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

Daniel Canseco-Gonzalez and Martin Albrecht

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DOI: 10.1039/c000000x

A series of RuII(η5-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 cyclometallation. Arenes dissociation was observed as a potential catalyst deactivation pathway.

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. Oxidation of alcohols to aldehydes and ketones has been achieved by oxidation with high-valent chromium or manganese oxides, or by Oppenauer-type oxidation involving the metal-catalyzed hydrogen transfer from the substrate to a sacrificial ketone such as cyclohexanone. Milder and often more selective methods were developed by Dess and Martin using hypervalent iodine, and by Ley with the introduction of per ruthenenate as catalyst in the presence of an N-oxide as terminal oxidant. 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 H2O2 or O2 as terminal oxidants, leading to substantial progress in particular in ruthenium-, palladium-, and copper-catalyzed alcohol oxidation, both homogeneously and heterogeneously.

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. Ruthenium-catalyzed protocols for the dehydrogenation of primary and secondary alcohols have been developed for example by the groups of Beller, Milstein, and Williams. 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. We recently observed that a ruthenium(II) cymene complex containing a triazolylidene ligand affords a catalyst precursor that readily oxidizes benzyl alcohol (BnOH) to benzaldehyde with concomitant release of H2. 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/alkyl systems and to exclusively alkyl substituents revealed a direct correlation between the ligand framework and the catalytic activity of the complexes.

Results and discussion
Synthesis of the complexes
The triazolium salts 1a–j were conveniently accessible through conventional copper-catalyzed click cycloaddition of the appropriate azide and alkyne, 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. Thus, reaction with Ag2O produced the silver carbene complexes 2a–j, which were isolated but not fully characterized due to their tendency to degrade. Analysis by 1H 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 disordered through a 180° rotation about the Ag–C9 bond. While this disorder hampered further refinement and precludes analysis of geometrical data, the X-ray diffraction analysis unambiguously showed a monomeric [Ag(trz)] complex as opposed to a cationic [Ag(NHC)2]+ structure as observed in many NHC silver complexes.
Carbene transfer from complexes 2a–j to [Ru(p-cymene)Cl]2 yielded triazolylidene ruthenium(II) complexes 3a–g 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 transmetallation. 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 transamination 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_{19} H 5.47 and 5.33 ppm in the [RuCl2(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_{19} 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 methyl group at C4 affects the high-field doublet stronger (δ_{19} H 5.16 and 4.98 ppm for 3g), suggesting steric interactions between the methyl 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_{19} H 5.13 and 4.23 ppm, and 5.00 and 4.62 ppm, respectively). The H NMR pattern of complex 3j is distinctly different and is characterized by a desymmetrization of the C-bound phenyl group due to cyclometalation, as briefly communicated.59,60 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_{19} H 2.9 ppm, while aryl substituents induce an upfield displacement by 0.05–0.4 ppm.

Comparison of the 13C NMR data and in particular of the carbene C5 resonance provides interesting trends. With alkyl wingtip groups on C4 and N1, a carbene resonance at δ_{19} 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_{19} 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 iPr (δ_{19} C 160.9, 160.5, and 160.4 ppm, respectively). Furthermore, introducing a mesityl rather than a phenyl substituent at C4 pronounces the highfield shift (δ_{19} 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_{19} 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 13C NMR frequencies with ligand donor properties.61

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_{aryl} bond is 2.061(4) Å, which is slightly shorter than in an analogue of 3b containing hexamethylbenzene rather than cymene as ancillary ligand,62 yet it is comparable to related [RuCl2(arenene)(NHC)] complexes.63 Also, the Ru–C_{triazole} distance to the cymene ligand is relatively short, 1.684(2) Å. The phenyl substituent is almost perpendicular to the heterocyclic carbone 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).

Scheme 1 Synthesis of triazolylidene ruthenium complexes 3.
characterized by two diagnostic doublets due to the cymene ligand ($\delta_1 5.12$ and 4.86 ppm), and a low-field $^{13}$C NMR resonance for the ruthenium-bound triazolylidene carbon at $\delta_1 160.5(\pm1)$ ppm.

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

Scheme 2 Synthesis of complexes 3k–m.

