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Wingtip substituents tailor the catalytic activity of ruthenium triazolylidene complexes in base-free alcohol oxidation†

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A series of Ru^{II} (η^6-arene) complexes with 1,2,3-triazolylidene ligands comprising different aryl and alkyl wingtip groups have been prepared and characterized by NMR spectroscopy, microanalysis, and in one case by X-ray diffraction. All complexes are active catalyst precursors for the oxidation of alcohols to the corresponding aldehydes/ketones without the need of an oxidant or base as additive. The wingtip groups have a direct impact on the catalytic activity, alkyl wingtips providing the most active species while aryl wingtip groups induce lower activity. An *N*-bound phenyl group was the most inhibiting wingtip group due to cyclometalation. Arene dissociation was observed as a potential catalyst deactivation pathway.

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Introduction

Carbonyls such as ketones and aldehydes are synthetically prevalent functional groups because of their outstanding versatility for derivatization. Amongst the various procedures to prepare carbonyl compound, they are accessible from alcohols as abundant precursors through selective oxidation procedures.[1] Oxidation of alcohols to aldehydes and ketones has been achieved by oxidation with high-valent chromium or manganese oxides,[2] or by Oppenauer-type oxidation involving the metal-catalyzed hydrogen transfer from the substrate to a sacrificial ketone such as cyclohexanone.[3] Milder and often more selective methods were developed by Dess and Martin using hypervalent iodine,[4] and by Ley with the introduction of perruthenate as catalyst in the presence of an *N*-oxide as terminal oxidant.[5] A drawback of these systems is the stoichiometric utilization of an oxidant, thus providing significant quantities of (sometimes toxic) side-products and a low atom-economy of the overall reaction. Much effort has therefore been devoted in recent years to use more benign oxidants such as H_2O_2 and O_2 as terminal oxidants,[6] leading to substantial progress in particular in ruthenium-[7] palladium-,[8] and copper-catalyzed alcohol oxidation,[9] both homogeneously and heterogeneously.[10]

Oxidant-free dehydrogenation of alcohols is comparatively rare, despite the obvious attractiveness of such a procedure in terms of waste, atom-economy, and possibly functional group tolerance. The recent quest for hydrogen as an alternative that does not impact the global carbon cycle has strongly stimulated research into acceptorless alcohol (and amine) dehydrogenation processes.[11] Ruthenium-catalyzed protocols for the dehydrogenation of primary and secondary alcohols have been developed for example by the groups of Beller, Milstein, and Williams.[12] In some cases, however, the formed product remains in the metal coordination sphere and is thus predisposed for further coupling to yield esters and acetals.[13] We recently observed that a ruthenium(II) cymene complex containing a triazolylidene ligand[14] affords a catalyst precursor that readily oxidizes benzyl alcohol (BnOH) to benzaldehyde with concomitant release of H_2.[15] We have now expanded our investigation of this clean oxidation process and have prepared a series of different triazolylidene complexes. Variation of the wingtip groups at the triazolylidene C4 and N1 positions from aryl groups to mixed aryl/alky systems and to exclusively alkyl substituents revealed a direct correlation between the ligand framework and the catalytic activity of the complexes.

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†Electronic supplementary information (ESI) available: Synthetic procedures for the triazolium salts and the silver carbene complexes, time-conversion profiles for alcohol oxidation, and crystallographic data of **3e**. CCDC 914595. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32939a

Results and discussion

Synthesis of the complexes

The triazolium salts **1a–j** were conveniently accessible through conventional copper-catalyzed click cycloaddition of the

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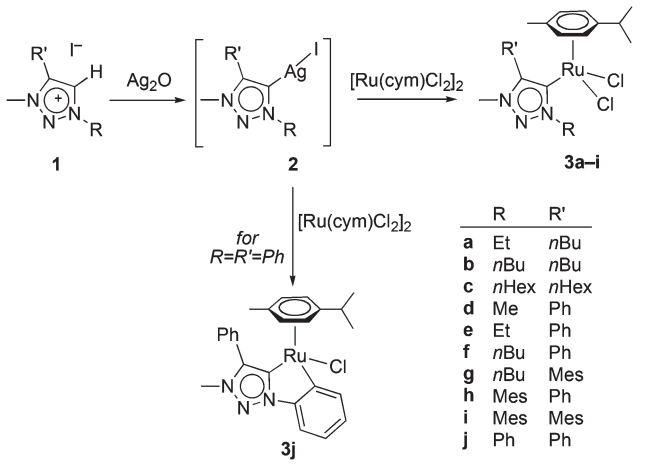

Scheme 1 Synthesis of triazolylidene ruthenium complexes **3**.

appropriate azide and alkyne,[16] followed by chemoselective methylation of the N3 position by using MeI (Scheme 1). Ruthenation of these triazolium salts was accomplished by transmetalation according to established procedures.[13a,15,17] Thus, reaction with Ag_2O produced the silver carbene complexes **2a–j**, which were isolated but not fully characterized due to their tendency to degrade. Analysis by ^{1}H NMR spectroscopy revealed the complete disappearance of the aromatic triazolium proton around 8.9–9.8 ppm along with minor shifts of the wingtip group signals as a consequence of the new chemical environment. The diarylated silver carbene complexes were considerably more stable. Crystals suitable for X-ray diffraction were obtained for **2j**, however, the refinement did not converge and showed a triazolylidene ligand that was strongly disorder through a 180° rotation about the Ag–C_{trz} bond. While this disorder hampered further refinement and precludes analysis of geometrical data, the X-ray diffraction analysis unambiguously showed a monomeric [AgI(trz)] complex as opposed to a cationic $[Ag(NHC)_2]^+$ structure as observed in many NHC silver complexes.[18]

