Bonding and catalytic application of ruthenium *N*-heterocyclic carbene complexes featuring triazole, triazolylidene and imidazolylidene ligands

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KEYWORDS. *N*-heterocyclic carbene, chelate, abnormal *N*-heterocyclic carbene, ruthenium, transfer hydrogenation.

source: https://doi.org/10.7892/boris.93946 | downloaded: 6.1.2020

ABSTRACT. The first mixed normal/abnormal NHC ruthenium(II) complexes bearing triazole/imidazole based ligands are presented. The ruthenium complexes show differing coordination geometries depending on the ligand sphere and the coordination of the triazole. Two Ru(II) monocarbene complexes have been obtained, with a 2-imidazolylidene carbene and the 1,2,3-triazoles acting as neutral nitrogen donors. In addition, a tridentate Ru(II) complex featuring a normal 2-imidazolylidene as well as two abnormal 1,2,3-triazolylidene carbene moieties is described. Both structural motifs are evaluated in transfer hydrogenation (TH) of acetophenone, with the electron rich Ru(II) tri-NHC exhibiting the highest conversion.

INTRODUCTION

For decades, catalytically active systems have been known to be stabilized by chelating ligands in organometallic chemisty.[1] Especially polydentate *N*-heterocyclic carbene (NHC) ligands with their strong donor ability show remarkable stability towards various oxidation states in transition metal complexes even under harsh conditions.[1a-e,1g,2] Bischelating[1g,3] and pincer ligands[1g,4] are amongst the most common ligand motifs of these complexes. Further development of the normal NHC systems recently led to a subclass of mesoionic or abnormal *N*-heterocyclic carbenes, namely the 1,2,3-triazolylidene ligands.[1c,5] 1,2,3-Triazolylidenes combine a significantly higher σ-donor strength compared to the widely used classical 2-imidazolylidenes with an almost unlimited synthetic access of the ligand precursors through the copper-catalyzed azide–alkyne cycloaddition reaction (CuAAC).[5d,5e,5g,6] A number of chelating triazolylidene transition metal complexes have been described in reports on catalytic as well as spectroscopic and electrochemical applications.[5g,6a,6b,7]

Ruthenium *N*-heterocyclic carbene complexes have been studied extensively for isomerization,[8] hydrogenation,[1g,9] metathesis[9c,10] and polymerization reactions,[11] due to their remarkable ability to adapt to a wide range of oxidation states and coordination geometries.[9a,12] Reports on chelating systems have increased over the years,[1g,8a,9a,10a] and specific design of ruthenium NHC complexes featuring multidentate carbene ligands allows for further insights into the mechanistic aspects of catalysis.[2c,13] Among various reports on the well-established imidazolylidene or triazolylidene carbenes with attached donor sites, the combination of imidazolylidene and triazolylidene carbenes with distinctly different properties is an interesting addition to known NHC pincer ligands with regard to structural and catalytic versatility.

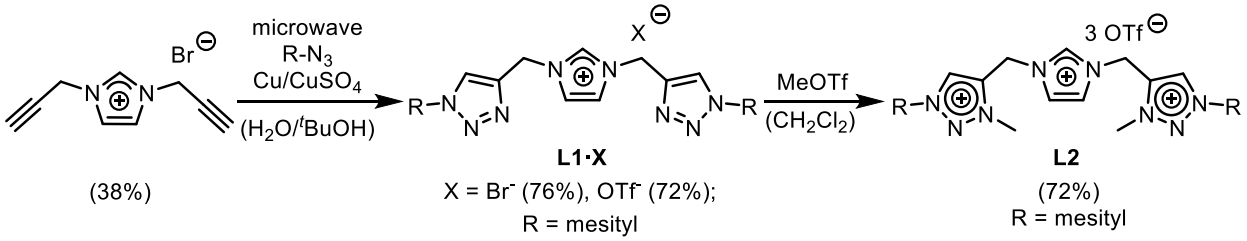
Consequently, the first examples of Ru(II) NHC complexes bearing chelating mixed normal/abnormal NHC ligands are reported here. The 1,2,3-triazole moieties can act either as neutral nitrogen donors or as abnormal/mesoionic carbenes, depending on the substitution pattern of the wingtip groups. Single-crystal X-ray diffraction in combination with NMR spectroscopy is employed to characterize the complexes both in solid state and in solution. Catalytic studies using the resulting monocarbene complexes as well as the tricarbene complex are in accordance with mechanistic considerations, and lead the way to a new class of chelating Ru(II) NHC complexes.

RESULTS AND DISCUSSION

Synthesis of ligand precursors.

The bis-triazole-functionalized *N*-heterocyclic carbene ligand precursor **L1** is readily accessible *via* conventional copper catalyzed dipolar [2+3] cycloaddition of mesityl azide and the corresponding functionalized alkyne (Scheme 1).[6e,14] Selective N-functionalization leads to the triazolium-imidazolium salt **L2** (Scheme 1).

Scheme 1. Synthesis of the ligand precursors **L1** and **L2**.



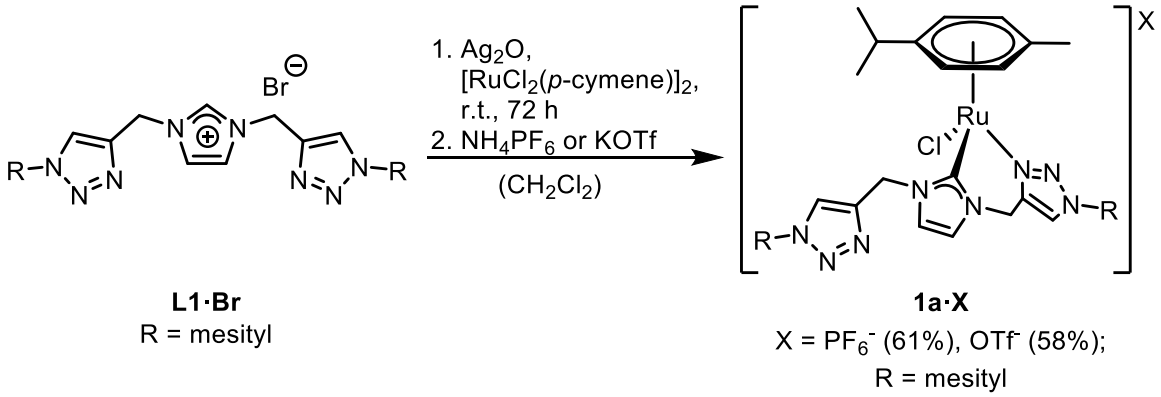
Ligand precursor **L1** shows different reactivity depending on its counter ion. *In situ* anion exchange from the bromide salt **L1·Br** (yield 76%) to the OTf^- analogue **L1·OTf** (yield 72%) in the reaction mixture is indicated by the characteristic upfield shift of the acidic imidazolium proton from δ_H 11.00 to 9.76 ppm ($CDCl_3$ solution), presumably as a consequence of lesser ion pairing in **L1·OTf**.[15] Methylation of the bis-triazole-functionalized precursor **L1·OTf** at the N3 position with MeOTf results in a cleaner reaction than with the bromide analogue and **L2** can be obtained in good yield (72%). The triazolium protons at δ_H = 8.69 ppm in **L2** show a significant downfield shift compared to the corresponding triazole precursor in the ^1H spectrum in addition to the strongly low field shifted signal of the methyl groups at the N3 position at δ_H = 4.41 ppm.

