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

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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 to afford complexes that 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 triazolylidenes 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(ɪ)-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 conditions[28,29] and consequently triazoles have become ubiquitous linkers for molecular components in various domains of (bio)chemistry, including materials science,[30–32] medicinal[33] 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.[26,43–45]

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 hydrogenations, giving rise to increased catalytic activities when compared to more classical analogs.[13,17,23,51–55]

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

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ligands, however, is much more scarce.[59,60] In pioneering work, Dyson and co-workers investigated the anticancer activity of Ru complexes of carbohydrate-functionalized NHC ligands,[60,61] though only few examples have explored the catalytic activity of such carbohydrate–NHC hybrid complexes.[8,22,62] Imidazolylidene systems functionalized with two carbohydrate wingtip groups, for example, induced up to 60% ee in asymmetric Rh(I)-catalyzed hydrosilylation of ketones.[62] We have demonstrated that deprotected carbohydrate substituents in NHC–Ir(III) complexes are beneficial for base-free alcohol and amine oxidation.[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 *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).[63] HRMS analysis (ESI+) confirmed formation of **1Glc** and **1Gal** by characteristic signals at m/z = 456.1985 and 456.1980, respectively (m/z = 456.1977 calculated for $[M + H]^+$). Also, ^{1}H NMR analysis showed the triazolyl CH resonance for both compounds **1Glc** and **1Gal** at 7.5 ppm. Importantly, only a single anomeric proton resonance was observed for each triazole as a doublet at δ_H 5.85 and 5.81, respectively, each with a coupling

constant of 9 Hz, which is consistent with stereoselective formation of β-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-bromo-ethanol and subsequent S_N2 reaction with NaN_3 according to literature procedures,[64,65] yielded 1-azidoethyl-2,3,4,6-tetra-acetylglucopyranoside, 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}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 β-conformation.

Carbohydrate-triazole compounds **1** and **2** were alkylated with Meerwein's reagent and isolated by precipitation from methanol to afford triazolium salts **3Glc**, **3Gal** and **4** in high to quantitative yields. A diagnostic downfield shift of *ca.* 1 ppm of the triazole CH resonance was observed upon alkylation (δ_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 *via* the well-established[25,66] transmetalation procedure using Ag_2O and
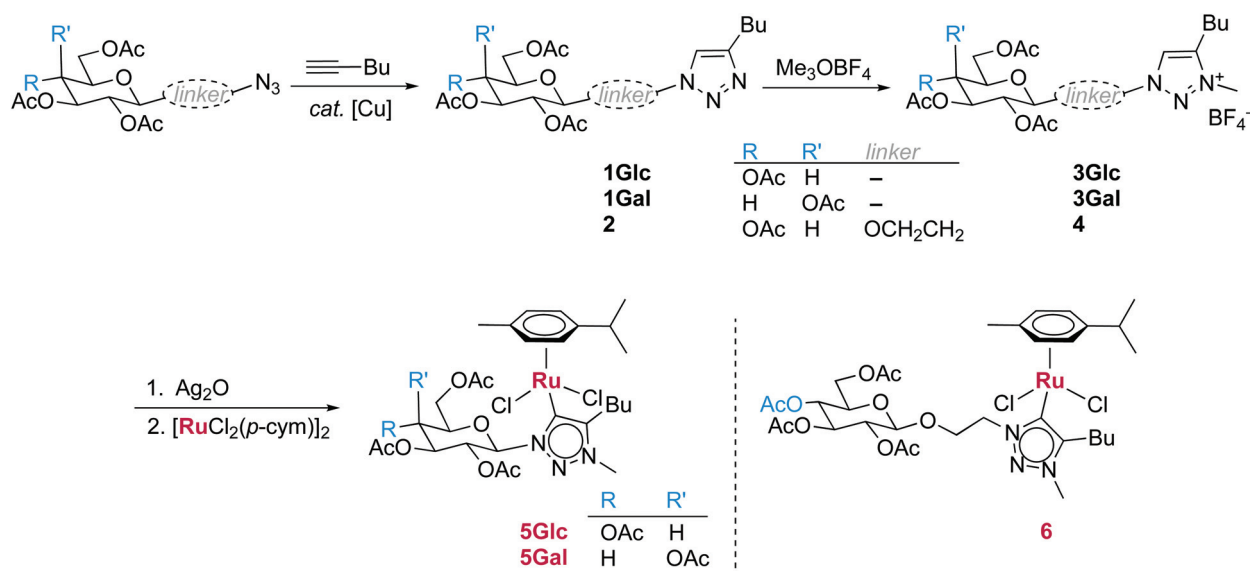
Scheme 1 Synthesis of complexes **5Glc**, **5Gal** and **6**.