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 BrOH as a model substrate (Eq. 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 benzylic alcohol catalyzed by triazolylidene ruthenium complexes

<table>
<thead>
<tr>
<th>[Ru]</th>
<th>N$_{mes}$–R</th>
<th>C$_{mes}$–R</th>
<th>conv’n 1 h</th>
<th>conv’n 16 h</th>
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<tbody>
<tr>
<td>3a</td>
<td>Et</td>
<td>Bu</td>
<td>55%</td>
<td>87%</td>
</tr>
<tr>
<td>3b</td>
<td>Bu</td>
<td>Bu</td>
<td>45%</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>3c</td>
<td>Hex</td>
<td>Hex</td>
<td>55%</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>3d</td>
<td>Me</td>
<td>Ph</td>
<td>35%</td>
<td>55%</td>
</tr>
<tr>
<td>3e</td>
<td>Et</td>
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<td>74%</td>
</tr>
<tr>
<td>3f</td>
<td>Bu</td>
<td>Ph</td>
<td>57%</td>
<td>82%</td>
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<tr>
<td>3g</td>
<td>Bu</td>
<td>Mes</td>
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<td>84%</td>
</tr>
<tr>
<td>3h</td>
<td>Mes</td>
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<td>36%</td>
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<tr>
<td>3l</td>
<td>Et</td>
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<td>69%</td>
</tr>
<tr>
<td>3m</td>
<td>Bu</td>
<td>Ph</td>
<td>60%</td>
<td>79%</td>
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<tr>
<td>4</td>
<td>Hex</td>
<td>Hex</td>
<td>37%</td>
<td>95%</td>
</tr>
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</table>

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

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$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$

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$\text{RuCl}_2(N_3)(\text{Mes})$ $\text{RuCl}_3(PPh_3)_3$
toluene-d₈ solutions of 3e and 4 to 110 °C for 16 h in the absence of any substrate. Only traces of free cymene were noted from 3e (< 3%) while substantial benzene dissociation was identified by the diagnostic ²H NMR signal at δH 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 3e 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 3e was decreasing to 33% in an exponential decay, and proportionally, formation of free cymene was detected by the characteristic aliphatic signals at δH 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-d₈). 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. After 16 h, only benzaldehyde and free cymene were detectable with integrals that suggest quantitative conversion of BnOH and 3e, respectively (anisole as internal standard). During the initial stages of the reaction, two complexes were identified in addition to 3e in small concentrations (ca. 5% and 15% relative to 3e, 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 H₆ sym resonances, whereas the major species is symmetric and displays only two H₆ sym signals. Their relative ratio as well as their proportion to complex 3e remained approximately constant over the course of the reaction. Based on the gradual but consistent drift of the BnOH methylene signal from δH 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), while the symmetric species may feature a two-legged pianostool geometry including a triazolylidene and a chloride ligand only (A, Scheme 3). 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 3e by a BnOH ligand, mediated by AgBF₄, 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 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.

### Table 2 Conversions of different alcohols with catalyst precursor 3c

<table>
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<th>substrate</th>
<th>product</th>
<th>conversion</th>
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<tr>
<td>1</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>62%</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>38%</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>32%</td>
</tr>
<tr>
<td>4</td>
<td>MeO₂C₆H₄OH</td>
<td>MeO₂C₆H₄O</td>
<td>82%</td>
</tr>
<tr>
<td>5</td>
<td>MeO₂C₆H₄OH</td>
<td>MeO₂C₆H₄O</td>
<td>48%</td>
</tr>
<tr>
<td>6</td>
<td>PhCO₂C₆H₄</td>
<td>PhCO₂C₆H₄</td>
<td>67%</td>
</tr>
<tr>
<td>7</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>39% (37%)</td>
</tr>
<tr>
<td>8</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>66% (66%)</td>
</tr>
<tr>
<td>9</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>96% (81%)</td>
</tr>
<tr>
<td>10</td>
<td>C₆H₅OH</td>
<td>C₆H₅O</td>
<td>61% (60%)</td>
</tr>
</tbody>
</table>

* Conditions: alcohol (0.2 mmol), 3c (0.01 mmol, 5 mol%) toluene (2 mL), 110 °C, 16 h; † values in parenthesis obtained with complex 3b; ‡ isolated yield: 35%; § isolated yield: 47%.
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(R)(H) alcohol complex as rate-limiting step 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 C₉₋₂ – 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 ESL. The carbene ruthenium complexes 3b–3d 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 (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.

Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland; residual solvents were also identified by ¹H NMR spectroscopy.