Synthesis of the ruthenium complexes.

Ruthenation of the imidazolium salt **L1·Br** is accomplished by a one-pot reaction mediated by Ag_2O at r.t. according to previously reported procedures (Scheme 2).[6a,7d] Successful complex formation of **1a** is only observed for the bromide salt ligand, whereas the OTf^- analogue does not yield any defined products under the applied reaction conditions. The corresponding ruthenium complex can be isolated as yellow powder and has been characterized as PF_6^- salt **1a·PF$_6$** and OTf^-

salt **1a·OTf** in 61 and 58% yield, respectively. Both complexes are stable towards moisture and air both in solid state and in solution.

Scheme 2. Ag_2O mediated one-pot synthesis of **1a·X** in dichloromethane at r.t.



L1·Br
R = mesityl

1a·X
X = PF_6^- (61%), OTf^- (58%);
R = mesityl

Complex **1a** is chelated by the ligand derived from **L1**, thus forming a cationic complex with coordination of the imidazolylidene and additional coordination of one triazole *via* the N3 nitrogen as evidenced by NMR spectroscopy and single crystal X-ray diffraction (Figure 1).

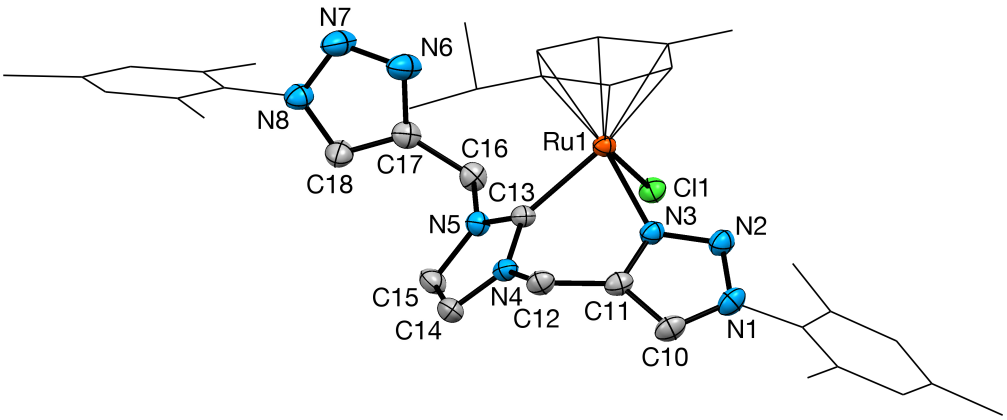


Figure 1. ORTEP style representation of the cationic complex fragment **1a·PF_6** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms and the $PF6^-$ counter ion are omitted for clarity. The coordinated *p*-cymene and the mesityl wingtip groups are displayed as wireframe for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C13, 2.049(3); Ru1–N3, 2.079(2); Ru1–

$C_{centroid}$, 1.707; Ru1–Cl1, 2.402(1); C13–Ru1–N3, 83.2(1); C13–Ru1–Cl1, 86.07(8); C13–Ru1–$C_{centroid}$, 131.39.

Suitable yellow crystals of **1a·PF$_6$** were obtained by slow diffusion of *n*-pentane into a solution of **1a·PF$_6$** in chloroform. X-ray diffraction reveals a classical three-legged piano stool geometry. The unit cell contains two crystallographically independent molecules with statistically identical structural parameters. Chelation of the triazole moiety produces a six-membered metallacycle with a bite angle C–Ru–N of 83.2(1)° and with Ru–C and Ru–N bond distances of 2.049(3) Å and 2.079(2) Å, respectively. The ruthenium carbene distance is in the range of previously reported bond lengths with similar bidentate ligand motifs, the ruthenium nitrogen distance on the other hand is slightly shorter than in related ruthenium(II) complexes.[16] A palladium(II) mono-NHC complex featuring a similar ligand motif, was described recently, however, no chelation was reported.[17] Interestingly, it was not possible to isolate the related neutral mono-NHC complex with two non-coordinated triazole moieties in our case.

Due to the coordination of one triazole moiety, desymmetrization of the ligand derived from **L1** took place, indicated by splitting of the signals in the ^{1}H NMR spectrum of complex **1a·PF$_6$**. Upon complexation, the triazole protons become inequivalent, with the non-coordinated triazole proton shifted to higher field compared to the coordinated one. The actual chemical shifts are strongly influenced by the counter ion and the deuterated solvent. For example, in **1a·PF$_6$** the coordinated triazole proton is shifted to δ_H 7.88 ppm, whereas the non-coordinated one shows a resonance at δ_H 7.33 ppm ($CDCl_3$ solution; for **1a·OTf** δ_H = 7.96 and 7.23 ppm in $CDCl_3$ solution, respectively).[18] Both bridging methylene groups (δ_H = 5.17 - 5.81 ppm) become inequivalent with the methylene group next to the coordinated triazole exhibiting very broad signals with no defined multiplicity. The methylene group next to the non-coordinated triazole on the other hand, is split