[RuCl$_2$(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 ^{1}H 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 ^{1}H resonance, corresponding to a triazolium CH group in the ligand precursor, and a characteristic[14] carbenic ^{13}C resonance at 167 ppm (**5**) or 163 ppm (**6**). The anomeric proton resonances in the spectra of **5** were further deshielded by 0.5–0.7 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 ^{1}H NMR spectrum, suggesting C_s symmetry of the complex. In contrast, the *p*-cymene ligand is dissymmetric in complexes **5Glc** and **5Gal** revealing four distinct resonances for the aromatic protons and two non-identical isopropyl CH$_3$ doublets at *ca.* 1.3 ppm for each complex. This splitting indicates restricted rotation about the Ru–C$_{NHC}$ 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 Ru$^{2+/3+}$ process at $E_{1/2}$ = +0.91 V *vs.* SCE and an irreversible oxidation at E_{pa} = +1.50 V (Fig. 1b, Table 1). **5Gal** and **6** showed very similar behavior with only slight shifts of the oxidation potentials. These redox features are reminiscent to those of the known[14,67] ruthenium complex [RuCl$_2$(cym)(trz^{BuBu})] **7** containing two *n*-butyl wingtip groups as triazolylidene 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 1 UV-Vis spectroscopic, and electrochemical properties of complexes **5Glc**, **5Gal**, **6** and **7**^{a}

Complex	λ_{max} (nm) [ε (M^{-1} cm^{-1})]	$E_{1/2}$ (V) [ΔE_p (mV)]^b	$E_{pa}{}^c$ (V)
5Glc	282 [5700], 236 (sh) [10 000]	0.91 [89]	1.50
5Gal	282 [5700], 236 (sh) [13 000]	0.96 [68]	1.52
6	272 [4500]	0.92 [226]	1.45
7	272 [4000]	0.91 [178]	1.44

^{a} All measurements in MeCN, sh = shoulder. ^{b} 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}, [NBu$_4$]PF$_6$ as the supporting electrolyte (0.1 mM). ^{c} Peak potential of irreversible oxidation.
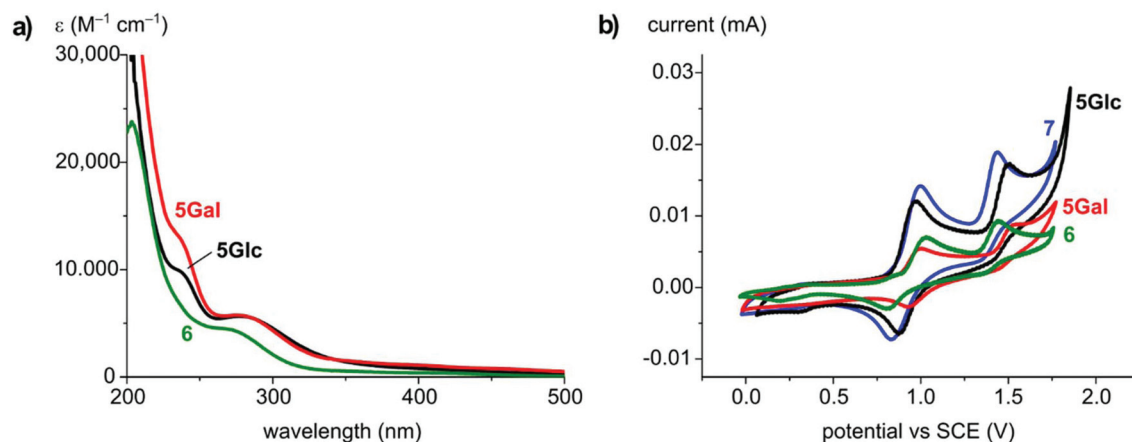
Fig. 1 (a) UV-Vis absorption spectra of **5Glc**, **5Gal** and **6** at room temperature in MeCN; and (b) cyclic voltammetry of **5Glc**, **5Gal**, **6**, and **7** in MeCN solution, scan rate 100 mV s^{-1}, [NBu$_4$]PF$_6$ as the supporting electrolyte (0.1 mM), complexes at 0.5 mM except **5Gal** (0.25 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 deacetylation 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_2O using 10 equiv. KOH and was confirmed by a HRMS (ESI+) signal at $m/z = 536.1684$, corresponding to $[M - 2Cl - H]^+$. Moreover, ^{1}H NMR analysis in D_2O 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_2O or $(CD_3)_2CDOD$ solution. Consequently, the more robust protected complexes **5** were used as pre-catalysts and complexes **8** were generated by *in situ* deprotection in the course of transfer hydrogenation catalysis.

