

**1,2,3-Triazolylidene Ruthenium(II)-Cyclometalated
Complexes and Olefin Selective Hydrogenation Catalysis**

Journal:	<i>Dalton Transactions</i>
Manuscript ID:	DT-ART-10-2014-003156.R1
Article Type:	Paper
Date Submitted by the Author:	05-Nov-2014
Complete List of Authors:	Bagh, Bidraha; University of Toronto, Chemistry McKinty, Adam; University of Toronto, Chemistry Lough, Alan; University of Toronto, Chemistry Stephan, Douglas; University of Toronto, Department of Chemistry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

1,2,3-Triazolylidene Ruthenium(II)-Cyclometalated Complexes and Olefin Selective Hydrogenation Catalysis

Bidraha Bagh, Adam M. McKinty, Alan J. Lough and Douglas W. Stephan*

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

DOI: 10.1039/b000000x

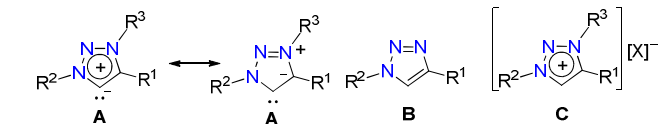
ABSTRACT: Silver(I) 1,2,3-triazol-5-ylidenes [(RCH₂C₂N₂(NMe)Ph)₂Ag][AgCl₂] (R = Ph **3a**, C₆H₂iPr₃ **3b**, C₆H₂Me₃ **3c**) and [(PhCH₂C₂N₂(NMe)R)₂Ag][AgCl₂] (R = C₆H₄Me **3d**, C₆H₄CF₃ **3e**) were synthesized and subsequently treated with RuHCl(PPh₃)₃ and RuHCl(H₂)(PCy₃)₂. The reaction of **3a** with RuHCl(PPh₃)₃ gave RuHCl(PPh₃)₂(PhCH₂C₂N₂(NMe)Ph) (**4a₁**) as the minor product and the cyclometalated complex RuCl(PPh₃)₂(PhCH₂C₂N₂(NMe)C₆H₄) (**4a₂**) as the major product. However, similar reaction with **3b** selectively formed the cyclometalated complex RuCl(PPh₃)₂((C₆H₂iPr₃)CH₂C₂N₂(NMe)C₆H₄) (**4b₂**). Similarly the silver(I) triazolylidenes **3a** and **3b** were reacted with RuHCl(H₂)(PCy₃)₂, gave RuHCl(PCy₃)₂(PhCH₂C₂N₂(NMe)Ph) (**5a₁**), RuCl(PCy₃)₂(PhCH₂C₂N₂(NMe)C₆H₄) (**5a₂**) and RuCl(PCy₃)₂((C₆H₂iPr₃)CH₂C₂N₂(NMe)C₆H₄) (**5b₂**), respectively. Species **3c**, **3d** and **3e** resulted in the cyclometalated complexes (**5c₂**, **5d₂** and **5e₂**) as the major products as well as the ruthenium-hydride complexes (**5c₁**, **5d₁** and **5e₁**) as the minor products. The cyclometalated species are derived from the ruthenium-hydride complexes via C(sp²)-H activation. These Ru-complexes were shown to act as hydrogenation catalyst precursors for olefinic substrates including those containing a variety of functional groups.

INTRODUCTION

The most common chemical transformation used in chemical industry is hydrogenation. Indeed, this reaction is essential for the preparation of a vast array of materials, polymers, pharmaceuticals, agrochemicals, fine chemicals and foodstuffs.¹ Among homogeneous catalysts used for hydrogenations, those derived from rhodium² and iridium³ complexes are common. While such precious metal systems are employed because of their activity, the expense and toxic nature of these metals has prompted effort to employ alternatives.⁴ Ruthenium compounds of the type RuHCl(CO)(NHC)(PPh₃) are effective catalysts for the hydrogenation of olefins.⁵ Albrecht et al. showed that ruthenium complexes of chelating NHCs acted as a very robust catalysts.⁶ In our own efforts we have recently communicated that a *cis-bis*-NHC ruthenium hydride complex exhibited remarkably selective catalyst for olefin hydrogenation.⁷ Noting that these catalysts do indeed contain electron rich Ru-centers, we considered the possibility of using of alternative donors.

1,3,4-trisubstituted-1,2,3-triazol-5-ylidenes (Figure 1 A) are a recent addition to the family of mesoionic N-heterocyclic carbenes (NHCs) that have attracted considerable attention in last five years.⁸ Precursors to these ligands namely 1,2,3-triazole (Figure 1 B) are readily synthesized by the Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes. This so-called 'click' reaction⁹ is highly modular and useful as it proceeds under mild reaction conditions, with high tolerance of functional groups and excellent yields. In 2008 the first transition metal complex of 1,2,3-triazolylidene was reported by Albrecht et al.

using the 1,2,3-triazolium salt (Figure 1 C) as precursor.¹⁰ While Bertrand *et al.* synthesized free 1,3,4-trisubstituted-1,2,3-triazol-5-ylidenes by the deprotonation of the 1,2,3-triazolium salt with KN(SiMe₃)₂ or KO^tBu,¹¹ these species are conveniently stabilized by complexation with Ag(I). These latter species can be exploited for transmetalation reactions and have been further exploited as ligands for novel metal catalysts in reactions such as oxidation of amines,¹² and water,¹³ alcohols,¹² oxidative coupling,¹² Suzuki coupling,¹⁴ and ring-opening and ring-closing metathesis.^{11a} In addition, in a recent report we have described three half-sandwich Ru(II) hydride complexes with 1,2,3-triazolylidene ligands which proved to be good hydrogenation catalysts for olefins.¹⁵ In this manuscript, we demonstrate that Ru-phosphine complexes of 1,2,3-triazolylidenes are readily accessible and highly effective and selective catalyst precursors for hydrogenation of functionalized olefins.



R¹ and R² = alkyl, benzyl or aryl; R³ = alkyl or benzyl; X = Br, I, OTf, PF₆, BF₄

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

EXPERIMENTAL SECTION

General Procedure. Syntheses of **1a-e** were performed in air

with ordinary solvents. All other 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 (pentane, hexanes, toluene, CH₂Cl₂) 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. CH₃CN was stored over CaH₂, distilled and degassed before use. Dry benzene was purchased from Aldrich and degassed before use. Deuterated solvents (C₆D₆, CDCl₃ and CD₂Cl₂) were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly. ¹H, ¹³C and ³¹P NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to SiMe₃ and referenced to the residual solvent signal (¹H and ¹³C) or relative to an external standard (³¹P, 85% H₃PO₄). 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. **1a**, **1b**, **1c**, **1d**, **1e**, **2a**, **2b**, **2c**, **3a**, **3b** and **3c** were synthesized according to literature procedure.¹⁶ RuHCl(PPh₃)₃ and RuHCl(H₂)(PCy₃)₂ was prepared following a modified literature procedure.¹⁷ As repeated elemental analysis of **3d** and **3e** failed to produce acceptable results, HRMS was performed as a further characterization.

Synthesis of [PhCH₂C₂HN₂(NMe)R][OTf] (R = C₆H₄Me **2d, C₆H₄CF₃ **2e**).** Identical synthetic procedures were followed for the preparation of **2d** and **2e**. MeOTf (11.00 mmol) was added dropwise to a solution of 1,2,3-triazole (10.00 mmol) in CH₂Cl₂ (20 mL) at r.t. The reaction mixture was stirred for 40 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.

2d: 1d (2.495 g, 10.00 mmol) and MeOTf (1.805 g, 11.00 mmol) yielded **2d** (3.747 g, 91%). ¹H NMR (CD₂Cl₂): δ 2.42 (s, 3H, CH₃), 4.23 (s, 3H, N-CH₃), 5.80 (s, 2H, CH₂), 7.33-7.63 (m, 9H, C₆H₅ and C₆H₄), 8.68 (s, 1H, triazolium-H). ¹³C NMR (CD₂Cl₂): δ 21.58 (CH₃), 39.03 (N-CH₃), 57.91 (CH₂), 119.20, 128.57, 129.43, 129.74, 129.97, 180.27, 130.68, 131.80, 143.19, 144.13 (C₆H₅, C₆H₄ and trizolium-C). Anal. Calcd for C₁₈H₁₈F₃N₃O₃S (413.41): C, 52.29; H, 4.39; N, 10.16. Found: C, 52.32; H, 4.34; N, 10.11.

2e: 1e (3.035 g, 10.00 mmol) and MeOTf (1.805 g, 11.00 mmol) yielded **2e** (4.229 g, 90%). ¹H NMR (CD₂Cl₂): δ 4.26 (s, 3H, N-CH₃), 5.82 (s, 2H, CH₂), 7.40-7.87 (m, 9H, C₆H₅ and C₆H₄), 8.78 (s, 1H, triazolium-H). ¹³C NMR (CDCl₃): δ 39.27 (N-CH₃), 58.14 (CH₂), 126.00, 126.91, 129.45, 129.80, 130.03, 130.39, 130.60, 131.49, 142.57 (C₆H₅, C₆H₄ and trizolium-C). Anal. Calcd for C₁₈H₁₅F₆N₃O₃S (467.39): C, 46.26; H, 3.23; N, 8.99. Found: C, 46.21; H, 3.25; N, 9.02.

