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Carbohydrate-Functionalized 1,2,3-Triazolylidene Complexes for Application in Base-Free Alcohol and Amine Oxidation

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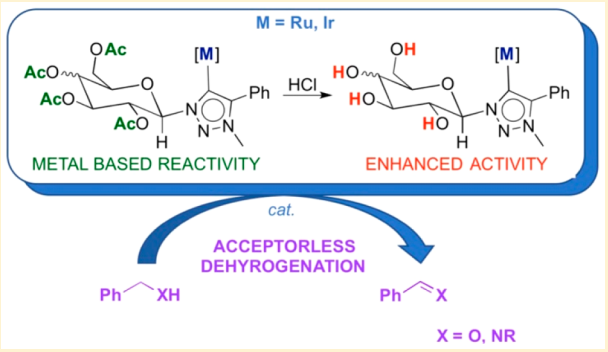
Supporting Information

ABSTRACT: Acetylglucose- and acetylgalactose-functionalized triazolylideneruthenium(II) and -iridium(III) complexes were synthesized and fully characterized. Subsequent carbohydrate deprotection yielded the first examples of glucose- and galactose-functionalized 1,2,3-triazolylideneiridium complexes. Base-free oxidation of alcohols and amines was used to probe the catalytic potential of the metal complexes and the influence of the carbohydrate wingtip group. Generally, the performance of these complexes is higher in amine oxidation than in alcohol oxidation. While the stereochemistry at the carbohydrate C4 position had no marked influence (galactose vs glucose), the ruthenium complexes typically exhibited higher substrate selectivity and product specificity compared to the analogous iridium species. Most noteworthy is the fact that the catalytic performance is significantly enhanced when the carbohydrate functionality is deprotected, suggesting an active role of the carbohydrate substituent in these transformations.



INTRODUCTION

Carbohydrates are one of the most abundant classes of biomolecules and have unique roles in nature including cellular recognition, structural rigidity, and a myriad of other biological functions.[1,2] A large diversity of carbohydrate molecules are available through structural and stereochemical variations. Moreover, the hydroxy groups on saccharides present unique possibilities as reactive sites for modification and hydrogen bonding.[3] The use of carbohydrate-based ligands for transition-metal catalysis is therefore a natural extension of these useful biomolecules, in particular for imparting asymmetric induction and substrate recognition.[4−12]

1,2,3-Triazolylidenes (trz's)[13−18] are a subclass of N-heterocyclic carbenes (NHCs) that are conveniently accessible via functional-group-tolerant copper-catalyzed click reactions.[17,19−23] Furthermore, these ligands have pronounced mesoionic properties,[15,16,24,25] which implies that the carbene has an adaptive donor strength that can stabilize low as well as high metal oxidation states.[26−29] These unique characteristics entailed the application of triazolylidenemetal complexes in a range of catalytic transformations including cross-coupling[30−36] and redox reactions such as amine and alcohol oxidation,[28,37−42] transfer hydrogenation,[39,42−45] and water oxidation.[26,46−48] Current trends in NHC chemistry are focusing on the development of functionalized ligand systems in which the ligand is noninnocent and can act, for example, as a potential proton shuttle during catalytic processes.[49−53] Carbohydrates are an attractive class of functional groups for such purposes because they provide ample opportunities to serve as hydrogen donors and acceptors to enhance the catalytic activity and selectivity. Surprisingly, however, only a few NHC metal complexes are known that are functionalized with a carbohydrate substituent, and even fewer of these have been applied in catalysis.[4,53−67] In particular, we are aware of only two reports that detail the synthesis and catalytic application of protecting-group-free carbohydrate NHC metal complexes.[54,60] Building on a previous study on carbohydrate-functionalized triazolylidene complexes, which used exclusively acetyl-protected sugar moieties,[55] we have now explored new glucose− and galactose−triazolylidene hybrid systems and disclosed protocols for the deprotection of carbohydrates on the metal complex. This work demonstrates that deprotection of the carbohydrate unit considerably enhances the catalytic activity and modifies the product selectivity, This modulation of the catalytic performance identifies carbohydrate−triazolylidene hybrids as attractive scaffolds for further optimization, in particular when considering the vast variability of the carbohydrate unit.

