triazol-5-ylidenes have been used as catalysts for ring-opening and ring-closing metathesis, Suzuki coupling, oxidative coupling and oxidation of water, alcohols and amines.[19] Very recently, we have reported the synthesis of Ru-triazolylidene complexes and exploited them for alcohols and amines oxidation.[20h] In this present report we describe the facile synthesis of a Ru-triazolylidene complexes and their use as highly efficient catalysts for hydrogenation of terminal, internal, cyclic and functionalized olefins.

RESULTS AND DISCUSSION

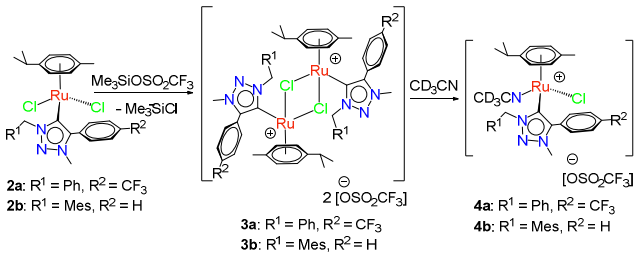
Synthesis and Characterization: The *bis*(1,2,3-triazolylidene) silver(I) complex **1a** was synthesized in good yield and subsequently treated with $[RuCl_2(p\text{-cymene})]_2$ resulting in formation of the species $[PhCH_2N_2(NMe)C_2(C_6H_4CF_3)]RuCl_2(p\text{-cymene})$ (**2a**) as a major product with the minor $C(sp^2)$-H activated product $[PhCH_2N_2(NMe)C_2(C_6H_3CF_3)]RuCl(p\text{-cymene})$ (**2a'**) (Scheme 1). Complexes **2a** and **2a'** were isolated from the crude solid by column chromatography using silica gel as stationary phase and a mixture of dichloromethane/acetone (9/1) as eluent. A yellow band which separated quickly was the cyclometalated complex **2a'** (4 %), whereas the second red-orange band was found to be the expected ruthenium(II) triazolylidene complex **2a** (81 %).



Scheme 1 Synthesis of **2a** and **2a'**.

Both complexes **2a** and **2a'** were fully characterized by ^1H, ^{13}C, ^{19}F NMR spectroscopy as well as elemental analysis. The NMR data shows a doublet at 1.11 ppm for CH_3 of *iso*-propyl moiety and a singlet at 6.18 ppm for benzylic-CH_2 suggesting that species **2a** is C_s symmetric. However, the ^1H NMR spectrum of the cyclometalated complex **2a'** displayed two doublets for both CH_3 of *iso*-propyl moiety (0.66 and 0.84 ppm) and benzylic-CH_2 (5.83 and 6.05 ppm), consistent with C_1 symmetry. While the ^1H NMR spectra, **2a** displayed two doublets (4.76 and 5.16 ppm) for the aromatic hydrogens of the *p*-cymene moiety, the corresponding signals for **2a'** showed four doublets (4.95, 5.28, 5.46 and 5.60 ppm). The Ru-C resonances appeared at 163.57 ppm for **2a** and 178.71 and 181.72 ppm for **2a'** in the respective ^{13}C NMR spectra. These data support the view that **2a** and **2a'** are derived from simple coordination of the triazolidene and metalation of the pendant arene, respectively. Very recently we reported related reactions of three *bis*(1,2,3-triazolylidene) silver(I) complexes with $[RuCl_2(p\text{-cymene})]_2$ with closely related outcomes.[20h] Similar cyclometalated triazolylidene complexes of ruthenium, iridium and palladium were also reported by Abrecht,[21] Fukuzawa[22] and Sankararaman.[23]

Complex **2a** and the related species **2b** derived from $MesCH_2N_2(NMe)C_2(C_6H_5)$ (Mes = $C_6H_2Me_3$), react with $Me_3SiOSO_2CF_3$ to form the cationic ruthenium species $[(PhCH_2N_2(NMe)C_2(C_6H_4CF_3))RuCl(p\text{-cymene})][OSO_2CF_3]$ (**3a**) and $[(MesCH_2N_2(NMe)C_2Ph)RuCl(p\text{-cymene})][OSO_2CF_3]$ (**3b**), respectively (Scheme 2). These cationic complexes are insoluble in most of the organic solvents although they are soluble to some extent in warm MeOD. ^1H NMR spectra of **3a** and **3b** displayed a doublet for CH_3 of *iso*-propyl moiety (**3a**: 1.21 ppm, **3b**: 1.30 ppm), a singlet for benzylic-CH_2 (**3a**: 5.94 ppm, **3b**: 5.90 ppm) and two doublets for aromatic hydrogens of the *p*-cymene moiety (**3a**: 5.15 and 5.60 ppm, **3b**: 5.65 and 5.87 ppm), suggesting that these species are C_s symmetric, similar to the parent compounds **2a** and **2b**. Compounds **3a** and **3b** dissolve in CD_3CN with a color change from orange-brown to yellow, inferring coordination of solvent yielding $[(PhCH_2N_2(NMe)C_2(C_6H_4CF_3))RuCl(p\text{-cymene})(CD_3CN)][OSO_2CF_3]$ (**4a**) and $[(PhCH_2N_2(NMe)C_2Ph)RuCl(p\text{-cymene})(CD_3CN)][OSO_2CF_3]$ (**4b**), respectively. This view was supported by the C_1 symmetric ^1H NMR data for **4a** and **4b**. The ^{13}C NMR data showed Ru-C resonances at 158.19 ppm and 154.29 ppm for **4a** and **4b**, respectively. As expected **4a** displayed two signals (-79.30 and -63.41 ppm) and **4b** displayed one signal (-79.30 ppm) in the respective ^{19}F NMR spectra. Coordination of acetonitrile was reversed upon standing under high vacuum for several hours, as **3a** and **3b**, respectively were cleanly regenerated.



