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Synthesis and catalytic alcohol oxidation and ketone transfer hydrogenation activity of donor-functionalized mesoionic triazolylidene ruthenium(II) complexes

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Abstract

We report on the synthesis of a variety of *C,E*-bidentate triazolylidene ruthenium complexes that comprise different donor substituents E (E = C: phenyl anion; E = O: carboxylate, alkoxide; E = N: pyridine at heterocyclic carbon or nitrogen). Introduction of these donor functionalities is greatly facilitated by the synthetic versatility of triazoles, and their facile preparation routes. Five different complexes featuring a *C,E*-coordinated ruthenium center with chloride/cymene spectator ligands and three analogous solvento complexes with MeCN spectator ligands were prepared and evaluated as catalyst precursors for direct base- and oxidant-free alcohol dehydrogenation, and for transfer hydrogenation using basic *i*PrOH as source of dihydrogen. In both catalytic reactions, the neutral/mono-cationic complexes with chloride/cymene spectator ligands performed better than the solvento ruthenium complexes. The donor functionality had a further profound impact on catalytic activity. For alcohol dehydrogenation, the *C,C*-bidentate phenyl-triazolylidene ligand induced highest conversions, while carboxylate or pyridine donor sites gave only moderate activity or none at all. In contrast, transfer hydrogenation is most efficient when a pyridyl donor group is linked to the triazolylidene via the heterocyclic carbon atom, providing turnover frequencies as high as 1400 h⁻¹ for cyclohexanone transfer hydrogenation. The role of the donor group is discussed in mechanistic terms.

Introduction

The functionalization of key ligands with donor groups for application in catalytic reactions has been much explored in coordination and organometallic chemistry,¹ since the potentially chelating nature of these donor groups offer electronic and coordinative flexibility that may facilitate different steps of a catalytic cycle.² While robust chelation imparts stability to a catalytically active species, hemilabile donor group coordination may be highly valuable for accessing transient intermediates in a catalytic cycle.³ Accordingly, the concept of chelation has found widespread application in N-heterocyclic carbene (NHC) chemistry.⁴ As a subclass of NHCs, mesoionic 1,2,3-triazolylidene ligands have recently gained significant attention,⁵ in parts because they combine the benefits of specific σ -donor properties, which are slightly stronger than classical imidazolium-derived systems,^{5a} together with vast synthetic flexibility of the ligand precursors.^{5c,6} The large majority of mesoionic triazolylidene complexes reported thus far feature monodentate ligands. Even though ligand tuning has been applied to tailor catalytic activity in various processes with such monodentate complexes,⁷ it is remarkable that the synthetic flexibility of the triazole ligand synthesis has not been exploited more extensively up to now for the introduction of chelating complexes. Examples with chelating triazolylidenes include ruthenium and iridium complexes featuring a chelating pyridyl-functionalized triazolylidene ligand for photosensitisation,⁸ water oxidation,⁹ and a series of rhodium and group 10 complexes.¹⁰

In light of the high versatility of [2+3] dipolar cycloaddition chemistry to access the corresponding 1,2,3-triazoles as carbene precursors,¹¹ we have been interested in expanding the range of chelating triazolylidene ligands in order to gain a better mechanistic understanding and eventually to rationally enhance the catalytic activity of triazolylidene complexes in ruthenium-catalyzed de- and transfer-hydrogenation reactions.¹² Therefore, we report here the synthesis and catalytic activity of a range of triazolylidene ruthenium complexes that feature different donor functionalization. In an attempt to maximize diversity, these donor-functionalized carbenes include (potentially) *C,O*-bidentate chelates featuring an alkoxide and a carboxylate donor group, *C,N*-bidentate that are distinguished by their bonding to either the triazole nitrogen or carbon, and *ortho*-metalated phenyl substituent that imparts a *C,C*-bidentate coordination mode of the triazolylidene. The catalytic activity of these ruthenium complexes in hydrogen transfer reactions and alcohol oxidation indicates that tailoring of the donor group is critical and leads to high turnover frequencies.

Results and discussion

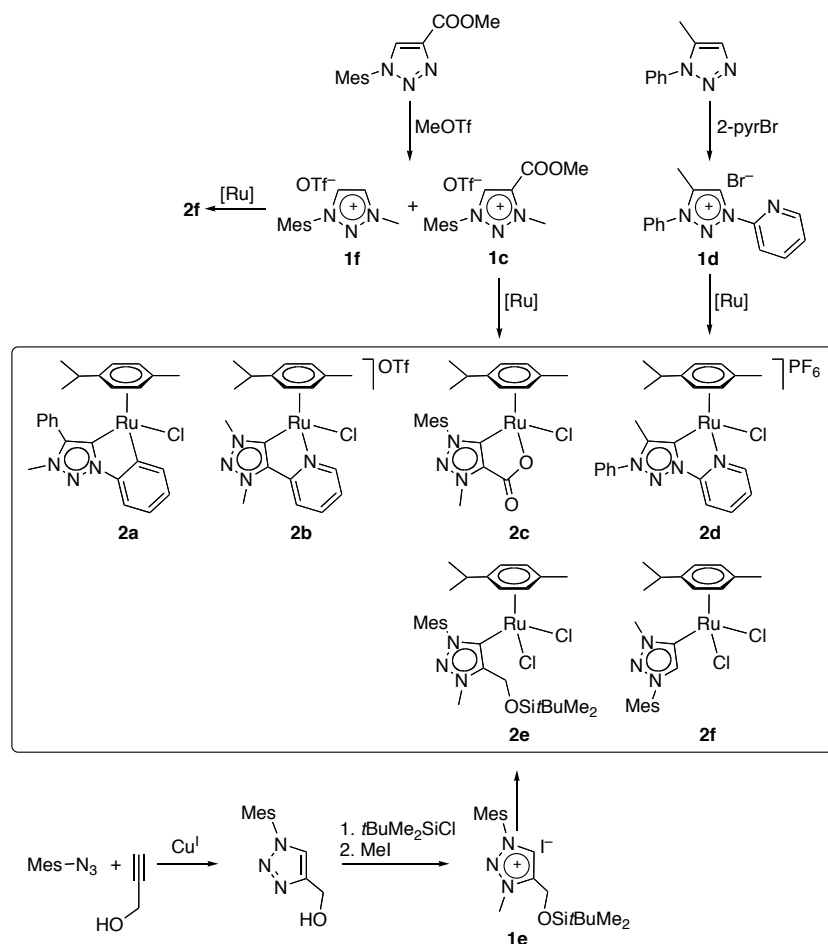
Synthesis of ligand precursors

The new triazolium salts **1c–e** were readily accessible via conventional dipolar [2+3] cycloaddition¹¹ of aryl azides and the corresponding alkyne, followed by selective *N*-functionalization. Due to the specific properties of the donor functionalities in these three triazolium salts (*i.e.* ester, imine, and protected alcohol), each synthesis followed a distinct pathway. Thus, methylation of the triazole precursor of **1c** at the N3 position with MeOTf gave a cleaner reaction than with MeI and proceeded in quantitative yield (98%). Elution over an ion exchange column gave the chloride analogue **1c'**. Successful anion exchange was indicated by the characteristic downfield shift of the acidic triazolium salt from δ_{H} 8.83 to 9.71 (CDCl₃ solution), presumably as a consequence of better ion pairing in **1c'**.¹³ Both salts are unstable over time and decarboxylation of **1c** was observed during recrystallization, cleanly yielding the triazolium salt **1f**. Similar decarboxylation was also observed during the quaternization of the triazole precursor with MeI under microwave conditions. The decarboxylation was confirmed spectroscopically by the absence of the carbonyl IR stretch vibration at 1751 cm⁻¹ and by the presence of two triazolium protons with equal intensity (δ_{H} 10.63 and 9.00) in the NMR spectrum, and by a single crystal X-ray diffraction analysis (Fig. S1).[†] The lability of the ester moiety in **1c** may open new opportunities for metallation of triazolium salts via decarboxylative methods.¹⁴