RESULTS AND DISCUSSION

Synthesis and Characterization of Glucosyl- and Galactosyltriazolylideneruthenium and -iridium Complexes. Minor modifications and optimization of the literature procedure reported by Kilpin and co-workers[55] for the synthesis of glucosyl−triazole **1a** and the corresponding

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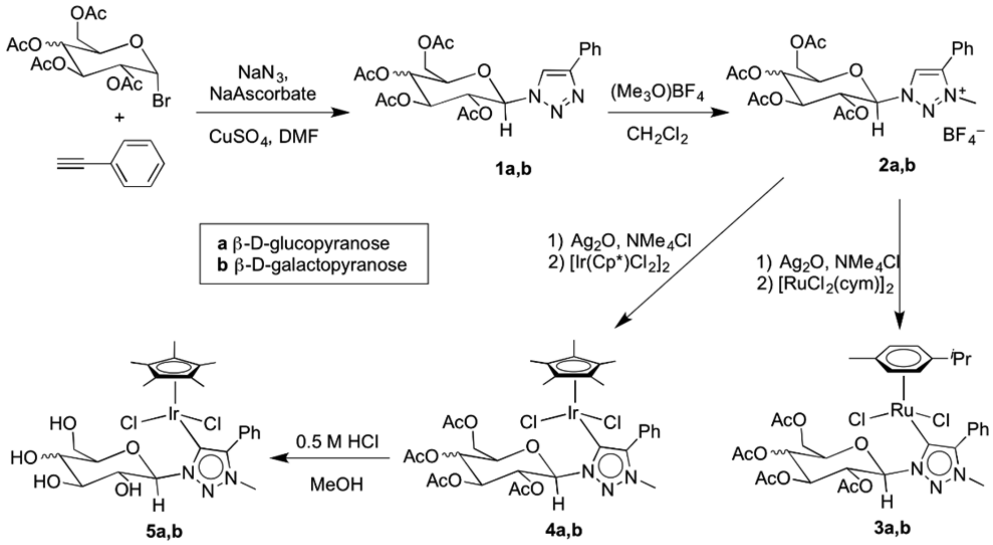
Scheme 1. Synthesis of β-Pyranosyl-Functionalized Triazolylidenemetal Complexes



ruthenium complex **3a** afforded the targeted carbohydrate-functionalized ruthenium and iridium complexes **3** and **4** (Scheme 1). Galactose−triazole **1b** was synthesized using copper(I)-catalyzed [3 + 2] cycloaddition of in situ generated β-galactosylazide and phenylacetylene (Scheme 1). Subsequent alkylation with $(Me_3O)BF_4$ yielded the novel galactose-functionalized triazolium salt **2b** (82%). The formation of **2b** was confirmed by ^{1}H NMR spectroscopy through the appearance of the NCH_3 resonance at 4.31 ppm and the downfield shift of the triazolium and anomeric protons (from δ_H = 8.05 and 5.90 to δ_H = 8.80 and 6.26, respectively). Synthesis of the pyranosyltriazolylideneruthenium(II) and -iridium(III) complexes **3** and **4** was accomplished through well-established silver transmetalation procedures.[15−17] Accordingly, treatment of the triazolium salts **2a** and **2b** with Ag_2O yielded the carbene silver intermediate, which was used in situ for transmetalation with either $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2(Cp^*)]_2$. Purification of the crude products by column chromatography afforded complexes **3** and **4** in high yields (71−86%) and high purity. In comparison to the reported literature procedure,[55] minor adjustments improved the purity of the crude products in our hands. For example, formation of the carbene silver species was optimized by a slight increase of the Ag_2O equivalents (from 0.5 to 0.6 mol equiv) and using pure acetonitrile (MeCN) as the solvent for this step rather than the CH_2Cl_2/MeCN mixture reported. Furthermore, transmetalation to iridium(III) required extended reaction times [24 h vs 2 h for ruthenium(II) complexes] to reach high yields of **4a** and **4b**.

The formation of complexes **3** and **4** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and, where possible, elemental analysis. Metalation was indicated in the ^{1}H NMR spectra by the disappearance of the triazolium proton resonance, as well as a diagnostic deshielding of the anomeric proton by 0.5−1 ppm (e.g., δ_H = 6.26 in **2b** vs 7.23 in **3b**). This low-field shift suggests a pronounced electronic perturbation at the anomeric position upon metal coordination of the carbene. The β-conformation of the carbohydrate in complexes **3** and **4** was retained according to ^{1}H NMR spectroscopy, as evidenced by the characteristic coupling constant ($^3J_{HH}$ = 9.1−9.7 Hz) between the carbohydrate H-1 and H-2 protons and by the presence of a single set of NMR resonances with no indication of any isomers formed.[68] The low symmetry of the complex is demonstrated by the resonances of the *p*-cymene ligand of the ruthenium(II) complexes **3a** and **3b**, featuring, e.g., two distinct doublets for the isopropyl CH_3 groups. This ligand desymmetrization is likely due to the large size of both triazole substituents, which limits rotation about the Ru−C_{trz} bond. No significant differences for the carbenic C atoms were noted in the ^{13}C NMR spectrum upon a comparison of the glucosyl- and galactosyl-substituted analogues. The carbenic C atoms resonate within the range reported for related ruthenium(II)[38,39,41,55,69,70] and iridium(III)[40,47,71−73] triazolylidene complexes.