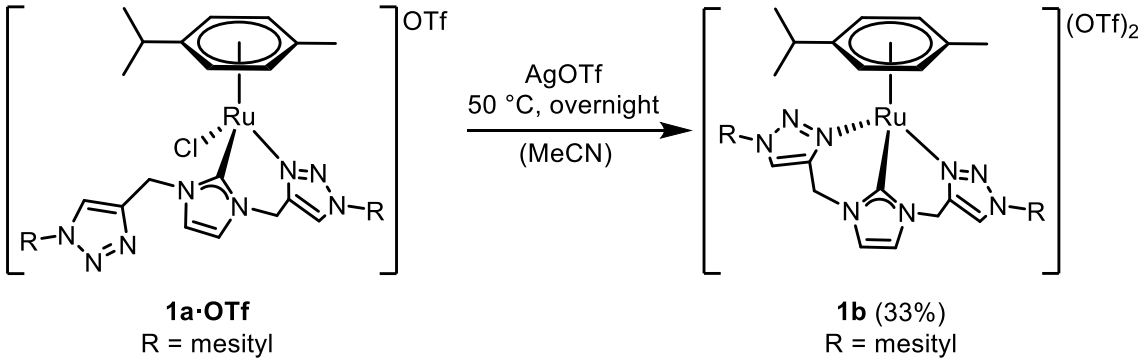
up into an AB doublet. In addition, the *meta* protons and the protons of the *ortho* methyl groups of the mesityl substituents become inequivalent upon complexation. The strong influence of the solvent is also evident, when **1a·OTf** is dissolved in DMSO-d_6. The previously broad signals become sharp and the methylene bridges split into two AB doublets (δ_H = 5.10 and 5.44 ppm, $^2J_{HH}$ = 15.7 and δ_H = 5.64 and 5.71 ppm, $^2J_{HH}$ = 16.0, respectively). Even the chemically inequivalent *para* methyl groups of the mesityl substituents as well as the methyl groups of the *p*-cymene are resolved. The desymmetrization pattern is also observed for the ^{13}C spectra for both **1a·PF$_6$** and **1a·OTf** regardless of the employed deuterated solvent.

A VT-NMR study at elevated temperatures (up to 100 °C) reveals no decoordination of the triazole moiety.[18] Instead, thermal dissociation of *p*-cymene and subsequent N-coordination of the second 1,2,3-triazole is observed in a DMSO-d_6 solution at 120 °C after 2 hours.[18] Upon chelation, the second triazole becomes almost equivalent with the already coordinated one with a downfield shift to δ_H = 8.78 ppm and the previously different methylene bridges exhibit a singlet signal at δ_H = 5.68 ppm. This splitting pattern is retained after purification and isolation of the resulting acetonitrile solvento complex with a singlet signal for the two coordinated triazole protons at δ_H = 8.07 ppm in a CD_3CN solution.[18] Due to the high symmetry in the ^{1}H NMR spectrum and the fact that the methylene bridges are chemically equivalent, a meridional structural motif of the ligand derived from **L1** is proposed. Complementary ESI-MS studies suggest the bonding of a chloride to the ruthenium center, which is in agreement with a *N,C,N*-tridentate coordinating ligand, an equatorially bound chloride and two acetonitrile ligands in axial positions.[18]

In order to evaluate the versatility of the ligand precursor **L1**, the synthesis of the corresponding tridentate cationic ruthenium(II) complex was attempted. Complex **1b** was prepared from complex

1a·OTf by AgOTf mediated abstraction of the chloride ligand in the presence of the coordinating solvent MeCN in 33% yield (Scheme 3).

Scheme 3. Synthesis of the tridentate complex **1b**.



1a·OTf
R = mesityl

1b (33%)
R = mesityl

Suitable single crystals of **1b** were obtained by slow diffusion of *n*-pentane into a solution of **1b** in chloroform/dichloromethane. The molecular structure of **1b** was established by single-crystal X-ray diffraction and confirms a three-legged piano stool geometry with the *N,C,N*-tridentate coordinated ligand in a facial bonding mode. Chelation gave two six-membered metallacycles with a Ru–C distance of 2.053(4) Å and Ru–N distances that are equal within standard deviations (Ru–N6 is 2.081(4) Å and Ru–N3 is 2.090(3) Å; Figure 2).

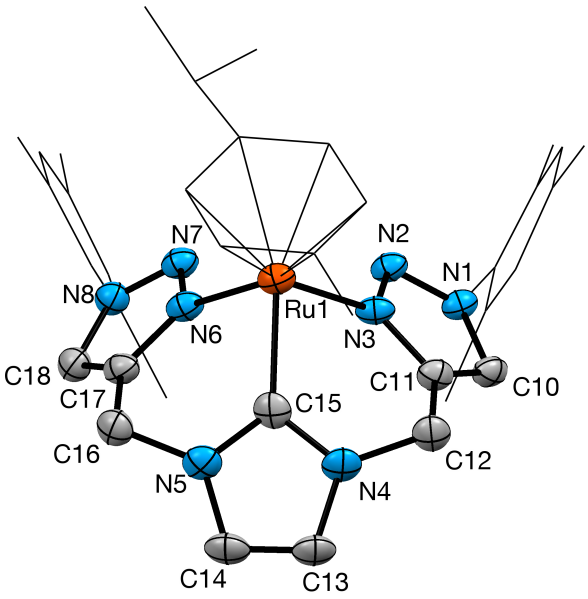


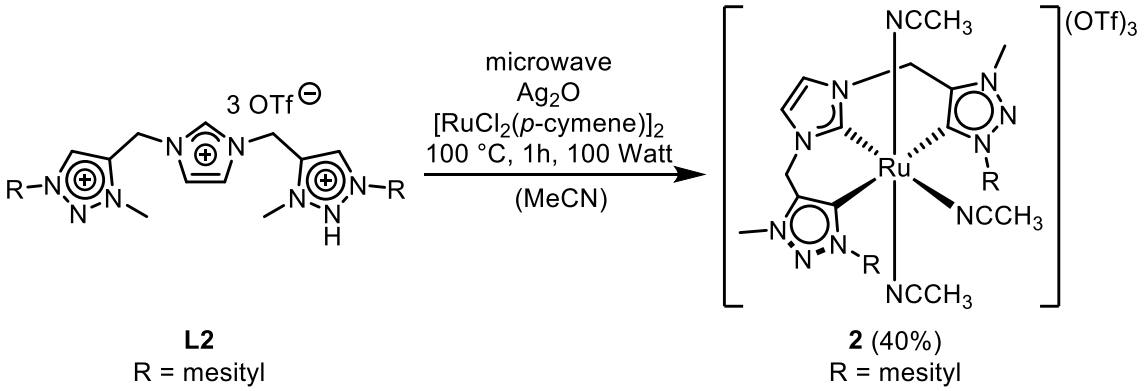
Figure 2. ORTEP style representation of the cationic complex fragment **1b** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms and OTf^- counter ions are omitted for clarity. The mesityl wingtip groups and the coordinated *p*-cymene are displayed as wireframe for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C15, 2.053(4); Ru1–N3, 2.090(3); Ru1–N6, 2.081(4); Ru1–$C_{centroid}$, 1.713; C15–Ru1–N3, 81.7(1); C15–Ru1–N6, 81.2(1); C15–Ru1–$C_{centroid}$, 133.00.

