Carbohydrate-functionalized N-heterocyclic carbene Ru(II) complexes: synthesis, characterization and catalytic transfer hydrogenation activity†

Joseph P. Byrne, † Pauline Musembi and Martin Albrecht *

Three Ru complexes containing carbohydrate/N-heterocyclic carbene hybrid ligands were synthesized that were comprised of a triazolylidene coordination site and a directly linked per-acetylated glucosyl (5Glc) or galactosyl unit (5Gal), or a glycosyl unit linked through an ethylene spacer (6). Electrochemical and UV-vis analysis indicate only minor perturbation of the electronic configuration of the metal center upon carbohydrate installation. Deprotection of the carbohydrate was accomplished under basic conditions, which were stable in solution over several hours, but decomposed in the solid state. Complexes 5 and 6 were used as pre-catalysts for transfer hydrogenation of ketones under basic conditions, i.e. conditions that lead to in situ deprotection of the carbohydrate entity. The carbohydrate directly influences the catalytic activity of the metal center. Remotely linked carbohydrates (complex 6) induce significantly lower catalytic activity than directly linked carbohydrates (complexes 5Glc, 5Gal), while unfunctionalized triazolylidene are an order of magnitude more active. These observations and substrate variations strongly suggest that substrate bonding is rate-limiting for transfer hydrogenation in these hybrid carbohydrate/triazolylidene systems.

Introduction

N-Heterocyclic carbenes (NHCs) act as versatile ligands for various catalytic systems,1 as well as for biological and materials applications.2 Ruthenium complexes of NHCs, in particular, have shown a broad range of catalytic activity,3–6 with application in olefin-metathesis,7–9 transfer hydrogenation,10–18 as well as oxidation of alcohols and amines,19–23 and water.24 1,2,3-Triazolylidenes have emerged as a particularly promising subclass of NHC ligands that are stronger σ-donors than Arduengo-type imidazolylidenes and easily accessible through Cu(i)-catalyzed azide–alkyne cycloaddition (CuAAC) ‘click’ chemistry.25 Because of these characteristics, they have found widespread applications in catalysis.26,27 CuAAC chemistry has excellent compatibility with most functional groups due to the mild reaction conditions28,29 and consequently triazolones have become ubiquitous linkers for molecular components in various domains of (bio)chemistry, including materials science,30–32 medicinal33 and supramolecular chemistry,34–37 as well as peptide/carbohydrate functionalisation.38–42 This CuAAC synthetic methodology allows the introduction of natural chiral pool motifs such as carbohydrates into triazoles, and thereby facilitates the decoration of 1,2,3-triazolylidene NHCs with functional wingtip substituents.39

The introduction of carbohydrate substituents on the triazolylidene scaffold is particularly attractive as this approach introduces functional groups in close proximity to the metal active site. Such cooperation of ligand sites and the metal center has been demonstrated in so-called bifunctional catalysts, as introduced elegantly with Noyori-type catalysts containing an amide functionality,46–48 and Shvo’s catalyst featuring a proximal oxygen functionality.49,50 Bifunctional NHC ligands have shown promise in a range of catalytic transformations including hydrogenuations, giving rise to increased catalytic activities when compared to more classical analogs.13,17,21,51–55

The use of carbohydrate motifs in homogenous transition metal catalysts has attracted considerable attention, particularly for introducing chirality and water solubility. Several complexes with carbohydrate-based phosphine and phosphinite ligand scaffolds have shown excellent performance in asymmetric catalysis.56–58 Similar work with N-heterocyclic carbene...
ligands, however, is much more scarce.\textsuperscript{59,60} In pioneering work, Dyson and co-workers investigated the anticancer activity of Ru complexes of carbohydrate-functionalized NHC ligands,\textsuperscript{60,61} though only few examples have explored the catalytic activity of such carbohydrate–NHC hybrid complexes.\textsuperscript{8,22,62} Imidazolylidene systems functionalized with two carbohydrate wingtip groups, for example, induced up to 60\% ee in asymmetric Rh(1)-catalyzed hydroisilylation of ketones.\textsuperscript{62} We have demonstrated that deprotected carbohydrate substituents in NHC–Ir(III) complexes are beneficial for base-free alcohol and amine oxidation.\textsuperscript{22} Based on these results, we became interested in exploiting this ligand design motif for transfer hydrogenation.

Herein we report three novel Ru–triazolylidene complexes that incorporate carbohydrate functionality, including their photophysical and electrochemical properties as well as their catalytic activity in transfer hydrogenation of ketones, which revealed that complexes are efficiently deprotected \textit{in situ} under the basic catalytic conditions.

**Results and discussion**

**Synthesis and characterization**

Triazole precursors 1 were synthesized in moderate yields by the CuAAC reaction from 1-hexyne and acetyl-protected anomeric azide derivatives of glucose and galactose (Scheme 1).\textsuperscript{63} HRMS analysis (ESI+) confirmed formation of 1\textsubscript{Glc} and 1\textsubscript{Gal} by characteristic signals at \(m/z = 456.1985\) and 456.1980, respectively (\(m/z = 456.1977\) calculated for [M + H]+). Also, \(^1\text{H}\) NMR analysis showed the triazolyl CH resonance for both compounds 1\textsubscript{Glc} and 1\textsubscript{Gal} at 7.5 ppm. Importantly, only a single anomeric proton resonance was observed for each triazole as a doublet at \(\delta_H = 5.85\) and 5.81, respectively, each with a coupling constant of 9 Hz, which is consistent with stereoselective formation of \(\beta\)-anomers of the monosaccharide moiety. The remaining carbohydrate CH resonances differed between the glucose and galactose derivative, and the acetyl protecting groups appeared as four singlets between 1.7 and 1.3 ppm.