Scheme 2 Synthesis of **3a-b** and **4a-b**.

Molecular structure analysis by X-ray diffraction revealed that **3a** is a cationic dimer with two chloride bridges between two ruthenium centres (Figure 2). The solid state structure shows an approximate C_2 symmetry with a C_2 axis passing through two chlorine atom. Ru-C bond distance of 2.085(3) Å is consistent with other ruthenium-triazolylidene complexes (1.99-2.09 Å).[24] The Ru-Cl bond distances of 2.4316(7) and 2.4493(8) Å, the Cl-Ru-Cl angle of 79.90(3)°] and the Ru-Cl-Ru angle of 100.10(3)° in **3a** are consistent with those seen in other complexes containing $Ru(\mu\text{-}Cl)_2Ru$ fragments, where the Ru-Cl bond distances lie in the range of 2.42-2.48 Å and Cl-Ru-Cl and Ru-Cl-

Ru bond angles fall in the range of 78-82° and 96-102°, respectively.[24] The cation-anion pair in **3a** show no close contacts.

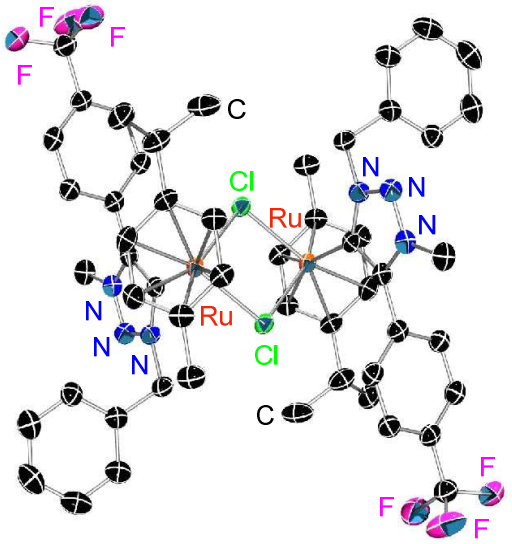
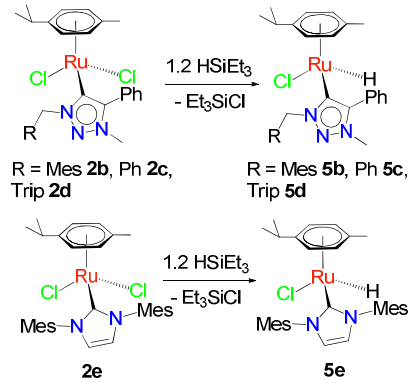


Fig. 2 Molecular structure of **3a** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and anions are omitted for clarity. Ru: orange, C: black, N: blue, Cl: green, F: pink.

We have recently exploited the series of Ru-triazolylidene complexes of the form $[RCH_2N_2(NMe)C_2Ph]RuCl_2$(*p*-cymene) [R = Mes **5b** (Mes = $C_6H_2Me_3$), Ph **5c**, Trip **5d** (Trip = $C_6H_2iPr_3$)] (Scheme 3) as moderate catalysts for oxidation of alcohols and benzylamines to aldehyde and imines respectively.[20h] These compounds reacted quantitatively with Et_3SiH at 25 °C to give the corresponding Ru-hydride complexes $[RCH_2N_2(NMe)C_2Ph]RuHCl$(*p*-cymene) (R = Mes **5b**, Ph **5c**, Trip **5d**), respectively (Scheme 3). Similarly, the known ruthenium-imidazolylidene complex (IMes)$RuCl_2$(*p*-cymene) **2e**[19] was converted to the hydride analogue (IMes)RuHCl(*p*-cymene) **5e** (Scheme 3). NMR data confirmed the formulations and the C_1 symmetry. The ^{1}H NMR spectra of **5b-e** showed four doublets (**5b**: 4.27, 4.54, 4.65, 5.42 ppm; **5c**: 4.20, 4.47, 4.49, 5.29 ppm; **5d**: 4.30, 4.52, 4.71, 5.43 ppm; **5e**: 3.76, 4.10, 4.34, 5.45 ppm) for the aromatic protons of the *p*-cymene fragment. Similarly, CH_3 protons of the *i*Pr group on the *p*-cymene moiety gave rise to two doublets (**5b**: 0.90, 1.00 ppm; **5c**: 0.80, 0.86 ppm; **5d**: 0.92, 1.01 ppm; **5e**: 1.01, 1.09 ppm). The hydride resonances appeared as singlets (**5b**: -6.60 ppm; **5c**: -6.74 ppm; **5d**: -6.59 ppm; **5e**: -7.02 ppm) in the up-field range of ^{1}H NMR spectra as expected. ^{13}C resonances for metal-bound carbon of the carbene were observed down-field at 171.06, 169.50, 169.41, and 186.10 ppm for **5b-e**, respectively. It is noteworthy that the reaction of Ru-halides with silanes has been recently exploited by Chatterjee and Gunanathan to generated Ru(II) and Ru(IV)-hydrides.[25]