Carbene transfer from complexes **2a–j** to [Ru(*p*-cymene)$Cl_2]_2$ yielded triazolylidene ruthenium(II) complexes **3a–i** in good to excellent yields (70–99% apart from **3a**), whereas **3j** was obtained in 35% yield only (Scheme 1). Generally, bulkier wingtip groups prolonged the reaction time for transmetalation. Complexes **3a–c** with alkyl wingtip groups were better soluble in chlorinated solvents and toluene than those with aromatic substituents. All complexes were stable towards moisture and air both in solution and in the solid state for several months.

Successful transruthenation was indicated by the characteristic NMR data. Specifically, formation of complexes **3a–j** was supported by the presence of resonances due to the cymene group and the triazolylidene ligand in equimolar ratio. The two doublets of the aryl protons of cymene shift to higher field upon triazolylidene coordination and provide a diagnostic probe for the nature of the triazolylidene wingtip groups. Thus, alkyl wingtip groups on both C4 and N1 induce a small upfield shift from δ_H 5.47 and 5.33 ppm in the [$RuCl_2$-(cymene)]$_2$ precursor to 5.35(1) and 5.02(1) ppm in complexes **3a–c**. Introduction of a phenyl group at C4 increases the upfield shift by some 0.2 ppm and the cymene protons resonate at δ_H 5.12(1) and 4.84(2) ppm in complexes **3d–f**. In both sets of complexes, the length of the alkyl substituents has no detectable impact on the resonance frequency. A mesityl group at C4 affects the high-field doublet stronger (δ_H 5.16 and 4.98 ppm for **3g**), suggesting steric interactions between the mesityl group and the cymene. Such interactions are expected to be more pronounced when both wingtip groups are bulky aryl groups, and indeed the cymene resonances are scattered over a broad range for the diaryl-substituted triazolylidene complexes **3h** and **3i** (δ_H 5.13 and 4.23 ppm, and 5.00 and 4.62 ppm, respectively). The ^{1}H NMR pattern of complex **3j** is distinctly different and is characterized by a desymmetrization of the *N*-bound phenyl group due to cyclometalation, as briefly communicated.[19,20] Similarly, the resonance frequency of the tertiary proton of the iPr group of cymene correlates with the set of wingtip substituents. With alkyl wingtips on N1 and C4, the septet appears around δ_H 2.9 ppm, while aryl substituents induce an upfield displacement by 0.05–0.4 ppm.

Comparison of the ^{13}C NMR data and in particular of the carbenic C5 resonance provides interesting trends. With alkyl wingtip groups on C4 and N1, a carbene resonance at δ_C 161.0(2) ppm is observed for complexes **3a–c**. No specific correlation between the length of the alkyl chain and the chemical shift was observed. Replacing the C-bound alkyl group with a phenyl substituent (complexes **3d–f**) increases the shielding of the carbene resonance slightly, δ_C 160.7(2) ppm. The upfield shift is counterintuitive when considering the electron-withdrawing character of aryl groups and thus implies a significant steric contribution to the NMR frequency. In line with such a notion, the carbene resonance is gradually shifting to higher field when increasing the length of the *N*-bound alkyl substituent from Me to Et to *n*Bu (δ_C 160.9, 160.5, and 160.4 ppm, respectively). Furthermore, introducing a mesityl rather than a phenyl substituent at C4 pronounces the high-field shift (δ_C 158.8 ppm for **3g**). With aryl substituents both on N1 and C4, the steric interactions are further altered and as a consequence, the NMR frequency does not follow any trend (δ_C 163.0 and 161.0 ppm for **3h** and **3i**, respectively). In its entirety, these chemical shift values underline the caution that needs to be applied when correlating ^{13}C NMR frequencies with ligand donor properties.[21]

An X-ray diffraction analysis was performed of a single crystal of **3e** as a representative example. The molecular structure (Fig. 1) confirmed the expected connectivity pattern and shows the typical three-legged piano-stool geometry with two chlorides and the triazolylidene ligand as the three 'legs'. The Ru–C_{trz} bond is 2.061(4) Å, which is slightly shorter than in an analogue of **3b** containing hexamethylbenzene rather than cymene as ancillary ligand,[15] yet it is comparable to related [$RuCl_2$(arene)(NHC)] complexes.[22] Also, the Ru–$C_{centroid}$ distance to the cymene ligand is relatively short, 1.684(2) Å. The phenyl substituent is almost perpendicular to the heterocyclic

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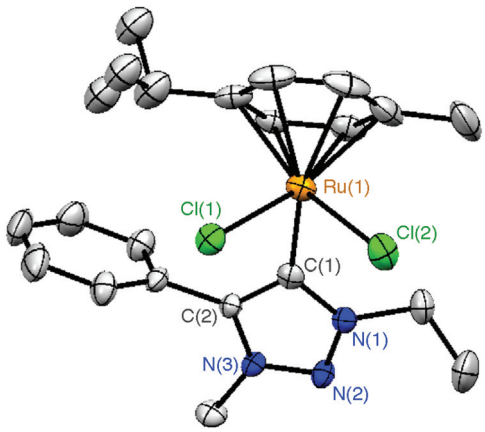
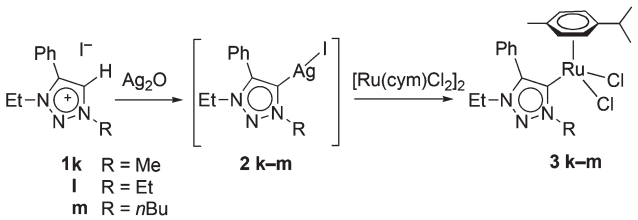