Glycosidation of peracetylated glucopyranose with 1-bromoethanol and subsequent S\textsubscript{N}2 reaction with NaN\textsubscript{3} according to literature procedures,\textsuperscript{64,65} yielded 1-azidoethyl-2,3,4,6-tetraacetylglucopyranoside, containing an ethylene spacer between the carbohydrate and azide functional groups. CuAAC of this azide with 1-hexyne (Scheme 1) yielded triazole 2, which gave a signal in HRMS analysis at \(m/z = 500.2236\), corresponding to [M + H]+ (calculated \(m/z = 500.2239\)). The triazolyl CH resonance appeared in the \(^1\text{H}\) NMR spectrum at 7.21 ppm and the anomeric proton resonance was much less deshielded than in the spectra of 1, appearing as a doublet at 4.40 ppm, which overlaps with a multiplet from the ethylene spacer. The anomeric coupling constant of 7.9 Hz is again consistent with a \(\beta\)-conformation.

Carbohydrate-triazole compounds 1 and 2 were alkylated with Meerwein’s reagent and isolated by precipitation from methanol to form triazolium salts 3\textsubscript{Glc}, 3\textsubscript{Gal} and 4 in high to quantitative yields. A diagnostic downfield shift of ca. 1 ppm of the triazole CH resonance was observed upon alkylation (\(\delta_H = 8.56, 8.50\) and 8.17, respectively) along with a new singlet corresponding to the triazolium \(N\) -methyl group. The anomeric proton resonances also shifted 0.2 – 0.4 ppm downfield. HRMS analysis revealed a M+ ion [M – BF\(_4\)]+ that is 14 amu higher than those of the corresponding triazole precursor [M + H]+ ions, indicative of successful methylation. These salts were used as ligand precursors without further purification.

Ruthenium(II) triazolylidene arene complexes 5 and 6 were synthesized from these triazolium salts \textit{via} the well-established\textsuperscript{25,66} transmetalation procedure using Ag\textsubscript{2}O and

![Scheme 1](image_url)
[RuCl₂(p-cym)]₂. The silver(i) carbene intermediate was not isolated, but its formation was monitored by disappearance of the triazolium CH resonance in the ¹H NMR spectrum and by HRMS analysis (m/z = 1045.3148 for [Ag(3Glc – H)₂]⁺). Isolation of the transmetalated ruthenium(II) complexes by flash chromatography provided microanalytically pure complexes 5 in good yields (60–80%), yet 6 in a only moderate 30% yield. Successful ruthenation was confirmed by HRMS analysis, showing signals for the [M – Cl]⁻ ion at m/z = 740.1885, 740.1886 and 784.2153, for 5Glc, 5Gal and 6, respectively. Complex formation was further supported via NMR analysis by the absence of the downfield ¹H resonance, corresponding to a 5Gal and 6 of the anomeric resonance upon ruthenation is negligible for bound to the 1,2,3-triazolylidene ligand. In contrast, the shift position upon complexation when the carbohydrate is directly field shift indicates electronic perturbation at the anomeric δ further deshielded by 0.5 ppm when compared to the triazolium precursors and significantly broadened, appearing at δ H 6.76 and 6.86 for 5Glc and 5Gal, respectively. This downfield shift indicates electronic perturbation at the anomeric position upon complexation when the carbohydrate is directly bound to the 1,2,3-triazolylidene ligand. In contrast, the shift of the anomeric resonance upon ruthenation is negligible for 6, which contains an ethylene spacer between the triazolylidene heterocycle and the carbohydrate unit. Moreover, complex 6 features two doublet resonances in the aromatic region due to the p-cymene ligand in the ¹H NMR spectrum, suggesting C₃ symmetry of the complex. In contrast, the p-cymene ligand is disymmetric in complexes 5Glc and 5Gal revealing four distinct resonances for the aromatic protons and two non-identical isopropyl CH₃ doublets at ca. 1.3 ppm for each complex. This splitting indicates restricted rotation about the Ru–CNC bond and hence a more rigid second coordination sphere imparted by the directly linked carbohydrate units.

The photophysical and electrochemical properties of 5Glc, 5Gal and 6 in MeCN solution were probed. UV-vis absorption spectra of both the new carbohydrate-derived complexes 5 show a strong absorption band at λ_max = 282 nm (ε 5700 M⁻¹ cm⁻¹) as well as a shoulder at 236 nm, both tentatively attributed to ligand-centered n–π*, π–π* transitions (Fig. 1a). In the spectrum of 6 an absorbance band at λ_max = 272 nm (ε 4500 M⁻¹ cm⁻¹) was observed. Additionally, all complexes feature a broad and weak charge transfer band between 300 and 500 nm, giving rise to the yellow-orange colour of the complexes.