In the case of **5b**, the geometry of the three-legged "piano-stool", half-sandwich complex was confirmed by an X-ray diffraction. Ru-C and Ru-Cl bond distances were found to be 2.037(3) and 2.435(1) Å, respectively. Interestingly, the Ru-H bond distance is found to be 1.73(2) Å, which is significantly longer that those previously reported for (IMes)RuHCl(CO)(PCy_3) [1.57(2) Å], ($C_3H_2(N(CH_2)_3OMe)_2$RuHCl(PPh_3)(IMes) [1.47(2) Å], ($C_3Cl_2(N(CH_2)_3OMe)_2$RuHCl(PPh_3)$_2$ [1.521(5) Å], ($C_3Cl_2(N(CH_2)_3OR)_2$RuHCl(PPh_3)$_2$ [R = *t*Bu: 1.59(7) Å, *t*Hex: 1.41(6) Å, Ph: 1.56(4) Å] and ($C_3H_2(N(CH_2)_3OMe)_2$RuHCl(PPh_3)(CO) [1.58(3) Å].[19] In **2c**, the C-Ru-H and C-Ru-Cl angles of 87.7(4)° and 88.93(9)°, respectively are similar to each other; while the Cl-Ru-H bond angle was found to be 77.2(1)°.



Scheme 3 Synthesis of **5b-e**.

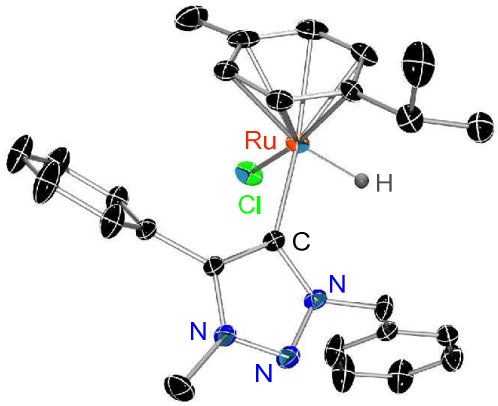


Fig. 3 Molecular structure of **5c** with thermal ellipsoids at the 50% probability level. All hydrogen atoms except the metal-hydride are omitted for clarity. Ru: orange, C: black, H: grey, N: blue, Cl: green.

Catalytic Hydrogenation of Olefins: The catalytic activity of the complexes **4a**, **4b** and **5b-e** for the hydrogenation of alkenes was investigated. Hydrogenation of olefins was performed at 50 °C under 4 atm of H_2, with a catalyst loading of 1 and 5 mol % and the reactions were monitored by ^{1}H NMR spectroscopy over 24 h (Table 1). Despite of the structural similarity with **E** (Figure 1), cationic ruthenium species **4a** and **4b** did not show any catalytic activity for the hydrogenation of olefins. However, the ruthenium-hydride species **5b-e** were active, displaying significant catalytic activity. Quantitative reduction of 1-hexene to hexane was observed in just 3 h with 5 mol % catalyst loading of **5d** (Entry 1). ^{1}H NMR measurements following this hydrogenation of 1-hexene clearly displayed the hydride resonance derived from **5d**, indicating that this species is robust. Addition of another equivalent of 1-hexene and replenishment of the H_2 atmosphere resulted in further reduction of 1-hexene to hexane, again being complete in 3 h. This process was repeated twice more with no loss of catalytic activity. Monitoring the

reduction by NMR spectroscopy revealed the transient isomerization of 1-hexene to 2-hexene was concurrent with the reduction of hexene to hexane.

Table 1 Hydrogenation Catalysis with **5b**, **5c**, **5d** and **5e**[a]

entry	substrate	product	cat	time/yield (h/%)[b]	cat	time/yield (h/%)[b]	cat	time/yield (h/%)[b]	cat	time/yield (h/%)[b]
1	1-hexene	hexane	**5d**	3/100	**5b**	4/100	**5c**	4/100	**5e**	8/100
2	1-hexene	hexane	**5d**[c]	7/100	**5b**[c]	8/96[d]	**5c**[c]	8/91[d]	**5e**[c]	8/52[d]
3	styrene	ethylbenzene	**5d**	8/48[d]	**5b**	8/39[d]	**5c**	8/35[d]	**5e**	24/83
4	2-hexene	hexane	**5d**	3/100	**5b**	4/100	**5c**	4/100	**5e**	8/100
5	2-methyl-2-butene	isopentane	**5d**	24/71	**5b**	24/63	**5c**	24/61	**5e**	24/32
6	stilbene	1,2-diphenylethane	**5d**	24/38	**5b**	24/31	**5c**	24/29	**5e**	24/12
7	cyclopentene	cyclopentane	**5d**	8/64[d]	**5b**	8/55[d]	**5c**	8/53[d]	**5e**	24/98
8	cyclohexene	cyclohexane	**5d**	8/61[d]	**5b**	8/52[d]	**5c**	8/51[d]	**5e**	24/94
9	cyclooctene	cyclooctane	**5d**	8/59[d]	**5b**	8/49[d]	**5c**	8/47[d]	**5e**	24/87
10	allyl alcohol	*n*-propanol	**5d**	3/100	**5b**	4/100	**5c**	4/100	**5e**	6/100
11	acrylaldehyde	propionaldehyde	**5d**	2/100	**5b**	3/100	**5c**	3/100	**5e**	4/100
12	3-buten-2-one	2-butanone	**5d**	4/100	**5b**	5/100	**5c**	5/100	**5e**	7/100
13	methyl 3-butenoate	methyl butyrate	**5d**	8/100	**5b**	8/81[d]	**5c**	8/83[d]	**5e**	24/89
14	acrylonitrile	propionitrile	**5d**	5/100	**5b**	7/100	**5c**	7/100	**5e**	8/76[d]
15	allylamine	propylamine	**5d**	8/63[d]	**5b**	8/49[d]	**5c**	8/42[d]	**5e**	24/91
16	2-vinyl pyridine	2-ethyl pyridine	**5d**	24/45	**5b**	24/37	**5c**	24/36	**5e**	24/18
17	*tert*-butyl vinyl ether	*tert*-butyl ethyl ether	**5d**	24/41	**5b**	24/29	**5c**	24/32	**5e**	24/15
18	phenyl vinyl sulfide	ethyl phenyl sulfide	**5d**	24/33	**5b**	24/24	**5c**	24/22	**5e**	24/12
19	1-vinylimidazole	1-ethylimidazole	**5d**	24/38	**5b**	24/28	**5c**	24/25	**5e**	24/13