Both the ruthenium carbon distance as well as the ruthenium nitrogen distances are similar to the distances found in complex **1a·PF$_6$** and are therefore within the range of previously reported bond lengths with similar multidentate ligand motifs.[16a,16b,16d] In the ^{1}H NMR spectrum the change from bidentate coordination to tridentate coordination is obvious due to symmetry-relation of the two triazole units which appear as a single set of signals. Upon coordination, the previously non-coordinated triazole proton becomes equivalent with the already coordinated triazole and is low field shifted to 8.10 ppm in CD_2Cl_2. The bridging methylene groups split into a single AB doublet (δ_H = 5.49 and 5.88 ppm, $^2J_{HH}$ = 16.2 Hz). Likewise, the *meta* protons become chemically equivalent as well as the protons of the *ortho* methyl groups of the mesityl substituents. A VT-NMR study reveals splitting of the broad mesityl substituent signals at lower temperatures with sharp signals at -90 °C.[18] No desymmetrization of the methylene linker between the

imidazolylidene and the triazole unit was observed at this temperature, and therefore the process leading to decoalescence might be attributed to a hindered rotation about the N_{trz}–C_{Mes} bond rather than a N-decoordination involving a species related to **1a**.

Ruthenation of the mixed imidazolium/triazolium salt **L2** is accomplished by a microwave mediated one-pot reaction according to a previously reported procedure (Scheme 4).[13a]

Scheme 4. Microwave-assisted synthesis of the mixed normal/abnormal ruthenium carbene compound **2**.



Monomeric Ru(II) complex **2** can be isolated as yellow powder and is stable towards air and moisture. The cationic complex is highly soluble in acetonitrile, but poorly soluble in non-polar solvents like Et_2O and *n*-pentane. Successful complexation is indicated by characteristic NMR data and single crystal X-ray diffraction (Figure 3).

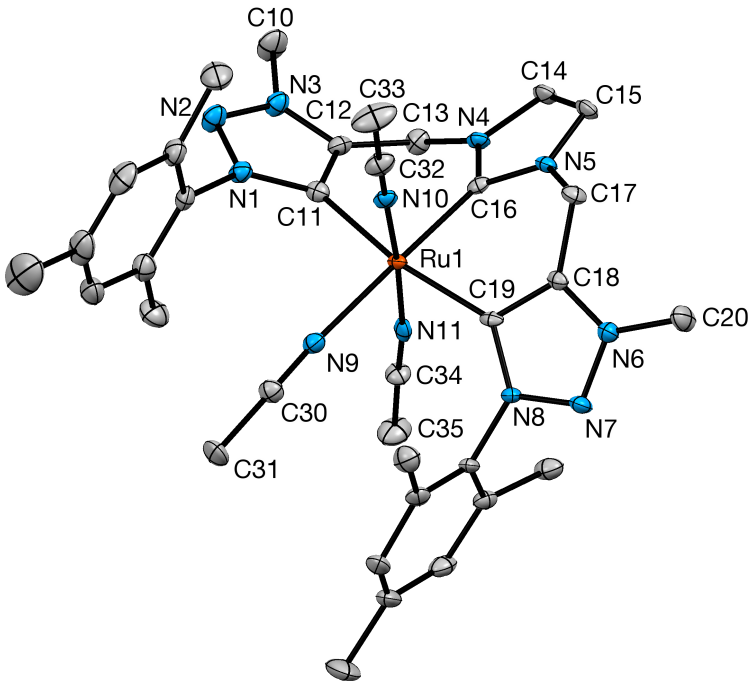


Figure 3. ORTEP style representation of the cationic complex fragment **2** with thermal ellipsoids shown at 50% probability. Hydrogen atoms and OTf^- counter ions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C11, 2.096(4); Ru1–C16, 2.015(5); Ru1–C19, 2.091(4); Ru1–N9, 2.102(4); Ru1–N10, 2.019(4); Ru1–N11, 2.015(4); C11–Ru1–C16, 85.3(2); C11–Ru1–C19, 170.1(2); C11–Ru1–N9, 95.5(2); C11–Ru1–N10, 92.5(2); C16–Ru1–N9, 179.1(2).

Suitable single crystals of **2** were obtained by slow diffusion of Et_2O into a solution of **1b** in MeCN. The complex exhibits a distorted octahedral geometry, with the mixed normal/abnormal NHC ligand being coordinated in a meridional fashion. In addition, *p*-cymene is substituted by three MeCN ligands, facilitating the observed meridional bonding mode. The Ru–C bond distance of the normal carbene of 2.015(5) Å is in the range of previously reported bond lengths featuring multidentate NHC ligands.[3a,13a,13e,19] The ruthenium carbene bond distances of the abnormal carbenes are identical within standard deviations (2.091(4) and 2.096(4) Å) and are slightly longer than previously reported bond lengths for abnormal triazolylidene ruthenium(II) complexes.[5d,6a,7a,7d,20] It is worth pointing out that the ligand parameters of complex **1b** and **2** are very similar.

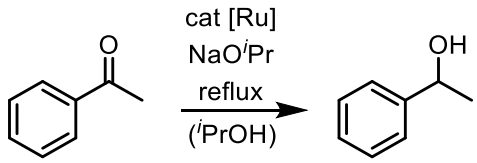
Meridional coordination of the ligand is also supported by NMR spectroscopy with a single signal for the two terminal methyl groups at the N3 position of the triazolylidene at δ_H = 4.20 ppm and two additional singlets for the methyl groups of the two mesityl substituents at δ_H = 2.33 and 1.88 ppm in the ^{1}H NMR spectrum. The methylene bridges in **2** are chemically equivalent and exhibit a singlet signal at δ_H 5.33 ppm, which also confirms the symmetrical meridional conformation especially when compared to the AB slitting pattern of the facial coordinating ligand in complex **1b**. In the ^{1}H NMR spectrum the coordinated acetonitrile ligands correspond to two signals at δ_H 1.96 and 2.03 ppm with integral three and six, respectively. The acetonitrile at δ_H 1.96 ppm corresponds to free acetonitrile, which is due to an exchange on NMR time scale. In the ^{13}C NMR spectrum only one set of signals is observed for the acetonitrile ligands, with the second set lying under the signals of the NMR solvent CD_3CN. The ^{13}C NMR spectrum also shows two characteristic independent carbene carbon shifts at δ_C = 172.6 and 185.3 ppm for the triazolylidene and imidazolylidene carbons, respectively.

To the best of our knowledge, complex **2** constitutes the first example of a mixed normal/abnormal tri-NHC complex of ruthenium reported to date and allows first insights into steric and electronic properties of this ligand motif. Especially the easy synthesis of the ligand precursor *via* dipolar [2+3] cycloaddition of mesityl azide and the corresponding functionalized alkyne will enable further tailoring of the steric properties of the wing tip groups.

