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

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ABSTRACT: Bis(1,2,3-triazolylidene) silver(I) complex 1a was reacted with [RuCl2(p-cymene)]2 to give the ruthenium complex [PhCH2N2(NMe)C2(C6H4CF3)]RuCl(p-cymene) (2a) as major product in addition to the minor C(sp^2)-H activated product [PhCH2N2(NMe)C2(C6H4CF3)]RuCl(p-cymene) (2a)*. Similar ruthenium complexes 2b, 2c, 2d and 2e with general formula RuCl2(p-cymene)(NHC) (NHC = MesCH2N2(NMe)C2Ph 2b, PhCH2N2(NMe)C2Ph 2c, TripCH2N2(NMe)C2Ph 2d, IMes 2e) were also synthesized. Subsequent reaction of Me3SiOSO2CF3 with 2a and 2b resulted in cationic ruthenium species [(PhCH2N2(NMe)C2(C6H4CF3)]RuCl(p-cymene)][OSO2CF3] (3a) and [(MesCH2N2(NMe)C2Ph)RuCl(p-cymene)][OSO2CF3] (3b), respectively. Complexes 3a and 3b dissolved in CD3CN to give [(PhCH2N2(NMe)C2(C6H4CF3)]RuCl(CD3CN)(p-cymene)][OSO2CF3] (4a) and [(MesCH2N2(NMe)C2Ph)RuCl(CD3CN)(p-cymene)][OSO2CF3] (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 RuCl2(p-cymene)(NHC) were reacted with Et3SiH 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(PPh3).2 This seminal discovery inspired countless developments and academic and industrial applications.3 Subsequent work by Osborn and Schrock,4 Crabtreeand Morris5 revealed the cationic hydrogenation precatalysts [(COD)Rh(P3Ph2)]+ and [(COD)Ir(py)(PCy3)]+, 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 coworkers7 and subsequently the groups of Chirik8 and Hanson9 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(PPh3) (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 ketones12 and other polar functional groups have emerged13, it was three decades after Wilkinson’s original work that a variety of Ru hydrogenation catalysts have emerged. Yi et al. described RuHCl(CO)(PCy3) (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)(PR3) (C)15 while in 2009, Albrecht et al. reported a series of cationic...
Ru-species with chelating NHC ligands (D, E) as robust hydrogenation catalysts for styrene,\textsuperscript{16} and more recently described the use of Ru-NHC for the transfer hydrogenation of olefins.\textsuperscript{17} Recently, we described a family of cis-bis-mixed-carbene Ru-hydride species (F-J) which provided catalysts selective for olefin hydrogenations\textsuperscript{18} or terminal olefins reduction.\textsuperscript{19}

1,2,3-triazol-5-ylidene complexes and exploited them for alcohols and as eluent. A yellow band which separated quickly was the stationary phase and a mixture of dichloromethane/acetonitrile (9/1) crude solid by column chromatography using silica gel as data shows a doublet at 1.11 ppm for CH\textsubscript{3}symmetric, corresponding signals for 2a and 2a\textsuperscript{'} were found to be the expected ruthenium(II) (NMe)C\textsubscript{3}Ru\textsubscript{2+}cationic ruthenium species (Figure 2). The solid state structure shows an approximate C\textsubscript{2} symmetry with a C\textsubscript{3} symmetric, similar to the parent compounds 2a and 2b. Compounds 3a and 3b dissolve in CD\textsubscript{3}CN with a color change from orange-brown to yellow, inferring coordination of solvent yielding [(PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)](CD\textsubscript{3}CN)[OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (4a) and [(PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)(CD\textsubscript{3}CN)][OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (4b), respectively. This view was supported by the C\textsubscript{16} symmetric \textsuperscript{1}H NMR data for 4a and 4b. The \textsuperscript{13}C NMR data showed Ru-C resonances at 151.19 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 \textsuperscript{19}F NMR spectra. Coordination of acetoniitrile was reversed upon standing under high vacuum for several hours, as 3a and 3b, respectively, were cleanly regenerated.