[a]Conditions: 0.10 mmol of substrate and 5 mol % of catalyst in CD_2Cl_2 at 50 °C under 4 atm of H_2. [b]Yields were determined by ^1H NMR spectroscopy. [c]1 mol % catalyst loading. [d]Quantitative reduction was observed in 24 h.

After 4 h, 1 mol % **5d**, gave rise to 1-hexene, 2-hexene and hexane in a ratio of ca. 15:25:60 (Entry 2). Nonetheless, reduction was complete after 7 h, thus indicating that both 1-hexene and 2-hexene are reduced by **5d**. This was further confirmed by the independent reduction of 2-hexene as this was reduced using 5 mol% **5d** in 3 h.

Species **5d** displayed much reduced activity for the reduction of styrene to ethylbenzene (Entry 3); however, quantitative reduction was observed in 24 h. **5d** was also utilized for the hydrogenation of the internal olefins, 2-hexene, 2-methyl-2-butene, stilbene, cyclpentene, cyclohexene and cyclooctene (Entries 4-9) although these proceeds in a much slower fashion.

The hydrogenation of olefins in molecules containing functional groups was also investigated. The catalyst **5d** was observed to be be highly effective in the rapid and selective reduction of olefinic fragments of allyl alcohol, acrylaldehyde, 3-buten-2-one, methyl 3-butenoate and acrylonitrile (Entries 10-14). The corresponding hydrogenation of allylamine (Entry 15) was slower but was complete reduction after 24 h. 2-vinylpyridine, *tert*-butyl vinyl ether, phenyl vinyl sulphide and 1-vinylimidazole (Entries 16-19) are reduced although in much slower reactions with yields of 33-45% after 24 h at 50°C and 4 atm of H_2 pressure.

Species **5b** and **5c** displayed similar catalytic selectivity for the reduction of olefinic residues in all substrates (Entries 1-19), although in general these catalysts were slightly slower than **5d**. For instant, in the case of the reduction of 1-hexene using 1 mol% catalysts gave 91 %, 96 % and 52% yield of hexane after 8 h using 1 mol% of **5b**, **5c** and **5e**, respectively. Similar trends were observed for the other substrates. In general, **5d** was found to be the most effective of the 4 catalysts evaluated herein, while the triazolium-based catalysts **5b-d** gave higher product yields than imidazolium-based catalyst **5e**. This is attributed greater donor ability of the triazolium ligands as well as the altered steric demands proximate to the metal centre. Presumably both features act in concert to facilitate ring slippage of the arene ligand prompting insertion of the olefin into the Ru-H bond and the subsequent hydrogenolysis of the transient Ru-alkyl intermediate. It is noted that no evidence of catalyst degradation was observed by NMR spectroscopy after several cycles of hydrogenation catalysis inferring arene slippage is transient and only partial affording olefin access to the metal center,

EXPERIMENTAL SECTION

General Procedure: All manipulations were carried out under an atmosphere of dry, oxygen free nitrogen atmosphere employing an Innovative Technology glove box and a Schlenk vacuum-line. Solvents (pentanes, hexanes, CH_3CN and CH_2Cl_2) were purified with 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. Deuterated solvents CD_2Cl_2 and C_6D_5Br were dried over calcium hydride, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly. CD_3CN and CD_3OD were degassed and stored over 3 Å molecular sieves. ^1H, ^{13}C and ^{19}F NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal. Chemical shifts are reported in ppm. Combustion analyses were performed in house, employing a Perkin-Elmer CHN Analyzer. All reagents were purchased from Aldrich and were used as received. **2b**, **2c**, **2d** and **2e** were synthesized as reported in literature.[16h,19]