The triazolium salt **1d** comprising a pyridine donor group at N3 was synthesized from the 1,5-disubstituted triazole precursor, which was prepared via an uncatalyzed cycloaddition of phenyl azide and an α -keto phosphorus ylide as alkyne equivalent (Scheme S1).¹⁵ Subsequent quaternization of N3 with bromopyridine at elevated temperatures followed by an anion exchange yielded **1d** in high yields. This procedure is superior to the classic copper catalyzed pathway, as the subsequent methylation of pyridyl-triazoles is unselective and provides a mixture of pyridinium and triazolium products.^{9b,16}

The triazolium salt **1e** containing a masked alkoxide donor group was synthesized via classical copper-catalyzed click cycloaddition¹¹ of mesityl azide and propargyl alcohol. The alcohol functionality was subsequently TBDMS-protected (TBDMS = tert-butyldimethylsilyl) to avoid complications in chemoselective alkylation and metallation. Notably, alkylation of the protected triazole with MeOTf induced cleavage of the TBDMS group even under mild conditions (1 eq. at RT). Better results were obtained when MeI was used as alkylation agent

(3.5 molequiv. MeI, 80 °C, 5h). Longer reaction times should be avoided, however, as slow cleavage of the alcohol protecting group was noted also with MeI.¹⁷ The ¹H NMR spectra of **1c** and **1e** show a low field resonance for the triazolium proton at C5 at δ_{H} 9.29 and 8.79 ppm for **1c** and **1e** respectively, which are downfield from their corresponding triazole precursors.



Scheme 1 Synthesis of the new complexes **2c–2f**.

Synthesis of the ruthenium cymene complexes

Ruthenation of triazolium salts **1c–f** was accomplished by a one-pot procedure mediated by Ag₂O according to established procedures^{9b} in 43% to 74% yield (Scheme 1). All complexes were stable towards moisture and air both in solution and in the solid state. The neutral complexes **2c** and **2e** were better soluble in chlorinated solvents and toluene than the cationic compound **2d**. Successful complexation was indicated by the characteristic NMR data, specifically by the disappearance of the aromatic triazolium proton around δ_{H} 8.8–9.7 ppm and by the presence of resonances due to the cymene group and the triazolylidene ligand in

equimolar ratio. In the ^{13}C NMR spectrum, the carbenic carbon resonance appears around 170 ppm for complexes **2c–e**, while the carboxylate group in **2c** resonates at δ_{C} 165.9 ppm.

While complexes **2e** and **2f** displayed the signature of a monodentate carbene ligand such as symmetry-related mesityl and cymene protons, respectively, spectroscopic data indicate chelating triazolylidene ligands in complexes **2c** and **2d**. Bidentate coordination was supported by the desymmetrization of the cymene ring, indicated by the four doublets between 5.4 and 4.6 ppm (**2c**) and between 6.1 and 5.8 ppm (**2d**). In addition, the two methyl groups of the isopropyl unit as well as the *meta* protons of the mesityl substituent of the triazolylidene ligand (in **2c**) become inequivalent upon complexation. Metal bonding of the pyridine unit in complex **2d** was further indicated by the characteristic^{9b} downfield shift of the *ortho* proton of the pyridyl substituent from δ_{H} 8.72 ppm in the ligand precursor **1d** to δ_{H} 9.24 ppm in the complex.

Chelation of the carboxylate group in **2c** is remarkable as it implies loss of the methyl group from the ester precursor **1c**. Presumably, ester hydrolysis is a consequence of the basic conditions entailed by Ag_2O and by the generation of OH^- ions upon formation of the silver triazolylidene intermediate.¹⁸ In the IR spectrum, the carbonyl vibration was observed at 1655 cm^{-1} as expected for a carboxylate group¹⁹ and similar to chelating imidazol-2-ylidene carboxylate ruthenium(II) complexes ($\nu_{\text{CO}} = 1630\text{ cm}^{-1}$),²⁰ yet at substantially lower energy than the CO vibration in the ester precursor **1c** ($\nu_{\text{CO}} = 1751\text{ cm}^{-1}$).

Unambiguous evidence for carboxylate chelation in **2c** was obtained by a single crystal X-ray diffraction analysis. The molecular structure (Fig. 1) confirmed the expected connectivity pattern as deduced from solution analysis and reveals the classical three-legged piano-stool geometry. Chelation of the carboxylate group produces a five-membered metallacycle with an acute bite angle ($\text{C1-Ru-O1 } 76.84(7)^\circ$) and with Ru–C and Ru–O bond distances of 2.0303(19) and 2.1444(15) Å, respectively. The latter is slightly longer than in the related imidazol-2-ylidene ruthenium(II) complex (Ru–O 2.079(8) Å),²⁰ while the Ru–C_{trz} bond is some 0.03–0.06 Å shorter than in analogous monodentate triazolylidene ruthenium complexes,^{7g} yet in good agreement with other chelating complexes, including the previously determined structures of **2a** and **2b** (2.0372(15) and 2.0318(12) Å, respectively).^{9b,10c}

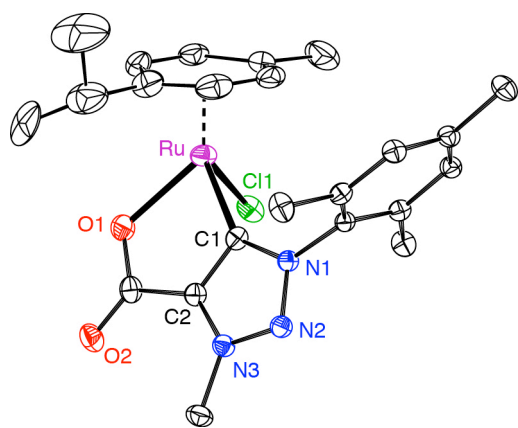


Figure 1 ORTEP representation of **2c** (50% probability, hydrogen atoms omitted for clarity). The cymene ring is disordered. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 2.0303(19), Ru(1)–O(1) 2.1444(15), Ru(1)–Cl(1) 2.4170(1), Ru(1)–C_{centroid} 1.679(5); C(1)–Ru(1)–O(1) 76.84(7), C(1)–Ru(1)–Cl(1) 86.65(1), O(1)–Ru(1)–Cl(1) 83.95(5), C(1)–Ru(1)–C_{centroid} 133.90(18), O(1)–Ru(1)–C_{centroid} 132.87(15).

Metallation of **1f** may occur principally at two positions due to the presence of two triazolium C–H sites. NMR spectroscopic analysis of the crude reaction product indicated, however, selective metallation of only one position. NOE experiments suggest a through-space interaction of the CH group of the triazolylidene and the *ortho* methyl group of the mesityl substituents, indicating metallation of the triazolium at the site proximal to the methyl substituents. This selectivity, probably imparted by the steric shielding of the mesityl substituents, was unequivocally confirmed by a crystallographic analysis (Fig. 2). Bond lengths and angles of this piano-stool complex are unsurprising and in good agreement with related monodentate ruthenium carbene complexes.^{7g,21}

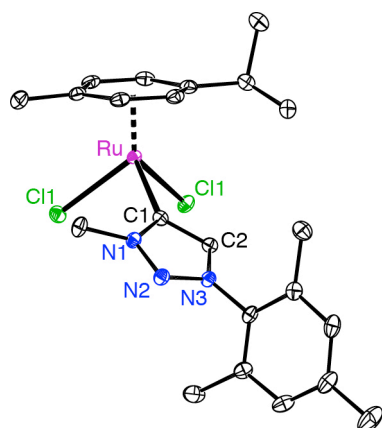
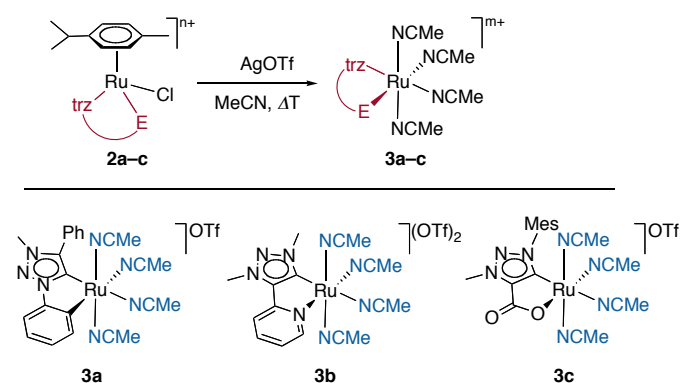


Figure 2 ORTEP representation of **2f** (50% probability, hydrogen atoms omitted for clarity and only one of the two independent molecules shown). The cymene ring is disordered.

Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 2.0573(17), Ru(1)–Cl(1) 2.4157(4), Ru(1)–Cl(2) 2.4274(4), Ru(1)–C_{centroid} 1.6867(8); C(1)–Ru(1)–Cl(1) 84.59(5), C(1)–Ru(1)–Cl(2) 87.78(5), C(1)–Ru(1)–C_{centroid} 129.06(6), Cl(1)–Ru(1)–Cl(2) 88.00(2).

Synthesis of solvento complexes

Selected solvento complexes were synthesized in order to evaluate the role of the spectator ligands in catalysis (see below). The complexes **3a–c** were prepared from the ruthenium(II) cymene precursors **2** by thermal replacement of the cymene ancillary ligand with MeCN and simultaneous AgOTf-mediated abstraction of the chloride ligand²² in 40–60% yield. These solvento complexes are more sensitive to air than their cymene counterparts and gradual degradation was indicated by a colour change from yellow to black over several days. Complexes **3a–c** are moderately soluble in chlorinated solvents and toluene, and better soluble in polar solvents such as MeCN, dichloroethane, 1,2-dichlorobenzene, and *t*BuOH.



Scheme 2 Synthesis of complexes **3a–c**.

Successful formation of the solvento complexes is deduced from the absence of cymene resonances and the presence of signals attributed to coordinated MeCN. Typically, only two sets of MeCN resonances were observed in 2:1 ratio, assigned to the mutually *trans* positioned MeCN ligands and one MeCN ligand *trans* to either the carbene or the chelating donor group. This pattern suggests that one MeCN ligand is kinetically very labile, which may be a direct consequence of the strong donor ability of the triazolylidene. The modification of the spectator ligands induces less steric congestion, which is demonstrated by the free rotation of the mesityl substituent (*cf* single resonance at δ_{H} 7.12 ppm for the aromatic protons). The carbenic carbon resonance shifts to lower field by approximately 3–4 ppm upon transformation of **2** to **3** (*e.g.* δ_{C} 176.2 ppm in **3c** vs 172.8 ppm in **2c**). No signs were observed

that would indicate metallacycle ring opening. For example in complex **3a**, four different proton signals for the N-bound phenyl group suggest a Ru–C_{Ph} bond that is robust under the applied reaction conditions. A single crystal X-ray diffraction analysis of **3a** is in agreement with this conclusion. The molecular structure (Fig. 3) reveals the surmised metallacycle due to *C,C*-bidentate chelation of the phenyl-substituted triazolylidene ligand. The ruthenium center is located at the center of a distorted octahedron. The bite angle C1–Ru–C10 of the chelating ligand is 80.03(7). The Ru–C_{trz} bond is slightly but significantly shorter than the Ru–C_{Ph} bond, 2.0394(17) vs 2.0538(17) Å. These bonds are shorter than those in the neutral ruthenium complex **2a**,^{10c} presumably a direct consequence of the lower electron density at ruthenium in a [Ru(NCMe)₄]²⁺ configuration as compared to the [RuCl(cym)]⁺ fragment. As expected, the Ru–N_{MeCN} bond lengths are strongly influenced by their *trans* ligand. The Ru–N4 and Ru–N5 bonds featuring a *C*-donor in *trans* position are substantially longer, than the Ru–N bond lengths of the mutually *trans* located MeCN ligands. Interestingly, the *trans* influence of the mesoionic triazolylidene ligand is almost identical to that of the anionic phenyl ligand (Ru–N(4) 2.1025(14) Å vs Ru–N(5) 2.1140(14) Å), which suggests a high relevance of the mesoionic (rather than a carbenic) limiting resonance structure.

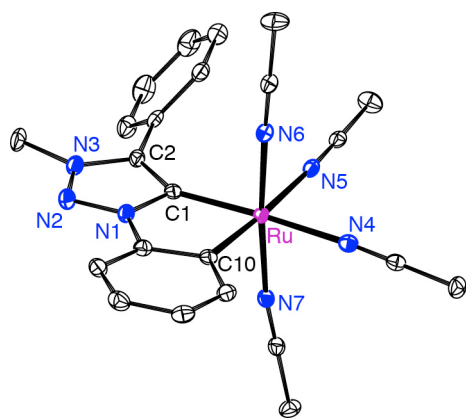


Figure 3 ORTEP representation of **3a** (50% probability, hydrogens and OTf[−] counterion omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1) 2.0394(17), Ru–C(10) 2.0538(17), Ru–N(4) 2.1025(14), Ru–N(5) 2.1140(14), Ru–N(6) 2.0093(14), Ru–N(7) 2.0231(14); C(1)–Ru–C(10) 80.03(7), C(1)–Ru–N(4) 174.67(6), N(4)–Ru–N(5) 88.33(5), C10(1)–Ru–N(7) 92.87(6), C10(1)–Ru–N(5) 176.68(6), N6(1)–Ru–N(7) 174.97(6).

Based on the established activity of N-heterocyclic carbene ruthenium complexes in hydrogen transfer reactions²³ and in dehydrogenative alcohol oxidation,^{7g,24} we were interested in exploring the effect of chelating groups in these types of catalytic transformations.

Catalytic alcohol oxidation

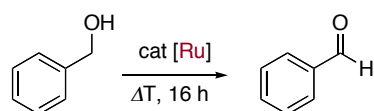
The ruthenium complexes **2a–e** and the corresponding solvento analogues **3a–c** were evaluated as catalyst precursors for the oxidant- and base-free oxidation of alcohols using benzyl alcohol (BnOH) as model substrate. The catalytic activity was monitored in a first set of experiments in toluene and in 1,2-dichlorobenzene (DCB; Table 1). Gradual formation of benzaldehyde was observed by ^1H NMR spectroscopy upon heating BnOH in the presence of 5 mol% of the triazolylidene ruthenium complex in a closed system. Time-resolved monitoring of the catalytic reaction suggest the pseudo-first order kinetics for product formation as expected for homogeneous systems.[†] The well-defined kinetic behavior provides a fairly accurate estimate of the time required for 50% conversion and of the turnover frequency at this conversion stage (TOF_{50}).

Evaluation of the data in Table 1 reveals several trends. Firstly, 1,2-dichlorobenzene is generally a better solvent for alcohol oxidation than toluene (*e.g.* entry 2 *vs* 8, entry 4 *vs* 10). Secondly, in all examples investigated here, the cymene complex **2** outperforms the analogous solvento complex **3** (*e.g.* entry 8 *vs* 9), presumably because of the stronger bonding of MeCN than the substrate ROH to the ruthenium center. An exception to this trend is the higher activity of **3b** as compared to **2b** in DCB, though the activity is very moderate in either case. Finally, chelation of a pyridine or carboxylate group (complexes **2b–d**) consistently induces lower activity than monodentate triazolylidenes, as demonstrated by the pyridine containing ruthenium complexes **2d** and **2b** (entries 10–14). The linkage of the pyridyl donor through either a triazolylidene carbon or nitrogen, *viz.* **2b** *vs* **2d**, has some impact (entries 10 *vs* 14), though conversions remained low with either catalyst precursor. Best results were obtained with the *C,C*-bidentate triazolylidene complex **2a** in DCB (entry 8). Turnover frequencies at 50% conversion reached 2.7 h^{-1} under optimized conditions. Raising the temperature above 110 °C had no beneficial effect, while lowering of the temperature resulted in a substantial drop of activity (entries 17–19). Polar solvents such as *t*BuOH inhibited catalytic activity (entry 20), presumably because of competitive bonding with the substrate to the ruthenium center in the active state (*i.e.* upon chloride dissociation).^{7g}

The monodentate triazolylidene complex **2e** provides up to 69% conversion (entry 6). We reasoned that the availability of an alkoxy-functionality as opposed to a silylether would be beneficial to catalytic activity for substrate deprotonation and potential catalyst activation through formation of an Ru–OR bond. Catalytic runs performed in the presence of NBu_4F for in-situ alcohol deprotection²⁵ indeed improved activity to some extent (entries 7,15).