**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\textsubscript{2}(p-cymene)]\textsubscript{2}, resulting in formation of the species [PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3}]RuCl(p-cymene) (2a) as a major product with the minor C(sp\textsuperscript{3})\textsubscript{3}H\textsubscript{3}activated product [PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3}]RuCl(p-cymene) (2a\textsuperscript{'}) (Scheme 1). Complexes 2a and 2a\textsuperscript{'} were isolated from the crude solid by column chromatography using silica gel as stationary phase and a mixture of dichloromethane/acetonitrile (9/1) as eluent. A yellow band which separated quickly was the cyclometalated complex 2a\textsuperscript{'} (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\textsuperscript{'} were fully characterized by \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F NMR spectroscopy as well as elemental analysis. The NMR data shows a doublet at 1.11 ppm for CH\textsubscript{3} of iso-propyl moiety and a singlet at 6.18 ppm for benzylic-CH\textsubscript{2} suggesting that species 2a is C\textsubscript{1} symmetric. However, the \textsuperscript{1}H NMR spectrum of the cyclometalated complex 2a\textsuperscript{'} displayed two doublets for both CH\textsubscript{3} of iso-propyl moiety (0.66 and 0.84 ppm) and benzylic-CH\textsubscript{2} (5.83 and 6.05 ppm), consistent with C\textsubscript{2} symmetry. While the \textsuperscript{1}H 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\textsuperscript{'} 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\textsuperscript{'} in the respective \textsuperscript{13}C NMR spectra. These data support the view that 2a and 2a\textsuperscript{'} 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\textsubscript{2}(p-cymene)]\textsubscript{2} with closely related outcomes.\textsuperscript{20b} Similar cyclometalated triazolylidene complexes of ruthenium, iridium and palladium were also reported by Abrecht,\textsuperscript{21} Fukuzawa\textsuperscript{22} and Sankararaman.\textsuperscript{23}

Complex 2a and the related species 2b derived from Mes\textsubscript{2}CH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3} (Mes = C\textsubscript{6}H\textsubscript{5}CF\textsubscript{3}), react with Me\textsubscript{3}SiOSO\textsubscript{2}CF\textsubscript{3} to form the cationic ruthenium species [(PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)][OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (3a) and [(MesCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)][OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (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. \textsuperscript{1}H NMR spectra of 3a and 3b displayed a doublet for CH\textsubscript{3} of iso-propyl moiety (3a: 1.21 ppm, 3b: 1.30 ppm), a singlet for benzylic-CH\textsubscript{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\textsubscript{2} symmetric, similar to the parent compounds 2a and 2b. Compounds 3a and 3b dissolve in CD\textsubscript{3}CN with a color change from orange-brown to yellow, inferring coordination of solvent yielding [(PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)](CD\textsubscript{3}CN)[OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (4a) and [(PhCH\textsubscript{2}N\textsubscript{2}(NMe)C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})RuCl(p-cymene)(CD\textsubscript{3}CN)][OSO\textsubscript{2}CF\textsubscript{3}]\textsubscript{2} (4b), respectively. This view was supported by the C\textsubscript{1} symmetric \textsuperscript{1}H NMR data for 4a and 4b. The \textsuperscript{13}C NMR data showed Ru-C resonances at 151.19 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 \textsuperscript{19}F NMR spectra.

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\textsubscript{2} symmetry with a C\textsubscript{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).\textsuperscript{24} The Ru-Cl bond distances of 2.4316(7) and 2.4493(8) Å, the CljRujCl and RuCljRuCl distances lie in the range of 2.42-2.48 Å and CljRu-Cl and Ru-CljRuCl distances lie in the range of 2.42-2.48 Å.