Synthesis of $[(PhCH_2C_2N_2(NMe)(C_6H_4CF_3))_2Ag][AgCl_2]$ (1a): A mixture of $[(PhCH_2N_2(NMe)C_2(C_6H_4CF_3))][OSO_2CF_3]$ (2.338 g, 5.00 mmol), Ag_2O (0.637 g, 2.75 mmol) and NMe_4Cl (0.603 g, 5.50 mmol) in a mixture of CH_2Cl_2 (10 mL) and CH_3CN (10 mL) was stirred at r.t. for 18 h under dark resulting in yellow solution

with grey precipitate. All volatiles were removed under vacuum to give a grey solid. It was extracted with CH_2Cl_2 (20 mL) and the solution was concentrated to ca. 4-5 mL. It was filtered through a plug of Celite. The solution was added dropwise to hexanes (20 mL) while stirring vigorously, which yielded 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 CH_2Cl_2 (4 mL) and the solution was added dropwise to well-stirred hexanes (20 mL) to give an off-white solid with colorless solution. The liquid was syringed off and the solid was dried under high vacuum to give **1a** (1.934 g, 84%) as pure product. ^{1}H NMR (CD_2Cl_2): δ 4.15 (s, 6H, N-CH_3), 5.61 (s, 4H, CH_2), 7.25-7.38 (m, 10H, C_6H_5), 7.66-7.76 (m, 8H, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 37.50 (N-CH_3), 59.57 (CH_2), 126.29, 128.72, 129.30, 130.35, 131.58, 131.88, 132.14, 134.69 (Ar-C), 148.09 (Ag-C). ^{19}F NMR (CD_2Cl_2): δ -63.20. MS (70 eV, ESI): m/z (rel intens) 741 (100) [$C_{34}H_{28}N_6F_6Ag^+$]. HRMS (ESI; m/z): calcd for $C_{34}H_{28}N_6F_6Ag$, 741.1331; found, 741.1326.

Synthesis of [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$]$RuCl_2$(*p*-cymene) (2a) and [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$]$RuCl_2$(*p*-cymene) (2a'). A mixture of bis(1,2,3-triazolylidene) silver(I) complex **1a** (0.921 g, 1.00 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (0.613 g, 1.00 mmol) in CH_2Cl_2 (15 mL) was stirred at r.t. for 16 h resulting in a red solution with white precipitate. The precipitate was filtered off and all volatiles were removed from the red solution to yield red solid (1.275 g) as crude products mixture. Elution on silica gel with a mixture of CH_2Cl_2/acetone (9/1) induced the separation of **2a** as the first yellow band and of **2a** as the second orange-red band. Removal of solvents under high vacuum yielded **2a'** (0.047 g, 4%) as a yellow solid and **2a** (1.011 g, 81%) as an orange-red solid.

2a: ^{1}H NMR (CD_2Cl_2): δ 1.11 (d, J = 7 Hz, 6H, CH_3 of *i*Pr), 1.73 (s, 3H, CH_3), 2.55 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.73 (s, 3H, N-CH_3), 4.76 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.16 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 6.18 (s, 2H, CH_2), 7.35-7.45 (m, 5H, C_6H_5), 7.71-7.79 (m, 4H, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 18.63 (CH_3), 22.61 (CH_3), 30.98 (CH), 37.77 (N-CH_3), 57.94 (CH_2), 82.76, 86.16, 97.11, 106.95 (Ar-C of *p*-cymene), 125.07, 128.59, 128.81, 129.03, 133.00, 136.73, 147.27 (Ar-C), 163.57 (Ru-C). ^{19}F NMR (CD_2Cl_2): δ -63.08. Anal. Calcd for $C_{27}H_{28}Cl_2F_3N_3Ru$ (623.50): C, 52.01; H, 4.53; N, 6.74. Found: C, 52.06; H, 4.50; N, 6.69.

2a': ^{1}H NMR (CD_2Cl_2): δ 0.66 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 0.84 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.97 (s, 3H, CH_3), 2.07 (sept, J = 7 Hz, 1H, CH of *i*Pr), 4.19 (s, 3H, N-CH_3), 4.95 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.28 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.46 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.60 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.83 (d, J = 14 Hz, 1H, CH of CH_2), 6.05 (d, J = 14 Hz, 1H, CH of CH_2), 7.17 (d, J = 7 Hz, 1H, C_6H_3), 7.38-7.47 (m, 6H, C_6H_3 and C_6H_5), 8.47 (s, 1H, C_6H_3). ^{13}C NMR (CD_2Cl_2): δ 18.98 (CH_3), 21.99 (CH_3 of *i*Pr), 22.90 (CH_3 of *i*Pr), 31.42 (CH of *i*Pr), 37.94 (N-CH_3), 56.42 (CH_2), 83.45, 87.40, 89.33, 93.16, 99.48, 104.24 (Ar-C of *p*-cymene), 119.19, 120.38, 127.76, 128.76, 129.38, 136.15, 138.10, 141.11, 151.41 (Ar-C), 178.71, 181.72 (Ru-C). ^{19}F NMR (CD_2Cl_2): δ -61.63. Anal. Calcd for $C_{27}H_{27}ClF_3N_3Ru$ (587.04): C, 55.24; H, 4.64; N, 7.16. Found: C, 55.19; H, 4.61; N, 7.19.

Synthesis of [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$)]$RuCl$(*p*-cymene)][$OSO_2CF_3$] (3a), [$PhCH_2N_2(NMe)C_2Ph$)]$RuCl$(*p*-cymene)][$OSO_2CF_3$] (3b), [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$)]$RuCl$(*p*-cymene)($CD_3CN$)][$OSO_2CF_3$] (4a) and [$PhCH_2N_2(NMe)C_2Ph$)]$RuCl$(*p*-cymene)($CD_3CN$)][$OSO_2CF_3$] (4b). A general procedure is described for the synthesis of **3a**/**3b** and **4a**/**4b**. A solution of $Me_3SiOSO_2CF_3$ in CH_2Cl_2 is added dropwise to a solution of **2a**/**2b** in CH_2Cl_2. The reaction mixture is stirred at r.t. for 18 h resulting in a red-brown solution. The solution is left at -35 °C for 48 h resulting in red-brown crystals. The crystals were dried under vacuum to give pure product.