Fig. 1 ORTEP representation of **3e** (50% probability, hydrogens omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.061(4), Ru(1)–Cl(1) 2.4183(11), Ru(1)–Cl(2) 2.466(12), Ru(1)–$C_{centroid}$ 1.684(2); C(1)–Ru(1)–Cl(1) 87.06(10), C(1)–Ru(1)–Cl(2) 89.95(13), Cl(1)–Ru(1)–Cl(2) 83.70(4).



Scheme 2 Synthesis of complexes **3k–m**.

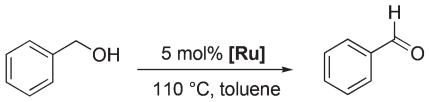
carbene plane. The tertiary proton of the cymene iPr group is located exactly on top of the center of the phenyl substituent (distance H to centroid 2.68 Å), suggesting an edge-to-face type hydrogen bond interaction. This interaction might be preserved in solution (*cf.* NMR shifts above).

For comparative reasons, complexes **3k–m** were prepared as analogues of **3d–f**. These complexes contain an ethyl rather than a methyl substituent at N3 (Scheme 2). The synthesis mirrors that of complexes **3d–f** with the exception that EtI was used for the alkylation of the corresponding triazoles rather than MeI. The spectroscopic trends were identical and complexes **3k–m** are characterized by two diagnostic doublets due to the cymene ligand (δ_H 5.12 and 4.86 ppm), and a low-field ^{13}C NMR resonance for the ruthenium-bound triazolylidene carbon at δ_C 160.5(±1) ppm.

Catalytic alcohol oxidation

The ruthenium complexes **3a–m** are catalyst precursors for the oxidant- and base-free oxidation of alcohols to ketones and aldehydes. The catalytic efficiency was evaluated by using BnOH as a model substrate (eqn (1)). Gradual oxidation to benzaldehyde was observed upon heating this substrate in toluene in the presence of catalytic quantities of the triazolylidene ruthenium complex. Benzaldehyde formation was monitored over time,† and conversions after 1 h and after 16 h are compiled in Table 1.

Table 1 Oxidation of benzyl alcohol catalyzed by triazolylidene ruthenium complexes[a]



(1)

[Ru]	N_{trz}–R	C_{trz}–R′	Conv'n 1 h	Conv'n 16 h
3a	Et	Bu	55%	87%
3b	Bu	Bu	45%	>98%
3c	Hex	Hex	55%	>98%
3d	Me	Ph	35%	55%
3e	Et	Ph	49%	74%
3f	Bu	Ph	57%	82%
3g	Bu	Mes	52%	84%
3h	Mes	Ph	16%	36%
3i	Mes	Mes	41%	63%
3j	Ph	Ph	14%	31%
3k	Me	Ph	31%	54%
3l	Et	Ph	53%	69%
3m	Bu	Ph	60%	79%
4	Hex	Hex	37%	95%
$[RuCl_2(cym)]_2$			<2%	17%
$[RuCpCl(PPh_3)_2]$			13%	15%

[a] Conditions: benzyl alcohol (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), toluene (2 mL), 110 °C.

Several trends evolve from this catalyst evaluation.

(i) The triazolylidene ligand imparts the catalytic activity as related commercial ruthenium complexes such as $[RuCl_2(cym)]_2$ or $[RuCpCl(PPh_3)_2]$ are considerably less competent than complexes **3**.

(ii) Variation of the remote substituents at N3 from methyl to ethyl has no detectable impact on the catalytic performance (*cf.* **3d–f** *vs.* **3k–m**). While the essentially identical performance of these systems is not surprising, these runs underpin the reproducibility of the catalytic activity and the well-defined nature of the most competent species.

(iii) In contrast to remote substitution, the catalytic activity is markedly affected by the type of wingtip substituents at the triazolylidene ligand. Generally, the presence of alkyl wingtip groups improves catalytic activity and longer alkyl chains induce better performance than shorter ones. This latter trend is supported by the increasing activity in the series **3a** < **3b** < **3c** for complexes containing alkyl wingtip groups only, and also in the series **3d** < **3e** < **3f** for complexes containing a phenyl wingtip at C4 and an alkyl substituents at N1.

(iv) The presence of a C-bound phenyl group has a minor impact on initial rates (*cf.* conversion after 1 h for the series **3a–c** *vs.* **3d–f**), though it compromises the long term stability of the catalytically active species and leads to incomplete conversion after 16 h. No significant difference was noted when replacing the phenyl wingtip group in **3f** with a mesityl substituent (**3g**).