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

To a solution of silver carbene 2 in CH₂Cl₂ (20 mL) was added [Ru(p-cymene)Cl₂]₂ (0.5eq). 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 CH₂Cl₂ and precipitated with Et₂O (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-cymene)Cl₂]₂ (105 mg, 0.17 mmol) in 16 h. The crude solid obtained after solvent evaporation was purified by column chromatography (SiO₂, CH₂Cl₂/acetone 3:1). The brown band was collected, concentrated to 2 mL and treated with cold Et₂O (50 mL), which induced the precipitation of 3a as a brown solid (135 mg, 83%). ¹H NMR (CDCl₃, 500 MHz): δ 5.53 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₁), 5.01 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₂), 4.70 (s, 2H, NCH₂CH₃), 3.98 (s, 3H, NCH₃), 2.97 (m, 2H, CH₃CH₂), 2.91 (sept. Jᵢ '= 7.0 Hz, 1H, CHMe₂), 2.02 (s, 3H, Cₐ₂–CH₂), 1.58 (m, 5H, NCH₂CH₃, Cₐ₂–CH₂CH₃), 1.47 (sext, Jᵢ '= 7.4 Hz, 2H, CH₂–CH₂CH₂CH₃), 1.28 (m, 3Jᵢ '= 7.0 Hz, 1H, CH–CH₃), 0.97 (t, Jᵢ '= 7.4 Hz, 3H, CH₃–CH₂CH₂CH₂CH₃), 13C{¹H} NMR (CDCl₃, 125 MHz): δ 161.2 (Cₐ˛–Ru), 147.6 (Cₐ₂–Ru), 147.5 (Cₐ–hex), 107.6, 97.5, 85.1, 82.6 (4 × Cₐ₂–Ru), 50.0 (NCH₃), 36.5 (NCH₃), 32.3 (Cₐ₂–CH₂), 30.9 (CHMe₂), 26.2 (Cₐ₂–CH₂CH₂), 23.3 (Cₐ₂–CH₂CH₂CH₂), 22.8 (CH–CH₃), 18.7 (Cₐ—CH₃), 16.3 (NCH₃), 14.1 (Cₐ₂–CH₂CH₂CH₂CH₃). No satisfactory elemental analysis could be obtained for this complex.