3a and 4a. A mixture of **2a** (0.465 g, 0.75 mmol) and $Me_3SiOSO_2CF_3$ (0.201 g, 0.90 mmol) in CH_2Cl_2 (10 mL) yielded **3a** (0.517 g, 94%) as red-brown crystals. **3a** was dissolved in CD_3CN to form **4a**. **3a:** ^{1}H NMR (CD_3OD): δ 1.21 (d, J = 7 Hz, 6H, CH_3 of *i*Pr), 1.94 (s, 3H, CH_3), 2.67 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.92 (s, 3H, N-CH_3), 5.15 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.60 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.94 (s, 2H, CH_2), 7.36-7.52 (m, 5H, C_6H_5), 7.75 (d, J = 7 Hz, 2H, C_6H_4), 7.92 (d, J = 7 Hz, 2H, C_6H_4). [Note: Due to the very poor solubility of **3a**, decent ^{13}C NMR spectrum was not obtained.] Anal. Calcd for $C_{28}H_{28}ClF_6N_3O_3RuS$ (737.12): C, 45.62; H, 3.83; N, 5.70. Found: C, 45.65; H, 3.81; N, 5.72. **4a:** ^{1}H NMR (CD_3CN): δ 1.15 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.19 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 2.00 (s, 3H, CH_3), 2.66 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.82 (s, 3H, N-CH_3), 5.27 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.31 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.64 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.66 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.73 (d, J = 14 Hz, 1H, CH of CH_2), 6.13 (d, J = 14 Hz, 1H, CH of CH_2), 7.33-7.48 (m, 5H, C_6H_5), 7.71 (d, J = 8 Hz, 2H, C_6H_4), 7.93 (d, J = 8 Hz, 2H, C_6H_4). ^{13}C NMR (CD_3CN): δ 18.86 (CH_3), 22.38 (CH_3), 22.79 (CH_3), 31.87 (CH), 38.65 (N-CH_3), 58.33 (CH_2), 83.40, 85.86, 88.59, 90.65, 102.36, 111.71 (Ar-C of *p*-cymene), 126.66, 129.28, 129.36, 129.65, 132.90, 133.35, 136.93, 146.06 (Ar-C), 159.18 (Ru-C). ^{19}F NMR (CD_3CN): δ -63.41, -79.30.

3b and 4b. A mixture of **2b** (0.210 g, 0.35 mmol) and $Me_3SiOSO_2CF_3$ (0.087 g, 0.39 mmol) in CH_2Cl_2 (3 mL) yielded **3b** (0.247 g, 91%) as red-brown crystals. **3b** was dissolved in CD_3CN to form **4b**. **3b:** ^{1}H NMR (CD_3OD): δ 1.30 (d, J = 7 Hz, 6H, CH_3 of *i*Pr), 2.20 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.41 (s, 6H, CH_3), 2.78 (sept, J = 7 Hz, 1H, CH of *i*Pr), 4.26 (s, 3H, N-CH_3), 5.65 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.87 (d, J = 6 Hz, 2H, Ar-H of *p*-cymene), 5.90 (s, 2H, CH_2), 7.01 (s, 2H, C_6H_2), 7.60-7.70 (m, 5H, C_6H_5). ^{13}C NMR (CD_3OD): δ 18.91 (CH_3), 19.86 (CH_3), 21.13 (CH_3), 22.28 (CH_3), 32.61 (CH), 39.22 (N-CH_3), 53.11 (CH_2), 78.49, 79.28, 79.70, 80.34 (Ar-C of *p*-cymene), 98.44, 102.66, 123.86, 126.37, 129.26, 130.57, 130.71, 132.82, 139.97, 141.38, 144.87 (Ar-C) [Note: Ru-C was not detected]. Anal. Calcd for $C_{31}H_{34}ClF_6N_3O_3RuS$ (779.20): C, 47.78; H, 4.40; N, 5.39. Found: C, 47.74; H, 4.44; N, 5.43. **4b:** ^{1}H NMR (CD_3CN): δ 1.21 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.24 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 2.12 (s, 3H, CH_3), 2.29 (s, 6H, CH_3 of Mes), 2.31 (s, 3H, CH_3 of Mes), 2.75 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.67 (s, 3H, N-CH_3), 5.36 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.39 (d, J = 14 Hz, 1H, CH og CH_2), 5.55 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.74 (d, J = 6 Hz, 1H, Ar-H of *p*-

cymene), 5.79 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 6.40 (d, J = 14 Hz, 1H, CH of CH_2), 6.98 (s, 2H, C_6H_5), 7.40-7.50 (m, 2H, C_6H_5), 7.54-7.65 (m, 3H, C_6H_5). ^{13}C NMR (CD_3CN): δ 19.15 (CH_3), 20.45 (CH_3), 21.11 (CH_3), 22.42 (CH_3), 23.15 (CH_3), 32.01 (CH), 38.22 (N-CH_3), 54.04 (CH_2), 83.13, 85.45, 88.77, 90.86, 103.01, 110.75 (Ar-C of *p*-cymene), 128.47, 129.44, 129.88, 131.04, 131.77, 139.73, 140.08, 147.50 (Ar-C), 155.61 (Ru-C). ^{19}F NMR (CD_3CN): δ -79.30.

