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1,2,3-Triazolylidene ruthenium(II)-cyclometalated complexes and olefin selective hydrogenation catalysis†

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Silver(I) 1,2,3-triazol-5-ylidenes $[(RCH_2C_2N_2(NMe)Ph)_2Ag][AgCl_2]$ (R = Ph **3a**, $C_6H_2iPr_3$ **3b**, $C_6H_2Me_3$ **3c**) and $[(PhCH_2C_2N_2(NMe)R)_2Ag][AgCl_2]$ (R = C_6H_4Me **3d**, $C_6H_4CF_3$ **3e**) were synthesized and subsequently treated with $RuHCl(PPh_3)_3$ and $RuHCl(H_2)(PCy_3)_2$. The reaction of **3a** with $RuHCl(PPh_3)_3$ gave $RuHCl(PPh_3)_2(PhCH_2C_2N_2(NMe)Ph)$ (**4a$_1$**) as the minor product and the cyclometalated complex $RuCl(PPh_3)_2(PhCH_2C_2N_2(NMe)C_6H_4)$ (**4a$_2$**) as the major product. However, similar reaction with **3b** selectively formed the cyclometalated complex $RuCl(PPh_3)_2((C_6H_2iPr_3)CH_2C_2N_2(NMe)C_6H_4)$ (**4b$_2$**). Similarly the silver(I) triazolylidenes **3a** and **3b** were reacted with $RuHCl(H_2)(PCy_3)_2$; gave $RuHCl(PCy_3)_2(PhCH_2C_2N_2(NMe)Ph)$ (**5a$_1$**), $RuCl(PCy_3)_2(PhCH_2C_2N_2(NMe)C_6H_4)$ (**5a$_2$**) and $RuCl(PCy_3)_2((C_6H_2iPr_3)CH_2C_2N_2(NMe)C_6H_4)$ (**5b$_2$**), respectively. Species **3c**, **3d** and **3e** resulted in the cyclometalated complexes (**5c$_2$**, **5d$_2$** and **5e$_2$**) as the major products as well as the ruthenium-hydride complexes (**5c$_1$**, **5d$_1$** and **5e$_1$**) as the minor products. The cyclometalated species are derived from the ruthenium-hydride complexes *via* $C(sp^2)$–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 rhodium[2] and iridium[3] 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 $RuHCl(CO)(NHC)(PPh_3)$ 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 (Fig. 1A) 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 (Fig. 1B) are readily synthesized by the Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes. This so-called 'click' reaction[9] 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-triazolydene was reported by Albrecht *et al.* using the 1,2,3-triazolium salt (Fig. 1C) 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 $KN(SiMe_3)_2$ or KO*t*Bu,[11] these species are conveniently stabilized by complexation with Ag(I). These latter species can be exploited for transmetallation reactions and have been further exploited as ligands for novel metal catalysts

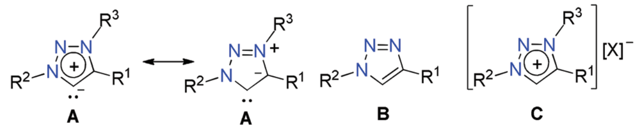

Fig. 1 1,2,3-Triazole species. R^1 and R^2 = alkyl, benzyl or aryl; R^3 = alkyl or benzyl; X = Br, I, OTf, PF_6, BF_4.

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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.

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, 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. CH_3CN was stored over CaH_2, distilled and degassed before use. Dry benzene was purchased from Aldrich and degassed before use. Deuterated solvents (C_6D_6, $CDCl_3$ and CD_2Cl_2) were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts are given relative to $SiMe_3$ and referenced to the residual solvent signal (^1H and ^{13}C) or relative to an external standard (^{31}P, 85% H_3PO_4). 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$(PPh_3)_3$ and RuHCl$(H_2)(PCy_3)_2$ 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 [$PhCH_2C_2HN_2(NMe)R$][OTf] (R = C_6H_4Me 2d, $C_6H_4CF_3$ 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 CH_2Cl_2 (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 × 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 (CD_2Cl_2): δ 2.42 (s, 3H, CH_3), 4.23 (s, 3H, N–CH_3), 5.80 (s, 2H, CH_2), 7.33–7.63 (m, 9H, C_6H_5 and C_6H_4), 8.68 (s, 1H, triazolium-H). ^{13}C NMR (CD_2Cl_2): δ 21.58 (CH_3), 39.03 (N–CH_3), 57.91 (CH_2), 119.20, 128.57, 129.43, 129.74, 129.97, 180.27, 130.68, 131.80, 143.19, 144.13 (C_6H_5, C_6H_4 and trizolium-C). Anal. Calcd for $C_{18}H_{18}F_3N_3O_3S$ (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 (CD_2Cl_2): δ 4.26 (s, 3H, N–CH_3), 5.82 (s, 2H, CH_2), 7.40–7.87 (m, 9H, C_6H_5 and C_6H_4), 8.78 (s, 1H, triazolium-H). ^{13}C NMR ($CDCl_3$): δ 39.27 (N–CH_3), 58.14 (CH_2), 126.00, 126.91, 129.45, 129.80, 130.03, 130.39, 130.60, 131.49, 142.57 (C_6H_5, C_6H_4 and trizolium-C). Anal. Calcd for $C_{18}H_{15}F_6N_3O_3S$ (467.39): C, 46.26; H, 3.23; N, 8.99. Found: C, 46.21; H, 3.25; N, 9.02.

Synthesis of [$(PhCH_2C_2N_2(NMe)R)_2Ag$][$AgCl_2$] (R = C_6H_4Me 3d, $C_6H_4CF_3$ 3e). Identical synthetic procedures were followed for the preparation of **3d** and **3e**. A mixture of triazolium salt (5.00 mmol), Ag_2O (2.75 mmol) and NMe_4Cl (5.50 mmol) in a 1 : 1 mixture of CH_2Cl_2 (10 mL) and CH_3CN (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 CH_2Cl_2 (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 CH_2Cl_2 (*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), Ag_2O (0.637 g, 2.75 mmol) and NMe_4Cl (0.603 g, 5.50 mmol) yielded **3d** (1.811 g, 89%). ^1H NMR (CD_2Cl_2): δ 2.41 (s, 3H, CH_3), 4.10 (s, 3H, N–CH_3), 5.54 (s, 2H, CH_2), 7.21–7.47 (m, 9H, C_6H_5 and C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 21.43 (CH_3), 37.71 (N–CH_3), 59.82 (CH_2), 124.79, 128.69, 129.22, 129.28, 129.55, 130.06, 134.81, 140.87, 149.60 (C_6H_5, C_6H_4 and trizolium-C). MS (70 eV, ESI): *m/z* (rel intens) 633 (100) [$C_{34}H_{34}N_6Ag^+$]. HRMS (ESI; *m/z*): calcd for $C_{34}H_{34}N_6Ag$, 633.1890; found, 633.1885.