However, NBu₄NF has an accelerating effect on its own.²⁶ catalytic oxidation of BnOH with complex **2a** in the presence of one equivalent of Bu₄NF increased the yield from 44% to 84% (entries 2 vs 16).

Table 1 Oxidation of benzyl alcohol with triazolylidene ruthenium complexes^a



Entry	[Ru]	Solvent	yield (%) ^b	TON
1	---	toluene	0	---
2	2a	toluene	44	9
3	3a	toluene	15	3
4	2b	toluene	6	1
5	3b	toluene	0	---
6	2e	toluene	69	14
7 ^c	2e	toluene	77	15
8	2a	DCB	77	15
9	3a	DCB	10	2
10	2b	DCB	18	4
11	3b	DCB	26	5
12	2c	DCB	3	0.6
13	3c	DCB	3	0.6
14	2d	DCB	4	0.8
15 ^c	2e	DCB	90	18
16 ^c	2a	toluene	84	17
17 ^d	2a	DCB	77	15
18 ^e	2a	DCB	30	6
19 ^e	2a	DCE	26	5
20 ^e	2a	<i>t</i> BuOH	0	---

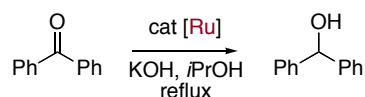
^a general reaction conditions: BnOH (0.2 mmol), [Ru] (0.01 mmol, 5 mo%), solvent (2 mL), 110 °C, 16 h, DCB = 1,2-dichlorobenzene, DCE = 1,2-dichloroethane; ^b yields determined by ¹H NMR integration (anisole as standard); ^c addition of NBu₄F (0.011 mmol); ^d at 130 °C; ^e at 80 °C.

In addition to their activity in catalyzing alcohol oxidations, the new ruthenium complexes **2** and **3** were investigated as catalysts for ketone reduction via transfer hydrogenation. Standard protocols were applied consisting of basic isopropanol as formal dihydrogen donor and benzophenone as model substrate. Typical conditions for catalyst screening employed a 100:10:1 ratio substrate/base/catalyst (S/B/C), and results of these experiments are compiled in Table 2. The impact of the donor function is significantly different than in alcohol dehydrogenation, which is not unexpected when considering the different modes of action. Alcohol dehydrogenation requires the substitution of a chloride ligand in complexes **2a–e** by

a substrate alcohol as initial step,^{7g} while transfer hydrogenation likely involves the exchange of chloride (or indeed a neutral ligand) by pre-formed isopropoxide.²⁷ As a consequence, the catalytic hydrogen transfer activity of the solvento complexes is only marginally lower than that of the analogous cymene complexes **2** (entries 4 vs 5, and 6 vs 7). Complex **2b** displays the highest performance and achieves full conversion within less than 30 min. The monodentate triazolylidene complex **2e** is less active, followed by complexes **2c** and **2d**, which do not achieve full conversion within 2 h (entries 6–9). Of note, the addition of a source of fluoride for the in-situ deprotection of the alcohol has a negative impact on the catalytic activity and induces a drop of the catalytic activity to the level of the carboxylate-functionalized triazolylidene complex **2c** (*cf* entries 6 and 10). Complexes **2a** and **3a** containing an anionic aryl ligand in addition to the mesoionic triazolylidene are essentially inactive and yields are identical to those observed in a blank experiment in the absence of any ruthenium source (entries 1–3). This different behavior demonstrates the strong donor ability of triazolylidene ligands, which results in a formally charge-neutralized ruthenium center and consequently in the preferred coordination of neutral rather than anionic ligands. Accordingly, this complex is better suited for alcohol oxidation, initiated by ROH coordination, rather than for transfer hydrogenation induced by RO⁻ coordination. In contrast, the pyridine chelated complex **2b** features a ruthenium center with relatively low electron density, which facilitates coordination of the RO⁻ anion, yet does not favor chloride dissociation to enable ROH bonding (*cf* excellent performance in transfer hydrogenation vs poor performance in alcohol dehydrogenation).

Transfer hydrogenation with these ruthenium complexes requires the presence of a base and reflux temperatures (entries 15–18). Lowering of the catalyst loading to 0.5 mol% is possible without significantly compromising yield or reaction time (entries 11,12). Time-dependent monitoring of the reaction did not reveal an induction period and showed pseudo-first order kinetics for substrate consumption and product formation.^{28†} According to these analyses, turnover frequencies at 50% conversion reach 680 h⁻¹, a value that is substantially higher than other carbene ruthenium transfer hydrogenation catalysts,²⁹ yet substantially lower than the most active species currently known for hydrogen transfer catalysis.³⁰ A further decrease of the concentration of the ruthenium pre-catalyst to 0.1 mol% provided a maximum turnover number of ca. 600, though the reaction does not proceed to completion under these conditions (entries 13,14).

Table 2. Catalytic transfer hydrogenation of benzophenone with ruthenium(II) complex^a

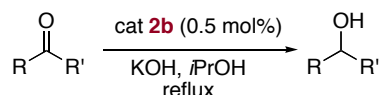


Entry ^a	[Ru]	mol%	Time (h)	yield (%) ^b	TON
1	---	---	0.5 / 16	0.6 / 11	---
2	2a	1	0.5 / 2	0.6 / 2	2
3	3a	1	0.5 / 2	1 / 5	5
4	2b	1	0.5 / 2	96 / 98	98
5	3b	1	0.5 / 2	84 / 98	98
6	2c	1	0.5 / 2	32 / 77	77
7	3c	1	0.5 / 2	25 / 70	70
8	2d	1	0.5 / 2	30 / 67	67
9	2e	1	0.5 / 2	46 / 95	95
10 ^c	2e	1	0.5 / 2	13 / 69	69
11	2b	0.5	0.5 / 2	91 / 99	198
12	3b	0.5	0.5 / 2	62 / 96	192
13	2b	0.1	0.5 / 2	25 / 52	520
14	3b	0.1	0.5 / 2	31 / 60	600
15 ^d	2b	0.5	0.5 / 2	0 / 0	---
16 ^d	3b	0.5	0.5 / 2	0 / 0	---
17 ^e	2b	0.5	0.5 / 2	0 / 1	2
18 ^e	3b	0.5	0.5 / 2	0 / 0.8	1.6

^a general reaction conditions: Benzophenone (1 mmol), KOH (0.1 mmol), [Ru] (0.01 mmol, 1 mol%), *i*PrOH (5 mL), reflux temperature; ^b determined by ¹H NMR spectroscopy; ^c with TBAF (0.011 mmol); ^d without base; ^e at 40 °C.

Complex **2b** was used under optimized catalyst concentration (0.5 mol%) for the transfer hydrogenation of a variety of substrates (Table 3). Diaryl, aryl-alkyl, as well as dialkyl ketones are readily hydrogenated under these conditions (entries 1–7). Aryl chlorides are fully preserved and no products from hydro-dehalogenation were detected (entry 2). Cyclohexanone is converted at a particularly high rate with TOF₅₀ up to 1400 h⁻¹. Acylpyridine is generally considered to be a difficult substrate because of potential *N,O*-bidentate chelation of either the starting material or the product to the catalytically active metal center, thus inhibiting catalytic turnovers.³¹ In line with this notion, this substrate is transfer hydrogenated substantially slower (TOF₅₀ 25 h⁻¹, entry 7). In contrast, esters are not suitable substrates and no hydrogenation was observed (entry 8).