Transfer Hydrogenation Catalysis. Complexes **1a** (for comparison reasons **1a·OTf** was used for all catalytic experiments), **1b** and **2** were investigated as catalyst precursors for ketone reduction *via* transfer hydrogenation. Standard protocols were applied consisting of basic 2-propanol as formal dihydrogen donor and acetophenone as model substrate (Scheme 5).[9b,13a] **1a**

(0.5 mol%), **1b** (0.5 mol%) and **2** (0.5 mol%) display catalytic activity in the presence of NaO*i*Pr (5 mol%) in 2-propanol at reflux conditions. Acetophenone is reduced to the corresponding alcohol 1-phenyl ethanol with 85%, 84% and 98% conversion within 180, 120 and 80 min, respectively, achieving turnover frequencies (TOFs) up to 1100 h^{-1} (summarized in Figure 4).[18]

Scheme 5. Catalytic transfer hydrogenation of acetophenone with mixed normal/abnormal NHC ruthenium complexes.



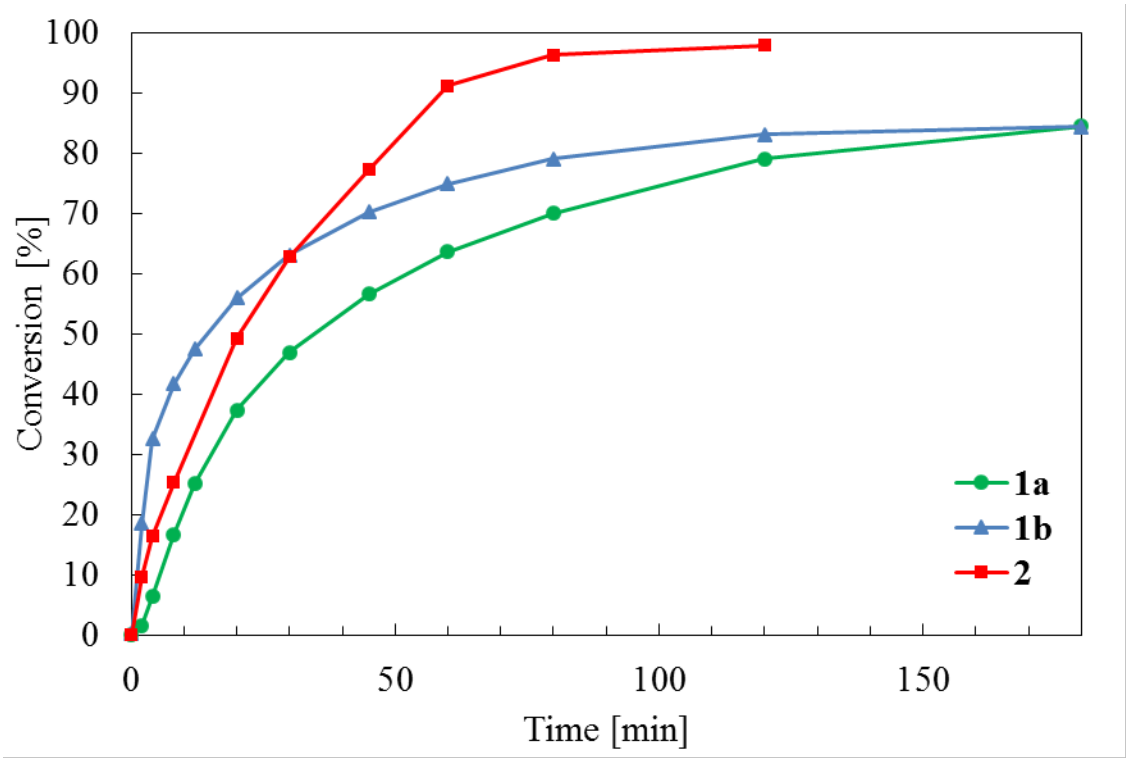


Figure 4. Catalytic performance of **1a**, **1b** and **2** in the transfer hydrogenation of acetophenone. Reaction conditions: acetophenone (1 mmol), NaO*i*Pr (0.05 mmol, 5 mol%), *i*PrOH 10 mL, catalyst loading (0.5 mol%), 82 °C. Conversions determined *via* GC analysis as average over two catalytic runs using anisole as internal standard.

Although the catalytic activity does not reach the highest reported reactivity for Ru TH pre-catalysts,[9b,9e,13a,16c,21] complexes **1a** and **1b** show comparable or significantly higher conversions than N-donor functionalized related compounds.[16a,16e,22] It is, however, noteworthy, that **1b**, with both triazole moieties coordinated to the ruthenium center, exhibits the highest (initial) turnover frequency (TOF_{2min}) of 1100 h^{-1} (19% conversion), compared to **1a** with a TOF_{4min} of 280 h^{-1} (6% conversion) and **2** with a TOF_{2min} of 580 h^{-1} (10% conversion). After reaching a conversion of 60% **1b** slows down significantly. The mixed normal/abnormal NHC complex **2** turned out to be a more robust TH precursor compared to the monocarbene complexes **1a** and **1b**, possibly due to a stronger chelating effect and a higher electron density at the metal center. Compound **2** establishes this novel structural motif as a viable alternative to existing Ru TH catalysts. The catalyst can be employed in low amounts of 0.5 mol%, in line with the expected high stability of the tridentate catalytic species.

CONCLUSION

The first Ru(II) mixed normal/abnormal NHC complexes derived from triazolium/imidazolium salts are presented. Two Ru(II) monocarbene complexes were obtained, with a 2-imidazolylidene skeleton and two 1,2,3-triazoles acting as neutral nitrogen donors. In addition, the tridentate Ru(II) complex featuring normal as well as abnormal carbene moieties is described. This unusual combination of one 2-imidazolylidene and two 1,2,3-triazolylidenes connected by methylene bridges constitutes the first example of a transition metal complex featuring a chelating mixed tri-NHC ligand. This combination of normal and abnormal NHC moieties potentially influences the

activity on the ruthenium complexes as catalyst precursors in transfer hydrogenation. Especially coordination of 1,2,3-triazole as neutral nitrogen donor vs. coordination as mesoionic triazolylidene ligand highlight the various possibilities of mixed NHC ligands for catalytic applications and provide a platform for further examination of this motif. Consequently, specific tailoring of the coordination geometry of ruthenium tri-NHC complexes holds great potential for the development of efficient homogeneous catalyst systems and will be further investigated. As so far no mixed NHC transition metal complexes have been reported, these results should be seen as an incentive to exploit the stabilizing properties of such tridentate ligand structures in the future.