3e: **2e** (2.338 g, 5.00 mmol), Ag_2O (0.637 g, 2.75 mmol) and NMe_4Cl (0.603 g, 5.50 mmol) yielded **3e** (1.934 g, 84%). ^1H NMR (CD_2Cl_2): δ 4.15 (s, 3H, N–CH_3), 5.61 (s, 2H, CH_2), 7.25–7.75 (m, 9H, C_6H_5 and C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 38.03 (N–CH_3), 59.86 (CH_2), 125.19, 126.27, 128.72, 129.30, 130.35, 131.58, 131.88, 132.14, 134.70, 148.09 (C_6H_5, C_6H_4 and trizolium-C). MS (70 eV, ESI): *m/z* (rel intens) 741 (100) [$C_{34}H_{28}N_6F_6Ag^+$]. HRMS (ESI; *m/z*): calcd for $C_{34}H_{28}N_6F_6Ag$, 741.1327; found, 741.1325.

Synthesis of RuHCl$(PPh_3)_2(PhCH_2C_2N_2(NMe)Ph)$ ($4a_1$) and RuCl$(PPh_3)_2(PhCH_2C_2N_2(NMe)C_6H_4)$ ($4a_2$). Toluene (30 mL) was added to a mixture of **3a** (0.395 g, 0.50 mmol) and RuHCl$(PPh_3)_3$ (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 × 10 mL). The red solid was dried to give crude product **4a$_2$** which was dissolved in appropriate solvent and crystallization gave dark red crystals as pure product **4a$_2$**. Dark red crystals were deposited from the pale red solution on standing, which were found to be a mixture of **4a$_1$** and **4a$_2$** in the ratio of 8.5 : 1.5.

4a$_2$: **3a** (0.395 g, 0.50 mmol) and RuHCl(PPh$_3$)$_3$ (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 **4a$_2$** (0.191 g, 21%). ^{1}H NMR (CDCl$_3$): δ 3.34 (s, 3H, N–CH$_3$), 4.86 (s, 2H, CH$_2$), 6.29–6.36 (m, 1H, Ar–H), 6.41–6.49 (m, 2H, Ar–H), 6.80 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar–H), 6.95–7.03 (m, 3H, Ar–H), 7.09–7.45 (m, 30H, Ar–H), 8.08 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar–H). ^{13}C NMR (CDCl$_3$): δ 36.59 (N–CH$_3$), 55.99 (CH$_2$), 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(C$_6$H$_4$) and Ru–C(triazolylidene)). ^{31}P NMR (CDCl$_3$): δ 37.70 (PPh$_3$). Anal. Calcd for C$_{52}$H$_{44}$ClN$_3$P$_2$Ru (909.40): C, 68.68; H, 4.88; N, 4.62. Found: C, 68.73; H, 4.85; N, 4.60.

4a$_1$: **4a$_1$** could not be isolated as a pure compound. The crude product (0.122 g) contained a mixture of **4a$_1$** and **4a$_2$** (8.5 : 1.5). Further crystallization from the mixture increased the amount of **4a$_2$**. ^{1}H NMR (CDCl$_3$): δ −27.49 (t, $^2J_{PH}$ = 24 Hz, 1H, RuH), 3.25 (s, 3H, Me), 4.77 (s, 2H, CH$_2$), 6.45–7.35 (m, 40H, Ar–H). ^{31}P NMR (CDCl$_3$): δ 46.33 (PPh$_3$).

Synthesis of RuCl(PPh$_3$)$_2$((C$_6$H$_2$iPr$_3$)CH$_2$C$_2$N$_2$(NMe)C$_6$H$_4$) (4b$_2$). Toluene (30 mL) was added to a mixture of **3b** (0.520 g, 0.50 mmol) and RuHCl(PPh$_3$)$_3$ (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 × 10 mL). The red solid (0.69 g) was dried to give crude product **4b$_2$** which was dissolved in CH$_2$Cl$_2$ (12 mL). Slow diffusion of Et$_2$O 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 **4b$_2$** (0.383 g, 37%). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.93 (d, $^3J_{HH}$ = 7 Hz, 12H, CH$_3$ of iPr), 1.26 (d, $^3J_{HH}$ = 7 Hz, 6H, CH$_3$ of iPr), 2.28 (sept, $^3J_{HH}$ = 7 Hz, 1H, CH of iPr), 2.89 (sept, $^3J_{HH}$ = 7 Hz, 2H, CH of iPr), 3.30 (s, 3H, N–CH$_3$), 5.22 (s, 2H, CH$_2$), 6.17 (d, $^3J_{HH}$ = 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, PPh$_3$), 7.91 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar–H). ^{13}C NMR (CD$_2$Cl$_2$): δ 24.04 (CH$_3$ of iPr), 24.98 (CH of iPr), 30.30 (CH$_3$ of iPr), 34.60 (CH of iPr), 36.49 (N–CH$_3$), 48.98 (CH$_2$), 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(C$_6$H$_4$) and Ru–C(triazolylidene)). ^{31}P NMR (CD$_2$Cl$_2$): δ 39.95 (PPh$_3$). Anal. Calcd for C$_{61}$H$_{62}$ClN$_3$P$_2$Ru (1035.64): C, 70.74; H, 6.03; N, 4.06. Found: C, 71.01; H, 5.99; N, 4.09.

Synthesis of RuHCl(PCy$_3$)$_2$(PhCH$_2$C$_2$N$_2$(NMe)Ph) (5a$_1$) and RuCl(PCy$_3$)$_2$(PhCH$_2$C$_2$N$_2$(NMe)C$_6$H$_4$) (5a$_2$). Benzene (10 mL) was added to a mixture of **3a** (0.197 g, 0.25 mmol) and RuHCl(H$_2$)(PCy$_3$)$_2$ (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 **5a$_2$** (0.291 g, *ca.* 60%) [it contains **5a$_1$** 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 **5a$_1$** and **5a$_2$**, was discarded. The red solution was left at −35 °C for 48 hours resulting in red crystals. The crystals were dried to give pure **5a$_1$** (0.038 g, 8%).