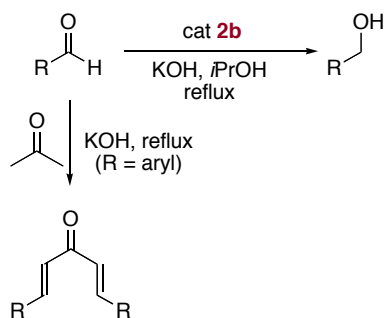
Table 3. Catalytic transfer hydrogenation of different substrate with complex **2b**^a



Entry	R	R'	Time (h)	conversion (%) ^b
1	C ₆ H ₅	CH ₃	0.5 / 2	86 / 98
2	<i>p</i> -ClC ₆ H ₄	CH ₃	0.5 / 2	63 / 97
3	C ₆ H ₅	C ₂ H ₅	0.5 / 2	83 / 98
4	(CH ₂) ₅		0.08 / 0.25	58 / 97
5	(CH ₂) ₄ CHCH ₃		0.5 / 2	73 / >99
6	CH ₃	CH ₂ CHMe ₂	0.5 / 2	68 / 98
7	2-pyridyl	CH ₃	2 / 24	34 / 88
8	C ₆ H ₅	OCH ₃	0.5 / 2	---
9	C ₆ H ₅	H	0.25 / 0.5	86 (12) / 99 (0) ^c
10 ^d	C ₆ H ₅	H	0.5 / 2	31 (18) / 44 (28) ^c
11	<i>p</i> -ClC ₆ H ₄	H	0.25 / 0.5	56 (27) / 60 (32) ^c
12	2-thiophenyl	H	0.5 / 2	64 (16) / 83 (32) ^c
13	2,4,6-(Me) ₃ C ₆ H ₂	H	0.5 / 2	18 / 52
14	3,4,5-(MeO) ₃ C ₆ H ₂	H	0.5 / 2	44 / 72
15	CH ₃ (CH ₂) ₃	H	0.5 / 2	34 / 39

^aReaction conditions: substrate (1 mmol), KOH (0.1 mmol), **2b** (0.01 mmol) in *i*PrOH (5 mL), reflux temperature; ^b conversion selectively to corresponding alcohol as determined by ¹H NMR spectroscopy; ^c major product from aldol condensation (alcohol in parentheses); ^d catalyst pre-heated with substrate and *i*PrOH for 10 min before addition of base.

Under the applied reaction conditions, aldehydes show a distinct reactivity pattern. Rather than being reduced to the primary alcohol, these substrates react predominantly with acetone, generated in the dehydrogenative half-cycle of a classical transfer hydrogenation sequence. With benzaldehyde as the substrate, double aldol condensation was unambiguously identified by the pertinent spectroscopic data of dibenzylidene acetone (Scheme 3). Analogous reactivity patterns were observed for chlorobenzaldehyde and thiophenyl aldehyde (entries 9–12). In contrast, polysubstituted aryl aldehydes fail to undergo such aldol condensation reactions and afford the hydrogenation product (entry 13,14), though at lower rates than observed for ketone conversion. Likewise, aliphatic aldehydes are transfer hydrogenated to the corresponding primary alcohol (entry 15). The fact that aldehyde hydrogenation is partially reversible (*cf* entry 9) suggests that complex **2b** may also be effective for hydrogen borrowing reactions.³² However, reaction of BnOH as primary alcohol with 1-phenethylalcohol in the presence of KOH (10 mol%) did not produce any coupled product in toluene nor in 1,2-dichlorobenzene.



Scheme 3 Ruthenium-catalyzed transfer hydrogenation of aldehydes with ketones and base-catalyzed aldol condensation of sterically unhindered aryl aldehydes with acetone.

Transfer hydrogenation of olefins³³ was evaluated by using cyclooctene and styrene as substrates. While the former was unreactive and no cyclooctane was detected, styrene hydrogenation was observed, albeit slowly, reaching about 15% conversion to ethylbenzene after 24 h. Obviously, complex **2b** is not very reactive towards olefinic double bonds.

Conclusions

A straightforward access to donor-functionalized mesoionic triazolylidene ruthenium complexes was disclosed. Introduction of donor functional groups into the triazolylidene skeleton influences the activity on the ruthenium complexes as catalyst precursors in alcohol oxidation and in transfer hydrogenation. The impact can be directly correlated with the propensity to form a reactive intermediate, *i.e.* with the potential to coordinate neutral ROH or a ionic alkoxide, respectively. These results highlight the potential of donor groups on the triazolylidene ligand for catalytic applications and provides an attractive strategy for further catalyst improvement to mediate such redox transformations. In addition, it will be attractive to combine both processes, ketone transfer hydrogenation and direct alcohol oxidation into a single cell as a potential approach to generate a hydrogen fuel cell that is based on simple alcohols. Work is in progress along these lines and aiming at replacing isopropanol with EtOH or MeOH.

Experimental section

General

The synthesis of 1-mesityl-4-methyl carboxylate-1,2,3-triazole,^{34,†} 1-phenyl-5-methyl-1,2,3-triazole,¹⁵ mesityl azide,³⁵ and of the ruthenium complexes **2a**,^{10c} **2b**,^{9b} and **3b**^{9b} was described previously. Solvents used for the reactions were purified using an alumina/catalyst column system (Thermovac Co.). All other reagents are commercially available and were used as received. Microwave reactions were carried out using a Biotage Initiator 2.5, operating at 100 W irradiation power. Unless specified otherwise, NMR spectra were recorded at 25 °C on Varian Innova spectrometers operating at 300, 400 or 500 MHz (¹H NMR) and 75, 100 or 125 MHz (¹³C{¹H} NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Microanalyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland; residual solvents were also identified by ¹H NMR spectroscopy.

Syntheses

Synthesis of 1-mesityl-1,2,3-triazol-4-yl methanol. Mesityl azide (1.0 g, 6.20 mmol), and propargyl alcohol (278 mg, 4.96 mmol) were suspended in a mixture of water (7 mL) and THF (7 mL). CuSO₄ (22 mg, 0.01 mmol), and sodium ascorbate (197 mg, 0.99 mmol) were added and the mixture was stirred for 6 h at 100 °C under microwave irradiation. After cooling, all volatiles were removed by evaporation and the residue was extracted with MeCN (2 × 100 mL). The combined organic phases were washed with water (2 × 60 mL), brine (2 × 50 mL), dried over MgSO₄, and evaporated to dryness. The residue was washed with pentane (50 mL) purified by flash chromatography (SiO₂; CH₂Cl₂/Et₂O 6:1) to give the pure triazole as a pale yellow powder (780 mg, 72%). ¹H NMR (CDCl₃, 500 MHz): δ 7.60 (s, 1H, H_{trz}), 6.99 (s, 2H, H_{mes}), 4.91 (s, 2H, CH₂OH), 2.58 (s, 1H, OH), 2.35 (s, 3H, ArCH₃), 1.96 (s, 6H, ArCH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 148.8 (C_{trz}-CH₂OH), 140.2, 135.3, 133.7, 129.3 (4 × C_{Mes}), 123.9 (C_{trz}-H), 56.8 (CH₂OH), 21.3 (Ar-CH₃), 17.5 (Ar-CH₃). Anal. Calcd for C₁₂H₁₅N₃O (217.27): C, 66.34; H, 6.96; N, 19.34. Found: C, 66.13; H, 6.91; N, 19.33.