Electrochemical analysis using cyclic voltammetry showed two oxidations for complex 5Glc, a quasi-reversible and presumably metal-based Ru²⁺/³⁺ process at E_{1/2} = +0.91 V vs. SCE and an irreversible oxidation at E_{pa} = +1.50 V (Fig. 1b, Table 1). 5Glc and 6 showed very similar behavior with only slight shifts of the oxidation potentials. These redox features are reminiscent to those of the known¹,⁶⁺⁺⁺ ruthenium complex [RuCl₂(cym)(trzBubBu)]⁺ 7 containing two n-butyl wingtip substituents (E_{1/2} = 0.91 V, E_{pa} = 1.4 V vs. SCE), indicating that the carbohydrate unit has no significant influence on the electron density at the ruthenium center, and that this unit is not redox active at these potentials.

**In situ** deprotection of 5Glc
Deprotection of the carbohydrate unit in complexes 5 and 6 is essential for exploiting the potential of the carbohydrate

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_max (nm) [ε (M⁻¹ cm⁻¹)]</th>
<th>E_{1/2} (V)</th>
<th>ΔE_p (mV)</th>
<th>E_{pa} (V)</th>
<th>E_{pc} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Glc</td>
<td>282 [5700], 236 (sh) [10 000]</td>
<td>0.91 [89]</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Gal</td>
<td>282 [5700], 236 (sh) [13 000]</td>
<td>0.96 [68]</td>
<td>1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>272 [4500]</td>
<td>0.92 [226]</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>272 [4000]</td>
<td>0.91 [178]</td>
<td>1.44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All measurements in MeCN, sh = shoulder. All potentials vs. SCE using Fc⁺/Fc as the internal standard (E_{1/2} = +0.40 V, ΔE_p = 72 mV), scan rate 100 mV s⁻¹, [NBu₄]PF₆ as the supporting electrolyte (0.1 mM). Peak potential of irreversible oxidation.

**Table 1.** UV-Vis spectroscopic, and electrochemical properties of complexes 5Glc, 5Gal, 6 and 7.

**Fig. 1.** (a) UV-Vis absorption spectra of 5Glc, 5Gal and 6 at room temperature in MeCN; and (b) cyclic voltammetry of 5Glc, 5Gal, 6, and 7 in MeCN solution, scan rate 100 mV s⁻¹, [NBu₄]PF₆ as the supporting electrolyte (0.1 mM), complexes at 0.5 mM except 5Glc (0.25 mM).
wingtip group for reductive catalytic processes and for promoting potentially bifunctional interactions involving the carbohydrate hydroxyl groups and the metal center. Such deprotection has been achieved only in a few specific cases.\(^{59,68,69}\) Recent results from our laboratory have demonstrated the decacylation of carbohydrate wingtip groups of iridium complexes in methanolic HCl.\(^{22}\) The ruthenium complexes 5 and 6, however, were not stable under these conditions and although deprotection was observed, simultaneous formation of significant amounts of free triazolium salt due to metal dissociation occurred. Acid-lability of Ru–triazolylidene bonds has been established by Grubbs, Bertrand, and co-workers in olefin methathesis catalysis.\(^7\) The Ru triazolylidene complexes were also not stable to conventional Zemplén deprotection conditions using methanolic NaOMe.\(^{70}\) However, stability tests of complex 5Glc under typical transfer hydrogenation conditions, i.e. KOH in iPrOH (20 mM) revealed rapid deprotection, which was accompanied by a color change of the reaction solution from orange to yellow (Scheme 2). Deprotection and formation of 8Glc was also accomplished in D\(_2\)O using 10 equiv. KOH and was confirmed by a HRMS (ESI\(^+\)) signal at \(m/z = 536.1684\), corresponding to [M – \(2\)Cl – H\(^+\)]. Moreover, \(^1\)H NMR analysis in D\(_2\)O showed the coalescence of the four distinct acetate signals of 5Glc into a single resonance consistent with the formation of KOAc (see ESI, Fig. S19†). In addition, the C\(^1\)–C\(^5\) carbohydrate ring proton resonances are shifted upfield upon deprotection. The asymmetry of the p-cymene ligand is retained, as indicated by two distinct isopropyl methyl signals at 1.13 and 1.29 ppm. Analogous results were observed for 5Gal, suggesting wider applicability of this method.

The deprotected complex 8Glc was not isolated as a pure solid since it displayed instability over the course of several hours upon drying. In addition, substantial amounts of degradation products were detected by \(^1\)H NMR spectroscopy over the course of 24 h when kept in either D\(_2\)O or (CD\(_3\))\(_2\)CDOD solution. Consequently, the more robust protected complexes 5 were used as pre-catalysts and complexes 8 were generated by \textit{in situ} deprotection in the course of transfer hydrogenation catalysis.