5a$_1$: ^{1}H NMR (CD$_2$Cl$_2$): δ −26.40 (t, $^2J_{PH}$ = 24 Hz, 1H, Ru–H), 0.81–2.05 (m, 66H, PCy$_3$), 4.15 (s, 3H, N–CH$_3$), 5.70 (s, 2H, CH$_2$), 6.57 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar–H), 7.33–7.40 (m, 6H, Ar–H), 7.51 (t, $^3J_{HH}$ = 8 Hz, 2H, Ar–H). ^{13}C NMR (CD$_2$Cl$_2$): δ 27.55, 28.52, 28.67, 30.01, 30.85, 36.53 (PCy$_3$), 38.75 (N–CH$_3$), 56.22 (CH$_2$), 124.33, 127.93, 128.04, 128.56, 128.80, 130.92, 131.59, 136.15, 144.87 (Ar–C). ^{31}P NMR (CD$_2$Cl$_2$): δ 41.08 (PCy$_3$). Anal. Calcd for C$_{52}$H$_{82}$ClN$_3$P$_2$Ru (947.70): C, 65.90; H, 8.72; N, 4.43. Found: C, 66.00; H, 8.68; N, 4.44.

5a$_2$: ^{1}H NMR (CD$_2$Cl$_2$): δ 0.75–2.11 (m, 66H, PCy$_3$), 4.24 (s, 3H, N–CH$_3$), 6.04 (s, 2H, CH$_2$), 7.28–7.74 (m, 9H, Ar–H). ^{31}P NMR (CD$_2$Cl$_2$): δ 24.28 (PCy$_3$).

Synthesis of RuCl(PCy$_3$)$_2$((C$_6$H$_2$iPr$_3$)CH$_2$C$_2$N$_2$(NMe)C$_6$H$_4$) (5b$_2$). Benzene (10 mL) was added to a mixture of **3b** (0.261 g, 0.25 mmol) and RuHCl(H$_2$)(PCy$_3$)$_2$ (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 × 10 mL). The solid was dried under high vacuum to give **5b$_2$** 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 **5b$_2$**. The solids were combined and dried thoroughly to give **5b$_2$** (0.409 g, 76%). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.92–2.16 (m, 84H, PCy$_3$ and CH$_3$ of iPr), 2.97 (sept, $^3J_{HH}$ = 7 Hz, 1H, CH of iPr), 3.07 (sept, $^3J_{HH}$ = 7 Hz, 2H, CH of iPr), 4.11 (s, 3H, N–CH$_3$), 5.58 (s, 2H, CH$_2$), 6.51 (t, $^3J_{HH}$ = 8 Hz, 1H, Ar–H), 6.60 (t, $^3J_{HH}$ = 8 Hz, 1H, Ar–H), 7.08 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar–H), 7.18 (s, 2H, Ar–H), 8.25 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar–H). ^{13}C NMR (CD$_2$Cl$_2$): δ 24.12, 26.99, 28.05, 28.33, 28.59, 30.69, 30.97, 31.53, 34.70, 37.09, 38.20 (PCy$_3$, CH and CH$_3$ of iPr), 49.28 (N–CH$_3$), 66.06 (CH$_2$), 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(C$_6$H$_4$) and Ru–C(triazolylidene)). ^{31}P NMR (CD$_2$Cl$_2$): δ 24.49. Anal. Calcd for C$_{61}$H$_{98}$ClN$_3$P$_2$Ru

(1071.92): C, 68.35; H, 9.22; N, 3.92. Found: C, 68.22; H, 9.21; N, 3.87.

Synthesis of $RuHCl(PCy_3)_2((C_6H_2Me_3)CH_2C_2N_2(NMe)Ph)$ (5c$_1$) and $RuCl(PCy_3)_2((C_6H_2Me_3)CH_2C_2N_2(NMe)C_6H_4)$ (5c$_2$). Benzene (10 mL) was added to a mixture of **3c** (0.230 g, 0.25 mmol) and $RuHCl(H_2)(PCy_3)_2$ (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 **5c$_2$** (0.281 g) as crude product. Crystallization from toluene solution at −35 °C gave pure **5c$_2$** (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 **5c$_1$** and **5c$_2$**, was discarded. The red solution was left at −35 °C for 48 hours resulting in red crystals. The crystals were dried to give pure **5c$_1$** (0.044 g, 9%).

5c$_1$: ^{1}H NMR (CD_2Cl_2): δ −26.49 (t, $^2J_{PH}$ = 24 Hz, 1H, Ru–H), 0.83–2.23 (m, 66H, PCy_3), 2.30 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 4.04 (s, 3H, N–CH_3), 5.28 (s, 2H, CH_2), 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). ^{13}C NMR (CD_2Cl_2): 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 (PCy_3 and CH_3), 52.38 (N–CH_3), 68.16 (CH_2), 124.21, 127.60, 129.23, 130.92, 131.84, 138.54, 138.97, 145.26 (Ar–C). ^{31}P NMR (CD_2Cl_2): δ 41.71 (PCy_3). Anal. Calcd for $C_{55}H_{88}ClN_3P_2Ru$ (989.78): C, 66.74; H, 8.96; N, 4.25. Found: C, 66.67; H, 8.93; N, 4.20.

5c$_2$: ^{1}H NMR (CD_2Cl_2): δ 1.08–2.23 (m, 66H, PCy_3), 2.30 (s, 3H, CH_3), 2.41 (s, 6H, CH_3), 4.23 (s, 3H, N–CH_3), 5.96 (s, 2H, CH_2), 6.98 (m, 1H, Ar–H), 7.52–7.79 (m, 4H, Ar–H), 8.01 (m, 1H, Ar–H). ^{13}C NMR (CD_2Cl_2): 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 (PCy_3 and CH_3), 49.04 (N–CH_3), 62.86 (CH_2), 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]. ^{31}P NMR (CD_2Cl_2): δ 23.96 (PCy_3). Anal. Calcd for $C_{55}H_{86}ClN_3P_2Ru$ (987.76): C, 66.88; H, 8.78; N, 4.25. Found: C, 66.81; H, 8.91; N, 4.26.

Synthesis of $RuHCl(PCy_3)_2(PhCH_2C_2N_2(NMe)(C_6H_4Me))$ (5d$_1$) and $RuCl(PCy_3)_2(PhCH_2C_2N_2(NMe)(C_6H_3Me))$ (5d$_2$). Benzene (10 mL) was added to a mixture of **3c** (0.210 g, 0.25 mmol) and $RuHCl(H_2)(PCy_3)_2$ (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 **5d$_2$** (0.295 g) as crude product. Crystallization from toluene solution at −35 °C gave pure **5d$_2$** (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 **5d$_1$** and **5d$_2$**. **5d$_1$** could not be isolated in pure form.