1-mesityl-4-(*tert*-butyldimethylsilyloxymethylene)-1,2,3-triazole. 1-mesityl-1,2,3-triazol-4-yl methanol (963 mg, 4.43 mmol), *t*BuMe₂SiCl (750 mg, 4.87 mmol), and 1-methylimidazole (1.09 g, 13.3 mmol) were dissolved in dry DMF (50 mL) under nitrogen atmosphere. The reaction mixture was allowed to proceed for 18 h at room temperature, then quenched with water (25 mL) and extracted with Et₂O (2 × 100 mL). The combined organic phases were washed with water (1 × 25 mL), brine (1 × 25 mL), dried over MgSO₄ and evaporated to

dryness. The residue was washed with pentane (50 mL) to afford the pure product as a pale yellow semi-solid. Solidification of the pure triazole occurred after 18 hours under high vacuum as a pale off-white solid (1200 mg, 82%). ^1H NMR (CDCl_3 , 500 MHz): δ 7.52 (s, 1H, H_{trz}), 6.98 (s, 2H, H_{mes}), 4.97 (s, 2H, CH_2OH), 2.35 (s, 3H, ArCH_3), 1.96 (s, 6H, ArCH_3), 0.91 (s, 9H, $\text{C}-\text{CH}_3$), 0.11 (s, 6H, CH_3 , SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 148.8 ($\text{C}_{\text{trz}}-\text{CH}_2\text{OH}$), 140.1, 135.3, 133.9, 129.2 ($4 \times \text{C}_{\text{Mes}}$), 123.6 ($\text{C}_{\text{trz}}-\text{H}$), 58.3 (CH_2OH), 25.9 ($\text{C}-\text{CH}_3$), 21.3 ($\text{Ar}-\text{CH}_3$), 18.4 (SiCMe_3), 17.5 ($\text{Ar}-\text{CH}_3$), -4.9 ($\text{Si}-\text{CH}_3$). Anal. Calcd for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{OSi}$ (331.53): C, 65.21; H, 8.82; N, 12.67. Found: C, 64.99; H, 8.96; N, 12.41.

Synthesis of $\mathbf{1c}\cdot\text{OTf}$. To a solution of 1-mesityl-4-methyl carboxylate-1,2,3-triazole (100 mg, 0.41 mmol) in Et_2O (15 mL) was added MeOTf (0.74 g, 0.45 mmol) and the mixture was stirred in a closed microwave tube for 20 h at RT. A white precipitate formed which was separated by filtration and washed with Et_2O (2×30 mL). All volatiles were removed in vacuo to afford pure $\mathbf{1c}\cdot\text{OTf}$ as a white solid. Colourless needles were obtained after crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (164 mg, 98%). ^1H NMR (CDCl_3 , 300 MHz): δ 8.83 (s, 1H, H_{trz}), 7.05 (s, 2H, H_{mes}), 4.70 (s, 3H, NCH_3), 4.04 (s, 3H, OCH_3), 2.37 (s, 3H, ArCH_3), 2.09 (s, 6H, ArCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 155.4 (COO), 143.1 (C_{mes}), 134.8 ($\text{C}_{\text{trz}}-\text{H}$), 134.7 (C_{mes}), 134.4 ($\text{C}_{\text{trz}}-\text{C}$), 131.0 (C_{mes}), 130.1 (C_{mes}), 54.3 (OCH_3), 41.8 (NCH_3), 21.3 ($\text{Ar}-\text{CH}_3$), 17.4 ($\text{Ar}-\text{CH}_3$). m/z : 260.1403 [$\text{M}-\text{OTf}$] $^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_3\text{O}_5\text{S}$ (409.38): C, 44.01; H, 4.43; N, 10.26. Found: C, 43.90; H, 4.34; N, 10.06.

Synthesis of $\mathbf{1c}\cdot\text{Cl}$. Compound $\mathbf{1c}\cdot\text{OTf}$ (200 mg, 0.49 mmol) was dissolved in MeOH (5 mL) and filtered slowly through an ion exchange column (Dowex 1×8 200–400 MESH Cl). The column was eluted with MeOH (2×10 mL). All volatiles of the eluate were removed in vacuo to afford $\mathbf{1c}\cdot\text{Cl}$ as a highly hygroscopic solid (142 mg, 98%). ^1H NMR (CDCl_3 , 300 MHz): δ 9.71 (s, 1H, H_{trz}), 7.06 (s, 2H, H_{mes}), 4.81 (s, 3H, NCH_3), 4.12 (s, 3H, OCH_3), 2.37 (s, 3H, ArCH_3), 2.18 (s, 6H, ArCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 155.8 (COO), 143.0 (C_{mes}), 135.8 ($\text{C}_{\text{trz}}-\text{H}$), 134.7 (C_{mes}), 134.3 ($\text{C}_{\text{trz}}-\text{C}$), 133.2 (C_{mes}), 131.1 (C_{mes}), 54.5 (OCH_3), 42.2 (NCH_3), 21.4 ($\text{Ar}-\text{CH}_3$), 18.0 ($\text{Ar}-\text{CH}_3$). HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_2^+$ 260.1399 Found 260.1410. IR (KBr): 1751 cm^{-1} (s, $\text{C}=\text{O}$).

Synthesis of $\mathbf{1d}$. A mixture of 1-phenyl-5-methyl-1,2,3-triazole (200 mg, 1.26 mmol) and 2-bromopyridine (198 mg, 1.26 mmol) in a sealed vial was heated at 160°C for 36 h. The brown residue obtained after evaporation of all volatiles was dissolved in water (50 mL) and excess

of KPF_6 was added resulting in an immediate precipitation of the compound. The mixture was stirred for 20 min and filtered. The residue was washed with water (2×10 mL) and Et_2O (10 mL). Recrystallization from $\text{MeCN}/\text{Et}_2\text{O}$ yielded analytically pure pale brown crystals of **1d**. (250 mg, 52%). ^1H NMR (CD_3CN , 500 MHz): δ 9.13 (s, 1H, H_{trz}), 8.72 (ddd, $J_{\text{HH}} = 4.8, 1.6, 0.8$, 1H, H_{py}), 8.26–8.19 (m, 2H, H_{ar}), 7.88–7.77 (m, 6H, H_{ar}), 2.61 (d, $J_{\text{HH}} = 0.64$, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 151.1 (C_{py}), 144.0 (C_{py}), 142.4 (C_{ar}), 141.3 (C_{py}), 134.0 ($\text{C}_{\text{trz-CH}_3}$), 132.9, 130.7, 127.8, 125.8, ($4 \times \text{C}_{\text{ar}}$), 125.7 ($\text{C}_{\text{trz-H}}$), 115.2 (C_{py}), 10.8 ($\text{C}_{\text{trz-CH}_3}$). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{F}_6\text{N}_4\text{P}$ (382.24): C, 44.99; H, 3.43; N, 14.66. Found: C, 44.00; H, 3.37; N, 14.46.

Synthesis of 1e. 1-mesityl-4-(tert-butylidimethylsilyloxymethylene)-1,2,3-triazole (300 mg, 0.90 mmol), and MeI (348 mg, 2.71 mmol) were added to dry MeCN (10 mL) and stirred for 6 h at 80°C under microwave irradiation. After cooling, all volatiles were removed by evaporation. The residue was washed with copious amounts of pentane. Recrystallization of the residue from hot acetone gave **1e** (70 mg, 88%). ^1H NMR (CDCl_3 , 500 MHz): δ 8.79 (s, 1H, H_{trz}), 7.03 (s, 2H, H_{mes}), 5.39 (s, 2H, CH_2O), 4.56 (s, 3H, NCH_3), 2.36 (s, 3H, ArCH_3), 2.11 (s, 6H, ArCH_3), 0.90 (s, 9H, SiC-CH_3 , TBDMS), 0.20 (s, 6H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 144.6 ($\text{C}_{\text{trz-C}}$), 142.8, 134.6, 131.3, ($3 \times \text{C}_{\text{mes}}$) 131.2 ($\text{C}_{\text{trz-H}}$), 130.1 (C_{mes}), 55.9 (CH_2O), 40.6 (NCH_3), 25.9 (C-CH_3), 21.4 (Ar-CH_3), 18.3 (CMe_3), 18.1 (Ar-CH_3), -4.9 (Si-CH_3). Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{IN}_3\text{OSi}$ (473.47): C, 48.20; H, 6.81; N, 8.87. Found: C, 47.73; H, 6.66; N, 8.67.