Synthesis of [(PhCH₂C₂N₂(NMe)R)₂Ag][AgCl₂] (R = C₆H₄Me **3d, C₆H₄CF₃ **3e**).** Identical synthetic procedures were followed

for the preparation of **3d** and **3e**. A mixture of triazolium salt (5.00 mmol), Ag₂O (2.75 mmol) and NMe₄Cl (5.50 mmol) in a 1:1 mixture of CH₂Cl₂ (10 mL) and CH₃CN (10 mL) was stirred at r.t. for 24 h under dark resulting in yellow solution with grey precipitate. All volatiles were removed under vacuum to give a grey solid which was extracted with CH₂Cl₂ (20 mL). The solution was concentrated to approximately one fourth to its original volume and filtered through a plug of Celite to get a clear solution. The solution was added dropwise to well-stirred hexanes (20 mL). This yielded a sticky precipitate with pale yellow solution. The solid was dried under vacuum resulted in a foamy solid. The solid was dissolved in minimum amount of CH₂Cl₂ (ca. 4-5 mL) and the solution was added dropwise to well-stirred hexanes (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 pure product.

3d: 2d (2.068 g, 5.00 mmol), Ag₂O (0.637 g, 2.75 mmol) and NMe₄Cl (0.603 g, 5.50 mmol) yielded **3d** (1.811 g, 89%). ¹H NMR (CD₂Cl₂): δ 2.41 (s, 3H, CH₃), 4.10 (s, 3H, N-CH₃), 5.54 (s, 2H, CH₂), 7.21-7.47 (m, 9H, C₆H₅ and C₆H₄). ¹³C NMR (CD₂Cl₂): δ 21.43 (CH₃), 37.71 (N-CH₃), 59.82 (CH₂), 124.79, 128.69, 129.22, 129.28, 129.55, 130.06, 134.81, 140.87, 149.60 (C₆H₅, C₆H₄ and trizolium-C). MS (70 eV, ESI): *m/z* (rel intens) 633 (100) [C₃₄H₃₄N₆Ag⁺]. HRMS (ESI; *m/z*): calcd for C₃₄H₃₄N₆Ag, 633.1890; found, 633.1885.

3e: 2e (2.338 g, 5.00 mmol), Ag₂O (0.637 g, 2.75 mmol) and NMe₄Cl (0.603 g, 5.50 mmol) yielded **3e** (1.934 g, 84%). ¹H NMR (CD₂Cl₂): δ 4.15 (s, 3H, N-CH₃), 5.61 (s, 2H, CH₂), 7.25-7.75 (m, 9H, C₆H₅ and C₆H₄). ¹³C NMR (CD₂Cl₂): δ 38.03 (N-CH₃), 59.86 (CH₂), 125.19, 126.27, 128.72, 129.30, 130.35, 131.58, 131.88, 132.14, 134.70, 148.09 (C₆H₅, C₆H₄ and trizolium-C). MS (70 eV, ESI): *m/z* (rel intens) 741 (100) [C₃₄H₂₈N₆F₆Ag⁺]. HRMS (ESI; *m/z*): calcd for C₃₄H₂₈N₆F₆Ag, 741.1327; found, 741.1325.

Synthesis of RuHCl(PPh₃)₂(PhCH₂C₂N₂(NMe)Ph) (4a₁**) and RuCl(PPh₃)₂(PhCH₂C₂N₂(NMe)C₆H₄) (**4a₂**).** Toluene (30 mL) was added to a mixture of **3a** (0.395 g, 0.50 mmol) and RuHCl(PPh₃)₃ (0.926 g, 1.00 mmol). The reaction mixture was stirred at 25 °C for 48 h resulting in a dark red solution with brown precipitate. The precipitate was filtered off and the solution was concentrated to ca. one fourth to its original volume. The concentrated solution was added dropwise to well stirred hexanes (30 mL) resulting in a red precipitate with pale red solution. The liquid was syringed off and the solid was washed with hexanes (3 x 10 mL). The red solid was dried to give crude product **4a₂** which was dissolved in appropriate solvent and crystallization gave dark red crystals as pure product **4a₂**. Dark red crystals were deposited from the pale red solution on standing, which were found to be a mixture of **4a₁** and **4a₂** in the ratio of 8.5:1.5.

4a₂: 3a (0.395 g, 0.50 mmol) and RuHCl(PPh₃)₃ (0.926 g, 1.00 mmol) yielded a red solid (0.482 g) as crude product. The crude product was dissolved in benzene (20 mL). Slow diffusion of hexanes into the benzene solution resulted in dark red crystals. Crystals were dried under high vacuum to give pure **4a₂** (0.191 g, 21%). ¹H NMR (CDCl₃): δ 3.34 (s, 3H, N-CH₃), 4.86 (s, 2H, CH₂), 6.29-6.36 (m, 1H, Ar-H), 6.41-6.49 (m, 2H, Ar-H), 6.80 (d,

$^3J_{\text{HH}} = 8$ Hz, 2H, Ar-H), 6.95-7.03 (m, 3H, Ar-H), 7.09-7.45 (m, 30H, Ar-H), 8.08 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H). ^{13}C NMR (CDCl_3): δ 36.59 (N-CH₃), 55.99 (CH₂), 118.83, 120.08, 122.96, 127.73, 128.70, 129.35, 134.48, 134.79, 135.09, 136.01, 139.77, 141.09, 153.53 (Ar-C), 173.39, 180.64 (Ru-C(C₆H₄)) and Ru-C(triazolylidene)). ^{31}P NMR (CDCl_3): δ 37.70 (PPh₃). Anal. Calcd for C₅₂H₄₄ClN₃P₂Ru (909.40): C, 68.68; H, 4.88; N, 4.62. Found: C, 68.73; H, 4.85; N, 4.60.

4a₁: **4a₁** could not be isolated as a pure compound. The crude product (0.122 g) contained a mixture of **4a₁** and **4a₂** (8.5:1.5). Further crystallization from the mixture increased the amount of **4a₂**. ^1H NMR (CDCl_3): δ -27.49 (t, $^2J_{\text{PH}} = 24$ Hz, 1H, RuH), 3.25 (s, 3H, Me), 4.77 (s, 2H, CH₂), 6.45-7.35 (m, 40H, Ar-H). ^{31}P NMR (CDCl_3): δ 46.33 (PPh₃).

Synthesis of RuCl(PPh₃)₂((C₆H₂*i*Pr₃)CH₂C₂N₂(NMe)C₆H₄) (4b₂**).** Toluene (30 mL) was added to a mixture of **3b** (0.520 g, 0.50 mmol) and RuHCl(PPh₃)₃ (0.926 g, 1.00 mmol). The reaction mixture was stirred at r.t. for 48 h resulting in a dark red solution with brown precipitate. The precipitate was filtered off and the solution was concentrated to ca. one fourth to its original volume. The concentrated solution was added dropwise to well stirred hexanes (30 mL) resulting in a red precipitate with pale red solution. The liquid was syringed off and the solid was washed with hexanes (3 x 10 mL). The red solid (0.69 g) was dried to give crude product **4b₂** which was dissolved in CH₂Cl₂ (12 mL). Slow diffusion of Et₂O into the solution resulted in dark red crystals. Dark red crystals were also deposited from the pale red solution on standing. Crystals were combined and dried under high vacuum to give pure **4b₂** (0.383 g, 37%). ^1H NMR (CD_2Cl_2): δ 0.93 (d, $^3J_{\text{HH}} = 7$ Hz, 12H, CH₃ of *i*Pr), 1.26 (d, $^3J_{\text{HH}} = 7$ Hz, 6H, CH₃ of *i*Pr), 2.28 (sept, $^3J_{\text{HH}} = 7$ Hz, 1H, CH of *i*Pr), 2.89 (sept, $^3J_{\text{HH}} = 7$ Hz, 2H, CH of *i*Pr), 3.30 (s, 3H, N-CH₃), 5.22 (s, 2H, CH₂), 6.17 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H), 6.40-6.45 (m, 2H, Ar-H), 7.01 (s, 2H, Ar-H), 7.05-7.42 (m, 30H, PPh₃), 7.91 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H). ^{13}C NMR (CD_2Cl_2): δ 24.04 (CH₃ of *i*Pr), 24.98 (CH of *i*Pr), 30.30 (CH₃ of *i*Pr), 34.60 (CH of *i*Pr), 36.49 (N-CH₃), 48.98 (CH₂), 118.75, 120.46, 121.85, 122.94, 124.38, 127.66, 128.70, 140.07, 149.56, 149.91, 154.64 (Ar-C), 174.27, 175.45 (Ru-C(C₆H₄) and Ru-C(triazolylidene)). ^{31}P NMR (CD_2Cl_2): δ 39.95 (PPh₃). Anal. Calcd for C₆₁H₆₂ClN₃P₂Ru (1035.64): C, 70.74; H, 6.03; N, 4.06. Found: C, 71.01; H, 5.99; N, 4.09.