5d$_2$: ^{1}H NMR (CD_2Cl_2): δ 0.89–2.05 (m, 66H, PCy_3), 2.24 (s, 3H, CH_3), 4.17 (s, 3H, N–CH_3), 5.81 (s, 2H, CH_2), 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). ^{13}C NMR (CD_2Cl_2): δ 21.78, 22.75, 27.08, 28.44, 30.31, 30.44, 30.63, 33.28, 34.54, 36.84, 37.12 (PCy_3, CH_3 and N–CH_3), 56.20 (CH_2), 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(C_6H_4) and Ru–C(triazolylidene)). ^{31}P NMR (CD_2Cl_2): δ 24.17 (PCy_3). Anal. Calcd for $C_{53}H_{82}ClN_3P_2Ru$ (959.71): C, 66.33; H, 8.61; N, 4.38. Found: C, 66.25; H, 8.56; N, 4.42.

5d$_1$: ^{1}H NMR (CD_2Cl_2): δ −26.30 (t, $^2J_{PH}$ = 24 Hz, 1H, Ru–H), 0.84–2.05 (m, 66H, PCy_3), 2.24 (s, 3H, CH_3), 4.17 (s, 3H, N–CH_3), 5.81 (s, 2H, CH_2), 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). ^{31}P NMR (CD_2Cl_2): δ 42.27 (PCy_3).

Synthesis of $RuHCl(PCy_3)_2(PhCH_2C_2N_2(NMe)(C_6H_4CF_3))$ (5e$_1$) and $RuCl(PCy_3)_2(PhCH_2C_2N_2(NMe)(C_6H_3CF_3))$ (5e$_2$). Benzene (10 mL) was added to a mixture of **3c** (0.240 g, 0.25 mmol) and $RuHCl(H_2)(PCy_3)_2$ (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 **5e$_2$** (0.305 g) as crude product. Crystallization from toluene solution at −35 °C gave pure **5e$_2$** (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 **5e$_1$** and **5e$_2$**. **5e$_1$** could not be isolated in pure form.

5e$_2$: ^{1}H NMR (CD_2Cl_2): δ 0.83–2.04 (m, 66H, PCy_3), 4.25 (s, 3H, N–CH_3), 5.85 (s, 2H, CH_2), 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). ^{13}C NMR (CD_2Cl_2): δ 26.98, 28.28, 28.31, 28.36, 30.48, 30.53, 36.70, 36.76, 36.82, 37.54 (PCy_3 and N–CH_3), 56.37 (CH_2), 114.08, 118.42, 127.95, 128.81, 129.67, 130.34, 136.04, 138.53, 143.40, 153.15 (CF_3 and Ar–C) 184.81, 186.88 (Ru–C(C_6H_4) and Ru–C(triazolylidene)). ^{31}P NMR (CD_2Cl_2): δ 23.58 (PCy_3). Anal. Calcd for $C_{53}H_{79}ClF_3N_3P_2Ru$ (1013.68): C, 62.80; H, 7.86; N, 4.15. Found: C, 62.87; H, 7.83; N, 4.18.

5e$_1$: ^{1}H NMR (CD_2Cl_2): δ −25.86 (t, $^2J_{PH}$ = 8 Hz, = 24 Hz, 1H, Ru–H), 0.82–2.11 (m, 66H, PCy_3), 4.28 (s, 3H, N–CH_3), 5.94 (s, 2H, CH_2), 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). ^{31}P NMR (CD_2Cl_2): δ 40.96 (PCy_3).

Hydrogenation of olefins in J. Young NMR tube

In a glove box, a sample of the appropriate metal complex **4a$_1$** (4.5 mg, 5 μmol, Note: **4a$_1$** contains 15% of **4a$_2$** as impurity) or **4a$_2$** (4.5 mg, 5 μmol) or **4b$_2$** (5.0 mg, 5 μmol) or **5b$_2$** (2.2 mg, 2 μmol), deuterated solvent (0.5 mL) (C_6D_6 for **4a$_1$** and CD_2Cl_2 for **4a$_2$** and **4b$_2$**) 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 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. ^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 **$5a_1$**/**$5b_2$**/**$5c_1$**/**$5c_2$**/**$5d_2$**/**$5e_2$** (2 μmol), CD_2Cl_2 (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 H_2 after purging five times with 50 atm of H_2. 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 N_2 stream, thus maintaining a dry, O_2-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 **$5e_2$** 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

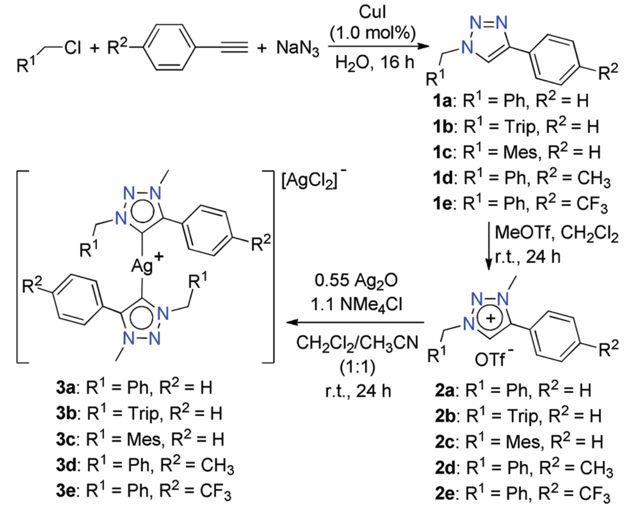
Non-hydrogen atomic scattering factors were taken from the literature tabulations.[19] The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, 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 ESI.†