(v) The unfavorable influence of aryl wingtip groups is further illustrated when considering the catalytic activity of complexes comprising aryl wingtip groups on both N1 and C4 (**3h–3i**). Initial activities are comparably moderate and final

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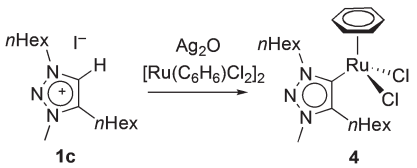
product yields are the lowest in the series tested. Wingtip C–H bond activation and ensuing cylcometalation may constitute a plausible catalyst deactivation pathway. Such a process has precedents both for phenyl and for mesityl substituents,[19,23] and may be induced by steric constraints (*cf.* NMR discussion above). Cyclometalated species are catalytically less competent as demonstrated by the low conversions observed with the preformed ruthenacycle **3j** and may thus account for the incomplete conversion when using phenyl-substituted triazolylidenes (**3d–m**).

(vi) The low activity of complex **3i** containing the triazolylidene analogue of IMes apparently disagrees with a carbene dissociation step as observed in other catalytic processes.[24] The di(mesityl)-substituted triazolylidene is arguably the most stable free carbene of the series evaluated here[14b] because acidic α-hydrogens in the wingtip substituents are absent. Hence this complex should lead to the lowest catalyst deactivation rate if carbene dissociation were relevant.

A potential catalyst activation step may involve the ancillary cymene ligand, either through edge-to-face hydrogen bonding to the substrate or through substitution by BnOH (or the solvent).[25] We evaluated this hypothesis by synthesizing complex **4**, *viz.* the benzene analogue of the most active catalyst precursor **3c** (eqn (2)).

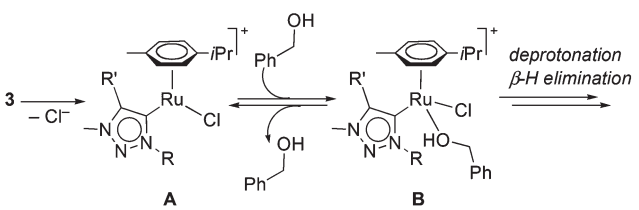


(2)

Complex **4** displayed similar catalytic activity to **3c**, though initial activities are lower (37% *vs.* 55%, *cf.* Table 1). Slower initial performance is inconsistent with hydrogen bonding of the substrate, which should be easier with benzene with less shielded C–H bonds than cymene. Moreover, the higher tendency of benzene compared to cymene to dissociate from the ruthenium coordination sphere disagrees with a catalyst activation step involving the arene ligand. Easier dissociation of benzene from complex **4** was confirmed NMR spectroscopically by heating toluene-d_8 solutions of **3c** and **4** to 110 °C for 16 h in the absence of any substrate. Only traces of free cymene were noted from **3c** (<3%) while substantial benzene dissociation was identified by the diagnostic ^{1}H NMR signal at δ_H 7.13 ppm when heating complex **4** (*ca.* 20% by NMR integration).

Further insight into the catalytic process was obtained from a catalytic experiment in deuterated toluene. A substantially larger ruthenium loading (25 mol%) was used in order to identify the fate of complex **3c** during the reaction. Interestingly, the rate of product formation was not accelerated with this higher ruthenium concentration (41% conversion after 0.5 h, 56% after 1 h), suggesting that the effective concentration of the catalytically active species is not increased. Over the first hour of reaction, the concentration of **3c** was decreasing to 33% in an exponential decay, and proportionally, formation of free cymene was detected by the characteristic aliphatic signals at δ_H 2.71 (septet), 2.15 (s), and 1.15 (d), while the pertinent aromatic doublets overlapped with residual protio signals of the reaction solvent (toluene-d_8). No formation of free triazolylidene or any triazolium salt was observed, however, which may point to the formation of colloidal ruthenium stabilized by a triazole derivative.[26] After 16 h, only benzaldehyde and free cymene were detectable with integrals that suggest quantitative conversion of BnOH and **3c**, respectively (anisole as internal standard). During the initial stages of the reaction, two complexes were identified in addition to **3c** in small concentrations (*ca.* 5% and 15% relative to **3c**, respectively) by the appearance of diagnostic doublets in the 4.9–5.4 ppm range. The minor of these two species is asymmetric and features four different H_{cym} resonances, whereas the major species is symmetric and displays only two H_{cym} signals.[27] Their relative ratio as well as their proportion to complex **3c** remained approximately constant over the course of the reaction. Based on the gradual but consistent drift of the BnOH methylene signal from δ_H 4.32 ppm to 4.30 ppm within the first hour of reaction, the asymmetric species was tentatively assigned to a cationic ruthenium (cymene) complex containing a triazolylidene ligand, a chloride, and a rapidly exchanging BnOH (**B**, Scheme 3),[28] while the symmetric species may feature a two-legged piano-stool geometry including a triazolylidene and a chloride ligand only (**A**, Scheme 3).[29] No resonances in the hydridic region were observed in the spectra. Based on this assumption, the rate-limiting step of the dehydrogenation process would consist of either alcohol deprotonation or β-hydrogen elimination. Attempts to synthesize the surmised intermediate by substituting one chloride in **3c** by a BnOH ligand, mediated by $AgBF_4$, have failed thus far.

The catalytic scope was evaluated with the best performing catalyst precursors, **3b** and **3c**, using different primary aliphatic and benzylic alcohols (Table 2). Aliphatic alcohols are converted substantially slower than BnOH and afford 30–60% of the corresponding aldehyde (entries 1–3). While the initial rate of oxidation was identical for all three *n*-alcohols (23% conversion after 1 h), catalyst deactivation occurred at different later stages of the reaction and led to the observed range of final conversions. Similar effects were observed with benzylic alcohols that contain a functional group on the aromatic ring (entries 4–6). Initial rates with 3,4-dimethoxybenzyl alcohol and 4-bromobenzyl alcohol were comparable to those



Scheme 3 Postulated activation pathway with formation of intermediates **A** and **B**.