Scheme 2 Synthesis of 3a-b and 4a-b.
bond distance is found to be 1.73(2) Å, which is significantly longer than those previously reported for 3a (1.41(6) Å,  Ph: 1.56(4) Å) and (C\(\text{Ph})_2\)Cl\(\text{RuHCl}(\text{N(CH}_3)_2\text{OMe})\) [1.521(5) Å], (C\(\text{Cl}_2\text{N(C\(\text{CH}_3\))OR})_2\text{RuHCl}(\text{PPh}_3)_2\) [R = tBu: 1.59(7) Å, tHex: 1.41(6) Å, Ph: 1.56(4) Å] and (C\(\text{H}_2\text{(N\(\text{CH}_3\))OMe})_2\text{RuHCl}(\text{PPh}_3)(\text{CO})_2\) [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)°.

Addition of another equivalent of 1-hexene and replenishment of the H\(\text{NMR}\) resonance derived from the reactions were monitored by H\(\text{NMR}\) spectroscopy over 24 h (Table 1). Despite of the structural similarity with catalytic activity for the hydrogenation of olefins. However, the ruthenium-hydride 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). 1H 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\(\text{NMR}\) 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

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| Conditions: 0.10 mmol of substrate and 5 mol % of catalyst in CD$_2$Cl$_2$ at 50 °C under 4 atm of H$_2$. | Yields were determined by $^1$H NMR spectroscopy. | *1 mol % catalyst loading. | 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, cyclopentene, 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 highly effective in the rapid and selective reduction of olefinic fragments of allyl alcohol, acrylaldehyde, 3-buten-2-one, methyl 3-butenone 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-5d 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 center. 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$_2$CN and CH$_2$Cl$_2$) 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$_2$Cl$_2$ and CD$_3$Br were dried over 3 Å molecular sieves. 1H, 13C and 19F NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to SiMe$_2$ 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, 2e, 2d and 2e were synthesized as reported in literature.

**Synthesis of [(PhCH$_2$)$_2$N$_2$(NMe)(C$_6$H$_4$Cl$_2$)$_2$]Ag[AgCl$_2$] (1a):**

A mixture of [(PhCH$_2$)$_2$N$_2$(NMe)$_2$C$_6$H$_4$Cl$_2$)]OSO$_2$CF$_3$ (2.338 g, 5.00 mmol), Ag$_2$O (0.637 g, 2.75 mmol) and NM$_2$Cl (0.603 g, 5.50 mmol) in a mixture of CH$_2$Cl$_2$ (10 mL) and CH$_2$CN (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\textsubscript{2}Cl\textsubscript{2} (20 mL) and the solution was concentrated to ca. 4-5 mL. It was filtered through a plug of Celite. The solution was discarded and the solid was dried under vacuum resulting in a foamy solid. The solid was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (4 mL) and 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 dissolvd in CH\textsubscript{2}Cl\textsubscript{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. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 4.15 (s, 6H, N-Ch\textsubscript{2}) , 5.61 (s, 4H, Ch\textsubscript{2}) , 7.25-7.38 (m, 10H, C\textsubscript{6}H\textsubscript{5}) , 7.66-7.76 (m, 8H, C\textsubscript{6}H\textsubscript{5}) . \textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 37.50 (N-Ch\textsubscript{2}) , 59.57 (Ch\textsubscript{2}) , 126.29, 128.72, 129.30, 130.35, 131.58, 131.88, 132.14, 134.69 (Ar-C) , 148.09 (Ag-C) . \textsuperscript{19}F NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) -63.20. MS (70 eV, ESI): m/z: (rel intens) 741 (100) [C\textsubscript{6}H\textsubscript{5}Nu\textsubscript{3}F\textsubscript{3}Ag] . HRMS (ESI; m/z): calculated for C\textsubscript{6}H\textsubscript{5}N\textsubscript{3}F\textsubscript{3}Ag: 741.1331; found: 741.1326.