Results and discussion

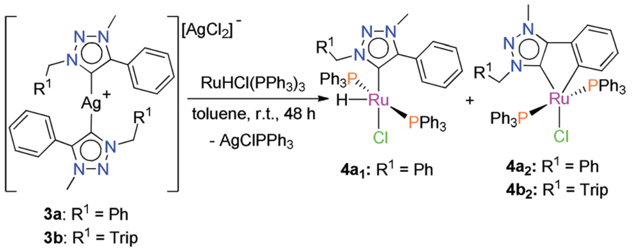
Synthesis and characterization

The 1,2,3-triazoles $[RCH_2C_2HN_3Ph]$ (R = Ph **1a**, $C_6H_2iPr_3$ **1b**, $C_6H_2Me_3$ **1c**) and $[PhCH_2C_2HN_3R]$ (R = C_6H_4Me **1d**, $C_6H_4CF_3$ **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-possition by reacting them with methyl triflate and thus generating $[RCH_2C_2HN_2(NMe)Ph)][OTf]$ (R = Ph **2a**, $C_6H_2iPr_3$ **2b**, $C_6H_2Me_3$ **2c**) and $[PhCH_2C_2HN_2(NMe)R][OTf]$ (R = C_6H_4Me **2d**, $C_6H_4CF_3$ **2e**), respectively (Scheme 1). By analogy to previous reports[10a,16a] subsequent reactions with Ag_2O afforded the stable silver(I) triazolylidenes species **3a–e** (Scheme 1). Mass spectrometry analysis were consistent with the formulation of these products with the general formula $[L_2Ag][AgCl_2]$[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)-triazolylidene complex **3a** was reacted with $RuHCl(PPh_3)_3$ to yield ruthenium-hydride complex $RuHCl(PPh_3)_2(PhCH_2C_2N_2(NMe)Ph)$ (**$4a_1$**) as the minor product and the cyclometalated complex $RuCl(PPh_3)_2(PhCH_2C_2N_2(NMe)C_6H_4)$ (**$4a_2$**) as the major product (Scheme 2). The cyclometalated complex **$4a_2$** was isolated in pure form and fully characterized, whereas the ruthenium-hydride complex **$4a_1$** was contaminated with **$4a_2$** (12–20%). The presence of triazolylidene moiety was observed in ^1H NMR spectra of **$4a_2$** and **$4a_1$**. For **$4a_1$**, a triplet at −27.49 ppm in the ^1H NMR spectrum and a doublet at 46.33 ppm in the ^{31}P NMR spectrum were observed, consistent with the presence of a hydride coupled to



Scheme 1 Synthesis of **1–3**.



Scheme 2 Synthesis of $\mathbf{4a_1}$, $\mathbf{4a_2}$ and $\mathbf{4b_2}$.

two phosphine moieties on ruthenium. A singlet at 37.70 ppm was observed in the ^{31}P NMR spectrum of $\mathbf{4a_2}$. In the ^{13}C NMR spectrum of $\mathbf{4a_2}$, the Ru–C(C_6H_4) and Ru–C(triazolylidene) resonances were observed at 173.39 and 180.64 ppm. The corresponding reaction of **3b** with $RuHCl(PPh_3)_3$ gave selectively the cyclometalated complex ($\mathbf{4b_2}$), which was isolated as dark red crystals (Scheme 2). ^{1}H and ^{13}C NMR spectra of $\mathbf{4b_2}$ confirmed the presence of the triazolylidene moiety in the complex while the ^{13}C resonances attributable to Ru–C(C_6H_4) and Ru–C(triazolylidene) were observed at 174.27 and 175.45 ppm. A singlet at 39.95 ppm in the ^{31}P NMR spectrum was consistent with the presence of two equivalent PPh_3 moieties.

Complexes $\mathbf{4a_1}$, $\mathbf{4a_2}$ and $\mathbf{4b_2}$ were characterized by X-ray molecular structure analysis. Single-crystal X-ray analysis of $\mathbf{4a_1}$ confirmed the formulation and revealed a five-coordinate square-pyramidal Ru-center where the triazolylidene moiety, chloride, and two phosphine ligands form the base of the pyramid and the hydride occupies the apex (Fig. 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 $\mathbf{4a_1}$ is 1.4809(9) Å, which is consistent with the Ru–H bond distances (1.41–1.59 Å) in previously report ruthenium-imidazolylidene complexes[5,7] and in contrast to that seen in a recently published half-sandwich Ru-triazolylidene complex (1.7310(23) Å).[15] Nonetheless, the Ru–C bond distance (1.9886(6) Å) in $\mathbf{4a_1}$ 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.

Single-crystal X-ray analyses of $\mathbf{4a_2}$ and $\mathbf{4b_2}$ revealed the five-coordinate distorted triagonal bipyramidal Ru centers where the two *trans* phosphine ligands occupy the apexes (Fig. 2b and 2c). In $\mathbf{4a_2}$, 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 $\mathbf{4b_2}$ are consistent with $\mathbf{4a_2}$. The Ru–C(triazolylidene) bond distances ($\mathbf{4a_2}$: 2.0079(3) Å, $\mathbf{4b_2}$: 1.9789(3) Å) are slightly shorter than the Ru–C(C_6H_4) bond distances ($\mathbf{4a_2}$: 2.0309(3) Å, $\mathbf{4b_2}$: 2.0356(3) Å). The Ru–Cl distances in $\mathbf{4a_2}$ (2.4582(7) Å) and $\mathbf{4b_2}$ (2.4634(8) Å) are comparable. In $\mathbf{4b_2}$ 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(C_6H_4): 143.62(1)°) are much wider than that expected for an ideal geometry. While the C–Ru–C angle (77.16(1)°) in $\mathbf{4a_2}$ is similar to that in $\mathbf{4b_2}$ (76.75(3)°), the Cl–Ru–C angles vary widely ($\mathbf{4a_2}$: Cl–Ru–C(triazolylidene): 165.01(8)°; Cl–Ru–C(C_6H_4): 117.38(8)°. $\mathbf{4b_2}$: Cl–Ru–C(triazolylidene): 139.63(1)°; Cl–Ru–C(C_6H_4): 143.62(1)°).

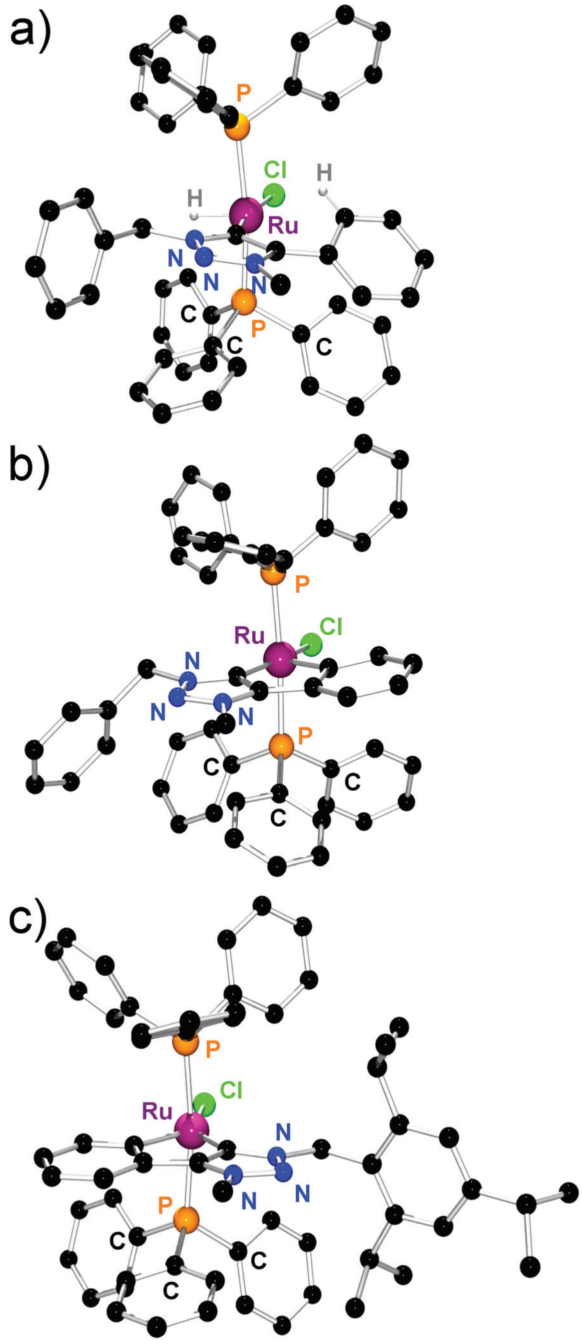
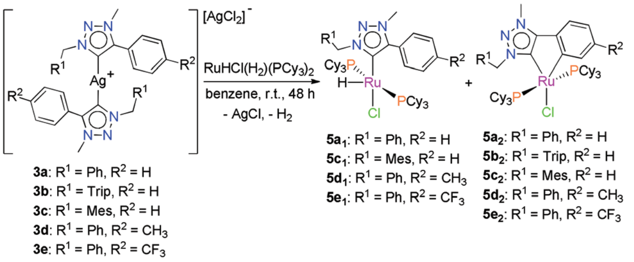