Synthesis of RuHCl(PCy₃)₂(PhCH₂C₂N₂(NMe)Ph) (5a₁**) and RuCl(PCy₃)₂(PhCH₂C₂N₂(NMe)C₆H₄) (**5a₂**).** Benzene (10 mL) was added to a mixture of **3a** (0.197 g, 0.25 mmol) and RuHCl(H₂)(PCy₃)₂ (0.350 g, 0.50 mmol). The reaction mixture was stirred at room temperature for 48 hours resulting in a red solution with brown precipitate. The brown solid was filtered off. The red solution was concentrated to ca. 2-3 mL and added dropwise to hexanes (15 mL) while stirring vigorously. This resulted in a red solution with orange precipitate. The solid was filtered off and dried under high vacuum to give **5a₂** (0.291 g, ca. 60%) [it contains **5a₁** as impurity (9%) and could not be isolated in pure form.]. The red solution was allowed to rest 18 hours at room temperature resulting in an orange semicrystalline precipitate and red solution. The semicrystalline precipitate, which

was a mixture of **5a₁** and **5a₂**, was discarded. The red solution was left at -35°C for 48 hours resulting in red crystals. The crystals were dried to give pure **5a₁** (0.038 g, 8%).

5a₁: ^1H NMR (CD_2Cl_2): δ -26.40 (t, $^2J_{\text{PH}} = 24$ Hz, 1H, Ru-H), 0.81-2.05 (m, 66H, PCy₃), 4.15 (s, 3H, N-CH₃), 5.70 (s, 2H, CH₂), 6.57 (d, $^3J_{\text{HH}} = 8$ Hz, 2H, Ar-H), 7.33-7.40 (m, 6H, Ar-H), 7.51 (t, $^3J_{\text{HH}} = 8$ Hz, 2H, Ar-H). ^{13}C NMR (CD_2Cl_2): δ 27.55, 28.52, 28.67, 30.01, 30.85, 36.53 (PCy₃), 38.75 (N-CH₃), 56.22 (CH₂), 124.33, 127.93, 128.04, 128.56, 128.80, 130.92, 131.59, 136.15, 144.87 (Ar-C). ^{31}P NMR (CD_2Cl_2): δ 41.08 (PCy₃). Anal. Calcd for C₅₂H₈₂ClN₃P₂Ru (947.70): C, 65.90; H, 8.72; N, 4.43. Found: C, 66.00; H, 8.68; N, 4.44.

5a₂: ^1H NMR (CD_2Cl_2): δ 0.75-2.11 (m, 66H, PCy₃), 4.24 (s, 3H, N-CH₃), 6.04 (s, 2H, CH₂), 7.28-7.74 (m, 9H, Ar-H). ^{31}P NMR (CD_2Cl_2): δ 24.28 (PCy₃).

Synthesis of RuCl(PCy₃)₂((C₆H₂*i*Pr₃)CH₂C₂N₂(NMe)C₆H₄) (5b₂**).** Benzene (10 mL) was added to a mixture of **3b** (0.261 g, 0.25 mmol) and RuHCl(H₂)(PCy₃)₂ (0.350 g, 0.50 mmol). The reaction mixture was stirred at room temperature for 48 hours resulting in a red solution with brown precipitate. The brown solid was filtered off. All volatiles were removed from the red solution resulting in a red solid which was washed with hexane (3 x 10 mL). The solid was dried under high vacuum to give **5b₂** as pure product (0.351 g). The hexane phase was allowed to rest for 48 hours during which time red crystals formed (0.058 g) as pure product **5b₂**. The solids were combined and dried thoroughly to give **5b₂** (0.409 g, 76%). ^1H NMR (CD_2Cl_2): δ 0.92-2.16 (m, 84H, PCy₃ and CH₃ of *i*Pr), 2.97 (sept, $^3J_{\text{HH}} = 7$ Hz, 1H, CH of *i*Pr), 3.07 (sept, $^3J_{\text{HH}} = 7$ Hz, 2H, CH of *i*Pr), 4.11 (s, 3H, N-CH₃), 5.58 (s, 2H, CH₂), 6.51 (t, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H), 6.60 (t, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H), 7.08 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H), 7.18 (s, 2H, Ar-H), 8.25 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, Ar-H). ^{13}C NMR (CD_2Cl_2): δ 24.12, 26.99, 28.05, 28.33, 28.59, 30.69, 30.97, 31.53, 34.70, 37.09, 38.20 (PCy₃, CH and CH₃ of *i*Pr), 49.28 (N-CH₃), 66.06 (CH₂), 117.52, 118.91, 122.03, 122.34, 125.50, 139.91, 143.65, 149.44, 150.04, 154.62 (Ar-C), 181.59, 182.66 (Ru-C(C₆H₄) and Ru-C(triazolylidene)). ^{31}P NMR (CD_2Cl_2): δ 24.49. Anal. Calcd for C₆₁H₉₈ClN₃P₂Ru (1071.92): C, 68.35; H, 9.22; N, 3.92. Found: C, 68.22; H, 9.21; N, 3.87.

Synthesis of RuHCl(PCy₃)₂((C₆H₂Me₃)CH₂C₂N₂(NMe)Ph) (5c₁**) and RuCl(PCy₃)₂((C₆H₂Me₃)CH₂C₂N₂(NMe)C₆H₄) (**5c₂**).** Benzene (10 mL) was added to a mixture of **3c** (0.230 g, 0.25 mmol) and RuHCl(H₂)(PCy₃)₂ (0.350 g, 0.50 mmol). The reaction mixture was stirred at room temperature for 48 hours resulting in a red solution with brown precipitate. The brown solid was filtered off. The red solution was concentrated to ca. 2-3 mL and added dropwise to hexanes (15 mL) while stirring vigorously. This resulted in a red solution with orange precipitate. The solid was filtered off and dried under high vacuum to give **5c₂** (0.281 g) as crude product. Crystallization from toluene solution at -35 °C gave pure **5c₂** (0.202 g, 40%). The red solution was allowed to rest 18 hours at room temperature resulting in an orange semicrystalline precipitate and red solution. The semicrystalline precipitate, which was a mixture of **5c₁** and **5c₂**, was discarded. The red solution was left at -35°C for 48 hours resulting in red crystals. The crystals were dried to give pure **5c₁** (0.044 g, 9%).

5c₁: ¹H NMR (CD₂Cl₂): δ -26.49 (t, ²J_{PH} = 24 Hz, 1H, Ru-H), 0.83-2.23 (m, 66H, PCy₃), 2.30 (s, 3H, CH₃), 2.31 (s, 6H, CH₃), 4.04 (s, 3H, N-CH₃), 5.28 (s, 2H, CH₂), 6.47 (d, ³J_{HH} = 8 Hz, 2H, Ar-H), 6.93 (s, 2H, Ar-H), 7.34 (t, ³J_{HH} = 8 Hz, 2H, Ar-H), 7.50 (t, ³J_{HH} = 8 Hz, 1H, Ar-H). ¹³C NMR (CD₂Cl₂): δ 21.08, 22.43, 23.07, 25.65, 27.01, 27.49, 28.06, 28.59, 30.77, 31.55, 32.00, 35.03, 38.78 (PCy₃ and CH₃), 52.38 (N-CH₃), 68.16 (CH₂), 124.21, 127.60, 129.23, 130.92, 131.84, 138.54, 138.97, 145.26 (Ar-C). ³¹P NMR (CD₂Cl₂): δ 41.71 (PCy₃). Anal. Calcd for C₅₅H₈₈ClN₃P₂Ru (989.78): C, 66.74; H, 8.96; N, 4.25. Found: C, 66.67; H, 8.93; N, 4.20.

5c₂: ¹H NMR (CD₂Cl₂): δ 1.08-2.23 (m, 66H, PCy₃), 2.30 (s, 3H, CH₃), 2.41 (s, 6H, CH₃), 4.23 (s, 3H, N-CH₃), 5.96 (s, 2H, CH₂), 6.98 (m, 1H, Ar-H), 7.52-7.79 (m, 4H, Ar-H), 8.01 (m, 1H, Ar-H). ¹³C NMR (CD₂Cl₂): δ 20.15, 21.18, 24.35, 27.14, 28.28, 29.42, 30.24, 30.64, 32.32, 33.22, 38.19, 39.26 (PCy₃ and CH₃), 49.04 (N-CH₃), 62.86 (CH₂), 122.37, 125.36, 128.64, 129.35, 129.81, 130.04, 132.28, 139.16, 140.65, 143.54 (Ar-C) [Note: Tertiary carbons were not detected]. ³¹P NMR (CD₂Cl₂): δ 23.96 (PCy₃). Anal. Calcd for C₅₅H₈₆ClN₃P₂Ru (987.76): C, 66.88; H, 8.78; N, 4.25. Found: C, 66.81; H, 8.91; N, 4.26.

Synthesis of RuHCl(PCy₃)₂(PhCH₂C₂N₂(NMe)(C₆H₄Me)) (5d₁) and RuCl(PCy₃)₂(PhCH₂C₂N₂(NMe)(C₆H₃Me)) (5d₂).

Benzene (10 mL) was added to a mixture of **3c** (0.210 g, 0.25 mmol) and RuHCl(H₂)(PCy₃)₂ (0.350 g, 0.50 mmol). The reaction mixture was stirred at room temperature for 48 hours resulting in a red solution with brown precipitate. The brown solid was filtered off. The red solution was concentrated to ca. 2-3 mL and added dropwise to hexanes (15 mL) while stirring vigorously. This resulted in a red solution with orange precipitate. The solid was filtered off and dried under high vacuum to give **5d₂** (0.295 g) as crude product. Crystallization from toluene solution at -35 °C gave pure **5d₂** (0.213 g, 42%). The red solution was allowed to rest 48 hours at room temperature resulting in an orange crystalline precipitate, which was a mixture of **5d₁** and **5d₂**. **5d₁** could not be isolated in pure form.