\textsuperscript{2} Synthesis of \([\text{PhCH}_{2}N\textsubscript{2}(\text{NMe})C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}Cu]Cl(\text{py-cyme})\) (2a) and \([\text{PhCH}_{2}N\textsubscript{2}(\text{NMe})C\textsubscript{6}H\textsubscript{5}C\textsubscript{6}H\textsubscript{5}Cu]Cl(\text{py-cyme})\) (2a'). A mixture of bis(1,2,3-triazolylidine) silver(II) complex 1a (0.921 g, 1.00 mmol) and [RuCl\textsubscript{3}(py-cyme)] (0.613 g, 1.00 mmol) in CH\textsubscript{2}Cl\textsubscript{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\textsubscript{2}Cl\textsubscript{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: \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 1.11 (d, \( J = 7 \) Hz, 6H, Ch\textsubscript{2} of iPr) , 1.73 (s, 3H, CH\textsubscript{3}) , 2.57 (sept, \( J = 7 \) Hz, 1H, CH of iPr) , 3.73 (s, 3H, N-Ch\textsubscript{2}) , 4.76 (d, \( J = 6 \) Hz, 2H, Ar-H of p-cyme) , 5.16 (d, \( J = 6 \) Hz, 2H, Ar-H of p-cyme) , 6.18 (s, 2H, CH\textsubscript{2}) , 7.35-7.45 (m, 5H, C\textsubscript{6}H\textsubscript{5}) , 7.71-7.79 (m, 4H, C\textsubscript{6}H\textsubscript{5}) . \textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 18.83 (CH\textsubscript{2}) , 22.61 (CH\textsubscript{3}) , 30.98 (CH\textsubscript{3}) , 37.77 (N-Ch\textsubscript{2}) , 57.94 (CH\textsubscript{2}) , 82.76, 86.16, 97.11, 106.95 (Ar-C of p-cyme) , 125.07, 128.59, 128.81, 129.03, 133.00, 136.73, 147.27 (Ar-C) , 163.57 (Ru-C) . \textsuperscript{19}F NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) -63.08. Anal. Calcd for C\textsubscript{29}H\textsubscript{26}F\textsubscript{4}N\textsubscript{3}Ru: C\textsubscript{28}H\textsubscript{26}F\textsubscript{4}N\textsubscript{3}Ru (623.50): C, 52.01; H, 4.53; N, 6.74. Found: C, 52.06; H, 4.50; N, 6.69.

2a': \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 0.66 (d, \( J = 7 \) Hz, 3H, Ch\textsubscript{3} of iPr) , 0.84 (d, \( J = 7 \) Hz, 3H, CH\textsubscript{2} of iPr) , 1.97 (s, 3H, CH\textsubscript{3}) , 2.07 (sept, \( J = 7 \) Hz, 1H, CH of iPr) , 4.19 (s, 3H, N-Ch\textsubscript{2}) , 4.95 (d, \( J = 6 \) Hz, 1H, Ar-H of p-cyme) , 5.28 (d, \( J = 6 \) Hz, 1H, Ar-H of p-cyme) , 5.46 (d, \( J = 6 \) Hz, 1H, Ar-H of p-cyme) , 5.60 (d, \( J = 6 \) Hz, 1H, Ar-H of p-cyme) , 5.83 (d, \( J = 14 \) Hz, 1H, CH of CH\textsubscript{2}) , 6.05 (d, \( J = 14 \) Hz, 1H, CH of CH\textsubscript{2}) , 7.17 (d, \( J = 7 \) Hz, 1H, C\textsubscript{6}H\textsubscript{5}) , 7.38-7.47 (m, 6H, C\textsubscript{6}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5}) , 8.47 (s, 1H, C\textsubscript{6}H\textsubscript{5}) . \textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 18.98 (CH\textsubscript{3}) , 21.99 (CH\textsubscript{2} of iPr) , 22.90 (CH\textsubscript{2} of iPr) , 31.42 (CH of iPr) , 37.94 (N-Ch\textsubscript{2}) , 56.42 (CH\textsubscript{2}) , 83.45, 87.40, 89.33, 93.16, 99.48, 104.24 (Ar-C of p-cyme) , 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) . \textsuperscript{19}F NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) -61.63. Anal. Calcd for C\textsubscript{29}H\textsubscript{26}F\textsubscript{4}N\textsubscript{3}Ru: C\textsubscript{28}H\textsubscript{26}F\textsubscript{4}N\textsubscript{3}Ru (587.04): C, 55.24; H, 4.64; N, 7.16. Found: C, 55.19; H, 4.61; N, 7.19.
Synthesis of [{MesCH$_2$N$_2$(NMe)$_2$C$_2$}RuHCl(p-cymene)] (5b).
A solution of Et$_3$SiH (0.141 g, 1.20 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise to a solution of 2b (0.599 g, 1.00 mmol) in CH$_2$Cl$_2$ (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 solid yellow as pure product 5b (0.552 g, 98%). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ -6.60 (s, 1H, Ru-H), 0.90 (d, J = 7 Hz, 3H, CH$_3$ of iPr), 1.00 (d, J = 7 Hz, 3H, CH$_3$ of iPr), 1.68 (s, 3H, CH$_3$), 1.91 (sept, J = 7 Hz, 1H, CH of iPr), 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$_6$H$_5$), 7.43-7.51 (m, 3H, C$_6$H$_5$), 7.57-7.66 (m, 2H, C$_6$H$_5$). $^1$C NMR (CD$_2$Cl$_2$): $\delta$ 18.87 (CH$_3$), 20.34 (CH$_3$), 21.18 (CH$_3$), 23.09 (CH$_3$), 23.82 (CH$_3$), 32.01 (CH$_3$), 37.25 (N-CH$_3$), 53.65 (CH$_3$), 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, 129.90, 132.18, 138.43, 139.03, 147.67 (Ar-C), 169.50 (Ru-C). Anal. Calcld for C$_9$H$_{18}$Cl$_2$N$_2$Ru: C, 64.89; H, 7.46; N, 7.45. Found: C, 64.89; H, 7.45; N, 7.45.