Fig. 2 POV-ray depiction of (a) $\mathbf{4a_1}$, (b) $\mathbf{4a_2}$ and (c) $\mathbf{4b_2}$: C, black; Cl, green; P, orange; N, blue; Ru, purple; H, gray. All hydrogen atoms except the hydride and the *ortho*-H of the phenyl moiety are omitted for clarity.

The silver(I)-triazolylidene complexes **3a–e** were also reacted with $RuHCl(H_2)(PCy_3)_2$ resulting in the formation of Ru–H



Scheme 3 Synthesis of **5a$_1$**, **5a$_2$**, **5b$_2$**, **5c$_1$**, **5c$_2$**, **5d$_1$**, **5d$_2$**, **5e$_1$** and **5e$_2$**.

complexes (**5a$_1$**, **5c$_1$**, **5d$_1$** and **5e$_1$**) as the minor products and the cyclometalated complexes (**5a$_2$**, **5c$_2$**, **5d$_2$** and **5e$_2$**) as the major products (Scheme 3). In the case of **3b**, reaction with RuHCl(H$_2$)(PCy$_3$)$_2$ gave exclusively the cyclometalated complex **5b$_2$** (Scheme 3). The complexes **5a$_1$**, **5b$_2$**, **5c$_1$**, **5c$_2$**, **5d$_2$** and **5e$_2$** were isolated as pure compounds and fully characterized (^{1}H, ^{13}C and ^{31}P NMR spectroscopy). However, isolation of pure **5a$_2$**, **5d$_1$** and **5e$_1$** proved problematic and thus were characterized by ^{1}H and ^{31}P NMR spectroscopy alone. Similar to the PPh$_3$-analogues, the present Ru–H complexes **5a$_1$**, **5c$_1$**, **5d$_1$** and **5e$_1$** displayed a triplet in the range of −25 to −27 ppm (**5a$_1$**: −26.40, **5c$_1$**: −26.49, **5d$_1$**: −26.30, **5e$_1$**: −25.86) in the respective ^{1}H NMR spectra and a doublet was observed in the range of 40 to 43 ppm (**5a$_1$**: 41.08, **5c$_1$**: 41.71, **5d$_1$**: 42.27, **5e$_1$**: 40.96) in the respective ^{31}P NMR spectra. A singlet in the range of 23 to 25 ppm (**5a$_2$**: 24.28, **5b$_2$**: 24.49, **5c$_2$**: 23.96, **5d$_2$**: 24.17, **5e$_2$**: 23.58) was observed in the ^{31}P NMR spectra of cyclometalated complexes **5a$_2$**–**e$_2$**. In the ^{13}C NMR spectra of the isolated cyclometalated species, the Ru–C(triazolylidene) and Ru–C(C$_6$H$_4$)/Ru–C(C$_6$H$_3$) resonances were observed in the range of 180 to 190 ppm (**5b$_2$**: 181.59 and 182.66, **5d$_2$**: 183.11 and 183.96, **5e$_2$**: 184.81, 186.88).

Formulation of complexes **5a$_1$** 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 (**5a$_1$** Ru–H$_{\text{ortho}}$: 2.058 Å; **4a$_1$**: 2.441 Å) (Fig. 3a). The Ru–H(hydride) bond distance in **5a$_1$** (1.545(4) Å) is slightly longer than that found in **4a$_1$** (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 **4a$_1$** and **5a$_1$** are similar while the C–Ru–P bond angles are **4a$_1$**: 93.92(6)° and **5a$_1$**: 94.48(6)°, and the Cl–Ru–P bond angles are 86.34(2)° and 87.00(2)°. Similar to **4a$_1$**, the benzyl group of the triazolylidene moiety in **5a$_1$** is oriented away from the ruthenium center.

Compound **5e$_2$** is a pseudo six-coordinate octahedral species (Fig. 3b), in contrast to **4a$_2$** and **4b$_2$** as it includes an agostic interaction between the Ru and a H on one of the PCy$_3$ ligands. However, this Ru–H(C$_6$H$_{11}$) distance (2.2442 Å) is slightly longer than the Ru–H(C$_6$H$_5$) distance (2.058 Å) seen in **5a$_1$**. The bond distances and angles about Ru in **5e$_2$** are similar to those seen in species **4a$_1$**, **4a$_2$** and **5a$_1$**.

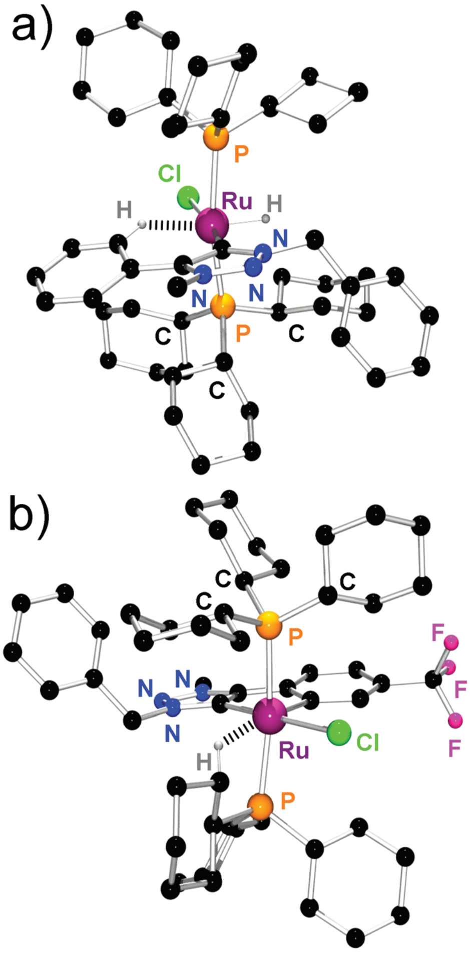


Fig. 3 POV-ray depiction of (a) **5a$_1$** and (b) **5e$_2$**: C, black; Cl, green; P, orange; N, blue; F, pink; Ru, purple; H, gray. All hydrogen atoms except the ruthenium bound hydrogens omitted for clarity.