Synthesis of [MesCH$_2$N$_2$(NMe)C$_2$Ph]RuHCl(*p*-cymene) (5b). A solution of Et_3SiH (0.141 g, 1.20 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **2b** (0.599 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at r.t. The reaction mixture was stirred at r.t. for 16 h resulting in a yellow-brown solution. All volatiles were removed from the solution under high vacuum resulting in a yellow-brown solid. The solid was washed with hexanes (3 x 10 mL) and dried under high vacuum to give yellow solid as pure product **5b** (0.552 g, 98 %). ^{1}H NMR (CD_2Cl_2): δ -6.60 (s, 1H, Ru-H), 0.90 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.00 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.68 (s, 3H, CH_3), 1.91 (sept, J = 7 Hz, 1H, CH of *i*Pr), 2.18 (s, 6H, CH_3), 2.21 (s, 3H, CH_3), 3.63 (s, 3H, N-CH_3), 4.27 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.54 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.65 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.42 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.86 (broad-s, 2H, CH_2), 6.83 (s, 2H, C_6H_2), 7.43-7.51 (m, 3H, C_6H_5), 7.57-7.66 (m, 2H, C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 18.87 (CH_3), 20.34 (CH_3), 21.18 (CH_3), 23.09 (CH_3), 23.82 (CH_3), 32.01 (CH), 37.52 (N-CH_3), 53.65 (CH_2), 79.29, 85.01, 85.69, 88.14, 97.80, 100.91 (Ar-C of *p*-cymene), 128.81, 129.18, 129.48, 129.69, 130.90, 132.18, 138.43, 139.03, 147.67 (Ar-C), 169.50 (Ru-C). Anal. Calcd for $C_{29}H_{36}ClN_3Ru$ (563.14): C, 61.85; H, 6.44; N, 7.46. Found: C, 61.89; H, 6.42; N, 7.45.

Synthesis of [PhCH$_2$N$_2$(NMe)C$_2$Ph]RuHCl(*p*-cymene) (5c). A solution of Et_3SiH (0.141 g, 1.20 mmol) in CH_2Cl_2 (4 mL) was added dropwise to a solution of **2c** (0.408 g, 0.73 mmol) in CH_2Cl_2 (5 mL) at r.t. The reaction mixture was stirred at 45 °C for 2 h resulting in a yellow-brown solution. All volatiles were removed from the solution under high vacuum resulting in a grey-yellow solid. The solid was washed with pentane (3 x 10 mL) and dried under high vacuum to give yellow solid as pure product **5b** (0.366 g, 96 %). X-ray quality crystals were grown by slow diffusion of pentane into a solution of **5b** in CH_2Cl_2. ^{1}H NMR (CD_2Cl_2): δ -6.74 (s, 1H, Ru-H), 0.80 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 0.86 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.56 (s, 3H, CH_3), 1.77 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.73 (s, 3H, N-CH_3), 4.20 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 4.47 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 4.49 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 5.29 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 5.81 (d, J = 14 Hz, 1H, CH_2), 6.17 (d, J = 14 Hz, 1H, CH_2), 7.19-7.30 (m, 3H, C_6H_5), 7.31-7.38 (m, 2H, C_6H_5), 7.41-7.51 (m, 3H, C_6H_5), 7.58-7.68 (m, 2H, C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 18.26 (CH_3), 22.52 (CH_3), 23.18 (CH_3), 31.37 (CH), 37.23 (N-CH_3), 56.89 (CH_2), 78.96, 84.58, 85.47, 87.37, 97.56, 100.16 (Ar-C of p-cymene), 127.75, 128.14, 128.40, 129.33, 130.25, 131.74, 136.76, 147.37 (Ar-C), 171.06 (Ru-C). Anal. Calcd for $C_{26}H_{30}ClN_3Ru$ (521.06): C, 59.93; H, 5.80; N, 8.06. Found: C, 60.02; H, 5.87; N, 8.01.

Synthesis of [TripCH$_2$N$_2$(NMe)C$_2$Ph]RuHCl(*p*-cymene) (5d). **5d** was synthesized following an identical synthetic procedure as described for the synthesis of **5c**. A mixture of Et_3SiH (0.070 g, 0.60 mmol) and **2d** (0.341 g, 0.50 mmol) in CH_2Cl_2 (8 mL) yielded **5d** as a yellow solid (0.311 g, 96 %). ^{1}H NMR (CD_2Cl_2): δ -6.59 (s, 1H, Ru-H), 0.92 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.01 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.09 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.11 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.20 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.92 (sept, J = 7 Hz, 1H, CH of *i*Pr), 2.85 (sept, J = 7 Hz, 1H, CH of *i*Pr), 2.98 (sept, J = 7 Hz, 1H, CH of *i*Pr), 3.64 (s, 3H, N-CH_3), 4.30 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 4.52 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 4.71 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 5.43 (d, J = 7 Hz, 1H, Ar-H of *p*-cymene), 5.82 (d, J = 14 Hz, 1H, CH_2), 6.06 (d, J = 14 Hz, 1H, CH_2), 7.01 (s, 2H, C_6H_2), 7.43-7.51 (m, 3H, C_6H_5), 7.56-7.64 (m, 2H, C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 18.84 (CH_3), 23.13 (CH_3), 23.75 (CH_3), 24.13 (CH_3), 24.33 (CH_3), 24.39 (CH_3), 30.21 (CH), 32.05 (CH), 34.71 (CH), 37.45 (N-CH_3), 51.87 (CH_2), 78.97, 85.39, 86.07, 87.59, 98.30, 100.53 (Ar-C of *p*-cymene), 121.66, 127.03, 128.83, 129.72, 130.84, 132.20, 147.77, 149.43, 149.76 (Ar-C), 169.41 (Ru-C). Anal. Calcd for $C_{35}H_{48}ClN_3Ru$ (647.30): C, 64.94; H, 7.47; N, 6.49. Found: C, 64.89; H, 7.45; N, 6.52.