Synthesis of [{PhCH$_2$N$_2$(NMe)$_2$C$_2$}RuHCl(p-cymene)] (5c).
A solution of Et$_3$SiH (0.141 g, 1.20 mmol) in CH$_2$Cl$_2$ (4 mL) was added dropwise to a solution of 2e (0.408 g, 0.73 mmol) in CH$_2$Cl$_2$ (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$_2$Cl$_2$. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ -6.74 (s, 1H, Ru-H), 0.80 (d, J = 7 Hz, 3H, CH$_3$ of iPr), 0.86 (d, J = 7 Hz, 3H, CH$_3$ of iPr), 1.56 (s, 3H, CH$_3$), 1.77 (sept, J = 7 Hz, 1H, CH of iPr), 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$_6$H$_5$), 7.31-7.38 (m, 2H, C$_6$H$_5$), 7.41-7.51 (m, 3H, C$_6$H$_5$), 7.58-7.68 (m, 2H, C$_6$H$_5$). $^1$C NMR (CD$_2$Cl$_2$): $\delta$ 18.26 (CH$_3$), 22.52 (CH$_3$), 23.18 (CH$_3$), 31.37 (CH$_3$), 37.23 (N-CH$_3$), 56.89 (CH$_3$), 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. Calcld for C$_{32}$H$_{45}$Cl$_2$N$_2$Ru (521.06): C, 59.93; H, 5.80; N, 8.06. Found: C, 60.02; H, 5.87; N, 8.01.
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 >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 F² minimizing the function w (F² - F½)² where the weight w is defined as 4F²/2σ (F²) and F₁ and F₂ 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 [RuCl₂(p-cymene)]; resulted in ruthenium(II)(p³-arene) complex 2a as major product. RuCl₂(p-cymene)(triazolylidene) 2a·b reacted with Me₃SiOSO₂CF₃ to generate cationic species 3a·b. 3a was found to be a dimer in the solid state. C₂D₂CN 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 (RCH₂N(Me)C₆H₅)RuHCl(p-cymene). Cationic species 4a·b were inactive for the hydrogenation of olefins. Of the triazolium species 5b·d, complex 5d (R = Tripp) 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-imidazolidine 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.

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**Notes and references**

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of [Pd(CH₂₃N(Me)(C₆H₅)₂)sO₂CF₃]; NMR spectra of 1a, 2a, 2′a, 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/c


TOC graphic

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\text{Functional group} \xrightarrow{\text{H}_2} \text{Functional group}
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