**Transfer hydrogenation catalysis**

To assess the suitability of the carbohydrate-functionalized carbene ruthenium complexes as pre-catalysts for base-promoted transfer hydrogenation of ketones, a model reaction with benzophenone was carried out under standard conditions,\(^{43}\) \textit{i.e.}, refluxing iPrOH as hydrogen source, KOH as activator, 100 : 10 : 1 substrate/base/catalyst ratio. For both 8Glc and 8Gal, both generated \textit{in situ} from the acetate-protected precursors 5Glc and 5Gal, respectively, the reaction proceeded to completion within 8 h, forming diphenylmethanol as the exclusive product (Table 2, entries 1 and 2). The results for both glucose- and galactose-derivatives were essentially identical, suggesting little influence of the remote carbohydrate C4 configuration and hence no relevance of a chair conformation of the pyranose ring.\(^{71}\) Complex 6 featuring an ethylene spacer between the triazolylidene and carbohydrate units showed decreased activity as pre-catalyst for the model reaction, when compared to those complexes with the carbohydrate directly linked to the triazolylidene, reaching only 57% within 8 h and incomplete conversion even after 24 h (84%, entry 3). In contrast, the unfunctionalized complex 7 generates a considerably faster catalyst and reaches completion in less than 2 h (TOF\(_{50} = 310\) h\(^{-1}\)). These differences point to a direct catalytic relevance of the carbohydrate functionality, either through chelation or through stabilization of substrates or intermediates within the catalytic cycle. The location of the carbohydrate is critical and proximal oxo functionalities are less inhibiting than the more remote functional group in complex 6.

Transfer hydrogenation of benzophenone by 5Glc was not impeded by elemental mercury. Thus, addition of Hg (0.2 g, ca. 1 mmol, 100 molequiv relative to Ru) after 2 h when the reaction has reached 34% substrate conversion proceeded to full conversion (entry 5). The initial decrease of activity was attributed to mass transfer limitations induced by the mercury drop. The preservation of catalytic activity supports a homogeneous catalyst as active species rather than significant dissociation of the triazolylidene ligand and formation of a heterogeneous layer as catalytically active phase.

Since the triazolylidene ligand is robustly coordinated to the ruthenium center, transfer hydrogenation allows for evaluating the asymmetric induction of the stereochemically well-defined carbohydrate functionality by using prochiral ketones. Similar carbohydrate-based ligands have previously been shown to be effective in asymmetric catalysis,\(^{58,62,72–75}\) including hydrosilylation of ketones.\(^{62}\) The enantioselectivity of 5Glc was probed with acetonophene as prochiral substrate for transfer hydrogenation (entry 6). The reaction proceeded at a lower rate than with benzophenone (TOF\(_{50} = 10\) vs. 20 h\(^{-1}\)), reaching 66% conversion after 8 h and full conversion after 24 h. Product analysis by chiral gas chromatography revealed negligible enantioselectivity (<2%, see ESI, Fig. S28†), indicating that chiral information from the carbohydrate wingtip group is not transferred to the substrate under these conditions. Modification of the chiral pocket and enhanced enantioselectivity may be induced through variation of the carbohydrate, drawing on the vast pool of pyranose and ribose structures present in nature.

In order to investigate electronic and steric influences on substrate reactivity as well as functional group tolerance, a small substrate scope was carried out with derivatives of

*Scheme 2* Synthesis of 8Glc by base-mediated deprotection of 5Glc.

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Dalton Trans., 2019, 48, 11838–11847 | 11841
benzophenone and acetophenone using 5Glc as pre-catalyst (entries 7–13). Using sterically more demanding 2-methylacetophenone as substrate in place of acetophenone led to a modest increase in activity (TOF50 = 13, entry 7). Very little variation of activity was noted when using electronically distinct substrates. For example, conversion of electron-withdrawing 4-bromoacetophenone (σp = +0.23, TOF50 = 8 h−1) and electron-donating 4-methoxyacetophenone (σp = −0.27, TOF50 = 7 h−1) was essentially identical (entries 8 and 9). Notably, neither substrate achieved full conversion after 24 h and thus proved less suitable than unsubstituted acetophenone. 4-Bromobenzophenone showed similar activity (TOF50 = 11, entry 10), implying a markedly decreased performance with respect to the unsubstituted benzophenone. Under the same conditions, benzaldehyde was not converted to the corresponding alcohol. Alcohol and amine substituents markedly inhibited catalytic activity and ketones with these functional groups reached conversions of only 10 and 15%, respectively after 8 h (entries 11 and 12). In contrast, di(2-pyridyl)ketone was converted much faster than benzophenone (TOF50 = 60 vs. 20 h−1, entry 13). This substrate scan suggests a few features of the catalytic transfer hydrogenation induced by 8Glc. First, the lack of influence of electronic substituent effects on the turnover frequency indicates that the rate-limiting step is not associated with substrate conversion. Moreover, the decrease of the rate for the conversion of substituted substrates, in particular in para position, hints to a steric bias and the requirement of sufficient space around the metal center for turnover to proceed. This observation renders β-hydrogen elimination from coordinated isopropoxide unlikely as rate-limiting step, as this step would be substrate-independent and lead to equal rates. Instead, these data suggest instead that substrate coordination is rate-limiting, a step that is obviously a function of the carbohydrate with the substrate. Substrate coordination may also involve decoordination of potentially chelating carbo-