Synthesis of [IMesCH$_2$N$_2$(NMe)C$_2$Ph]RuHCl(*p*-cymene) (5e). **5e** was synthesized following an identical synthetic procedure as described for the synthesis of **5c**. A mixture of Et_3SiH (0.141 g, 1.20 mmol) and **2e** (0.613 g, 1.00 mmol) in CH_2Cl_2 (15 mL) yielded **5e** as a brown solid (0.550 g, 95 %). ^{1}H NMR (CD_2Cl_2): δ -7.02 (s, 1H, Ru-H), 1.01 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.09 (d, J = 7 Hz, 3H, CH_3 of *i*Pr), 1.70 (s, 3H, CH_3), 1.80 (sept, J = 7 Hz, 1H, CH of *i*Pr), 2.09 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 3.76 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.10 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 4.34 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 5.46 (d, J = 6 Hz, 1H, Ar-H of *p*-cymene), 6.97 (s, 2H, C_2H_2), 7.06 (s, 4H, C_6H_2). ^{13}C NMR (CD_2Cl_2): δ 17.63, 18.34, 18.69, 20.85, 21.34, 25.21, 25.58 (CH_3), 32.34 (CH), 72.95, 83.89, 88.43, 93.95 (Ar-C of *p*-cymene), 122.50, 128.79, 128.89, 136.33, 138.42, 138.96 (Ar-C and C_2H_2), 186.12 (Ru-C). Anal. Calcd for $C_{31}H_{40}ClN_2Ru$ (577.19): C, 64.51; H, 6.99; N, 4.85. Found: C, 64.59; H, 7.04; N, 4.82.

Hydrogenation of olefins by 5b, 5c, 5d and 5e. In a glove box, a sample of the appropriate ruthenium-hydride complex **5b** (5.2 mg, 10 μmol) or **5c** (5.6 mg, 10 μmol) or **5d** (6.5 mg, 10 μmol) or **5e** (5.8 mg, 10 μmol), CD_2Cl_2 (0.5 mL) and substrate (0.2 mmol in case of 5 mol% catalyst loading and 1 mmol in case of 1 mol% catalyst loading) were combined in a vial. The mixture was transferred to a J. Young tube and the J. Young tube was sealed. On a Schlenk line, the reaction mixture was degassed four times using the freeze-pump-thaw method. The sample was then frozen once more in liquid nitrogen and 4 atm of H_2 was added. The J. Young tube was sealed again and warmed to room temperature and then placed in an oil bath pre-heated to 50 °C. ^{1}H NMR spectra were measured at appropriate intervals and relative integration of substrate and product peaks were used to determine the composition of the mixture.

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 >99.5% complete data to a 2θ value of at least 55°. The data were collected at 150(±2) K for all. The data integration and absorption corrections were performed with the Bruker Apex 2 software package.[26]

X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations.[27] 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 $\omega (F_o-F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma (F_o^2)$ 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

The reaction of silver(I) triazolylidene **1a** and $[RuCl_2(p\text{-cymene})]_2$ resulted in ruthenium(II)(η^6-arene) complex **2a** as major product and cyclometalated species **2a'** as minor product. $RuCl_2$(*p*-cymene)(triazolylidene) **2a-b** reacted with $Me_3SiOSO_2CF_3$ to generate cationic species **3a-b**. **3a** was found to be a dimer in the solid state. CD_3CN coordinated to the metal centres in **3a-b** to form **4a-b**. Ru-complexes of 1,2,3-triazol-5-ylidenes **2b-d** are readily prepared and converted to the Ru-hydride complexes **5b-d** of the form $(RCH_2N_2(NMe)C_2Ph]RuHCl(p\text{-cymene})$. Cationic species **4a-b** were inactive for the hydrogenation of olefins. Of the triazolium species **5b-d**, complex **5d** (R = Trip) proved to be the most active hydrogenation catalyst, although all of these species are effective hydrogenation catalysts for terminal, internal and cyclic and functionalized olefins. These species exhibited higher catalytic activity than the closely related ruthenium-imidazolylidene complex **5e**. We are continuing to examine the impact of the modification of carbene donors in our continuing efforts to develop new olefin-selective hydrogenation catalysts. The results of these efforts will be reported in due course.

Acknowledgement. The financial support of LANXESS Inc., the NSERC of Canada, and the Ontario Centres of Excellence are gratefully acknowledged. DWS is grateful for the award of a Canada Research Chair.

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of $[PhCH_2N_2(NMe)C_2(C_6H_4CF_3)][OSO_2CF_3]$; NMR spectra of **1a**, **2a**, **2a'**, **3a**, **3b**, **4a**, **4b**, **5b**, **5c**, **5d** and **5e**. CIF for all structural studies have been deposited. **3a**: CCDC 1018320; **5c**: CCDC 1007295; See DOI: 10.1039/b000000x/

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