EXPERIMENTAL SECTION

General Comments. All reactions were performed under an atmosphere of dry argon in oven-dried glassware using standard Schlenk techniques. All reagents were purchased from commercial sources and used without further purification. Mesityl azide[23] and [Ru(*p*-cymene)Cl_2]$_2$[24] were synthesized according to literature procedures.

Microwave reactions were carried out using a CEM Discover microwave synthesizer, operating at 100 W irradiation power. Chromatographic separations were performed using silica gel (40 - 63 μm). NMR spectra were recorded with a Bruker Avance DPX 400, a Bruker Avance III 400 and a Bruker Avance I 500 spectrometer at a temperature of 298 K. The spectra were referenced to the residual solvent signals in parts per million (ppm). Abbreviations for NMR multiplicities are: singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m). Coupling constants *J* are given in Hz. All ^{13}C NMR spectra are 1H decoupled. Electrospray ionization spectra (ESI) were obtained on a Thermo Scientific LCQ/Fleet spectrometer by Thermo Fisher Scentific. GC analysis was done with an HP 6890 GC system using an Agilent DB-225ms column (24.8 m x 250 μm x 0.25 μm).

Elemental analyses were performed in the microanalytical laboratories of Technische Universität München and University College Dublin.

Synthesis of 1,3-dipropargylimidazolium bromide.[25] A solution of imidazole (2.04 g 30.0 mmol) in dry tetrahydrofuran (40 mL) was slowly added to a solution of sodium hydride (1.31 g, 732.7 mmol) in dry tetrahydrofuran (40 mL). After stirring for 15 min at room temperature, a solution of propargyl bromide (80% in toluene, 8.32 mL, 75.0 mmol) in dry THF (20 mL) was added quickly at 0 °C. The reaction mixture was allowed to warm to r.t. and stirred overnight, before stirring for 2 h at 60 °C. The solution was cooled down to 0 °C and precipitated with Et_2O (100 mL). The brown residue was dissolved in methanol and precipitated with Et_2O (100 mL). Subsequently, the residue was suspended in acetonitrile and filtrated. The filtrate was concentrated under reduced pressure and washed with cold acetone to yield 1,3-dipropargylimidazolium bromide (2.59 g, 38%) as a colorless powder.

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 9.50 (s, 1H, H_{im}), 7.91 (d, ^3J = 1.6 Hz, 2H, H_{im}), 5.30 (d, ^3J = 2.5 Hz, 4H, CH_2), 3.87 (t, ^4J = 2.6 Hz, 2H, C*H*).

^{13}C NMR (100.62 MHz, DMSO-d_6): δ = 136.2 (C_{im}), 122.7 (C_{im}), 79.1 (C_q), 76.0 (*C*H), 38.8 (*C*H_2).

Anal. Calcd for $C_9H_9BrN_2$ (225.09): C, 48.03; H, 4.03; N, 12.45. Found: C, 47.69; H, 3.85; N, 12.16.

Synthesis of L1·Br. Mesityl azide (161 mg, 1.00 mmol), and 1,3-dipropargylimidazolium bromide (113 mg, 0.50 mmol) were suspended in a mixture of water (2 mL) and *tert*-BuOH (2 mL). $CuSO_4$ (11.2 mg, 0.07 mmol), and copper powder (1.59 mg, 0.03 mmol) were added and the mixture was stirred for 2 h at 100 °C under microwave irradiation. After cooling, the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with

aqueous ammonia (3 × 15 mL) and brine (3 × 15 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and precipitated with pentane (50 mL) to give the pure triazole/imidazole ligand **L1·Br** as a pale brown powder (208 mg, 76%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 11.00 (s, 1H, H_{im}), 8.27 (s, 2H, H_{trz}), 7.68 (s, 2H, H_{im}), 6.94 (s, 4H, CH_{mes}), 5.86 (s, 4H, CH_2), 2.33 (s, 6H, CH_3), 1.88 (s, 12H, CH_3).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 140.5 ($C_{q,mes}$), 140.0 ($C_{q,trz}$), 137.9 (C_{im}), 134.9 ($C_{q,mes}$), 133.0 ($C_{q,mes}$), 129.3 (CH$_{mes}$), 127.0 (CH$_{trz}$), 122.3 (CH$_{im}$), 44.5 (CH$_2$), 21.2 (CH$_{3\,para}$), 17.5 (CH$_{3\,ortho}$).

MS-ESI (*m*/*z*): [**L1·Br**-Br]$^+$ 467.23.

Synthesis of L1·OTf. In order to obtain **L1·OTf** instead of the bromide salt, KOTf (235mg, 1.25 mmol) was added to the reaction mixture prior to extraction with CH_2Cl_2. The pure triazole/imidazole ligand **L1·OTf** is obtained as an off white powder (221 mg, 72%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 9.76 (s, 1H, H_{im}), 8.10 (s, 2H, H_{trz}), 7.65 (s, 2H, H_{im}), 6.95 (s, 4H, CH_{mes}), 5.70 (s, 4H, CH_2), 2.33 (s, 6H, CH_3), 1.88 (s, 12H, CH_3).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 140.5 ($C_{q,mes}$), 149.7($C_{q,trz}$), 136.9 (C_{im}), 134.9 ($C_{q,mes}$), 133.0 ($C_{q,mes}$), 129.3 (CH$_{mes}$), 126.9 (CH$_{trz}$), 122.6 (CH$_{im}$), 44.6 (CH$_2$), 21.2 (CH$_{3\,para}$), 17.4 (CH$_{3\,ortho}$).

MS-ESI (*m*/*z*): [**L1·OTf**-OTf]$^+$ 467.28.

Anal. Calcd for $C_{28}H_{31}F_3N_8O_3S$ (616.66): C, 54.54; H, 5.07; N, 18.17; S, 5.20. Found: C, 54.42; H, 5.13; N, 18.09; S, 4.99.

Synthesis of L2. To a solution of **L1·OTf** (400 mg, 0.65 mmol) in CH_2Cl_2 (20 mL) was added MeOTf (255 mg, 1.56 mmol) and the mixture was stirred in a closed Schlenk tube overnight at RT. The white suspension was concentrated to half its original volume, and the product was precipitated with diethyl ether. The raw brown solid was purified *via* repeated precipitation from

MeCN/Et_2O. Washing with *n*-pentane and removal of the residual solvent under reduced pressure yielded **L2** (442 mg, 72 %) as a colorless solid.