Synthesis of 1f. The triazolium salt **1d** is unstable and it decomposes over time to form **1f**. Analytically pure beige crystals of compound **1f** were obtained from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. ^1H NMR (400 MHz, CDCl_3): δ 10.63 (s, 1H, H_{trz}), 9.00 (s, 1H, H_{trz}), 7.02 (s, 2H, H_{mes}), 4.75 (s, 3H, NCH_3), 2.34 (s, 3H, CH_3), 2.01 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.8 (C_{mes}), 134.8 (C_{mes}), 134.4 ($\text{C}_{\text{trz-H}}$), 133.1 ($\text{C}_{\text{trz-H}}$), 131.4 (C_{mes}), 130.1 (CH_{mes}), 41.2 (NCH_3), 21.4 ($\text{C}_{\text{mes-CH}_3}$), 17.6 ($\text{C}_{\text{mes-CH}_3}$). HRMS (ESI^+ , 30 V): m/z : 202.1057; calculated for $[\text{M-Cl}]^+$ 202.2755.

Synthesis of 2c. A mixture of **1c**·**OTf** or **1c**·**Cl** (409 mg, 1.00 mmol), Ag_2O (116 mg, 0.5 mmol) and $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ (300 mg, 0.49 mmol) in CH_2Cl_2 (30 mL) was stirred in the dark at room temperature for 15 h and then filtered through Celite. The solvent was removed in vacuo and the red-orange residue was purified by gradient column chromatography (SiO_2 ,

CH₂Cl₂/acetone 4:1 to 4:3) to obtain **2c** as a red-orange solid. Analytically pure crystals of **2c** were obtained by recrystallization from CH₂Cl₂/pentane (238 mg, 43%). ¹H NMR (CDCl₃, 500 MHz): δ 7.14 (s, 1H, H_{mes}), 7.10 (s, 1H, H_{mes}), 5.42 (d, ³J_{HH} = 6.0 Hz, 1H, H_{cym}), 5.36 (d, ³J_{HH} = 6.0 Hz, 1H, H_{cym}), 5.07 (d, ³J_{HH} = 5.6 Hz, 1H, H_{cym}), 4.63 (d, ³J_{HH} = 5.6 Hz, 1H, H_{cym}), 4.33 (s, 3H, NCH₃), 2.42–2.40 (m, 4H, CHMe₂ + ArCH₃), 2.14 (s, 6H, ArCH₃), 1.83 (s, 3H, C_{cym}–CH₃), 1.01 (d, ³J_{HH} = 7.1 Hz, 3H, CH–CH₃), 0.98 (d, ³J_{HH} = 7.1 Hz, 3H, CH–CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 172.8 (C_{trz}–Ru), 165.9 (COO), 141.4 (C_{mes}), 137.1 (C_{trz}–C), 134.8 (C_{mes}), 134.7 (C_{mes}), 129.9 (C_{mes}), 128.9 (C_{mes}), 101.7, 93.3, 90.4, 85.7, 81.2, 81.0 (6 × C_{cym}), 36.3 (NCH₃), 30.7 (CHMe₂), 22.7 (CH–CH₃), 21.5 (CH–CH₃), 21.3 (Ar–CH₃), 18.5 (C_{cym}–CH₃), 18.4 (Ar–CH₃), 17.4 (Ar–CH₃). IR (CDCl₃): ν = 1655 cm⁻¹ (s, C=O). Anal. Calcd for C₂₃H₂₈ClN₃O₂Ru (515.09) × 0.5 CH₂Cl₂: C, 50.63; H, 5.24; N, 7.54. Found: C, 50.65; H, 5.33; N, 7.23.

Synthesis of 2d. Complex **1d** (50 mg, 0.13 mmol), Ag₂O (30 mg, 0.13 mmol) and [Ru(*p*-cym)Cl₂]₂ (40 mg, 0.065 mmol) in dry CH₂Cl₂ (6 mL) were stirred in the dark at room temperature for 40 h and then filtered through Celite. After evaporation of the solvent the residue was re-dissolved in CH₂Cl₂ and Et₂O (50 mL) was added. Compound **2d** was obtained as a yellow solid which was collected by filtration and dried in vacuo (63 mg, 74%). ¹H NMR (CD₃CN, 400 MHz): δ 9.24 (d, J_{HH} = 6.0 Hz, 1H, H_{py}), 8.10 (m, 2H, H_{ar}), 7.72–7.60 (m, 6H, H_{ar}), 6.04, 6.00, 5.88, 5.80 (4 × d, ³J_{HH} = 6.0 Hz, 1H, H_{cym}), 2.81 (s, 3H, C_{trz}–CH₃), 2.68 (sept, ³J_{HH} = 7.0 Hz, 1H, CHMe₂), 2.04 (s, 3H, C_{cym}–CH₃), 1.15, 1.11 (2 × d, ³J_{HH} = 7.0 Hz, 3H, CH–CH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 168.3 (C_{trz}–Ru), 155.7 (C_{py}), 145.1 (C_{py}), 141.4 (C_{ar}), 141.3 (C_{py}), 134.5 (C_{trz}–Me), 132.1, 130.4, 126.8, 125.9, (4 × C_{ar}), 114.7 (C_{ar}), 89.6, 89.2, 87.9, 85.5 (4 × C_{cym}), 31.5 (CHMe₂), 22.5, 22.3 (2 × CH–CH₃), 18.5 (C_{cym}–CH₃), 12.2 (C_{trz}–CH₃). HRMS (ESI) Calcd for C₂₄H₂₆N₄ClRu⁺ 507.0889 Found 507.0878.

Synthesis of 2e. Compound **1e** (120 mg, 0.25 mmol), Ag₂O (30 mg, 0.13 mmol) and [Ru(*p*-cym)Cl₂]₂ (78 mg, 0.13 mmol) in dry CH₂Cl₂ (40 mL) were stirred in the dark at room temperature for 20 h and then filtered through Celite. After evaporation of the solvent, a yellow residue was obtained which was washed with pentane (100 mL). Redissolving the solid in 2 mL of MeOH and filtration through a small pad of neutral alumina afforded **2e** as a pale yellow powder. Analytically pure **2e** was obtained by recrystallization from CH₂Cl₂/Et₂O (99 mg, 60%). ¹H NMR (CDCl₃, 500 MHz): δ 7.04 (s, 2H, H_{ar}), 5.08 (d, ³J_{HH} = 5.9 Hz, 2H, H_{cym}), 4.89 (s, 2H, CH₂O), 4.74 (s_{broad}, 2H, H_{cym}), 4.14 (s, 3H, NCH₃), 2.39 (s, 3H, ArCH₃),

2.25 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 1H, CHMe_2), 2.19 (s, 6H, ArCH_3), 1.87 (s, 3H, $\text{C}_{\text{cym}}\text{-CH}_3$), 1.11 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, CH-CH_3), 0.94 (s, 9H, C-CH_3), 0.18 (s, 6H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 168.8 ($\text{C}_{\text{trz}}\text{-Ru}$), 166.8 ($\text{C}_{\text{trz}}\text{-CH}_2$), 146.4, 140.5, 136.4, 129.0 ($4 \times \text{C}_{\text{Mes}}$), 101.5, 94.0, 83.5 ($3 \times \text{C}_{\text{cym}}$), 56.9 (CH_2O), 37.9 (NCH_3), 31.7 (CHMe_2), 26.1 (C-CH_3), 23.3 (CHCH_3), 21.3 (ArCH_3), 18.5 ($\text{C}_{\text{cym}}\text{-CH}_3$), 18.3 (CMe_3 , TBDMS), 18.2 (ArCH_3), -5.2 (Si-CH_3). Anal. Calcd for $\text{C}_{29}\text{H}_{45}\text{Cl}_2\text{N}_3\text{RuSi} \times 0.5 \text{Et}_2\text{O}$: (688.80): C, 54.05; H, 7.32; N, 6.10. Found: C, 54.60; H, 6.88; N, 6.47.