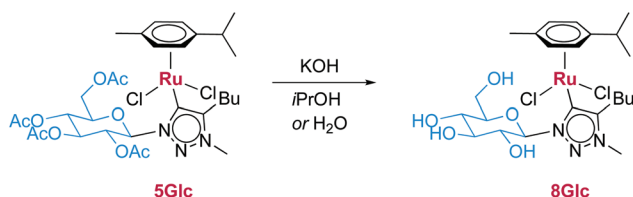### Transfer hydrogenation catalysis

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 con-

ditions,[43] *i.e.*, refluxing iPrOH as hydrogen source, KOH as activator, 100 : 10 : 1 substrate/base/complex ratio. For both **8Glc** and **8Gal**, both generated *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 acetophenone 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**.

Table 2 Catalytic activity of Ru complexes for transfer hydrogenation of various carbonyl substrates[a]

Entry	Complex	Substrate	Conversion[b] (%)		TOF$_{50}$[c] (h^{-1})	σ_p[d]
			8 h	24 h		
1	**5Glc**		98	>98	20	0
2	**5Gal**		>98	>98	22	0
3	**6**		57	84	9	0
4	**7**		>98	>98	310	0
5	**5Glc**[e]		62	>98	8	0
6	**5Glc**		66	98	10	0
7	**5Glc**		74	98	13	—
8	**5Glc**		56	75	8	+0.23
9	**5Glc**		51	77	7	−0.27
10	**5Glc**		62	74	11	+0.23
11	**5Glc**		10	16	—	−0.36
12	**5Glc**		15	31	—	−0.66
13	**5Glc**		97	>98	60	—

[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 ^{1}H NMR analysis. [c] TOF$_{50}$ (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.

benzophenone and acetophenone using **5Glc** as pre-catalyst (entries 7–13). Using sterically more demanding 2-methyl-acetophenone as substrate in place of acetophenone led to a modest increase in activity (TOF$_{50}$ = 13, entry 7). Very little variation of activity was noted when using electronically distinct substrates. For example, conversion of electron-withdrawing 4-bromoacetophenone (σ_p = +0.23, TOF$_{50}$ = 8 h^{-1}) and electron-donating 4-methoxyacetophenone (σ_p = −0.27, TOF$_{50}$ = 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 (TOF$_{50}$ = 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 (TOF$_{50}$ = 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 turn-over 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 affected by the steric demand and the potential (hydrogen bond) interactions of the carbohydrate with the substrate. Substrate coordination may also involve decoordination of potentially chelating carbo-

hydrate hydroxy groups from the ruthenium center. This decoordination is accelerated with soft pyridyl coordinating groups (entry 13), which may rationalize the enhanced conversion rate observed with this substrate. In contrast, phenol and aniline functional groups are presumably too acidic and deprotonated under the basic reaction conditions, leading to a strongly coordinating ligand 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 triazolylidene-bound glucose substantially enhances turnover rates compared to more remote carbohydrate functionalization, though it reduces activity compared to unfunctionalized carbene complexes. This prominent role of the carbohydrate substituent provides opportunities for further catalyst engineering towards other transformations involving hydrogen transfer such as oxidations or hydrogen borrowing processes, as well as by modulation of the carbohydrate entity using other pyranoses or furanoses to exploit their beneficial properties in catalysis.

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.[63–65] Ag$_2$O was used after regeneration by heating to >160 °C under vacuum. Dry, degassed solvents were obtained by filtration over columns of dried aluminium oxide under a positive pressure of argon. NMR spectra were recorded on Bruker spectrometer operating at room temperature. Chemical shifts (δ in ppm, J in Hz) were referenced to residual solvent resonances and are reported downfield from SiMe$_4$. High resolution mass spectrometry and elemental analysis were performed by the Analytical Research Services at University of Bern.