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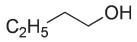
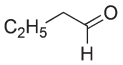
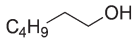
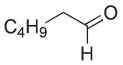
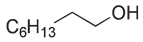
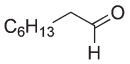
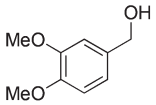
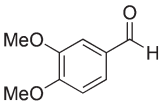
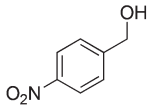
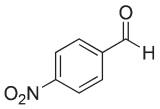
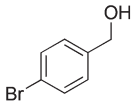
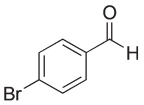
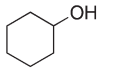
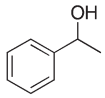
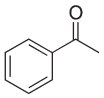
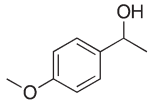
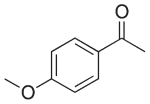
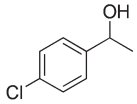
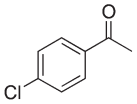
Table 2 Conversions of different alcohols with catalyst precursor **3c**[a]

Entry	Substrate	Product	Conversion[b]
1			62%
2			38%
3			32%
4			82%[c]
5			48%
6			67%
7			39% (37%)
8			66% (66%)
9			96%[d] (81%)
10			61% (60%)

[a] Conditions: alcohol (0.2 mmol), **3c** (0.01 mmol, 5 mol%), toluene (2 mL), 110 °C, 16 h. [b] Values in parenthesis obtained with complex **3b**. [c] Isolated yield: 35%. [d] Isolated yield: 47%.

measured for BnOH (51% and 47%, respectively, after 1 h), yet deactivation of the catalytically competent species halts the reaction and inhibits full conversion.

Under standard conditions, also secondary alcohols were oxidized to produce the corresponding ketones with moderate to excellent conversions. The observed trends are similar to those deduced for primary alcohols. Thus, aliphatic alcohols such as cyclohexanol were relatively poor substrates (<40% conversion), whereas benzylic secondary alcohols were converted efficiently, especially when the phenyl group contained electron-donating groups. Electron-withdrawing groups gave lower conversions, indicating reduced catalytic rates upon depletion or pronounced polarization of the electron density in the α-C–H bond that is activated during the alcohol oxidation process. This observation is in agreement with β-H elimination of a putative Ru–OR alkoxide or a Ru–O(H)(R) alcohol complex as rate-limiting step[30] and corroborates the conclusions drawn from *in situ* NMR analysis.

Conclusions

A series of triazolylidene ruthenium(II) complexes were prepared as catalyst precursors for the base- and oxidant-free dehydrogenation of alcohols to the corresponding carbonyl compounds. Variation in the triazolylidene ligand framework allowed trends to be established. Specifically, aryl wingtip groups induce lower activity than alkyl groups, and longer alkyl substituents lead to slightly better performance than shorter alkyl chains. As a particular case, the *N*-bound phenyl group undergoes spontaneous C_{Ph}–H bond activation and affords a cyclometalated complex with low catalytic activity in alcohol oxidation. Primary and secondary benzylic alcohols gave the corresponding aldehydes and ketones in good to excellent yields, while aliphatic alcohols were insufficiently converted, which may provide opportunities for selective oxidation. The absence of base and oxidant is appealing in terms of atom economy and experimental setup and should allow for wide functional group tolerance. Future work should be directed towards lowering the reaction temperature and catalyst loading. A deeper mechanistic understanding of the dehydrogenation process will be pivotal to achieve these goals and to make the process widely applicable.

Experimental section

General

All solvents used for the reaction were purified using an alumina/catalyst column system (Thermovac Co.). The synthesis of the new triazolium salts and the new carbene silver complexes are detailed in the ESI.† The carbene ruthenium complexes **3b**,[15] **3e**,[14a] and **3j**[19] were synthesized as described previously. 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 (^{1}H NMR) and 75, 100 or 125 MHz (^{13}C{^{1}H} 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. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland; residual solvents were also identified by ^{1}H NMR spectroscopy.

General procedure for the syntheses of the triazolylidene ruthenium(II) complexes 3

To a solution of silver carbene **2** in CH_2Cl_2 (20 mL) was added [Ru(*p*-cymene)Cl_2]$_2$ (0.5 eq.). The mixture was stirred at room temperature for the time indicated and then filtered through Celite. All volatiles were removed *in vacuo* at room temperature. The residue was washed with pentane (3 × 25 mL), dried, and dissolved in a minimum amount of CH_2Cl_2 and precipitated

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with Et_2O (100 mL). The precipitate was collected and dried *in vacuo*.