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Substrate</th>
<th>Conversionb (%)</th>
<th>TOF50c (h−1)</th>
<th>σp d</th>
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<tbody>
<tr>
<td>1</td>
<td>5Glc</td>
<td>98</td>
<td>&gt;98</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5Gal</td>
<td>&gt;98</td>
<td>&gt;98</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>57</td>
<td>84</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>&gt;98</td>
<td>&gt;98</td>
<td>310</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>5Glc</td>
<td>66</td>
<td>98</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>5Glc</td>
<td>74</td>
<td>98</td>
<td>13</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>5Glc</td>
<td>56</td>
<td>75</td>
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<tr>
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<td>5Glc</td>
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<tr>
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<td>5Glc</td>
<td>15</td>
<td>31</td>
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<tr>
<td>12</td>
<td>5Glc</td>
<td>97</td>
<td>&gt;98</td>
<td>60</td>
<td>—</td>
</tr>
</tbody>
</table>

a General reaction conditions: Ru complex (0.01 mmol), substrate (1.0 mmol), KOH (0.05 mL, 2 M, 0.1 mmol), 2-propanol (5 mL) at reflux. 

b Determined by 1H NMR analysis. 

c TOF50 (mol product)/(mol pre-catalyst) at 50% conversion. 

d Hammett parameter of aryl para-substituent. 

e Elemental Hg (ca. 1 mmol) added after 2 h.
to exploit their beneficial properties as well as by modulation of the carbohydrate entity using transfer such as oxidations or hydrogen borrowing processes, or the formation of carbene complexes. This prominent role of the carbohydrate functionality has a profound impact on catalytic activity in transfer hydrogenation of ketones. Directly transferring hydrogen to remote sites is possible using soft pyridyl coordinating ligands which is even more diﬃcult to be displaced by the carbonyl group for catalytic turnover (entries 11 and 12).

Conclusions

We have successfully synthesized and characterized new carbohydrate–NHC Ru complexes. Deprotection of acetylated carbohydrate unit on the ruthenium complex was achieved in situ under basic conditions in protic solvents without aﬀecting the Ru–triazolylidene bond and aﬀording the ﬁrst example of an unprotected carbohydrate–NHC system with Ru. This method provides access to hydroxy-functionalized carbene complexes, even though their isolation is compromised by stability issues. The carbohydrate functionality has a profound impact on catalytic activity in transfer hydrogenation of ketones. Directly transferring hydrogen to remote sites is possible using soft pyridyl coordinating ligands which is even more diﬃcult to be displaced by the carbonyl group for catalytic turnover (entries 11 and 12).

Experimental section

General

Unless otherwise stated, all reagents were obtained from commercial suppliers and used as received. Carbohydrate azide precursors were prepared according to modiﬁed literature procedures. 

General synthesis of triazoles

Acetylated pyranosyl azide (1 000 g, 2.68 mmol) and 1-hexyne (0.31 mL, 2.7 mmol) were reacted in the presence of CuSO4·5H2O (0.270 g, 1.07) and sodium ascorbate (0.530 g, 2.68 mmol) in tert-butanol–water mixture (1:1, 20 mL), at room temperature for 3 days. The reaction mixture was diluted with EDTA (20 mL, 0.2 M in 1.0 M NaH2O2 solution) and extracted into CH2Cl2 (3 × 20 mL). The organic layers were combined, washed with brine, dried over MgSO4 and ﬁltered through Celite, yielding a white solid (1) or yellow oil (2).

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-butyl-1,2,3-triazole (1Glc). Yield: 0.512 g, (42%). Anal. calcd for C20H29N3O9Na+ [M + Na]+: C 52.74, H 6.42, N 9.23%; found C 53.09, H 6.83, N 8.86%. HRMS (m/z) [ESI+]: Calculated for C20H29O9N3Na+: M + Na+] m/z = 456.1977; found m/z = 456.1985. 1H NMR (CDCl3, 400 MHz): δ = 0.93 (t, 3H, JHH = 7.5 Hz, butyl CH3), 1.31–1.41 (m, 2H, butyl CH3), 1.61–1.73 (m, 2H, butyl CH3), 1.87, 2.03, 2.07, 2.08 (4 × s, 3H, C(O)CH3), 2.72 (t, 2H, JHH = 7.5 Hz, CtrzCH2), 3.99 (ddd, 1H, JHH = 9.0, 5.1, 2.1 Hz, glucosyl C1H), 4.14 (dd, 1H, JHH = 2.1 Hz, JHH = 12.6 Hz, glucosyl C2H), 4.30 (dd, 1H, JHH = 5.1 Hz, JHH = 12.6 Hz, glucosyl C3H), 5.23 (app t, 1H, glucosyl C4H), 5.34–5.49 (m, 2H, glucosyl C5H and C6H), 5.81 (d, 1H, JHH = 9.0 Hz, glucosyl C7H), 7.51 (s, 1H, CtrzH). 13C{1H} NMR (CDCl3, 100 MHz): δ = 13.9 (butyl CH3), 20.3, 20.66, 20.69, 20.8 (4 × C(O)CH3), 22.3 (butyl CH3), 25.3 (butyl CH3), 31.3 (CtrzCH2), 61.7 (glucosyl C7H), 67.9, 70.4, 72.9, 75.3 (4 × glucosyl C2H), 83.5 (glucosyl C8H), 119.0 (CtrzH), 149.5 (Ctrz–Bu), 169.1, 169.5, 170.0, 170.6 (4 × C=O), FT-IR (ATR, cm−1): 3070 (w), 2928 (w), 2357, 1746 (s, C=O), 1436, 1436, 1216 (s), 1094, 1041 (s), 928.