^{1}H NMR (400.13 MHz, CD_3CN): δ = 9.31 (s, 1H, H_{im}), 8.69 (s, 2H, H_{trz}), 7.79 (d, J = 1.6 Hz, 2H, H_{im}), 7.16 (s, 4H, CH_{mes}), 5.88 (s, 4H, CH_2), 4.41 (s, 6H, NCH_3), 2.37 (s, 6H, CH_3), 2.04 (s, 12H, CH_3).

^{13}C NMR (100.62 MHz, CD_3CN): δ = 144.0 ($C_{q,mes}$), 139.5 (C_{im}), 138.9 ($C_{q,trz}$), 135.7 ($C_{q,mes}$), 133.8 (CH$_{trz}$), 132.1 ($C_{q,mes}$), 130.7 (CH$_{mes}$), 125.0 (C_{im}), 42.8 (CH$_2$), 40.2 (NCH$_3$), 21.2 (CH$_{3\,para}$), 17.3 (CH$_{3\,ortho}$).

MS-ESI (*m*/*z*): [**L2**-OTf]$^+$ 795.10; [**L2**-2OTf]$^{2+}$ 323.07; [**L2**-3OTf]$^{3+}$ 165.80.

Anal. Calcd for $C_{32}H_{37}F_9N_8O_9S_3$ (944.86): C, 40.68; H, 3.95; N, 11.86; S, 10.18. Found: C, 40.61; H, 4.01; N, 11.79; S, 10.15.

Synthesis of complex 1a. A mixture of **L1·Br** (75.1 mg, 0.14 mmol), Ag_2O (14.6 mg, 0.06 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (38.6 mg, 0.06 mmol) in CH_2Cl_2 (10 mL) was stirred in the dark at room temperature for 72 h. The suspension was filtered through celite and the solvent was removed under reduced pressure.

a) isolated as **1a·PF$_6$**. The pale brown residue was dissolved in CH_2Cl_2 (5 mL), NH_4PF_6 (30.8 mg, 0.19 mmol) was added and the mixture was stirred at room temperature for 5 h and subsequently filtered through celite. Precipitation with *n*-pentane and drying under reduced pressure yields **1a·PF$_6$** as yellow solid. Analytically pure yellow crystals of **1a·PF$_6$** were obtained by recrystallization from $CHCl_3$/*n*-pentane (68 mg, 61%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.91 (s, 1H, H_{im}), 7.88 (s, 1H, $H_{trz,coord}$), 7.33 (s, H, H_{trz}), 7.22 (s, 1H, H_{im}), 6.99 (s, 2H, CH_{mes}), 6.98 (s, 2H, CH_{mes}), 5.92 (d, J = 5.8 Hz, 2H, H_{cym}), 5.81 (d, J = 11.5 Hz, 1H, CH_2), 5.64 (d, J = 5.4 Hz, 2H, H_{cym}), 5.59 (m, 1H, CH_2), 5.51 (d, J = 5.8 Hz, 1H,

CH_2), 5.17 (d, J = 16.0 Hz, 1H, CH_2), 2.87 (sept, 1H, CHMe$_2$), 2.35 (s, 6H, C$_{mes}$CH_3), 2.21 (s, 3H, C$_{cym}$CH_3), 1.99 (s, 6H, C$_{mes}$CH_3), 1.95 (s, 6H, C$_{mes}$CH_3), 1.23 (d, J = 6.8 Hz, 6H, CH$_{cym}$CH_3).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 173.8, 142.1, 141.1, 140.4, 135.1, 135.0, 133.3, 132.8, 129.5, 129.3, 126.3, 125.8, 124.3, 121.9, 111.5, 102.3, 87.9, 87.5, 87.4, 83.8, 46.0, 44.3, 31.5, 24.0, 21.3, 21.3, 21.1, 19.0, 17.6, 17.5.

^{31}P NMR (161.97 MHz, $CDCl_3$): δ = -144.4 (sept, PF$_6$).

MS-ESI (m/z): [**1a·PF$_6$**-PF$_6$]$^+$ 737.19.

Anal. Calcd for $C_{37}H_{44}ClF_6N_8PRu$ x 0.67 $CHCl_3$ (961.88): C, 47.03; H, 4.68; N, 11.65. Found: C, 47.33; H, 4.67; N, 11.80.

b) isolated as **1a·OTf**. The pale brown residue is dissolved in CH_2Cl_2 (5 mL), KOTf (35.6 mg, 0.19 mmol) was added and the mixture was stirred at room temperature overnight and subsequently filtered through celite. Precipitation with *n*-pentane and drying under reduced pressure yielded **1a·OTf** (64.8 mg, 58%) as light brown solid.

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 8.71 (s, 1H, $H_{trz,coord}$), 8.48 (s, 1H, H_{trz}), 7.73 (d, J = 1.8 Hz, 1H, H_{im}), 7.58 (d, J = 1.8 Hz, 1H, H_{im}), 7.16 (s, 2H, CH_{mes}), 7.13 (s, 2H, CH_{mes}), 6.01(m, 2H, H_{cym}), 5.85 (m, 2H, H_{cym}), 5.71 (d, J = 16.0 Hz, 1H, CH_2), 5.64 (d, J = 6.0 Hz, 1H, CH_2), 5.44 (d, J = 15.4 Hz, 1H, CH_2), 5.10 (d, J = 15.9 Hz, 1H, CH_2), 2.77 (sept, 1H, CHMe$_2$), 2.35 (s, 3H, C$_{mes}$CH_3), 2.34 (s, 3H, C$_{mes}$CH_3), 2.06 (s, 3H, C$_{cym}$CH_3), 1.95 (s, 6H, C$_{mes}$CH_3), 1.92 (s, 6H, C$_{mes}$CH_3), 1.15 (d, J = 6.9 Hz, 3H, CH$_{cym}$CH_3), 1.10 (d, J = 6.8 Hz, 3H, CH$_{cym}$CH_3).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 173.5, 142.2, 141.1, 140.5, 135.0, 134.9, 132.8, 129.5, 129.3, 126.2, 124.5, 121.8, 111.1, 102.4, 88.1, 87.6, 87.4, 83.8, 45.8, 44.6, 31.5, 23.9, 21.3, 21.3, 21.2, 19.1, 17.7, 17.4.

MS-ESI (m/z): [**1a·OTf**-OTf]$^+$ 737.18.

Anal. Calcd for $C_{38}H_{44}ClF_3N_8O_3RuS$ (886.40): C, 51.49; H, 5.00; N, 12.64; S, 3.62. Found: C, 51.25; H, 5.23; N, 12.33; S, 3.55.