Complex 3a. According to the general method from silver carbene **2a** (138 mg, 0.34 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (105 mg, 0.17 mmol) in 16 h. The crude solid obtained after solvent evaporation was purified by column chromatography (SiO_2, CH_2Cl_2–acetone 3 : 1). The brown band was collected, concentrated to 2 mL and treated with cold Et_2O (50 mL), which induced the precipitation of **3a** as a brown solid (135 mg, 83%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 5.35 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 5.01 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.70 (s_{broad}, 2H, NCH_2CH_3), 3.98 (s, 3H, NCH_3), 2.97 (m, 2H, C_{trz}–CH_2), 2.91 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, $CHMe_2$), 2.02 (s, 3H, C_{cym}–CH_3), 1.58 (m, 5H, NCH_2CH_3, C_{trz}–CH_2CH_2), 1.47 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, C_{trz}–$CH_2CH_2CH_2$), 1.28 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH–CH_3), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, C_{trz}–$CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 161.2 (C_{trz}–Ru), 147.6 (C_{trz}–Bu), 107.6, 97.5, 85.1, 82.6 (4 × C_{cym}), 50.0 (NCH_2), 36.5 (NCH_3), 32.3 (C_{trz}–CH_2), 30.9 ($CHMe_2$), 26.2 (C_{trz}–CH_2CH_2), 23.3 (C_{trz}–$CH_2CH_2CH_2$), 22.8 (CH–CH_3), 18.7 (C_{cym}–CH_3), 16.3 (NCH_2CH_3), 14.1 (C_{trz}–$CH_2CH_2CH_2CH_3$). No satisfactory elemental analysis could be obtained for this complex.

Complex 3c. According to the general method from silver carbene **2c** (188 mg, 0.39 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (118 mg, 0.19 mmol) in 16 h. The crude solid was purified by column chromatography (SiO_2, CH_2Cl_2–acetone 3 : 1). The brown band was collected and concentrated to 2 mL. Addition of cold Et_2O induced the precipitation of **3c** as a brown solid (184 mg, 74%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 5.35 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 5.02 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.59 (br, 2H, NCH_2), 3.97 (s, 3H, NCH_3), 2.96 (m, 2H, C_{trz}–CH_2), 2.88 (m, 1H, $CHMe_2$), 2.01 (s, 3H, C_{cym}–CH_3), 1.98 (m, 2H, NCH_2CH_2), 1.42 (m, 4H, $CH_{2\ hex}$), 1.33–1.28 (m, 16H, $CH_{2\ hex}$, CH–CH_3), 0.90 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 161.2 (C_{trz}–Ru), 147.5 (C_{trz}–hex), 107.2, 97.3, 85.2, 82.7 (4 × C_{cym}), 54.9 (NCH_2), 36.5 (NCH_3), 31.8 ($CHMe_2$) 31.2, 30.9, 30.2, 29.2, 26.8, 26.6, 22.9, 22.8, 22.3 (9 × $CH_{2\ hex}$), 22.7 (CH–CH_3), 18.8 (C_{cym}–CH_3), 14.3, 14.2 (2 × $CH_{3\ hex}$). Anal. Calcd for $C_{25}H_{43}Cl_2N_3Ru$ (557.19) × 0.5 H_2O: C, 52.99; H, 7.83; N, 7.42. Found: C, 52.68; H, 7.44; N, 7.47.

Complex 3d. According to the general method from silver carbene **2d** (330 mg, 0.80 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (247 mg, 0.40 mmol) in 2 h. Yield: 154 mg (40%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.63 (m, 2H, H_{Ph}), 7.47 (m, 3H, H_{Ph}), 5.12 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.86 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.45 (s, 3H, NCH_3), 3.72 (s, 3H, NCH_3), 2.61 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 1.86 (s, 3H, C_{cym}–CH_3), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 160.9 (C_{trz}–Ru), 148.6 (C_{trz}–Ph), 131.9, 129.9, 128.7, 128.0 (4 × C_{Ph}), 104.9, 97.4, 84.2, (3 × C_{cym}), 42.6, 36.7 (2 × NCH_3), 30.6 ($CHMe_2$), 22.5 (CH–CH_3), 18.4 (C_{cym}–CH_3). Anal. Calcd for $C_{20}H_{25}Cl_2N_3Ru$ (479.40): C, 50.11; H, 5.26; N, 8.76. Found: C, 49.87; H, 5.22; N, 8.74.

Complex 3f. According to the general method from silver carbene **2f** (140 mg, 0.32 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (95 mg, 0.16 mmol) in 2 h. Yield: 161 mg (99%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.62 (m, 2H, H_{Ph}), 7.46 (m, 3H, H_{Ph}), 5.12 (d, $^3J_{HH}$ = 5.8 Hz, 2H, H_{cym}), 4.85 (d, $^3J_{HH}$ = 5.8 Hz, 2H, H_{cym}), 4.77 (m, 2H, NCH_2), 3.71 (s, 3H, NCH_3), 2.57 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 2.03 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 1.84 (s, 3H, C_{cym}–CH_3), 1.48 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2$), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH–CH_3), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 160.8 (C_{trz}–Ru), 147.9 (C_{trz}–Ph), 132.0, 129.9, 129.0, 128.0 (4 × C_{Ar}), 104.9, 97.0, 84.4, 84.2 (4 × C_{cym}), 54.8 (NCH_2), 36.7 (NCH_3), 33.1 (NCH_2CH_2), 30.6 ($CHMe_2$), 22.5 (CH–CH_3), 20.2 ($NCH_2CH_2CH_2$), 18.3 (C_{cym}–CH_3), 13.9 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{24}H_{33}Cl_2N_3Ru$ (521.48): C, 53.83; H, 6.21; N, 7.85. Found: C, 53.55; H, 6.12; N, 7.67.