It is interesting to note that reaction of [RuCl$_2$(*p*-cymene)]$_2$ with silver(I) triazolylidenes **3a**, **3b** and **3c**, gave cyclometalated species as minor products (2–5%) with the (*p*-cymene)RuCl$_2$-(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 ruthium-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(sp^2)–H bond activation resulting in cyclomatalation with liberation of H$_2$ being the driving force. To confirm this, **5a$_1$** was dissolved in CD$_2$Cl$_2$ and the solution was monitored by ^{31}P NMR spectroscopy. A doublet at 41.1 ppm arising from **5a$_1$** slowly decreased while a singlet at 24.3 ppm corresponding to **5a$_2$** grew in (Fig. 4). After 6 days complete conversion to **5a$_2$** was observed. Similarly in the ^{1}H NMR spectra, the hydride triplet at −26.40 ppm corresponding to **5a$_1$** disappeared in 6 days.

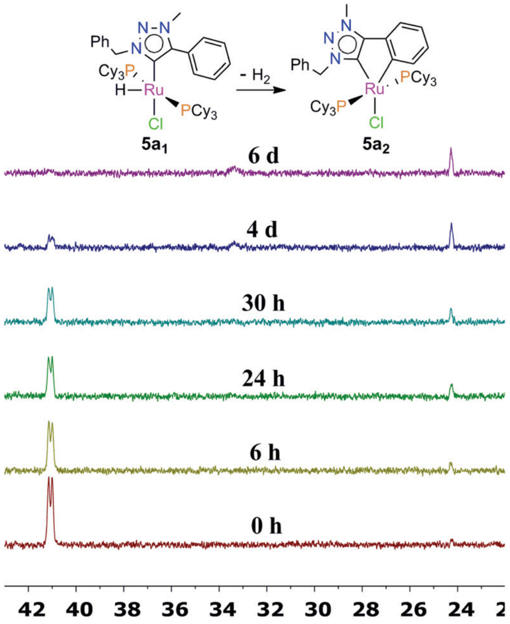
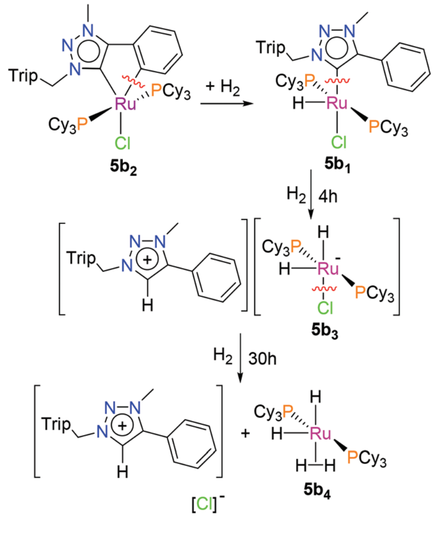


Fig. 4 Conversion of $5a_1$ to $5a_2$ monitored by ^{31}P NMR spectroscopy.

Addition of hydrogen (4 atm) to a solution of the cyclometalated species **$5b_2$** in a sealed J. Young NMR tube and monitoring by ^1H and ^{31}P NMR spectroscopy revealed a fast reaction in which **$5b_2$** reacted with one equivalent of H_2 yielding the hydride complex **$5b_1$** (Scheme 4) with the characteristic ^1H NMR hydride resonance at −26.13 ppm and the doublet (41.05 ppm) in ^{31}P NMR spectrum. After 4 h under H_2 **$5b_1$** reacted further, generating the triazolium cation $[(C_6H_2iPr_3)CH_2C_2HN_2(NMe)Ph]^+$ and anionic ruthenium-dihydride complex **$5b_3$** as evidenced by the ^1H NMR resonances at 10.51 ppm and −8.37 ppm respectively and the ^{31}P resonance at 75.79 ppm. The latter species **$5b_3$** slowly degraded after 30 h affording a new species **$5b_4$** which exhibited a broad hydride resonance at −12.25 ppm and ^{31}P resonance at 53.53 ppm. The ratio of the triazolium-hydrogen peak and the broad hydride peak was 1 : 4, suggested the formulation of **$5b_4$** as $RuH_2(H_2)(PCy_3)_2$ (Scheme 4). Although this species could not be isolated, the broad ^1H NMR signal is consistent with facile interchange of the hydrides and η^2-H_2 sites. Interestingly the closely related species $Ru_2H_4(H_2)(PCy_3)_4$ displays a similarly broad peak at −12.5 ppm[24] while the ^{31}P NMR resonance from **$5b_4$** (53.53 ppm) is similar to those seen for $RuHI(H_2)(PCy_3)_2$ (56 ppm) and $RuHCl(H_2)(PCy_3)_2$ (54 ppm).[25]



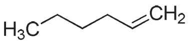
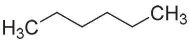
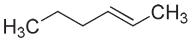
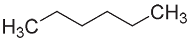
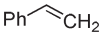
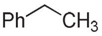
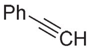
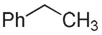
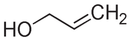
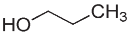
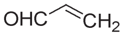
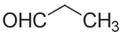
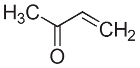
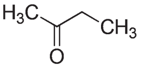
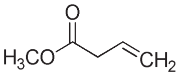
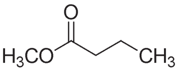
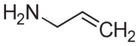
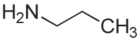
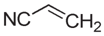
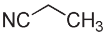
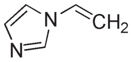
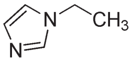
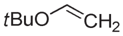
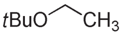
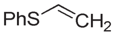
Scheme 4 Generation of $5b_1$, $5b_3$ and $5b_4$.