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 CuSO$_4$·5H$_2$O (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 NH$_4$OH$_{(aq)}$ solution) and extracted into CH$_2$Cl$_2$ (3 × 20 mL). The organic layers were combined, washed with brine, dried over MgSO$_4$ 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 C$_{20}$H$_{29}$N$_3$O$_9$ (455.464 g mol^{-1}): C 52.74, H 6.42, N 9.23%; found C 53.09, H 6.03, N 8.86%. HRMS (*m/z*) (ESI+): Calculated for C$_{20}$H$_{30}$O$_9$N$_3$$^+$ [M + H]$^+$ *m/z* = 456.1977; found *m/z* = 456.1985. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.93 (t, 3H, $^3J_{H,H}$ = 7.5 Hz, butyl CH$_3$), 1.31–1.41 (m, 2H, butyl CH$_2$), 1.61–1.73 (m, 2H, butyl CH$_2$), 1.87, 2.03, 2.07, 2.08 (4 × s, 3H, C(O)CH$_3$), 2.72 (t, 2H, $^3J_{H,H}$ = 7.5 Hz, C$_{trz}$CH$_2$), 3.99 (ddd, 1H, $^3J_{H,H}$ = 9.0, 5.1, 2.1 Hz, glucosyl C^{5}H), 4.14 (dd, 1H, $^3J_{H,H}$ = 2.1 Hz, $^2J_{H,H}$ = 12.6 Hz, glucosyl C^{6}H), 4.30 (dd, 1H, $^3J_{H,H}$ = 5.1 Hz, $^2J_{H,H}$ = 12.6 Hz, glucosyl C^{6}H), 5.23 (app t, 1H, glucosyl C^{4}H), 5.34–5.49 (m, 2H, glucosyl C^{2}H and C^{3}H), 5.85 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, glucosyl C^{1}H), 7.51 (s, 1H, C$_{trz}$H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 13.9 (butyl CH$_3$), 20.3, 20.66, 20.69, 20.8 (4 × C(O)CH$_3$), 22.3 (butyl CH$_2$), 25.3 (butyl CH$_2$), 31.3 (C$_{trz}$CH$_2$), 61.7 (glucosyl C^{6}H$_2$), 67.9, 70.4, 72.9, 75.3 (4 × glucosyl C$^{2-5}$H, 85.9 (glucosyl C^{1}H), 119.0 (C$_{trz}$H), 149.5 (C$_{trz}$–Bu), 169.1, 169.5, 170.0, 170.6 (4 × C=O). FT-IR (ATR, cm^{-1}): 3070 (w), 2928 (w), 2357 (w), 1746 (s, C=O), 1436, 1366, 1216 (s), 1093, 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 C$_{20}$H$_{29}$N$_3$O$_9$ (455.464 g mol^{-1}): C 52.74, H 6.42, N 9.23%; found C 52.70, H 6.34, N 9.03%. HRMS (*m/z*) (ESI+): Calculated for C$_{20}$H$_{30}$O$_9$N$_3$$^+$ [M + H]$^+$ *m/z* = 456.1977; found *m/z* = 456.1980; calculated for C$_{20}$H$_{29}$O$_9$N$_3$Na$^+$ [M + Na]$^+$ *m/z* = 478.1796; found *m/z* = 478.1799. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.94 (t, 3H, $^3J_{H,H}$ = 7.4 Hz, butyl CH$_3$), 1.30–1.42 (m, 2H, butyl CH$_2$), 1.62–1.71 (m, 2H, butyl CH$_2$), 1.88, 2.01, 2.05, 2.22 (4 × s, 3H, C(O)CH$_3$), 2.73 (t, 2H, $^3J_{H,H}$ = 7.4 Hz, C$_{trz}$CH$_2$), 4.11–4.24 (m, 3H, galactosyl C^{5}H + C^{6}H$_2$), 5.23 (dd, 1H, $^3J_{H,H}$ = 10.3, 3.3 Hz, galactosyl C^{4}H), 5.50–5.61 (m, 2H, galactosyl C^{2}H + C^{3}H), 5.81 (d, 1H, $^3J_{H,H}$ = 9.3 Hz, galactosyl C^{1}H), 7.55 (s, 1H, C$_{trz}$H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 13.8 (butyl CH$_3$), 20.2, 20.5, 20.63, 20.64 (4 × C(O)CH$_3$), 22.2 (butyl CH$_2$), 25.3 (butyl CH$_2$), 31.3 (C$_{trz}$CH$_2$), 61.2 (galactosyl C^{6}H$_2$), 66.9, 67.8, 70.9, 74.0 (galactosyl C$^{2-5}$H, 86.2 (galactosyl C^{1}H), 118.8 (C$_{trz}$H), 149.2 (C$_{trz}$–Bu), 169.1, 169.8, 169.9, 170.3 (4 × C=O); FT-IR (ATR, cm^{-1}): 2958 (w), 2929 (w), 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-azidoethyl-glucopyranoside (1.250 g, 2.99 mmol), yielding **2** as a pale yellow oil (1.335 g, 89%), which was used without further purification. Gradient flash chromatography (SiO$_2$; CH$_2$Cl$_2$ to CH$_2$Cl$_2$/CH$_3$OH 95 : 5) was used to obtain the product as an off-white hygroscopic solid. HRMS (*m/z*) (ESI+): Calculated for C$_{22}$H$_{34}$N$_3$O$_{10}$$^+$ *m/z* = 500.2239 [M + H]$^+$; found *m/z* = 500.2236. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.92 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH$_3$), 1.31–1.48 (m, 2H, butyl CH$_2$), 1.57–1.72 (m, 2H, butyl CH$_2$), 1.93, 1.98, 2.00, 2.07 (4 × s, 3H, C(O)CH$_3$), 2.56–2.80 (m,