Complex 3g. According to the general method from silver carbene **2g** (225 mg, 0.46 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (140 mg, 0.23 mmol) in 16 h. Yield: 186 mg (72%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.02 (s, 2H, H_{Mes}), 5.16 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H_{cym}), 4.99 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H_{cym}), 4.77 (t, $^3J_{HH}$ = 8.0 Hz, 2H, NCH_2), 3.62 (s, 3H, NCH_3), 2.76 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, $CHMe_2$), 2.36 (s, 3H, Mes–CH_3), 2.13 (s, 6H, Mes–CH_3), 1.97 (m, 2H, NCH_2CH_2), 1.92 (s, 3H, C_{cym}–CH_3), 1.46 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH–CH_3), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 158.5 (C_{trz}–Ru), 145.4 (C_{trz}–Mes), 140.5, 139.3, 128.9, 126.3 (4 × C_{Mes}), 110.2, 105.1, 86.7, 84.5 (4 × C_{cym}), 55.8 (NCH_2), 35.9 (NCH_3), 33.9 (NCH_2CH_2), 30.5 ($CHMe_2$), 22.4 (CH–CH_3), 21.5, 21.4 (2 × $MesCH_3$), 20.2 (C_{cym}–CH_3), 18.4 ($NCH_2CH_2CH_2$), 14.2 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{26}H_{37}Cl_2N_3Ru$ (563.14) × 1/3 CH_2Cl_2: C, 53.44; H, 6.41; N, 7.10. Found: C, 53.06; H, 6.47; N, 7.03.

Complex 3h. According to the general method from silver carbene **2h** (300 mg, 0.59 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (179 mg, 0.29 mmol) in 2 h. Yield: 239 mg (70%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 8.00 (m, 2H, H_{Ar}), 7.58 (m, 3H, H_{Ar}), 6.90 (s, 2H, H_{Ar}), 5.13 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.23 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 3.95 (s, 3H, NCH_3), 2.85 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, $CHMe_2$), 2.31 (s, 3H, $ArCH_3$), 2.06 (s, 6H, $ArCH_3$), 1.80 (s, 3H, C_{cym}–CH_3), 1.16 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 163.0 (C_{trz}–Ru), 142.7 (C_{trz}–Ph), 139.5, 135.3, 132.2, 130.4, 130.2, 130.0, 128.9, 128.5 (8 × C_{Ar}), 107.1, 97.2, 88.9, 80.9 (4 × C_{cym}), 37.7 (NCH_3), 30.7 ($CHMe_2$), 22.7 (CH–CH_3), 21.4, 18.8 (2 × $ArCH_3$), 18.1 (C_{cym}–CH_3). Anal. Calcd for $C_{28}H_{33}Cl_2N_3Ru$ (583.11) × 0.5 CH_2Cl_2: C, 54.68; H, 5.47; N, 6.71. Found: C, 54.83; H, 5.38; N, 6.81.

Complex 3i. According to the general method from silver carbene **2i** (94 mg, 0.17 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (52 mg, 0.09 mmol) in 16 h. Yield: 82 mg (77%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.00 (s, 2H, H_{Mes}), 6.90 (s, 2H, H_{Mes}), 5.00 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.62 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 3.65 (s, 3H, NCH_3), 2.61 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, $CHMe_2$), 2.38, 2.33 (2 × s, 3H, Mes–CH_3), 2.19, 2.16 (2 × s, 6H, Mes–CH_3), 1.80 (s, 3H, C_{cym}–CH_3), 1.06 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 161.0 (C_{trz}–Ru), 142.8 (C_{trz}–Mes), 138.7, 138.3, 136.2, 134.4, 130.2, 129.7, 129.0, 128.6 (8 × C_{Mes}), 102.5, 95.0, 86.8, 85.2 (4 × C_{cym}), 36.2 (NCH_3), 30.3

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($CHMe_2$), 22.5 (CH–CH_3), 21.3, 20.6, 18.8, 18.2 (4 × Mes–CH_3), 17.8 (C_{cym}–CH_3). Anal. Calcd for $C_{31}H_{39}Cl_2N_3Ru$ (625.16) × H_2O: C, 57.85; H, 6.42; N, 6.53. Found: C, 57.58; H, 6.07; N, 6.60.

Complex 3k. According to the general method from silver carbene **2k** (150 mg, 0.35 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (108 mg, 0.18 mmol) in 2 h, affording **3k** as a red powder (70 mg, 80%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.63 (m, 2H, H_{Ph}), 7.47 (m, 3H, H_{Ph}), 5.12 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.86 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}) 4.46 (s, 3H, NCH_3), 4.03 (q, $^3J_{HH}$ = 7.3 Hz, 2H NCH_2), 2.58 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 1.84 (s, 3H, C_{cym}–CH_3), 1.34 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3) 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 160.5 (C_{trz}–Ru), 147.9 (C_{trz}–Ph), 132.2, 129.8, 128.7, 127.9 (4 × C_{Ph}), 104.6, 97.3, 84.2, 84.1 (4 × C_{cym}), 45.4 (NCH_2), 42.6 (NCH_3), 30.6 ($CHMe_2$), 22.5 (CH–CH_3), 18.4 (C_{cym}–CH_3), 14.8 (NCH_2CH_3). Anal. Calcd for $C_{21}H_{27}Cl_2N_3Ru$ (493.43): C, 51.12; H, 5.52; N, 8.52. Found: C, 50.93; H, 5.39; N, 8.28.