5d₂: ¹H NMR (CD₂Cl₂): δ 0.89-2.05 (m, 66H, PCy₃), 2.24 (s, 3H, CH₃), 4.17 (s, 3H, N-CH₃), 5.81 (s, 2H, CH₂), 6.48 (d, ³J_{HH} = 8 Hz, 1H, Ar-H), 7.06 (d, 1H, Ar-H), 7.31-7.42 (m, 5H, Ar-H), 7.96 (s, 1H, Ar-H). ¹³C NMR (CD₂Cl₂): δ 21.78, 22.75, 27.08, 28.44, 30.31, 30.44, 30.63, 33.28, 34.54, 36.84, 37.12 (PCy₃, CH₃ and N-CH₃), 56.20 (CH₂), 118.82, 118.94, 127.84, 127.98, 128.69, 132.61, 136.51, 137.11, 143.38, 154.31 (Ar-C) 183.11, 183.96 (Ru-C(C₆H₄) and Ru-C(triazolylidene)). ³¹P NMR (CD₂Cl₂): δ 24.17 (PCy₃). Anal. Calcd for C₅₃H₈₂ClN₃P₂Ru (959.71): C, 66.33; H, 8.61; N, 4.38. Found: C, 66.25; H, 8.56; N, 4.42.

5d₁: ¹H NMR (CD₂Cl₂): δ -26.30 (t, ²J_{PH} = 24 Hz, 1H, Ru-H), 0.84-2.05 (m, 66H, PCy₃), 2.24 (s, 3H, CH₃), 4.17 (s, 3H, N-CH₃), 5.81 (s, 2H, CH₂), 6.40-6.57 (m, 2H, Ar-H), 7.01-7.11 (m, 1H, Ar-H), 7.29-7.43 (m, 4H, Ar-H) 7.97 (s, 1H, Ar-H). ³¹P NMR (CD₂Cl₂): δ 42.27 (PCy₃).

Synthesis of RuHCl(PCy₃)₂(PhCH₂C₂N₂(NMe)(C₆H₄CF₃)) (5e₁) and RuCl(PCy₃)₂(PhCH₂C₂N₂(NMe)(C₆H₃CF₃)) (5e₂).

Benzene (10 mL) was added to a mixture of **3c** (0.240 g, 0.25 mmol) and RuHCl(H₂)(PCy₃)₂ (0.350 g, 0.50 mmol). The reaction mixture was stirred at room temperature for 48 hours

resulting in a red solution with brown precipitate. The brown solid was filtered off. The red solution was concentrated to ca. 2-3 mL and added dropwise to hexanes (15 mL) while stirring vigorously. This resulted in a red solution with orange precipitate. The solid was filtered off and dried under high vacuum to give **5e₂** (0.305 g) as crude product. Crystallization from toluene solution at -35 °C gave pure **5e₂** (0.193 g, 38%). The red solution was allowed to rest 48 hours at room temperature resulting in an orange crystalline precipitate, which was a mixture of **5e₁** and **5e₂**. **5e₁** could not be isolated in pure form.

5e₂: ¹H NMR (CD₂Cl₂): δ 0.83-2.04 (m, 66H, PCy₃), 4.25 (s, 3H, N-CH₃), 5.85 (s, 2H, CH₂), 6.91 (d, ³J_{HH} = 8 Hz, 1H, Ar-H), 7.23 (d, ³J_{HH} = 8 Hz, 1H, Ar-H), 7.31-7.44 (m, 5H, Ar-H), 8.43 (s, 1H, Ar-H). ¹³C NMR (CD₂Cl₂): δ 26.98, 28.28, 28.31, 28.36, 30.48, 30.53, 36.70, 36.76, 36.82, 37.54 (PCy₃ and N-CH₃), 56.37 (CH₂), 114.08, 118.42, 127.95, 128.81, 129.67, 130.34, 136.04, 138.53, 143.40, 153.15 (CF₃ and Ar-C) 184.81, 186.88 (Ru-C(C₆H₄) and Ru-C(triazolylidene)). ³¹P NMR (CD₂Cl₂): δ 23.58 (PCy₃). Anal. Calcd for C₅₃H₇₉ClF₃N₃P₂Ru (1013.68): C, 62.80; H, 7.86; N, 4.15. Found: C, 62.87; H, 7.83; N, 4.18.

5e₁: ¹H NMR (CD₂Cl₂): δ -25.86 (t, ²J_{PH} = 8 Hz, = 24 Hz, 1H, Ru-H), 0.82-2.11 (m, 66H, PCy₃), 4.28 (s, 3H, N-CH₃), 5.94 (s, 2H, CH₂), 7.38-7.49 (m, 3H, Ar-H), 7.59-7.71 (m, 2H, Ar-H), 7.76-7.93 (m, 3H, Ar-H) 9.37 (s, 1H, Ar-H). ³¹P NMR (CD₂Cl₂): δ 40.96 (PCy₃).

Hydrogenation of Olefins in J. Young NMR Tube. In a glove box, a sample of the appropriate metal complex **4a₁** (4.5 mg, 5 μmol, Note: **4a₁** contains 15% of **4a₂** as impurity) or **4a₂** (4.5 mg, 5 μmol) or **4b₂** (5.0 mg, 5 μmol) or **5b₂** (2.2 mg, 2 μmol), deuterated solvent (0.5 mL) (C₆D₆ for **4a₁** and CD₂Cl₂ for **4a₂** and **4b₂**) and substrate (0.1 mmol) 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 H₂ 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. ¹H NMR spectra were measured at appropriate intervals and relative integration of substrate and product peaks were used to determine the composition of the mixture.

Hydrogenation of Olefins in Parr Reactor. In a glove box, a sample of the appropriate metal complex **5a₁/5b₂/5c₁/5c₂/5d₁/5e₂** (2 μmol), CD₂Cl₂ (0.5 mL) and substrate (0.1 mmol) were combined in a vial. The vial was placed in the Parr reactor and was sealed inside the glove box. The Parr reactor was pressurized with 50 atm of H₂ after purging five times with 50 atm of H₂. The hydrogenation was run for 3 h. The pressure was released and ¹H NMR spectra were measured from the reaction mixture. Relative integration of substrate and product peaks was 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 N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data

collection strategies were determined using Bruker Apex 2 software and optimized to provide >96.6% complete data. In The data were collected at 150(±2) K for all. Data for compound **5e** 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.¹⁸

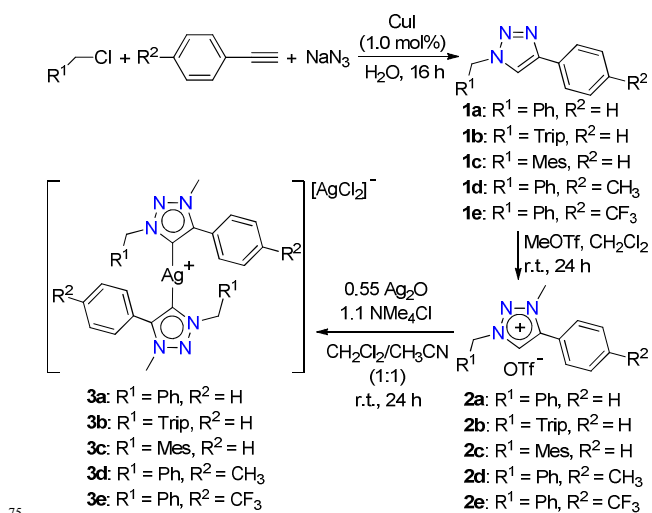
X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations.¹⁹ The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F_o , 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.

RESULTS AND DISCUSSION

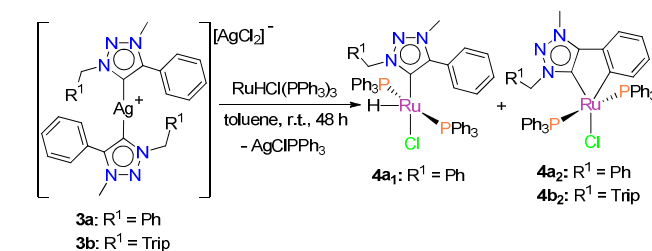
Synthesis and Characterization: The 1,2,3-triazoles [RCH₂C₂HN₃Ph] (R = Ph **1a**, C₆H₂iPr₃ **1b**, C₆H₂Me₃ **1c**) and [PhCH₂C₂HN₃R] (R = C₆H₄Me **1d**, C₆H₄CF₃ **1e**) were readily synthesized in excellent yield by treating a mixture of appropriate chloro-derivatives, terminal alkyne and sodium azide in distilled water in presence of catalytic amount of Cu(I) (Scheme 1).¹⁶ The reaction is regioselective and 1,4-disubstituted 1,2,3-triazoles were the only products. Thereafter, **1a**, **1b**, **1c**, **1d** and **1e** were methylated selectively at N3-position by reacting them with methyl triflate and thus generating [RCH₂C₂HN₂(NMe)Ph][OTf] (R = Ph **2a**, C₆H₂iPr₃ **2b**, C₆H₂Me₃ **2c**) and [PhCH₂C₂HN₂(NMe)R][OTf] (R = C₆H₄Me **2d**, C₆H₄CF₃ **2e**), respectively (Scheme 1). By analogy to previous reports^{10a, 16a} subsequent reactions with Ag₂O afforded the stable silver(I) triazolylienes species **3a-e** (Scheme 1). Mass spectrometry analysis were consistent with the formulation of these products with the general formula [L₂Ag][AgCl₂]^{16a} as the major peaks at m/z = 605.16, 857.44, 689.25, 633.19 and 741.13 were observed in the mass spectra of **3a-e**, respectively.