Hydrogenation catalysis

The catalytic activity of **$4a_1$**, **$4a_2$**, **$4b_2$** and **$5b_2$** for hydrogenation of alkenes and alkyne was investigated (Table 1). At 50 °C under 4 atm of H_2, with catalyst precursor loadings of 2 or 5 mol%, hydrogenation of olefins was performed and monitored by ^1H NMR spectroscopy. In the presence of **$4a_1$** or **$4a_2$**, 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 **$4b_2$**. In contrast, **$5b_2$** 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 **$4a_1$**, **$4a_2$** and **$4b_2$** displayed much slower activity for the hydrogenation of 2-hexene (**$4a_1$**: 100% in 12 h, **$4a_2$**: 100% in 12 h, **$4b_2$**: 100% in 10 h). Similarly the conversion of styrene to ethylbenzene by **$5b_2$** (100% in 8 h) was much faster than **$4a_1$** (16 h), **$4a_2$** (14 h) and **$4b_2$** (12 h). Similarly **$5b_2$** 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 **$4a_1$**, **$4a_2$** or **$4b_2$** as a catalyst precursor although these were much slower, yielding styrene : ethylbenzene ratios of 4 : 96 for **$4b_2$**, 16 : 84 for **$4a_2$** and 23 : 77 for **$4a_1$** after 24 h.

The ability of the derived catalysts to tolerate functional groups was also investigated. Using similar reaction conditions allylalcohol, 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 **$5b_2$**, fast and complete reduction of the olefinic residues in allylalcohol (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 **$4a_1$**, **$4a_2$** and **$4b_2$** displayed lower reactivity for most of these functionalized substrates, although quantitative reduction was observed for allylalcohol, acrylaldehyde, 3-buten-2-one, methyl-3-buteneoate and allylamine after 24 h. Nonetheless, it should be noted that 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)

Table 1 Hydrogenation catalysis with **$4a_1$**, **$4a_2$**, **$4b_2$** and **$5b_2$**[a]

Entry	Substrate	Product	Cat.	*t*/Conversion[b] (h/%)	Cat.	*t*/Conversion[b] (h/%)	Cat.	*t*/Conversion[b] (h/%)	Cat.	*t*/Conversion[b] (h/%)
1			**$4a_1$**	6/100	**$4a_2$**	6/100	**$4b_2$**	5/100	**$5b_2$**	2/100
2			**$4a_1$**	12/100	**$4a_2$**	12/100	**$4b_2$**	10/100	**$5b_2$**	4/100
3			**$4a_1$**	16/100	**$4a_2$**	14/100	**$4b_2$**	12/100	**$5b_2$**	8/100
4			**$4a_1$**	24/84[c]	**$4a_2$**	24/84[c]	**$4b_2$**	24/96[c]	**$5b_2$**	14/100
5			**$4a_1$**	12/100	**$4a_2$**	12/100	**$4b_2$**	10/100	**$5b_2$**	3/100
6			**$4a_1$**	12/100	**$4a_2$**	10/100	**$4b_2$**	8/100	**$5b_2$**	3/100
7			**$4a_1$**	20/100	**$4a_2$**	18/100	**$4b_2$**	16/100	**$5b_2$**	6/100
8			**$4a_1$**	14/100	**$4a_2$**	14/100	**$4b_2$**	12/100	**$5b_2$**	4/100
9			**$4a_1$**	20/100	**$4a_2$**	20/100	**$4b_2$**	16/100	**$5b_2$**	8/100
10			**$4a_1$**	24/89	**$4a_2$**	24/92	**$4b_2$**	24/100	**$5b_2$**	14/100
11			**$4a_1$**	24/77	**$4a_2$**	24/86	**$4b_2$**	24/100	**$5b_2$**	10/100
12			**$4a_1$**	24/19	**$4a_2$**	24/22	**$4b_2$**	24/31	**$5b_2$**	24/65
13			**$4a_1$**	24/25	**$4a_2$**	24/32	**$4b_2$**	24/38	**$5b_2$**	24/78

[a] Conditions: 0.20 mmol of substrate and 5 mol % (**$4a_1$**, **$4a_2$**, **$4b_2$**) and 2 mol % (**$5b_2$**) of catalyst precursor in CD_2Cl_2 at 50 °C under 4 atm of H_2. [b] Conversions were determined by ^1H NMR spectroscopy. [c] Rest of the product was observed to be styrene.

has been reported to be an olefin selective hydrogenation catalyst[15] with activity similar to that of **$4a_1$**, **$4a_2$** and **$4b_2$**.

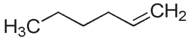
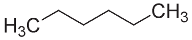
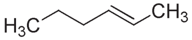
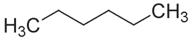
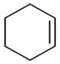
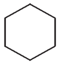
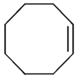
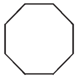
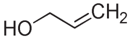
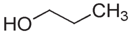
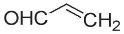
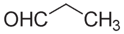
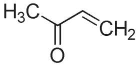
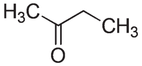
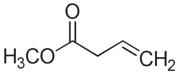
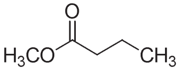
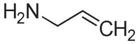
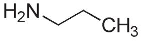
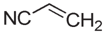
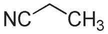
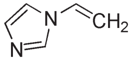
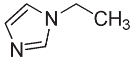
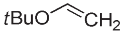
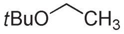
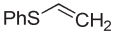
Given the previous success with previously reported Ru-NHC-carbene complexes,[7] 2 mol% **$5a_1$**, **$5b_2$**, **$5c_1$**, **$5c_2$**, **$5d_2$** or **$5e_2$** were tested under similar conditions. Thus hydrogenations of a series of linear and cyclic olefins were examined at 25 °C under high pressure (50 atm) of H_2 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, allylalcohol, acrylaldehyde, 3-buten-2-one and methyl-3-buteneoate. Reduction of allylamine, *tert*-butyl vinyl ether and phenyl vinyl sulfide was either complete or close, but showed moderate activity 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 PCy_3 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 H_2 to regenerate the catalyst. The conversion of **$5b_1$** to **$5b_3$** and **$5b_4$** observed on prolonged exposure to H_2 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(sp^2)–H activation by the ruthenium-hydride with liberation of H_2. 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 presumable a result of the additional steric protection of the metal centre by the tris-isopropylphenyl substituent. Analogous ruthenium-PCy_3 complexes **$5a_1$**, **$5b_2$**, **$5c_1$**, **$5c_2$**, **$5d_2$** and **$5e_2$** dis-

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 CD_2Cl_2 at r.t. under 50 atm of H_2 for 3 h. [b] Conversions were determined by ^{1}H NMR spectroscopy.

played enhanced reactivity. This is thought to result from the greater electron donating ability of PCy_3 compared to PPh_3. 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.

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