1-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-4-butyl-1,2,3-triazole (1Gal). Yield: 0.560 g (46%). Anal. calcd for C20H30O9N3Na+: M + Na+) m/z = 478.1976; found m/z = 478.1999. 1H NMR (CDCl3, 400 MHz): δ = 0.94 (t, 3H, JHH = 7.4 Hz, butyl CH3), 1.30–1.42 (m, 2H, butyl CH3), 1.62–1.71 (m, 2H, butyl CH3), 1.88, 2.01, 2.05, 2.22 (4 × s, 3H, C(O)CH3), 2.73 (t, 2H, JHH = 7.4 Hz, CtrzCH2), 4.11–4.24 (m, 3H, galactosyl C5H and C6H, 5.23 (dd, 1H, JHH = 10.3, 3.3 Hz, galactosyl C7H), 5.50–5.61 (m, 2H, galactosyl C8H and C9H), 5.81 (d, 1H, JHH = 9.3 Hz, galactosyl C10H), 7.55 (s, 1H, CtrzH). 13C{1H} NMR (CDCl3, 100 MHz): δ = 13.8 (butyl CH3), 20.2, 20.5, 20.63, 20.64 (4 × C(O)CH3), 22.2 (butyl CH3), 25.3 (butyl CH3), 31.3 (CtrzCH2), 61.2 (galactosyl C7H), 66.9, 67.8, 70.9, 74.0 (galactosyl C8H), 86.2 (galactosyl C9H), 118.8 (CtrzH), 149.2 (Ctrz–Bu), 169.1, 169.8, 169.9, 170.3 (4 × C=O), FT-IR (ATR, cm−1): 2958 (w), 2929 (w), 2914 (s), 1743 (s, C=O), 1369, 1218 (s), 1044 (s), 923.

1-(2,4-(Butyl-1,2,3-triazol-1-yl)ethoxy)-1-deoxy-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (2). The product was prepared according to the general procedure from 2,3,4,6-tetra-O-acetyl-1-azido-2-deoxy-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (1.25 g, 2.99 mmol), yielding 2 as a pale yellow oil (1.335 g, 89%), which was used without further puriﬁcation. Gradient flash chromatography (SiO2; CH2Cl2 to CH2Cl2/CH3OH 95 : 5) was used to obtain the product as an off-white hygroscopic solid. HRMS (m/z) [ESI+]: Calculated for C23H31N3O10m/z = 500.2239 [M + H]+; found m/z = 500.2236. 1H NMR (300 MHz, CDCl3): δ = 0.92 (t, 3H, JHH = 7.3 Hz, butyl CH3), 1.31–1.48 (m, 2H, butyl CH3), 1.57–1.72 (m, 2H, butyl CH2), 1.93, 1.98, 2.00, 2.07 (4 × s, 3H, C(O)CH3), 2.56–2.80 (m, 2H, butyl CH2).
2H, butyl CH$_2$), 3.68 (ddd, 1H, $^3$J$_{H,H}$ = 10.0, 4.8, 2.4 Hz, glucosyl C$_4^H$), 3.90 (ddd, 1H, $^1$J$_{H,H}$ = 10.4 Hz, $^3$J$_{H,H}$ = 8.5, 3.4 Hz, ethylene CH$_2$F), 4.06–4.29 (m, 3H, ethylene CH$_2$ + glucosyl C$_6^H$), 4.39–4.59 (m, 2H, ethylene CH$_2$), 4.46 (d, 1H, $^3$J$_{H,H}$ = 7.9 Hz, glucosyl C$_3^H$), 4.98 (dd, 1H, $^1$J$_{H,H}$ = 9.5, 7.9 Hz, glucosyl C$_3^H$), 5.05 (dd, 1H, $^3$J$_{H,H}$ = 10.0, 9.5 Hz, glucosyl C$_4^H$), 5.16 (t, 1H, $^3$J$_{H,H}$ = 9.5 Hz, glucosyl C$_3^H$), 7.31 (s, 1H, C$_{5^H}$).$^{13}$C(NMR) (75 MHz, CDCl$_3$); $\delta$ = 13.8 (butyl CH$_3$), 20.5, 20.5, 20.7, 20.7 (4 × C(O)CH$_3$), 22.3, 25.4, 31.5 (3 × butyl CH$_3$), 49.8 (CH$_3$), 61.8 (CH$_3$), 68.3, 71.0, 72.0, 72.5 (glucosyl C$_5^2$H$_2$), 100.6 (glucosyl C$_1^H$), 122.0 (C$_{5^H}$), 148.3 (C$_{5^H}$–Bu), 169.2, 169.4, 170.1, 170.5 (4 × C=O); FT-IR (ATR, cm$^{-1}$): 2935 (w), 1744 (s, C=O), 1432, 1365, 1211 (s), 1032 (s), 907.