The silver(I)-triazolyliene complex **3a** was reacted with RuHCl(PPh₃)₃ to yield ruthenium-hydride complex RuHCl(PPh₃)₂(PhCH₂C₂N₂(NMe)Ph) (**4a₁**) as the minor product and the cyclometalated complex RuCl(PPh₃)₂(PhCH₂C₂N₂(NMe)C₆H₄) (**4a₂**) as the major product (Scheme 2). The cyclometalated complex **4a₂** was isolated in pure form and fully characterized, whereas the ruthenium-hydride

complex **4a₁** was contaminated with **4a₂** (12-20 %). The presence of triazolyliene moiety was observed in ¹H NMR spectra of **4a₂** and **4a₁**. For **4a₁**, a triplet at -27.49 ppm in the ¹H NMR spectrum and a doublet at 46.33 ppm in the ³¹P NMR spectrum were observed, consistent with the presence of a hydride coupled to two phosphine moieties on ruthenium. A singlet at 37.70 ppm was observed in the ³¹P NMR spectrum of **4a₂**. In the ¹³C NMR spectrum of **4a₂**, the Ru-C(C₆H₄) and Ru-C(triazolyliene) resonances were observed at 173.39 and 180.64 ppm. The corresponding reaction of **3b** with RuHCl(PPh₃)₃ gave selectively the cyclometalated complex (**4b₂**), which was isolated as dark red crystals (Scheme 2). ¹H and ¹³C NMR spectra of **4b₂** confirmed the presence of the triazolyliene moiety in the complex while the ¹³C resonances attributable to Ru-C(C₆H₄) and Ru-C(triazolyliene) were observed at 174.27 and 175.45 ppm. A singlet at 39.95 ppm in the ³¹P NMR spectrum was consistent with the presence of two equivalent PPh₃ moieties.



Scheme 1 Synthesis of 1-3.



Scheme 2 Synthesis of **4a₁**, **4a₂** and **4b₂**.

Complexes **4a₁**, **4a₂** and **4b₂** were characterized by X-ray molecular structure analysis. Single-crystal X-ray analysis of **4a₁** confirmed the formulation and revealed a five-coordinate square-pyramidal Ru-center where the triazolyliene moiety, chloride, and two phosphine ligands form the base of the pyramid and the hydride occupies the apex (Figure 2a). The two phosphine ligands are *trans* to each other with Ru-P bond distances of 2.3171(5) and 2.3253(5) Å. The Ru-H bond distance in **4a₁** is 1.4809(9) Å, which is consistent with the Ru-H bond distances (1.41-1.59 Å) in previously report ruthenium-imidazolyliene complexes^{5, 7} and in contrast to that seen in a recently published half-sandwich Ru-triazolyliene complex (1.7310(23) Å).¹⁵ Nonetheless, the Ru-C bond distance (1.9886(6) Å) in **4a₁** is consistent with other

ruthenium-triazolylidene complexes [1.98-2.10 Å]. Ru-Cl bond distance [2.4812 (4) Å] is found to be in the expected range.^{11a,12,15-16} The *ortho*-H of the phenyl moiety is in close proximity of the metal center; (2.441 Å). The sum of P-Ru-Cl angles [90.03(2)° and 87.37(2)°] and P-Ru-C angles [95.09(5)° and 89.20(5)°] is ca. 362°. The benzyl group of the triazolylidene moiety is oriented away from the ruthenium center.

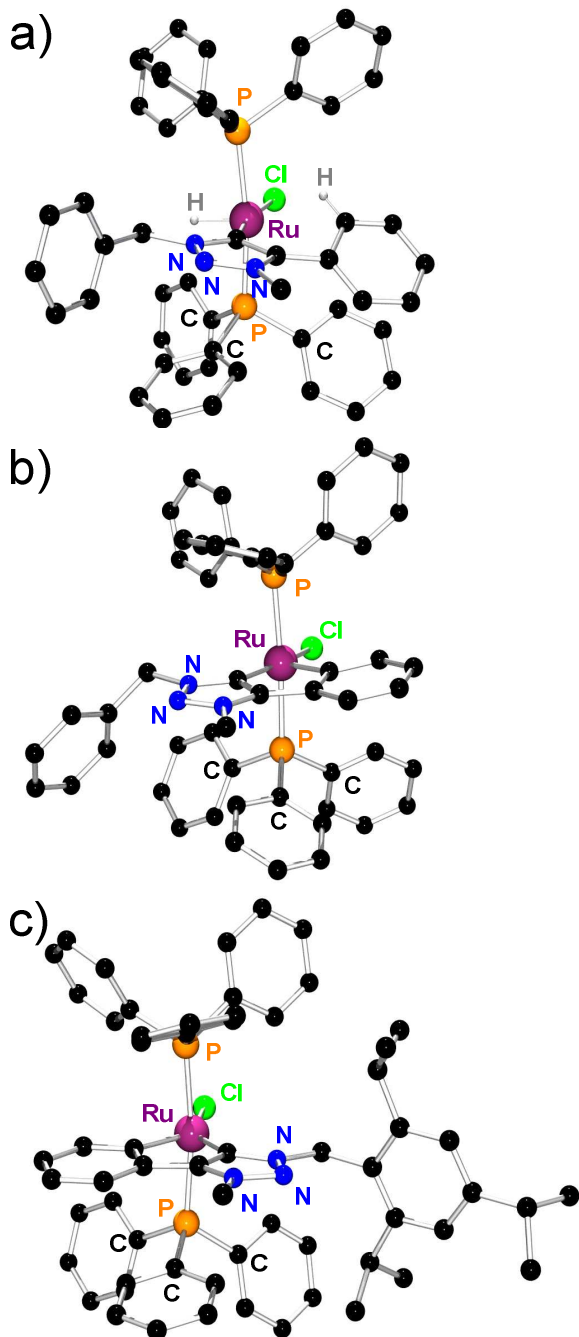


Fig. 2 POV-ray depiction of a) **4a₁**, b) **4a₂** and c) **4b₂**: C, black; Cl, green; P, orange; N, blue; Ru, purple; H, gray. All hydrogen atoms except the hydride and the *ortho*-H of the phenyl moiety are omitted for clarity.

Single-crystal X-ray analyses of **4a₂** and **4b₂** revealed the five-coordinate distorted trigonal bipyramidal Ru centers where the two *trans* phosphine ligands occupy the apexes (Figure 2b, 2c). In

4a₂, the Ru-P distances are 2.3337(6) Å and 2.3412(6) Å and P-Ru-P angle is 175.67(2)°. The Ru-P distances (2.3457(8) Å and 2.3481(9) Å) and P-Ru-P angle (170.91(3)°) in **4b₂** are consistent with **4a₂**. The Ru-C(triazolylidene) bond distances (**4a₂**: 2.0079(3) Å, **4b₂**: 1.9789(3) Å) are slightly shorter than the Ru-C(C₆H₄) bond distances (**4a₂**: 2.0309(3) Å, **4b₂**: 2.0356(3) Å). The Ru-Cl distances in **4a₂** (2.4582(7) Å) and **4b₂** (2.4634(8) Å) are comparable. In **4b₂** the C-Ru-C angle is 76.75(3)° which is much narrower than ideal 120°, whereas Cl-Ru-C angles (Cl-Ru-C(triazolylidene): 139.63(1)°; Cl-Ru-C(C₆H₄): 143.62(1)°) are 25 much wider than that expected for an ideal geometry. While the C-Ru-C angle (77.16(1)°) in **4a₂** is similar to that in **4b₂** (76.75(3)°), the Cl-Ru-C angles vary widely (**4a₂**: Cl-Ru-C(triazolylidene): 165.01(8)°; Cl-Ru-C(C₆H₄): 117.38(8)°. **4b₂**: Cl-Ru-C(triazolylidene): 139.63(1)°; Cl-Ru-C(C₆H₄): 143.62(1)°).

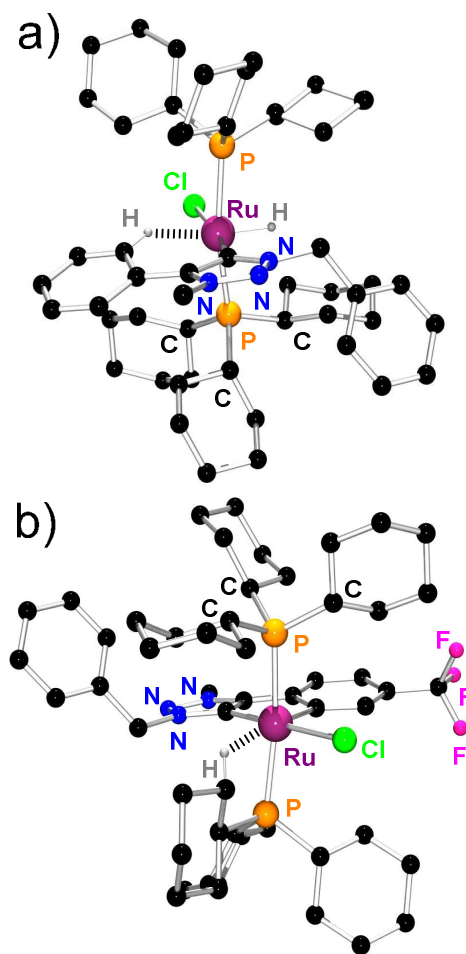
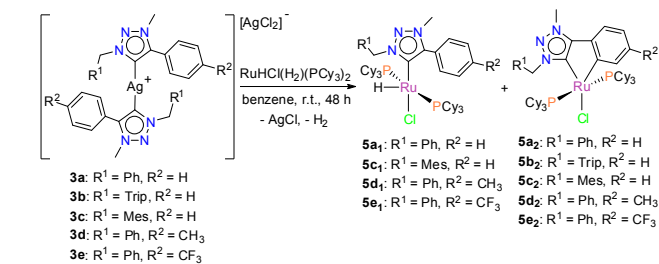


Fig. 3 POV-ray depiction of a) **5a₁** and b) **5e₂**: C, black; Cl, green; P, orange; N, blue; F, pink; Ru, purple; H, gray. All hydrogen atoms except the ruthenium bound hydrogens omitted for clarity.