Complex 3l. According to the general method from silver carbene **2l** (175 mg, 0.40 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (123 mg, 0.20 mmol) in 2 h. Yield: 90 mg (89%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.62 (m, 2H, H_{Ph}), 7.45 (m, 3H, H_{Ph}), 5.12 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.89–4.85 (m, 4H, 2H_{cym}, 2H, NCH_2) 4.02 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 2.57 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 1.83 (s, 3H, C_{cym}–CH_3), 1.62 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3), 1.33 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 160.5 (C_{trz}–Ru), 147.2 (C_{trz}–Ph), 132.2, 129.7, 128.9, 127.9 (4 × C_{Ph}), 104.9, 96.8, 84.4, 84.0 (4 × C_{cym}), 50.2, 45.5 (2 × NCH_2), 30.5 ($CHMe_2$), 22.5 (CH–CH_3), 18.3 (C_{cym}–CH_3), 16.2, 14.8 (2 × NCH_2CH_3). Anal. Calcd for $C_{22}H_{29}Cl_2N_3Ru$ (507.46): C, 52.07; H, 5.76; N, 8.28. Found: C, 51.78; H, 5.63; N, 8.01.

Complex 3m

According to the general method from silver carbene **2m** (140 mg, 0.30 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (93 mg, 0.15 mmol) in 2 h, yielding **3m** as a red-brown powder (69 mg, 86%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.62 (m, 2H, H_{Ph}), 7.46 (m, 3H, H_{Phr}), 5.13 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.86 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 4.78 (m, 2H, NCH_2CH_2), 4.03 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 2.54 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 2.05 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 1.82 (s, 3H, C_{cym}–CH_3), 1.48 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2$), 1.33 (t, 2H, $^3J_{HH}$ = 7.3 Hz, NCH_2CH_3), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH–CH_3), 0.99 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 160.4 (C_{trz}–Ru), 147.2 (C_{trz}–Ph), 132.3, 129.7, 128.9, 127.9 (4 × $C_{Ar/Ph}$), 104.5, 96.8, 84.4, 84.2 (4 × C_{cym}), 54.8 (NCH_2CH_2), 45.4 (NCH_2CH_3), 33.1 (NCH_2CH_2), 30.9 ($CHMe_2$), 22.6 (CH–CH_3), 20.2 ($NCH_2CH_2CH_2$), 18.2 (C_{cym}–CH_3), 14.8 (NCH_2CH_3), 13.9 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{24}H_{33}Cl_2N_3Ru$ (535.51): C, 53.83; H, 6.21; N, 7.85. Found: C, 53.55; H, 6.12; N, 7.67.

Complex 4

In a one-pot reaction **1c** (220 mg, 0.58 mmol), Ag_2O (67 mg, 0.29 mmol) and [Ru(benzene)Cl_2]$_2$ (144 mg, 0.29 mmol) in CH_2Cl_2 (40 mL) were stirred at room temperature for 48 h and then filtered through Celite. The crude residue was purified by column chromatography (SiO_2, CH_2Cl_2–acetone 3 : 1). The red band was collected and concentrated to 5 mL. Addition of cold Et_2O induced the precipitation of **4** as a brown solid (110 mg, 38%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 5.48 (s, 6H, $H_{benzene}$), 4.59 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2(CH_2)_4CH_3$), 3.97 (s, 3H, NCH_3), 3.05 (s_{broad}, 2H, C_{trz}–$CH_2(CH_2)_4CH_3$), 1.97 (q, $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2CH_2(CH_2)_3CH_3$), 1.60 (s_{broad}, 2H, $CH_{2\ hex}$), 1.43 (m, 4H, $CH_{2\ hex}$), 1.33 (m, 8H, $CH_{2\ hex}$) 0.91 (m, 6H, $N(CH_2)_5CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 158.2 (C_{trz}–Ru), 147.8 (C_{trz}–hex), 85.99 ($C_{benzene}$), 54.9 (NCH_2, Hex), 36.5 (NCH_3), 31.8 ($NCH_2CH_2(CH_2)_3CH_3$), 31.7, 31.2, 30.5, 29.8, 29.2, (5 × CH_2, Hex), 26.8 (C_{trz}–$CH_2(CH_2)_4CH_3$), 26.2, 22.8, 22.7, 22.3 (4 × CH_2, Hex), 14.3, 14.2 (2 × CH_3, Hex). Anal. Calcd for $C_{21}H_{35}Cl_2N_3Ru$ (501.49): C, 50.29; H, 7.03; N, 8.38. Found: C, 49.69; H, 6.85; N, 8.12.

General procedure for alcohol oxidations

A mixture of the alcohol (0.2 mmol) and the appropriate ruthenium complex **3** or **4** (0.01 mmol), and anisole (0.2 mmol) or hexamethylbenzene (0.2 mmol, for the oxidation of *para*-methoxy-1-phenethyl alcohol) as internal standard was refluxed in toluene (2 mL) in a closed vial. Aliquots were taken at specific times, diluted with $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.

Crystallographic details

Crystals suitable for single crystal structure analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **3e**. A suitable crystal was mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe and Cie, 2002) equipped with a graphite-monochromator. Data collection was performed at −50 °C using Mo-Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 135 mm. The structure was solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97.[31] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULscanABS as implemented in PLATON03.[32] Complex **3e** crystallized with one disordered molecule of pentane per asymmetric unit and featured partial disorder in the *n*-butyl group. CCDC number 914595 contains the supplementary crystallographic data for this paper.

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