Complex 3b

According to the general method from silver carbene 2b (188 mg, 0.39 mmol) and [Ru(p-cymene)Cl₂]₂ (118 mg, 0.19 mmol) in 16 h. The crude solid was purified by column chromatography (SiO₂, CH₂Cl₂/acetone 3:1). The brown band was collected and concentrated to 2 mL. Addition of cold Et₂O induced the precipitation of 3c as a brown solid (184 mg, 74%). ¹H NMR (CDCl₃, 500 MHz): δ 5.53 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₁), 5.02 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₂), 4.59 (br, 2H, NCH₃), 3.97 (s, 3H, NCH₃), 2.96 (m, 2H, CH₃CH₂), 2.88 (m, 1H, CH₂hex), 1.33–1.28 (m, 16H, CH₂hex, CH–CH₃), 1.18 (t, Jᵢ '= 7.0 Hz, 6H, CH₂–CH₃), 1.58 (m, 5H, NCH₂CH₃, Cₐ₂–CH₂CH₃), 147.5 (Cₐ–hex), 107.2, 97.3, 85.2, 82.7 (4 × Cₐ₂–Ru), 54.9 (NCH₃), 36.5 (NCH₃), 31.8 (CHMe₂), 31.2, 30.9, 30.2, 29.2, 26.8, 26.6, 22.9, 22.8, 22.3 (9 × CH₃), 22.7 (CH–CH₃), 18.8 (Cₐ—CH₃), 14.3, 14.2 (2 × CH₃). Anal. Calcd for C₃H₃N₂Ru: 557.19 × 0.5 H₂O: 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-cymene)Cl₂]₂ (247 mg, 0.40 mmol) in 2 h. Yield: 154 mg (40%). ¹H NMR (CDCl₃, 500 MHz): δ 7.63 (m, 2H, Hₗ₃), 7.47 (m, 3H, Hₗ₄), 5.12 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₁), 4.86 (d, Jᵢ '= 5.9 Hz, 2H, Hₗ₂), 4.45 (s, 3H, NCH₃), 3.72 (s, 3H, NCH₃), 2.61 (sept, Jᵢ '= 6.9 Hz, 1H, CHMe₂), 1.86 (s, 3H, Cₐ₂–CH₂), 1.13 (m, Jᵢ '= 6.9 Hz, 6H, CH–CH₃), 13C{¹H} NMR (CDCl₃, 125 MHz): δ 160.9 (Cₐ˛–Ru), 148.6 (Cₐ₂–Ru), 131.9, 129.9, 128.7, 128.0 (4 × Cₐ₂–Ru), 104.9, 97.4, 84.2, (3 × Cₐ—CH₃), 42.6, 36.7 (2 × NCH₃), 30.6 (CHMe₂), 22.5 (CH–CH₃), 18.4 (Cₐ—CH₃). Anal. Calcd for C₉H₁₅N₂Ru: 549.40: 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-cymene)Cl₂] (95 mg, 0.16 mmol) in 2 h. Yield: 161 mg (99%). 1H NMR (CDCl₃, 500 MHz): δ 7.62 (m, 2H, Hₙₙ), 7.46 (m, 3H, H₃ₙ), 5.12 (d, 1J_HH = 5.8 Hz, 2H, H₃ₙ). 13C{¹H} NMR (CDCl₃, 125 MHz): δ 163.0 (C=O, Ru), 139.5, 135.3, 132.2, 130.4, 130.2, 130.0, 128.9, 128.5 (8 × C₆H₅), 107.1, 97.2, 88.9, 80.9 (4 × C₇H₇), 37.7 (NCH₃), 30.7 (CH₂C₇H₇), 22.7 (CH₂, C₇H₇), 21.4, 18.8 (2 × CH₂), 18.1 (CH₃C₇H₇). Anal. Calcd for C₂₅H₂₄Cl₄Ru (583.11): 0.55 Cl₂C₇H₇; 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-cymene)Cl₂] (52 mg, 0.09 mmol) in 16 h. Yield: 82 mg (77%). 1H NMR (CDCl₃, 500 MHz): δ 7.00 (s, 2H, Hₙₙ), 6.90 (s, 2H, H₃ₙ), 5.00 (d, 1J_HH = 5.9 Hz, 2H, H₃ₙ). 13C{¹H} NMR (CDCl₃, 125 MHz): δ 7.16 (7.0 Hz, 1H, CHMe). 1H NMR (CDCl₃, 400 MHz): δ 4.62 (d, 3J_HH = 5.9 Hz, 2H, H₃ₙ), 3.65 (s, 3H, NCH₃), 2.61 (sept, 1J_HH = 7.0 Hz, 1H, CHMe₂). 1H NMR (CDCl₃, 500 MHz): δ 7.30 (7.3 Hz, 1H, CHMe₂). 1H NMR (CDCl₃, 500 MHz): δ 2.85 (d, 1J_HH = 7.0 Hz, 1H, CHMe₂). 1H NMR (CDCl₃, 500 MHz): δ 2.76 (sept, 1J_HH = 7.0 Hz, 1H, CHMe₂). 1H NMR (CDCl₃, 500 MHz): δ 2.06 (s, 6H, ArCH₂). 1H NMR (CDCl₃, 500 MHz): δ 0.98 (t, 3J_HH = 7.4 Hz, 3H, CH₃CH₂CH₃).
Complex 4
In a one-pot reaction 1e (220 mg, 0.58 mmol), Ag3O (67 mg, 0.29 mmol) and [Ru(benzene)Cl2]2 (144 mg, 0.29 mmol) in CH2Cl2 (40 mL) were stirred at room temperature for 48 h and then filtered through Celite. The crude residue was purified by column chromatography (SiO2, CH2Cl2/acetone 3:1). The red band was collected and concentrated to 5 mL. Addition of cold Et2O induced the precipitation of 4 as a brown solid (110 mg, 38%).

Notes and references
For an example of two entries 1 in Table 2) suggests that the colloidal material is, or rapidly becomes, catalytically inactive.

Chemical shifts are for the minor species \( \delta_1 = 5.36, 5.13, 5.06, 5.00 \) (4 \( \times d, J_{HH} = 6 \text{ Hz}, 1H \)), major species: \( \delta_0 = 5.25, 4.90 \) (2 \( \times d, J_{HH} = 6 \text{ Hz}, 2H \)).


For an example of two-legged ruthenium arene systems, see: A. D. Phillips, K. Thommes, R. Scopolittì, C. Gandoiì, M. Albrecht, K.


(a) F. Bernardi, J. D. Scholten, G. H. Fecher, J. Dupont and J. Morais, Chem. Phys. Lett., 2009, 479, 113–116; (b) P. Lara, O. Rivada-Wheelerm, S. Conoêîro, R. Poteau, K. Philippot and B. Chaudret, Angew. Chem., Int. Ed., 2011, 50, 12080–12084; (c) the cessation of catalytic conversion at various points of reaction (cf entries 1-3 in Table 2) suggests that the colloidal material is, or rapidly becomes, catalytically inactive.