2H, butyl CH_2), 3.68 (ddd, 1H, $^3J_{H,H}$ = 10.0, 4.8, 2.4 Hz, glucosyl C^5H), 3.90 (ddd, 1H, $^2J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 8.5, 3.4 Hz, ethylene CHH), 4.06–4.29 (m, 3H, ethylene CHH + glucosyl C^6H_2), 4.39–4.59 (m, 2H, ethylene CH_2), 4.46 (d, 1H, $^3J_{H,H}$ = 7.9 Hz, glucosyl C^1H), 4.98 (dd, 1H, $^3J_{H,H}$ = 9.5, 7.9 Hz, glucosyl C^2H), 5.05 (dd, 1H, $^3J_{H,H}$ = 10.0, 9.5 Hz, glucosyl C^4H), 5.16 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, glucosyl C^3H), 7.31 (s, 1H, $C_{trz}H$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 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_2), 49.8 (CH_2), 61.8 (CH_2), 68.0 (CH_2), 68.3, 71.0, 72.0, 72.5 (glucosyl $C^{2-5}H$), 100.6 (glucosyl C^1H), 122.0 ($C_{trz}H$), 148.3 (C_{trz}–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_3OBF_4 (0.067 g, 0.45 mmol) were dissolved in dry CH_2Cl_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-ᴅ-glucopyranosyl)-4-butyl-3-methyl-1,2,3-triazol-3-ium tetrafluoroborate (3Glc). According to the general procedure, reaction of **1Glc** (0.200 g, 0.44 mmol) and Me_3OBF_4 (0.067 mg, 0.45 mmol) yielded **3Glc** (0.240 g, 98%). Anal. calcd for $C_{21}H_{32}N_3O_9BF_4$ (557.303 g mol^{-1}): C 45.26, H 5.79, N 7.54%; found C 45.13, H 5.01, N 7.27%; HRMS (*m/z*) (ESI+): Calculated for $C_{21}H_{32}O_9N_3^+$ $[M − BF_4]^+$ *m/z* = 470.2133; found *m/z* = 470.2136. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH_3), 1.39–1.54 (m, 2H, butyl CH_2), 1.69–1.83 (m, 2H, butyl CH_2), 2.02, 2.03, 2.06, 2.08 (4 × s, 3H, $C(O)CH_3$), 2.75–2.99 (m, 2H, butyl CH_2), 4.12–4.45 (m, 6H, glucosyl C^5H + C^6H_2 + NCH_3), 5.26 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, glucosyl C^4H), 5.42 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, glucosyl C^3H), 5.62 (t, 1H, $^3J_{H,H}$ = 9.0 Hz, glucosyl C^2H), 6.20 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, glucosyl C^1H), 8.56 (s, 1H, $C_{trz}H$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.7 (butyl CH_3), 20.5, 20.70, 20.74, 20.9 (4 × $C(O)CH_3$), 22.3, 23.4, 28.9 (3 × butyl CH_2), 38.4 (NCH_3), 61.2 (glucosyl C^6H_2), 67.3, 69.6, 72.9, 75.5 (galactosyl $C^{2-5}H$), 87.5 (glucosyl C^1H), 128.6 ($C_{trz}H$), 145.8 (C_{trz}–Bu), 169.6, 169.87, 169.93, 170.7 (4 × $C{=}O$); FT-IR (ATR, cm^{-1}): 2968 (w), 2359, 1747 (s, $C{=}O$), 1434, 1371 (s), 1215 (s), 1024 (br, s, BF_4), 927.

1-(2,3,4,6-Tetra-*O*-acetyl-β-ᴅ-galactopyranosyl)-4-butyl-3-methyl-1,2,3-triazol-3-ium tetrafluoroborate (3Gal). According to the general procedure, **1Gal** (0.200 g, 0.44 mmol) and Me_3OBF_4 (0.067 mg, 0.45 mmol) were reacted to yield **3Gal** (0.246 g, 100%). HRMS (*m/z*) (ESI+): Calculated for $C_{21}H_{32}O_9N_3^+$ $[M − BF_4]^+$ *m/z* = 470.2133; found *m/z* = 470.2127. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH_3), 1.39–1.56 (m, 2H, butyl CH_2), 1.64–1.82 (m, 2H, butyl CH_2), 2.01, 2.04, 2.07, 2.21 (4 × s, 3H, $C(O)CH_3$), 2.77–2.97 (m, 2H, butyl CH_2), 4.10–4.46 (m, 6H, galactosyl C^5H + C^6H_2 + NCH_3), 5.31 (dd, 1H, $^3J_{H,H}$ = 10.1, 3.3 Hz, galactosyl C^3H), 5.56 (d, 1H, $^3J_{H,H}$ = 3.3 Hz, galactosyl C^4H), 5.67 (t, 1H, $^3J_{H,H}$ = 9.5 Hz,

galactosyl C^2H), 6.12 (d, 1H, $^3J_{H,H}$ = 9.5 Hz, galactosyl C^1H), 8.50 (s, 1H, $C_{trz}H$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.6 (butyl CH_3), 20.4, 20.5, 20.7, 20.7 (4 × $C(O)CH_3$), 22.2, 23.3, 28.9 (3 × butyl CH_2), 38.2 (N–CH_3), 60.8 (galactosyl C^6H_2), 66.8, 67.2, 70.7, 74.8 (galactosyl $C^{2-5}H$, 88.0 (galactosyl C^1H), 128.0 ($C_{trz}H$), 145.7 (C_{trz}–Bu), 169.6, 169.9, 170.0, 170.5 (4 × $C{=}O$); FT-IR (ATR, cm^{-1}): 3121 (w), 2962 (w), 1745 (s, $C{=}O$), 1370, 1210 (s), 1034 (s, br, BF_4), 922, 496.