**General synthesis of triazolium salts**

The triazole compound (0.44 mmol) and Me$_3$OBF$_4$ (0.067 g, 0.45 mmol) were dissolved in dry CH$_2$Cl$_2$ (30 mL) and stirred at room temperature for 16 h. Then MeOH (0.5 mL) was added and stirring continued for 30 min. All volatiles were evaporated under reduced pressure. The residue was dissolved in a minimum of MeOH and stored at −20 °C, yielding the triazolium salt as a white solid. 3Gal and 4 were hygroscopic and were therefore used without further purification.

**1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-butyl-3-methyl-1,3,3-triazol-1-ium tetrafluoroborate (3Glc).** According to the general procedure, reaction of 1Glc (0.200 g, 0.44 mmol) and Me$_3$OBF$_4$ (0.067 mg, 0.45 mmol) yielded 3Glc (0.240 g, 98%). Anal. calc. for C$_{31}$H$_{45}$N$_3$O$_9$RuCl$_2$ [M + BF$_4$]$^-$; m/z = 540.1313; found m/z = 540.1314.

**General synthesis of Ru(n) complexes**

The triazolium salt (0.43 mmol), Ag$_2$O (0.060 g, 0.26 mmol) and Me$_3$NCl (0.057 g, 0.52 mmol) were suspended in dry CH$_2$CN (50 mL) and stirred in the absence of light at room temperature for 5 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (25 mL), filtered through Celite and concentrated under reduced pressure. CH$_2$Cl$_2$ (20 mL) and [Ru(p-cym)$_2$Cl$_2$]$_2$ (0.099 g, 0.16 mmol) were added and the mixture was stirred for 3 h. The reaction mixture was cooled in an ice bath, filtered through Celite, and evaporated to dryness. The red residue was purified by gradient flash chromatography (SiO$_2$: CH$_2$Cl$_2$ to CH$_2$Cl$_2$/acetone 9:1).

**Ru complex 5Glc**

From 3Glc (0.240 g) according to the general procedure, 5Glc was obtained (0.189 g, 80%). Anal. calc. for C$_{31}$H$_{45}$N$_3$O$_9$RuCl$_2$ (775.683 g mol$^{-1}$): C 48.00, H 5.85, N 5.42%; found C 48.06, H 5.39, N 5.84%. HRMS (m/z) (ESI$^+$): Calculated for C$_{31}$H$_{45}$N$_3$O$_9$RuCl$_2$ $^+$ [M + Cl]$^+$; m/z = 174.1882; found m/z = 174.1885. $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 8.11 (d, 1H, $^3$J$_{H,H}$ = 10.5 Hz, butyl CH$_3$), 1.28, 1.31, 1.34, 1.36 (4 × butyl CH$_3$), 88.1 (galactosyl C$_{5^H}$), 128.6 (C$_{5^H}$), 145.8 (C$_{5^H}$–Bu), 169.6, 169.8, 169.9, 170.7 (4 × C=O); FT-IR (ATR, cm$^{-1}$): 2995 (w), 2848(w), 1744 (s, C=O), 1435, 1369, 1218 (s), 1034 (s, br, BF$_4$).
C(O)CH₃), 2.88–3.08 (m, 3H, butyl CH₂ + CHMe₂), 3.97–4.09 (m, 4H, NCH₃ + glucosyl C₂H), 4.12–4.27 (m, 2H, glucosyl C₂H₃), 5.00 (d, 1H, 3J₁H-H = 5.8 Hz, C₆H₃), 5.14–5.26 (m, 2H, Ccym-H + glucosyl C₂H), 5.30–5.43 (m, 2H, CHcym + glucosyl C₂H), 5.53 (d, 1H, 3J₁H-H = 5.8 Hz, Ccym-H), 6.01 (t, 1H, 3J₁H-H = 9.4 Hz, glucosyl C₂H), 6.76 (br s, 1H, glucosyl C₂H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 14.0 (butyl CH₃), 18.8 (cym-CH₃), 20.71, 20.74, 20.97, 21.12 (4 × C(O)CH₃), 22.27, 23.0 (2 × CH-CH₂), 23.2 (butyl CH₂), 26.3 (butyl CH₂), 30.8 (CHMe₂), 31.8 (butyl CH₂), 37.3 (NCH₃), 62.3 (glucosyl C₂H₆), 68.3 (glucosyl C₂H₇), 70.1 (glucosyl C₂H₇), 74.1 (glucosyl C₆H₃), 74.5 (glucosyl C₂H₇), 80.7, 81.9, 86.3, 86.8 (4 × Ccym-H), 87.1 (glucosyl C₂H₇), 97.6 (Ccym), 108.3 (Ccym), 148.0 (Ctrz-Ru), 161.7 (Cirz-Ru), 169.2, 169.6, 170.1, 170.5 (4 × C═O); FT-IR (ATR, cm⁻¹): 2957 (w), 1747 (s, C═O), 1433, 1365, 1212 (s), 1032, 972.