The silver(I)-triazolylidene complexes **3a-e** were also reacted with RuHCl(H₂)(PCy₃)₂ resulting in the formation of Ru-H complexes (**5a₁**, **5c₁**, **5d₁** and **5e₁**) as the minor products and the cyclometalated complexes (**5a₂**, **5c₂**, **5d₂** and **5e₂**) as the major products (Scheme 3). In the case of **3b**, reaction with RuHCl(H₂)(PCy₃)₂ gave exclusively the cyclometalated complex **5b₂** (Scheme 3). The complexes **5a₁**, **5b₂**, **5c₁**, **5c₂**, **5d₁** and **5e₂**

were isolated as pure compounds and fully characterized (^1H , ^{13}C and ^{31}P NMR spectroscopy). However, isolation of pure **5a₂**, **5d₁** and **5e₁** proved problematic and thus were characterized by ^1H and ^{31}P NMR spectroscopy alone. Similar to the PPh_3 -analogues, the present Ru-H complexes **5a₁**, **5c₁**, **5d₁** and **5e₁** displayed a triplet in the range of -25 to -27 ppm (**5a₁**: -26.40, **5c₁**: -26.49, **5d₁**: -26.30, **5e₁**: -25.86) in the respective ^1H NMR spectra and a doublet was observed in the range of 40 to 43 ppm (**5a₁**: 41.08, **5c₁**: 41.71, **5d₁**: 42.27, **5e₁**: 40.96) in the respective ^{31}P NMR spectra. A singlet in the range of 23 to 25 ppm (**5a₂**: 24.28, **5b₂**: 24.49, **5c₂**: 23.96, **5d₂**: 24.17, **5e₂**: 23.58) was observed in the ^{31}P NMR spectra of cyclometalated complexes **5a₂**-**e₂**. In the ^{13}C NMR spectra of the isolated cyclometalated species, the Ru-C(triazolylidene) and Ru-C(C_6H_4)/Ru-C(C_6H_3) resonances were observed in the range of 180 to 190 ppm (**5b₂**: 181.59 and 182.66, **5d₂**: 183.11 and 183.96, **5e₂**: 184.81, 186.88).



Scheme 3 Synthesis of **5a₁**, **5a₂**, **5b₂**, **5c₁**, **5c₂**, **5d₁**, **5d₂**, **5e₁** and **5e₂**.

Formulation of complexes **5a₁** was further confirmed by X-ray crystallography revealing six-coordinate distorted octahedral geometries about Ru if one considers the agostic interaction with the *ortho*-hydrogen of the pendant phenyl ring (**5a₁** Ru-H_{ortho}: 2.058 Å; **4a₁**: 2.441 Å) (Figure 3a). The Ru-H(hydride) bond distance in **5a₁** (1.545(4) Å) is slightly longer than that found in **4a₁** (1.4809(9) Å) while the *trans* phosphine give rise to Ru-P bond distances of 2.3700(6) and 2.3743(5) Å. The Ru-C and Ru-Cl bond distances are found to be 1.987(2) and 2.4896(6) Å, respectively. The Ru-P, Ru-C and Ru-Cl bond distances in both **4a₁** and **5a₁** are similar while the C-Ru-P bond angles are **4a₁**: 93.92(6) $^\circ$ and **5a₁**: 94.48(6) $^\circ$, and the Cl-Ru-P bond angles are 86.34(2) $^\circ$ and 87.00(2) $^\circ$. Similar to **4a₁**, the benzyl group of the triazolylidene moiety in **5a₁** is oriented away from the ruthenium center.

Compound **5e₂** is a pseudo six-coordinate octahedral species (Figure 3b), in contrast to **4a₂** and **4b₂** as it includes an agostic interaction between the Ru and a H on one of the PCy₃ ligands. However, this Ru-H(C_6H_5) distance (2.2442 Å) is slightly longer than the Ru-H(C_6H_3) distance (2.058 Å) seen in **5a₁**. The bond distances and angles about Ru in **5e₂** are similar to those seen in species **4a₁**, **4a₂** and **5a₁**.

It is interesting to note that reaction of $[\text{RuCl}_2(\text{p-cymene})]_2$ with silver(I) triazolylidene complexes **3a**, **3b** and **3c**, gave cyclometalated species as minor products (2-5 %) with the (p-cymene)RuCl₂(triazolylidene) as major product (80-90 %).^{16a} Herein, use of RuHCl(PPh_3)₃ as the synthon is shown to reverse this pattern. Precedent for such intramolecular C-H activation of iridium and ruthenium-triazolylidene complexes have been reported recently by the groups of Albrecht^{13, 20} and Fukuzawa.²¹ In addition, a cyclometalated Pd-triazolylidene complex has also

been described.²² Conceptually these species are similar to metallated NHC complexes.²³

In the formation of **4** and **5**, it is reasonable to suggest that the Ru-H species is formed initially followed by intramolecular C(sp²)-H bond activation resulting in cyclometalation with liberation of H₂ being the driving force. To confirm this, **5a₁** was dissolved in CD₂Cl₂ and the solution was monitored by ^{31}P NMR spectroscopy. A doublet at 41.1 ppm arising from **5a₁** slowly decreased while a singlet at 24.3 ppm corresponding to **5a₂** grew in (Figure 4). After 6 days complete conversion to **5a₂** was observed. Similarly in the ^1H NMR spectra, the hydride triplet at -26.40 ppm corresponding to **5a₁** disappeared in 6 days.

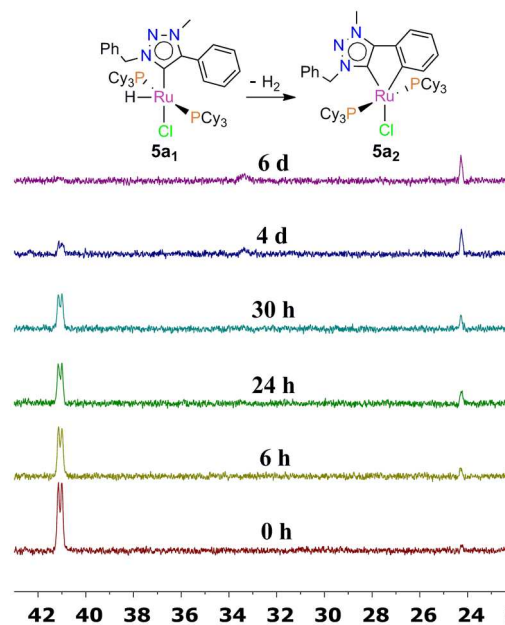
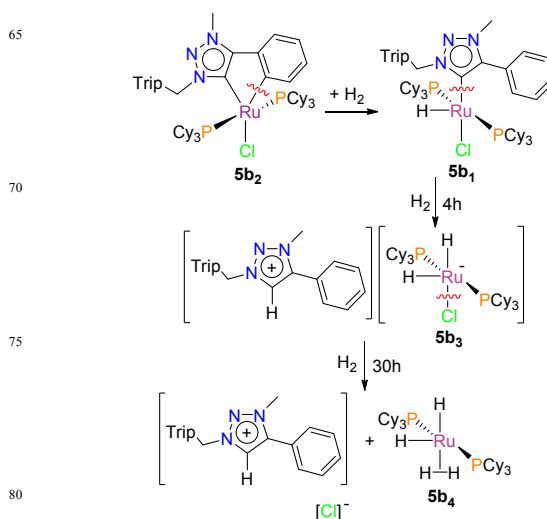


Fig. 4 Conversion of **5a₁** to **5a₂** monitored by ^{31}P NMR spectroscopy.



Scheme 4 Generation of **5b₁**, **5b₃** and **5b₄**.