1-(2-(4-Butyl-3-methyl-1,2,3-triazolium-1-yl)ethoxy)-1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-ᴅ-glucopyranose tetrafluoroborate (4). According to the general procedure, **2** (0.250 g, 0.50 mmol) and Me_3OBF_4 (0.075 mg, 0.51 mmol) were reacted and yielded **4** (0.255 g, 84%). HRMS (*m/z*) (ESI+): Calculated for $C_{23}H_{36}O_{10}N_3^+$ *m/z* = 514.2395 $[M − BF_4]^+$; found *m/z* = 514.2387. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH_3), 1.41 (quintet, 2H $^3J_{H,H}$ = 7.4 Hz, butyl CH_2), 1.60–1.75 (m, 2H, butyl CH_2), 1.92, 1.95, 1.96, 2.01 (4 × s, 3H, $C(O)CH_3$), 2.67–2.86 (m, 2H, butyl CH_2), 3.75 (ddd, 1H, J = 10.2, 4.7, 2.3 Hz, glucosyl C^5H), 4.00–4.28 (m, 7H, NCH_3 + ethylene CH_2 + glucosyl C^6H_2), 4.60 (d, 1H, $^3J_{H,H}$ = 7.9 Hz, glucosyl C^1H), 4.64–4.79 (m, 2H, ethylene CH_2), 4.82 (dd, 1H, $^3J_{H,H}$ = 9.6, 7.9 Hz, glucosyl C^2H), 4.95 (t, 1H, $^3J_{H,H}$ = 9.6 Hz, glucosyl C^4H), 5.12 (t, 1H, $^3J_{H,H}$ = 9.6 Hz, glucosyl C^3H), 8.17 (s, 1H, $C_{trz}H$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.3 (butyl CH_3), 20.4, 20.4, 20.46, 20.53 (4 × $OC(O)CH_3$), 21.9, 22.7, 28.5 (3 × butyl CH_2), 37.2 (N–CH_3), 53.6 (ethylene CH_2), 61.5 (glucosyl C^6H_2), 66.5 (ethylene CH_2), 68.1, 71.0, 71.7, 72.4 (glucosyl $C^{2-5}H$), 100.4 (glucosyl C^1H), 128.4 ($C_{trz}H$), 144.5 (C_{trz}–Bu), 169.4, 169.6, 169.8, 170.5 (4 × $C{=}O$); FT-IR (ATR, cm^{-1}): 2959 (w), 2848(w), 1744 (s, $C{=}O$), 1435, 1369, 1218 (s), 1034 (s, br, BF_4), 908.

General synthesis of Ru(ɪɪ) complexes

The triazolium salt (0.43 mmol), Ag_2O (0.060 g, 0.26 mmol) and Me_4NCl (0.057 g, 0.52 mmol) were suspended in dry CH_3CN (50 mL) and stirred in the absence of light at room temperature for 5 h. The reaction mixture was diluted with CH_2Cl_2 (25 mL), filtered through Celite and concentrated under reduced pressure. CH_2Cl_2 (20 mL) and $[Ru(p\text{-cym})Cl_2]_2$ (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_2Cl_2 to CH_2Cl_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. calcd for $C_{31}H_{45}N_3O_9RuCl_2$ (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 $C_{31}H_{45}N_3O_9RuCl^+$ *m/z* = 740.1882 $[M − Cl]^+$; found *m/z* = 740.1885. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH_3), 1.32 (d, 3H, $^3J_{H,H}$ = 6.9 Hz, $CHCH_3$), 1.34 (d, 3H, $^3J_{H,H}$ = 6.9 Hz, $CHCH_3$), 1.46 (quintet, 2H, $^3J_{H,H}$ = 7.3 Hz, butyl CH_2), 1.54–1.64 (br s, 2H, butyl CH_2), 1.93 (s, 3H, $C(O)CH_3$), 1.97 (s, 3H, cym–CH_3), 2.02, 2.04, 2.06 (3 × s, 3H,