Synthesis of complex 1b. A mixture of **1a·OTf** (150 mg, 0.17 mmol) and AgOTf (52.2 mg, 0.20 mmol) in MeCN (3 mL) was stirred in the dark at 50 °C overnight and then filtered through celite. The mixture was dissolved in CH_2Cl_2 and precipitated with Et_2O. Precipitation from MeCN with Et_2O and drying under reduced pressure yielded **1b** as light yellow solid. Analytically pure yellow crystals of **1b** were obtained by recrystallization from $CHCl_3$/CH_2Cl_2/*n*-pentane (55 mg, 33%).

^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 8.10 (s, 2H, H_{trz}), 7.54 (s, 2H, H_{im}), 7.00 (s, 4H, CH_{mes}), 5.97 (d, J = 6.3 Hz, 2H, H_{cym}), 5.88 (d, J = 16.2 Hz, 2H, CH_2), 5.88 (d, J = 6.4 Hz, 2H, H_{cym}), 5.49 (d, J = 16.2 Hz, 2H, CH_2), 2.79 (sept, J = 7.4 Hz, 1H, CHMe$_2$), 2.34 (s, 6H, C$_{mes}$CH_3), 2.31 (s, 3H, C$_{cym}$CH_3), 1.84 (s, 12H, C$_{mes}$CH_3), 1.28 (d, J = 6.9 Hz, 6H, CH$_{cym}$CH_3).

^{13}C NMR (100.62 MHz, CD_3CN): δ = 176.6 (C_{im}), 144.8 (C_{trz}), 142.6 ($C_{q,mes}$), 135.7 ($C_{q,mes}$), 133.3 ($C_{q,mes}$), 130.3 (*C*H$_{mes}$), 127.6 (*C*H$_{trz}$), 125.0 (*C*H$_{im}$), 91.4 (*C*H$_{cym}$), 87.0 (*C*H$_{cym}$), 45.7 (*C*H$_2$), 32.5 (*C*H$_{cym}$Me$_2$), 22.7 (CH$_{cym}$(*C*H$_3$)$_2$), 21.1 (*C*H$_{3,mes,para}$), 19.4 (*C*H$_{3,cym}$), 17.5 (*C*H$_{3,mes,ortho}$).

^{19}F NMR (376.46 MHz, CD_2Cl_2): δ = -78.9 (s, OTf).

MS-ESI (*m*/*z*): [**1b**-OTf]$^+$ 850.89, [**1b**-2OTf]$^{2+}$ 351.21.

Anal. Calcd for $C_{39}H_{44}F_6N_8O_6RuS_2$ x 0.5 CH_2Cl_2 (1042.47): C, 45.51; H, 4.35; N, 10.75; S, 6.15. Found: C, 45.53; H, 4.41; N, 10.93; S, 6.58.

Synthesis of complex 2. 5 mL of acetonitrile was added to a mixture of **L2** (150 mg, 0.159 mmol), Ag_2O (54.1 mg, 0.233 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (47.6 mg, 0.078 mmol). The orange mixture was stirred for 1 h at 100 °C under microwave irradiation. After cooling, the mixture was filtered over celite and the volatiles were removed under reduced pressure. The residue was

purified by column chromatography (SiO_2; CH_2Cl_2 : MeCN = 1:1) to give **2** as pale yellow powder. Clear yellow crystals were obtained after crystallization from MeCN/Et_2O by slow diffusion (63 mg, 40%).

^{1}H NMR (400.13 MHz, CD_3CN): δ = 7.36 (s, 2H, H_{im}), 7.05 (s, 4H, CH_{mes}), 5.33 (s, 4H, CH_2), 4.20 (s, *6*H, NCH_3), 2.33 (s, 6H, C_{mes}CH_3), 2.03 (s, 6H, CH_3CN), 1.96 (d s, 3H, CH_3CN), 1.88 (s, 12H, C_{mes}CH_3).

^{13}C NMR (100.62 MHz, CD_3CN): δ = 185.3 (C_{im}), 172.6 (C_{trz}), 141.3 (C_{trz}), 141.0 ($C_{q,mes}$), 137.3 ($C_{q,mes}$), 136.3 ($C_{q,mes}$), 129.6 (*C*H$_{mes}$), 124.9 (CH$_3$*C*N), 123.1 (*C*H$_{im}$), 45.2 (*C*H$_2$), 37.3 (N*C*H$_3$), 21.1 (*C*H$_{3,mes,para}$), 17.4 (*C*H$_{3,mes,ortho}$), 4.3 (*C*H$_3$CN).

^{19}F NMR (376.46 MHz, CD_3CN): δ = -79.4 (s, OTf).

MS-ESI (*m*/*z*): [**2**-OTf]$^+$ 867.35, [**2**-OTf-MeCN]$^+$ 826.35, [**2**-OTf-2MeCN]$^+$ 785.56, [**2**-OTf-3MeCN]$^+$ 745.08, [**2**-2OTf-MeCN]$^{2+}$ 338.58, [**2**-2OTf-2MeCN]$^{2+}$ 318.30, [**2**-2OTf-3MeCN]$^{2+}$ 297.22.

Anal. Calcd for $C_{37}H_{43}F_6N_{11}O_6RuS_2$ x MeCN (1058.06): C, 44.27; H, 4.38; N, 15.89. Found: C, 44.20; H, 4.39; N, 15.91.

Transfer Hydrogenation Catalysis. Catalytic transfer hydrogenation reactions were carried out under an argon atmosphere in Schlenk tubes. In a typical experiment, the reactor was charged with 2-propanol (9.8 ml), the ketone (1 mmol), anisole (50.5 μL) and the respective amount of catalyst (0.5 mol%).[9b,13a] The mixture was heated to reflux for 1 min and a 0.1 M solution of NaO*i*Pr in 2-propanol (200 μL, 0.05 mmol, 5 mol%) was added to the stirred mixture. 0.5 mL aliquots of the reaction mixture were taken at the required reaction times and immediately cooled down to 0 °C, filtered over a short pad of silica and quenched with 1 mL of diethyl ether in a GC vial.

Subsequently, the mixture was analyzed by gas chromatography. The conversion of the ketone and the yield of alcohol were calculated according to the internal standard.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org. For detailed information on NMR Data and Transfer Hydrogenation Catalysis and Crystallographic Data see Supporting Information. Crystallographic Data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC XXX (**1a**·$\mathbf{PF_6}$), XXX (**1b**) and XXX (**3**). This data is available free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

M.H. is grateful for the financial support of the TUM Graduate School of Chemistry. Dr. A. Pöthig's and Christian Jandl's support with crystallographic data is greatly appreciated. M. Weindl's support with NMR spectroscopy is greatly appreciated.

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