Synthesis of 2f. A mixture of **1f** (120.4 mg, 0.5 mmol), Ag_2O (50 mg, 0.21 mmol) and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (128.6 mg, 0.21 mmol) in dry CH_2Cl_2 (10 mL) was stirred in the dark at room temperature for 15 h. After filtration through Celite and solvent evaporation, the orange solid was washed with Et_2O (2×25 mL) and dried in vacuo. Analytically pure orange crystals of compound **2f** were obtained in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (186 mg, 73%). ^1H NMR (400 MHz, CDCl_3): δ 7.72 (s, 1H, H_{prz}), 6.96 (s, 2H, H_{mes}), 5.33 (d, $^3J_{\text{HH}} = 5.8$ Hz, 2H, H_{cym}), 5.20 (d, $^3J_{\text{HH}} = 5.8$ Hz, 2H, H_{cym}), 4.43 (s, 3H, NCH_3), 2.71 (sept, $^3J_{\text{HH}} = 7.0$ Hz, 1H, $\text{C}_{\text{cym}}\text{CHMe}_2$), 2.32 (s, 3H, $\text{C}_{\text{mes}}\text{CH}_3$), 2.16 (s, 3H, $\text{C}_{\text{cym}}\text{CH}_3$), 1.97 (s, 6H, $\text{C}_{\text{mes}}\text{CH}_3$), 1.20 (d, $^3J_{\text{HH}} = 7.0$ Hz, 6H, $\text{C}_{\text{cym}}\text{CHMe}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 165.8 ($\text{C}_{\text{trz}}\text{-Ru}$), 141.3 (C_{mes}), 135.9 ($\text{C}_{\text{trz}}\text{-H}$), 134.4 (C_{mes}), 132.6 (C_{mes}), 129.6 (CH_{mes}), 104.1 (C_{cym}), 100.5 (C_{cym}), 84.6 (CH_{cym}), 84.1 (CH_{cym}), 41.1 (NCH_3), 31.0 (CHMe_2), 22.6 (CH-CH_3), 21.3 ($\text{C}_{\text{mes}}\text{-CH}_3$), 18.8 ($\text{C}_{\text{cym}}\text{-CH}_3$), 17.6 ($\text{C}_{\text{mes}}\text{-CH}_3$). HRMS (ESI^+ , 30 V): m/z : 472.1096; calculated for $[\text{M-Cl}]^+$ 472.0088.

Synthesis of 3a. Complex **2a** (66 mg, 0.13 mmol) and AgOTf (54 mg, 0.21 mmol) in dry MeCN (10 mL) were stirred at reflux for 18 h. The mixture was filtered through Celite and all volatiles were evaporated under reduced pressure. The residue was washed with pentane yielding compound **3a** as a yellow solid which was collected and dried in vacuo (39 mg, 45%). Analytically pure **3a** was obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. ^1H NMR (CDCl_3 , 400 MHz): δ 7.92 (dd, $J_{\text{HH}} = 7.4, 1.2$ Hz, 1H, H_{ar}), 7.63–7.45 (m, 6H, H_{ar}), 7.04 (td, $J_{\text{HH}} = 7.4, 1.2$ Hz, 1H, H_{ar}), 6.95 (td, $J_{\text{HH}} = 7.4, 1.2$ Hz, 1H, H_{ar}), 4.02 (s, 3H, NCH_3), 2.50 (s, 3H, CH_3CN), 1.96 (s, 6H, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 125 MHz): δ 175.6 ($\text{C}_{\text{ph}}\text{-Ru}$), 171.6 ($\text{C}_{\text{trz}}\text{-Ru}$), 149.5 ($\text{C}_{\text{trz}}\text{-Ph}$), 148.6, 141.4, 132.4, 130.7, 130.4 ($5 \times \text{C}_{\text{ar}}$), 129.8 (MeCN), 127.2 (C_{ar}), 122.1, 118.7 ($2 \times \text{MeCN}$), 113.8 (C_{ar}), 38.0 (NCH_3), 4.6, 4.3 ($2 \times \text{CH}_3\text{CN}$). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{F}_3\text{N}_7\text{O}_3\text{RuS}$ (649.06) $\times 0.5 \text{CH}_2\text{Cl}_2$: C, 42.58; H, 3.65; N, 14.19. Found: C, 42.31; H, 3.31; N, 13.84.

Synthesis of 3c. Complex **2c** (29 mg, 0.056 mmol) and AgOTf (24 mg, 0.093 mmol) in dry MeCN (5 mL) were stirred at reflux for 18 h. The mixture was filtered through Celite and all volatiles were evaporated under reduced pressure. The residue was washed with pentane yielding compound **3c** as a yellow solid which was collected and dried in vacuo (19 mg, 51%). Analytically pure **3c** was obtained by recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (CDCl₃ 400 MHz): δ 7.12 (s, 2H, H_{mes}), 4.36 (s, 3H, NCH₃), 2.34 (s, 3H, ArCH₃), 2.27 (s, 6H, CH₃CN), 2.04 (s, 6H, ArCH₃), 1.79 (s, 3H, CH₃CN). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 176.2 (C_{trz}-Ru), 167.5 (COO), 141.5 (C_{mes}), 136.7 (C_{mes}), 136.5 (C_{trz}-COO), 129.9 (C_{mes}), 125.9 (C_{mes}), 123.7, 122.2 (2 × MeCN), 36.8 (NCH₃), 21.2 (Ar-CH₃), 17.4 (Ar-CH₃), 4.1, 3.7 (2 × CH₃CN). HRMS (ESI⁺) Calcd for C₂₁H₂₆N₇O₂Ru⁺: 510.1191 Found 510.1190.

General Procedure for Alcohol Oxidations

A mixture of the alcohol (0.2 mmol) and the appropriate ruthenium complex **2** or **3** (0.01 mmol), and anisole (0.2 mmol) as internal standard was refluxed in the selected solvent (2 mL) in a closed vial. Aliquots were taken at specific times, diluted with CDCl₃ and analyzed by ¹H NMR spectroscopy.

General Catalytic Procedure for Transfer Hydrogenation

The catalyst (1–0.1 mol%), *i*PrOH (5 mL) and a solution of KOH (2M, 0.05 mL, 0.1 mmol) were added to a one-neck round-bottom flask equipped with a magnetic stirring bar. The mixture was stirred at reflux for 10 minutes. Ketone (1.0 mmol) was added and heating was continued. Aliquots (0.2 mL) were taken after 30 minutes and 2 h, poured into cyclohexane or dichloromethane (2 mL), filtered through Celite or SiO₂ in a Pasteur pipette. All volatiles were removed under vacuum. Conversions were determined by ¹H NMR spectroscopy using CDCl₃ as solvent.

Crystallographic details

Crystal data for complexes **2c** and **3a** were collected by using an Agilent Technologies SuperNova. A diffractometer fitted with an Atlas detector that uses monochromated Mo-K_α radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed.³⁶ The structures

were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on F^2 for all data using SHELXL-97.³⁷ Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Crystallographic details are summarized in Tables S3–S6. CCDC numbers 968356–968359 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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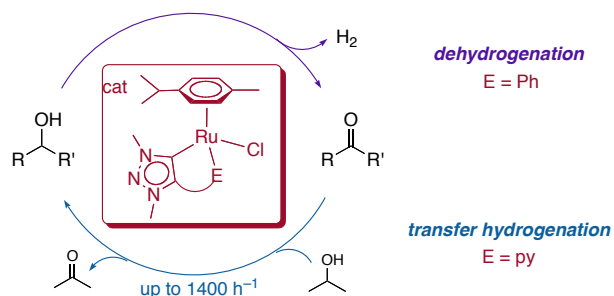
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Table of contents entry



Depending on the donor functionality, triazolylidene ruthenium complexes are catalytically highly active in either alcohol oxidation or ketone transfer hydrogenation.