C(O)CH$_3$), 2.88–3.08 (m, 3H, butyl CH$_2$ + CHMe$_2$), 3.97–4.09 (m, 4H, NCH$_3$ + glucosyl C^{5}H), 4.12–4.27 (m, 2H, glucosyl C^{6}H$_2$), 5.00 (d, 1H, $^3J_{H,H}$ = 5.8 Hz, C$_{cym}$H), 5.14–5.26 (m, 2H, C$_{cym}$H + glucosyl C^{4}H), 5.30–5.43 (m, 2H, C$_{cym}$H + glucosyl C^{3}H), 5.53 (d, 1H, $^3J_{H,H}$ = 5.8 Hz, C$_{cym}$H), 6.01 (t, 1H, $^3J_{H,H}$ = 9.4 Hz, glucosyl C^{2}H), 6.76 (br s, 1H, glucosyl C^{1}H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 14.0 (butyl CH$_3$), 18.8 (cym–CH$_3$), 20.71, 20.74, 20.97, 21.12 (4 × C(O)CH$_3$), 22.7, 23.0 (2 × CH–CH$_3$), 23.2 (butyl CH$_2$), 26.3 (butyl CH$_2$), 30.8 (CHMe$_2$), 31.8 (butyl CH$_2$), 37.3 (NCH$_3$), 62.3 (glucosyl C^{6}H$_2$), 68.3 (glucosyl C^{4}H), 70.1 (glucosyl C^{2}H), 74.1 (glucosyl C^{3}H), 74.5 (glucosyl C^{5}H), 81.1, 81.9, 86.3, 86.8 (4 × C$_{cym}$H), 87.1 (glucosyl C^{1}H), 97.6 (C$_{cym}$), 108.3 (C$_{cym}$), 148.0 (C$_{trz}$–Bu), 167.1 (C$_{trz}$–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, 922.

Ru complex 5Gal

From **3Gal** (0.223 g) according to the general procedure, **5Gal** was obtained (0.138 g, 60%). Anal. calcd 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 47.37, H 5.65, N 5.00%. HRMS (m/z) (ESI+): Calculated for C$_{31}$H$_{45}$N$_3$O$_9$RuCl$^+$ m/z = 740.1882 [M − Cl]$^+$; found m/z = 740.1886. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.95 (t, 3H, $^3J_{H,H}$ = 7.2 Hz, butyl CH$_3$), 1.30, 1.33 (2 × d, 3H, $^3J_{H,H}$ = 6.9 Hz, CHCH$_3$), 1.40–1.55 (m, 2H, butyl CH$_2$), 1.60–1.90 (br s, 2H, butyl CH$_2$), 1.92 (s, 3H, C(O)CH$_3$), 1.97 (s, 3H, cym–CH$_3$), 1.99, 2.02, 2.23 (3 × s, 3H, C(O)CH$_3$), 2.85–3.14 (m, 3H, butyl CH$_2$ + CHMe$_2$), 4.08 (s, 3H, NCH$_3$), 4.11–4.28 (m, 3H, galactosyl C^{5}H + C^{6}H$_2$), 4.97 (d, 1H, $^3J_{H,H}$ = 5.8 Hz, C$_{cym}$H), 5.15–5.26 (m, 2H, C$_{cym}$H + galactosyl CH), 5.37 (d, 1H, $^3J_{H,H}$ = 5.8 Hz, C$_{cym}$H), 5.46–5.63 (m, 2H, C$_{cym}$H + galactosyl CH), 6.17 (t, 1H, $^3J_{H,H}$ = 9.7 Hz, galactosyl C^{2}H), 6.86 (br s, 1H, galactosyl C^{1}H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 14.0 (butyl CH$_3$), 18.8 (cym–CH$_3$), 20.6, 20.90, 20.92, 21.26 (4 × C(O)CH$_3$), 22.4 (CHCH$_3$), 23.2 (butyl CH$_2$), 26.3 (CHMe$_2$), 31.1 (butyl CH$_2$), 31.8 (butyl CH$_2$), 37.2 (NCH$_3$), 62.1 (galactosyl C^{6}H$_2$), 67.5 (galactosyl C^{2}H), 68.4 (galactosyl C^{3}H), 72.1 (galactosyl C^{4}H), 73.7 (galactosyl C^{5}H), 80.7, 81.9, 86.0, 87.0 (4 × C$_{cym}$H), 87.6 (galactosyl C^{1}H), 98.1 (C$_{cym}$), 108.3 (C$_{cym}$), 148.0 (C$_{trz}$–Bu), 167.1 (C$_{trz}$–Ru), 169.5, 169.9, 170.27, 170.28 (4 × C=O); FT-IR (ATR, cm^{-1}): 2956 (w), 1748 (s, C=O), 1367, 1216 (s), 1051, 921.