Addition of hydrogen (4 atm) to a solution of the cyclometalated species **5b₂** in a sealed J. Young NMR tube and monitoring by ^1H and ^{31}P NMR spectroscopy revealed a fast reaction in which **5b₂** reacted with one equivalent of H₂ yielding

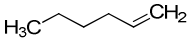
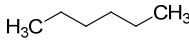
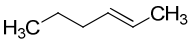
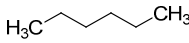




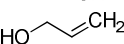
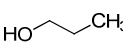
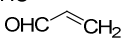
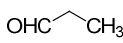
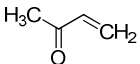
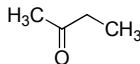
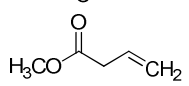
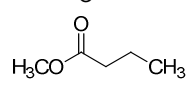
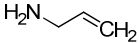
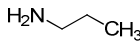


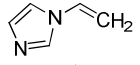
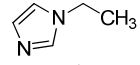
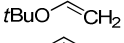
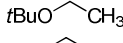


the hydride complex **5b₁** (Scheme 4) with the characteristic ¹H NMR hydride resonance at -26.13 ppm and the doublet (41.05 ppm) in ³¹P NMR spectrum. After 4 h under H₂ **5b₁** reacted further, generating the triazolium cation $[(C_6H_2iPr_3)CH_2C_2HN_2(NMe)Ph]^+$ and anionic ruthenium-dihydride complex **5b₃** as evidenced by the ¹H NMR resonances at 10.51 ppm and -8.37 ppm respectively and the ³¹P resonance at 75.79 ppm. The latter species **5b₃** slowly degraded after 30 h affording a new species **5b₄** which exhibited a broad hydride resonance at -12.25 ppm and ³¹P resonance at 53.53 ppm. The ratio of the triazolium-hydrogen peak and the broad hydride peak was 1:4, suggested the formulation of **5b₄** as RuH₂(H₂)(PCy₃)₂ (Scheme 4). Although this species could not be isolated, the broad ¹H NMR signal is consistent with facile interchange of the hydrides and η²-H₂ sites. Interestingly the closely related species Ru₂H₄(H₂)(PCy₃)₄ displays a similarly broad peak at -12.5 ppm²⁴ while the ³¹P NMR resonance from **5b₄** (53.53 ppm) is similar to those seen for RuH(H₂)(PCy₃)₂ (56 ppm) and RuHCl(H₂)(PCy₃)₂ (54 ppm).²⁵

Hydrogenation Catalysis: The catalytic activity of **4a₁**, **4a₂**, **4b₂** and **5b₂** for hydrogenation of alkenes and alkyne was investigated (Table 1). At 50 °C under 4 atm of H₂, with catalyst precursor loadings of 2 or 5 mol %, hydrogenation of olefins was performed and monitored by ¹H NMR spectroscopy. In the presence of **4a₁** or **4a₂**, quantitative reduction of 1-hexene to hexane was observed in 6 h. Similarly complete hydrogenation of 1-hexene was observed in 5 h for species **4b₂**. In contrast, **5b₂** led to complete hydrogenation of 1-hexene in just 2 h while the reduction of 2-hexene to hexane was observed in 4 h. Species **4a₁**, **4a₂** and **4b₂** displayed much slower activity for the hydrogenation of 2-hexene (**4a₁**: 100 % in 12 h, **4a₂**: 100 % in 12

h, **4b₂**: 100 % in 10 h). Similarly the conversion of styrene to ethylbenzene by **5b₂** (100 % in 8 h) was much faster than **4a₁** (16 h), **4a₂** (14 h) and **4b₂** (12 h). Similarly **5b₂** hydrogenated phenylacetylene to styrene and styrene to ethylbenzene simultaneously. Thus the reaction mixture yielded phenylacetylene: styrene: ethylbenzene in a ratio of 30: 50: 20 after 6 h, whereas the phenylacetylene was fully consumed in 10 h affording a styrene: ethylbenzene of 40: 60 and complete conversion to ethylbenzene in 14 h. The related hydrogenation of phenylacetylene was achieved using **4a₁**, **4a₂** or **4b₂** as a catalyst precursor although these were much slower, yielding styrene: ethylbenzene ratios of 4: 96 for **4b₂**, 16: 84 for **4a₂** and 23: 77 for **4a₁** after 24 h.

The ability of the derived catalysts to tolerate functional groups was also investigated. Using similar reaction conditions allyl alcohol, acrylaldehyde, 3-buten-2-one, methyl-3-buteneoate, allylamine, acrylonitrile, 1-vinylimidazole, tert-butyl vinyl ether and phenyl vinyl sulfide were used as substrates for catalytic hydrogenations. In the presence of **5b₂**, fast and complete reduction of the olefinic residues in allyl alcohol (3 h), acrylaldehyde (3 h), 3-buten-2-one (6 h) and methyl-3-buteneoate (4 h) was observed. In contrast, the hydrogenation of olefins with donor groups such as allylamine (8 h), acrylonitrile (14 h), 1-vinylimidazole (10 h), tert-butyl vinyl ether (65 % in 24 h) and phenyl vinyl sulfide (78 % in 24 h) were much slower. Catalysts derived from **4a₁**, **4a₂** and **4b₂** displayed lower reactivity for most of these functionalized substrates, although quantitative reduction was observed for allyl alcohol, acrylaldehyde, 3-buten-2-one, methyl-3-buteneoate and allylamine after 24 h. Nonetheless, it should be noted that

Table 1 Hydrogenation catalysis with **4a₁**, **4a₂**, **4b₂** and **5b₂**.^a

entry	substrate	product	cat	t / conversion (h / %) ^b	cat	t / conversion (h / %) ^b	Cat	t / conversion (h / %) ^b	cat	t / conversion (h / %) ^b
1			4a₁	6 / 100	4a₂	6 / 100	4b₂	5 / 100	5b₂	2 / 100
2			4a₁	12 / 100	4a₂	12 / 100	4b₂	10 / 100	5b₂	4 / 100
3			4a₁	16 / 100	4a₂	14 / 100	4b₂	12 / 100	5b₂	8 / 100
4			4a₁	24 / 84 ^c	4a₂	24 / 84 ^c	4b₂	24 / 96 ^c	5b₂	14 / 100
5			4a₁	12 / 100	4a₂	12 / 100	4b₂	10 / 100	5b₂	3 / 100
6			4a₁	12 / 100	4a₂	10 / 100	4b₂	8 / 100	5b₂	3 / 100
7			4a₁	20 / 100	4a₂	18 / 100	4b₂	16 / 100	5b₂	6 / 100
8			4a₁	14 / 100	4a₂	14 / 100	4b₂	12 / 100	5b₂	4 / 100
9			4a₁	20 / 100	4a₂	20 / 100	4b₂	16 / 100	5b₂	8 / 100
10			4a₁	24 / 89	4a₂	24 / 92	4b₂	24 / 100	5b₂	14 / 100
11			4a₁	24 / 77	4a₂	24 / 86	4b₂	24 / 100	5b₂	10 / 100
12			4a₁	24 / 19	4a₂	24 / 22	4b₂	24 / 31	5b₂	24 / 65
13			4a₁	24 / 25	4a₂	24 / 32	4b₂	24 / 38	5b₂	24 / 78

^a Conditions: 0.20 mmol of substrate and 5 mol % (**4a₁**, **4a₂**, **4b₂**) and 2 mol % (**5b₂**) of catalyst precursor in CD₂Cl₂ at 50 °C under 4 atm of H₂. ^b Conversions were determined by ¹H NMR spectroscopy. ^c Rest of the product was observed to be styrene.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 2 Hydrogenation catalysis with **5a**₁, **5b**₂, **5c**₁, **5c**₂, **5d**₂ and **5e**₂.^a

entry	substrate	product	cat	conversion (%) ^b	cat	conversion (%) ^b	cat	conversion (%) ^b	cat	conversion (%) ^b	cat	conversion (%) ^b	cat	conversion (%) ^b
1			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
2			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
3			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
4			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
5			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
6			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
7			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
8			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
9			5a ₁	100	5b ₂	100	5c ₁	100	5c ₂	100	5d ₂	100	5e ₂	100
10			5a ₁	86	5b ₂	97	5c ₁	90	5c ₂	92	5d ₂	92	5e ₂	83
11			5a ₁	43	5b ₂	51	5c ₁	46	5c ₂	48	5d ₂	46	5e ₂	40
12			5a ₁	69	5b ₂	80	5c ₁	70	5c ₂	74	5d ₂	74	5e ₂	67
13			5a ₁	90	5b ₂	100	5c ₁	94	5c ₂	94	5d ₂	93	5e ₂	88
14			5a ₁	93	5b ₂	100	5c ₁	95	5c ₂	97	5d ₂	97	5e ₂	91

^a Conditions: 0.20 mmol of substrate and 2 mol% of catalyst in CD₂Cl₂ at r.t. under 50 atm of H₂ for 3 h. ^b Conversions were determined by ¹H NMR spectroscopy.

in all cases the functional groups remained unaltered, leading only to exclusive hydrogenation of the olefinic residues. It is interesting to note that complexes with general formula RuHCl(*p*-cymene)(triazolylidene) has been reported to be an olefin selective hydrogenation catalyst¹⁵ with activity similar to that of **4a**₁, **4a**₂ and **4b**₂.

Given the previous success with previously reported Ru-NHC-carbene complexes,⁷ 2 mol% **5a**₁, **5b**₂, **5c**₁, **5c**₂, **5d**₂ or **5e**₂ were tested under similar conditions. Thus hydrogenations of a series of linear and cyclic olefins were examined at 25 °C under high pressure (50 atm) of H₂ in a Parr reactor (Table 2). Of the species tested, **5b**₂ was found to be most effective, Nonetheless all complexes effected quantitative reduction of 1-hexene, 2-hexene, cyclopentene, cyclohexene, cyclooctene, allyl alcohol, acrylaldehyde, 3-buten-2-one and methyl-3-butenolate. Reduction of allylamine, *tert*-butyl vinyl ether and phenyl vinyl sulfide was either complete or close, but showed moderate reactivity for acrylonitrile and 1-vinylimidazole.