**Ru complex 5Gal**

From 3Gal (0.223 g) according to the general procedure, 5Gal was obtained (0.138 g, 60%). Anal. calcld for C₃₁H₄₅N₃O₉RuCl₂ (775.683 g mol⁻¹): C 48.00, H 5.85, N 5.42%; found C 47.37, H 5.89, N 5.42%. HRMS (m/z) (ESI⁺): Calculated for C₃₁H₄₅N₃O₉RuCl₂·(H₂O) (837.751 g mol⁻¹): [M+H]⁺; found [M+H]⁺ = 784.2144 [M+H]⁺; found [M+H]⁺ = 784.2153. ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, 3H, 3J₁H-H = 7.2 Hz, butyl CH₃), 1.30, 1.33 (2 × d, 3H, 3J₁H-H = 6.9 Hz, CHcym), 1.40–1.55 (m, 2H, butyl CH₂), 1.60–1.90 (br s, 2H, butyl CH₂), 1.92 (s, 3H, C(O)CH₃), 1.97 (s, 3H, cym-CH₃), 1.99, 2.02, 2.23 (3 × s, 3H, C(O)CH₃), 2.85–3.14 (m, 4H, butyl CH₂ + CHMe₂), 4.08 (s, 3H, NCH₃), 4.11–4.28 (m, 3H, galactosyl C₂H + C₆H₃), 4.97 (d, 1H, 3J₁H-H = 5.8 Hz, Ccym-H), 5.15–5.26 (m, 2H, Ccym-H + galactosyl CH), 5.37 (d, 1H, 3J₁H-H = 5.8 Hz, Ccym-H), 5.46–5.63 (m, 2H, Ccym-H + galactosyl CH), 6.17 (t, 1H, 3J₁H-H = 9.7 Hz, galactosyl C₂H₃), 6.86 (br s, 1H, 1H, 3J₁H-H = 6.8 Hz, CHcym). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 14.0 (butyl CH₃), 18.8 (cym-CH₃), 20.6, 20.90, 20.92, 21.26 (4 × C(O)CH₃), 22.4 (CHMe₂), 23.2 (butyl CH₂), 26.3 (CHMe₂), 31.1 (butyl CH₂), 31.8 (butyl CH₂), 37.2 (NCH₃), 62.1 (galactosyl C₂H₆), 67.5 (galactosyl C₂H₇), 68.4 (galactosyl C₂H₇), 72.1 (galactosyl C₂H₇), 73.7 (galactosyl C₆H₃), 80.7, 81.9, 86.0, 87.0 (4 × Ccym-H), 87.6 (galactosyl C₂H₇), 98.1 (Ccym), 108.3 (Ccym), 148.0 (Cirz-Ru), 161.7 (Cirz-Ru), 169.5, 169.9, 170.27, 170.28 (4 × C═O); FT-IR (ATR, cm⁻¹): 2956 (w), 1748 (s, C═O), 1361, 1216 (s), 1051, 921.

**In situ deprotection of 5Glc**

Complex 5Glc (4 mg, 5 μmol) was dissolved in D₂O (0.5 mL) and KOH (0.2 M in D₂O, 0.05 mL, 0.05 mmol) was added, which induces an immediate color change from orange to yellow. HRMS (m/z) (ESI⁺): Calculated for C₃₃H₄₉N₃O₁₀RuCl⁺ (536.1704 [M - 2Cl - H]⁺); found m/z = 536.1684. ¹H NMR (300 MHz, D₂O): δ = 1.13 (d, 3H, 3J₁H-H = 6.8 Hz, CHcym), 1.21 (t, 3H, 3J₁H-H = 6.9 Hz, butyl CH₃), 1.29 (d, 3H, 3J₁H-H = 6.8 Hz, CHcym), 1.61–2.10 (m, 4H, butyl CH₂), 2.08 (s, 12H, CH₂COOK) 2.24 (s, 1H, cym-CH₃), 2.52–2.72 (m, 1H, CHcym), 2.95–3.20 (m, 2H, butyl CH₂), 3.47–3.60 (m, 1H, glucosyl CH), 3.60–3.76 (m, 2H, glucosyl CH), 3.76–4.03 (m, 2H, glucosyl CH), 4.15 (d, 1H, J = 10.7 Hz, glucosyl C₂H₇), 4.35 (s, 3H, NCH₃), 5.04–5.13 (m, 1H, Ccym-H), 5.23 (d, 1H J = 8.2 Hz, glucosyl C₂H₇), 5.45 (d, 1H, 3J₁H-H = 6.1 Hz, Ccym-H), 5.77 (d, 1H, 3J₁H-H = 5.7 Hz, Ccym-H), 5.82 (d, 1H, 3J₁H-H = 5.7 Hz, Ccym-H).

**General procedure for transfer hydrogenation catalysis**

The Ru complex (0.01 mmol) was dissolved in iPrOH (5 mL) and aqueous KOH was added (2 M, 0.05 mL, 0.10 mmol). Hexamethylenzene was added as an internal standard. The solution was heated to reflux for 20 min, then the ketone (1.00 mmol) was added and stirring at reflux was continued. Aliquots of the reaction mixture were sampled at given times and analyzed by diluting into CDCl₃ and measuring ¹H NMR spectra to monitor reaction progress.

**Conflicts of interest**

There are no conflicts to declare.

**Funding sources**

We acknowledge generous support from the European Commission for a Marie Skłowska Curie Individual Fellowship to J. P. B. (Grant 749549) and from the European Research Council (CoG 615653), as well as the Swiss-European Mobility Programme for a visiting fellowship for P. M. to Bern.

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