Ru complex 6

Reaction of **4** (0.220 g) according to the general procedure afforded complex **6** (0.096 g, 30%). Anal. calcd for C$_{33}$H$_{49}$N$_3$O$_{10}$RuCl$_2$·(H$_2$O) (837.751 g mol^{-1}), C 47.31, H 6.14, N 5.02%; found C 47.49, H 5.89, N 4.70%. HRMS (m/z) (ESI+): Calculated for C$_{33}$H$_{49}$N$_3$O$_{10}$RuCl$^+$ m/z = 784.2144 [M − Cl]$^+$; found m/z = 784.2153. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.96 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, butyl CH$_3$), 1.30 (d, 6H, $^3J_{H,H}$ = 6.9 Hz, CHCH$_3$), 1.46 (m, 2H, butyl CH$_2$), 1.55–1.70 (br s, 2H, butyl CH$_2$), 1.98 (s, 3H, C(O)CH$_3$), 1.99–2.04 (m, 9H, cym–CH$_3$ + 2 × C(O)CH$_3$), 2.07 (s, 3H, C(O)CH$_3$), 2.86–3.09 (m, 3H, butyl CH$_2$ + CHMe$_2$), 3.75 (ddd, 1H, $^3J_{H,H}$ = 10.1, 4.6, 2.4 Hz, glucosyl C^{5}H), 3.98 (s, 3H, NCH$_3$), 4.08–4.19 (m, 2H, ethylene CHH + glucosyl C^{6}HH), 4.22–4.38 (m, 2H, ethylene CHH + glucosyl C^{6}HH), 4.65

(d, 1H, $^3J_{H,H}$ = 8.0 Hz, glucosyl C^{1}H). 4.83 (dtd, 2H, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 8.0, 5.8 Hz, ethylene CH$_2$), 4.95 (dd, 1H, $^3J_{H,H}$ = 9.5, 8.0 Hz, glucosyl C^{2}H), 5.07–5.14 (m, 3H, glucosyl C^{4}H + C$_{cym}$H), 5.20 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, glucosyl C^{3}H), 5.37 (dd, 1H, $^3J_{H,H}$ = 5.8, 1.3 Hz, C$_{cym}$H), 5.40 (dd, 1H, $^3J_{H,H}$ = 5.8, 1.3 Hz, C$_{cym}$H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 13.9 (butyl CH$_3$), 18.5 (cym–CH$_3$), 20.59, 20.61, 20.8, 22.5 (4 × C(O)CH$_3$), 22.8 (CHCH$_3$), 23.1 (butyl CH$_2$), 26.0 (CHMe$_2$), 30.7 (butyl CH$_2$), 31.8 (butyl CH$_2$), 36.4 (NCH$_3$), 53.8 (ethylene CH$_2$), 61.9 (glucosyl C^{6}H$_2$), 68.3 (glucosyl CH), 68.7 (ethylene CH$_2$), 71.4, 71.9, 72.9 (3 × glucosyl CH), 82.4, 82.9, 85.1, 85.2 (4 × C$_{cym}$H), 96.7 (C$_{cym}$), 100.5 (glucosyl C^{1}H), 107.4 (C$_{cym}$), 147.6 (C$_{trz}$–Bu), 163.0 (C$_{trz}$–Ru), 169.2, 169.5, 170.1, 170.6 (4 × C=O).

In situ deprotection of 5Glc

Complex **5Glc** (4 mg, 5 μmol) was dissolved in D$_2$O (0.5 mL) and KOH (0.2 M in D$_2$O, 0.05 mL, 0.05 mmol) was added, which induces an immediate color change from orange to yellow. HRMS (m/z) (ESI+): Calculated for C$_{23}$H$_{36}$N$_3$O$_5$Ru$^+$ m/z = 536.1704 [M − 2Cl − H]$^+$; found m/z = 536.1684. ^{1}H NMR (300 MHz, D$_2$O): δ = 1.13 (d, 3H, $^3J_{H,H}$ = 6.8 Hz, CHCH$_3$), 1.21 (t, 3H, $^3J_{H,H}$ = 6.9 Hz, butyl CH$_3$), 1.29 (d, 3H, $^3J_{H,H}$ = 6.8 Hz, CHCH$_3$), 1.61–2.10 (m, 4H, butyl CH$_2$), 2.08 (s, 12H, CH$_3$COOK) 2.24 (s, 1H, cym–CH$_3$), 2.52–2.72 (m, 1H, CHMe$_2$), 2.95–3.20 (m, 2H, butyl CH$_2$), 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 C^{6}H), 4.35 (s, 3H, NCH$_3$), 5.04–5.13 (m, 1H, C$_{cym}$H), 5.23 (d, 1H J = 8.2 Hz, glucosyl C^{1}H), 5.45 (d, 1H, $^3J_{H,H}$ = 6.1 Hz, C$_{cym}$H), 5.77 (d, 1H, $^3J_{H,H}$ = 5.7 Hz, C$_{cym}$H), 5.82 (d, 1H, $^3J_{H,H}$ = 5.7 Hz, C$_{cym}$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). Hexamethylbenzene 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 CDCl$_3$ and measuring ^{1}H NMR spectra to monitor reaction progress.

Conflicts of interest

There are no conflicts to declare.

Funding sources

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