The mechanism of the hydrogenation catalysis is thought to begin with the rapid conversion of the cyclometallated species to **5b**₁. Dissociation of PCy₃ from **5b**₁ is then thought to provide the

catalytically active species allowing for a cycle of reactivity involving coordination of olefin, insertion into the Ru-H and reaction with H₂ to regenerate the catalyst. The conversion of **5b**₁ to **5b**₃ and **5b**₄ observed on prolonged exposure to H₂ were slow and these species are thought not to impact on the catalytic cycle. Nonetheless, mechanistic studies are continuing.

Conclusions

A series of 1,2,3-triazolylidene complexes of Ru have been prepared and characterized. While ruthenium-hydride complexes are seen as minor by-products, the major products are ones in which the ligand is cyclometalated. The cyclometalated species are generated via C(sp²)-H activation by the ruthenium-hydride with liberation of H₂. Ruthenium-triphenylphosphine complexes (**4a**₁, **4a**₂ and **4b**₂) were effective catalyst precursors for hydrogenation of olefins. Interestingly the C-H activated catalyst precursor **4b**₂ showed better activity presumably a result of the additional steric protection of the metal centre by the *tris*-isopropylphenyl substituent. Analogous ruthenium-PCy₃ complexes **5a**₁, **5b**₂, **5c**₁, **5c**₂, **5d**₂ and **5e**₂ displayed enhanced reactivity. This is thought to result from the greater electron

donating ability of PCy₃ compared to PPh₃. In addition, these species were olefin-selective, tolerating a variety of functional groups. The preparation of new, modified carbene-complexes are the subject of continuing study in our 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

Department of Chemistry, University of Toronto, 80 St George St, Toronto, Ontario, Canada, M5S3H6; Tel: 01-416-946-3294; E-mail: dstephan@chem.utoronto.ca

† Electronic Supplementary Information (ESI) available: CIF for all structural studies have been deposited CCDC 1028679-1028683 See DOI: 10.1039/b000000x/

- H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner and M. Studer, *Adv. Synth. Catal.*, 2003, **345**, 103-151.
- (a) J. F. Young, J. A. Osborn, H. Jardine and G. Wilkinson, *Chem. Commun.*, 1965, 131-132; (b) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2143-2147; (c) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 4450-4455.
- R. H. Crabtree and G. E. Morris, *J. Organomet. Chem.*, 1977, **135**, 395-403.
- (a) Z. Strassberger, M. Mooijman, E. Ruijter, A. H. Alberts, C. d. Graaff, R. V. A. Orru and G. Rothenberga, *Appl. Organomet. Chem.*, 2010, **24**, 142-146; (b) Z. Strassberger, M. Mooijman, E. Ruijter, A. H. Alberts, A. G. Maldonado, R. V. A. Orru and G. Rothenberg, *Adv. Synth. Catal.*, 2010, **352**, 2201-2210.
- (a) H. M. Lee, D. C. Smith, Z. He, E. D. Stevens, C. S. Yi and S. P. Nolan, *Organometallics* 2001, **20**, 794-797; (b) U. L. Dharmasena, H. M. Foucault, E. N. dos Santos, D. E. Fogg and S. P. Nolan, *Organometallics*, 2005, **24**, 1056-1058.
- C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy and M. Albrecht, *Organometallics* 2009, **28**, 5112-5121.
- (a) C. L. Lund, M. J. Sgro, R. Cariou and D. W. Stephan, *Organometallics*, 2012, **31**, 802-805; (b) T. E. Wang, C. Prankevicus, C. L. Lund, M. J. Sgro and D. W. Stephan, *Organometallics*, 2013, **32**, 2168-2177.
- (a) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755-766; (b) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, **49**, 8810-8849; (c) A. Krüger and M. Albrecht, *Aust. J. Chem.*, 2011, **64**, 1113-1117; (d) M. Albrecht, *Chimia* 2009, **63**, 105-110; (e) P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **51**, 596-609.
- (a) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596-2599; (b) C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057-3064; (c) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004; (d) J. E. Hein and V. V. Fokin, *Chem. Soc. Rev.*, 2010, **39**, 1302-1315; (e) L. Liang and D. Astruc, *Chem. Soc. Rev.*, 2011, **255**, 2933-2945.
- (a) P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534-13535; (b) J. D. Crowley, A.-L. Lee and K. J. Kilpin, *Aust. J. Chem.*, 2011, **64**, 1118-1132; (c) K. F. Donnelly, A. Petronilho and M. Albrecht, *Chem. Commun.*, 2013, **49**, 1145-1159.
- (a) J. Bouffard, B. K. Keitz, R. Tonner, G. Guisado-Barrios, G. Frenking, R. H. Grubbs and G. Bertrand, *Organometallics*, 2011, **30**, 2617-2627; (b) G. Guisado-Barrios, J. Bouffard, B. Donnadiou and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, **49**, 4759-4762.
- A. Prades, E. Peris and M. Albrecht, *Organometallics*, 2011, **30**, 1162-1167.
- R. Lalrempuia, N. D. McDaniel, H. Mueller-Bunz, S. Bernhard and M. Albrecht, *Angew. Chem. Int. Ed.*, 2010, **49**, 9765-9768.
- (a) T. Karthikeyan and S. Sankaraman, *Tetrahedron Lett.*, 2009, **50**, 5834-5837; (b) T. Nakamura, K. Ogata and S. i. Fukuzawa, *Chem. Lett.*, 2010, **39**, 920-922.
- B. Bagh and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 15638-15645.
- (a) B. Bagh, A. M. McKinty, A. J. Lough and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 12842-12850; (b) H. Hikori, K. Ogata and S.-i. Fukuzawa, *Synlett.*, 2013, **24**, 843-846.
- M. Viciano, M. Feliz, R. Corberan, J. A. Mata, E. Clot and E. Peris, *Organometallics*, 2007, **26**, 5304-5314.
- Bruker Inc., 2013.
- D. T. Cromer and J. T. Waber, *Int. Tables X-Ray Crystallogr.*, 1974, **4**, 71-147.
- (a) A. Petronilho, M. Rahman, J. A. Woods, H. Al-Sayyed, H. Müller-Bunz, J. M. D. MacElroy, S. Bernhard and M. Albrecht, *Dalton Trans.*, 2012, **41**, 13074-13080; (b) K. F. Donnelly, R. Lalrempuia, H. Müller-Bunz and M. Albrecht, *Organometallics*, 2012, **31**, 8414-8419.
- K. Ogata, S. Inomata and S. Fukuzawa, *Dalton Trans.*, 2013, **42**, 2362-2365.
- R. Saravanakumar, V. Ramkumar and S. Sankaraman, *Organometallics*, 2011, **30**, 1689-1694.
- (a) Y. Ohki, T. Hatanaka and K. Tatsumi, *J. Am. Chem. Soc.*, 2008, **130**, 17174-17186; (b) J. M. S. Cardoso and B. Royo, *Chem. Commun.*, 2012, **48**, 4944-4946; (c) M. J. Chilvers, R. F. R. Jazzar, M. F. Mahon and M. K. Whittlesey, *Adv. Synth. Catal.*, 2003, **345**, 1111-1114; (d) S. Burling, M. F. Mahon, B. M. Paine, M. K. Whittlesey and J. M. J. Williams, *Organometallics*, 2004, **23**, 4537-4539; (e) S. Burling, E. Mas-Marza, J. E. V. Valpuesta, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2009, **28**, 6676-6686; (f) C. Zhang, Y. Zhao, B. Li, H. Song, S. Xu and B. Wang, *Dalton Trans.*, 2009, 5182-5189; (g) C. Zhang, B. Li, H. Song, S. Xu and B. Wang, *Organometallics*, 2011, **30**, 3029-3036; (h) A. A. Danopoulos and P. Braunstein, *Dalton Trans.*, 2013, **42**, 7276-7280; (i) A. Labande, N. Debono, A. Sournia-Saquet, J.-C. Daran and R. Poli, *Dalton Trans.*, 2013, **42**, 6531-6537; (j) C. Y. Tang, N. Phillips, M. J. Kelly and S. Aldridge, *Chem. Commun.*, 2012, **48**, 11999-12001; (k) X. Liu and P. Braunstein, *Inorg. Chem.*, 2013, **52**, 7367-7379; (l) A. M. Oertel, J. Freudenreich, V. R. J. Gein, L. F. Veiros and M. J. Chetcuti, *Organometallics*, 2011, **30**, 10323-10326; (m) J. H. Lee, K. S. Yoo, C. P. Park, J. M. Olsen, S. Sakaguchi, G. K. S. Prakash, T. Mathew and K. W. Jung, *Adv. Synth. Catal.*, 2009, **351**, 563-568; (n) O. Rivada-Wheelaghan, B. Donnadiou, C. Maya and S. Conejero, *Chem. Eur. J.*, 2010, **16**, 10323-10326; (o) O. Rivada-Wheelaghan, M. A. Ortuño, J. Diez, A. Lledó and S. Conejero, *Angew. Chem. Int. Ed.*, 2012, **51**, 3936-3939.
- T. Arliguie, B. Chaudret, R. H. Morris and A. Sella, *Inorg. Chem.*, 1988, **27**, 598-599.
- B. Chaudret, G. Chug, O. Eisenstein, S. A. Jackson, F. J. Lahoz and J. A. Lopez, *J. Am. Chem. Soc.*, 1991, **113**, 2314-2316.

TOC Graphic