Attempts to deprotect the acetylated pyranose complexes **3** and **4** initially focused on base-mediated cleavage of the acetyl groups. However, the standard conditions (NaOMe/MeOH)[60,74−76] only yielded mixtures of compounds, as evidenced by ^{1}H NMR spectroscopy of the crude sample. In contrast, exposure of complexes **4a** and **4b** to methanolic HCl for 2 days cleanly afforded iridium complexes **5a** and **5b**. Deprotection of the carbohydrate was confirmed by ^{1}H NMR spectroscopy, first by the loss of the acetate resonances in the 2.20−1.90 ppm region and second by the appearance of the hydroxy resonances between 6.10 and 4.50 ppm (deuterated dimethyl sulfoxide solutions). Also, deprotection induced a noticeable upfield shift of the anomeric ^{1}H resonance in both **5a** and **5b** by diagnostic values of 1.2 and 1.4 ppm, respectively. The large coupling constant ($^3J_{HH}$ = 9.1 ± 0.1 Hz) indicates full retention of the carbohydrate β-conformation.[68] The free carbohydrate-functionalized complexes **5a** and **5b** are soluble in organic solvents such as CH_2Cl_2, methanol (MeOH), and MeCN as well as in H_2O. In contrast, the parent acetyl-protected complexes **4a** and **4b** are only sparingly soluble in H_2O. The long reaction times for deprotection, together with the high yields of complexes **5a** and **5b** (>80%), demonstrate the remarkably high stability of the carbene−iridium bond under acidic conditions. The robust nature of the iridium−triazolylidene bond has been noted previously for related iridium(III) complexes in water oxidation catalysis under acidic conditions.[61] Similar deprotection methodologies were attempted for the ruthenium complexes; however, a mixture of products as well as demetalation of **3a** and **3b** was observed in the crude reaction mixture, including $[Ru(p\text{-cymene})Cl_2]_2$ and

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several unidentified products, suggesting a lower stability of the Ru−C_{trz} bond compared to the Ir−C_{trz} bond.

Inversion of the synthetic protocol toward deprotected carbohydrate-functionalized triazolylidene complexes **5** by first deprotection of the carbohydrate moiety of compound **2** and subsequent metalation was unsuccessful in our hands. Carboyhdrate deprotection under classical conditions using NaOMe in MeOH resulted in deacylation and also in the complete cleavage of the triazolium unit.

Crystallographic Characterization of Carbohydrate-Functionalized Carbene Complex 5a. Single-crystal X-ray diffraction analysis of complex **5a** confirmed the bonding pattern and, in particular, demonstrates that the β-configuration of the carbohydrate is retained throughout the synthesis of these complexes (Figure 1). The bonding around iridium

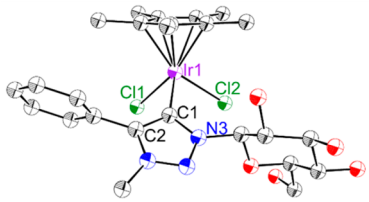
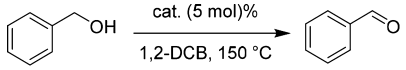


Figure 1. ORTEP plot of one of four crystallographically independent molecules in the unit cell of **5a** (50% probability; H atoms and cocrystallized MeOH are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir1−C1, 2.073(7); Ir1−Cl1, 2.4522(18); Ir1−Cl2, 2.4409(17); Ir−Cp*(centroid), 1.807; Ir1−C1−C2, 130.0(5); Ir1−C1−N3, 127.4(5).

reveals no significant deviations compared with a related complex containing two phenyl wingtip groups on the triazolylidene ligand.[71] Furthermore, the carbohydrate moiety displays the expected chair conformation. Interestingly, the unit cell contained four crystallographically independent complex molecules, two of which had the C-6 hydroxyl substituent facing toward the Cp* ligand, while this substituent is pointing away from the metal center in the other two molecules. A network of hydrogen-bonding interactions between the independent molecules of **5a** and MeOH span the unit cell. Each molecule also displays short contacts between the chlorido ligands and the carbohydrate hydroxy groups at positions 2 and 3 of an adjacent molecule, although no intramolecular hydrogen-bonding patterns were identified.

Acceptorless Oxidation of Benzyl Alcohol. Metal complexes with trz ligands have been used in base-free catalytic oxidation, an attractive transformation with fewer side products in comparison to classical oxidation methodologies.[28,37−42] Furthermore, pendant functional groups are known to enhance the catalytic activity of dehydrogenative oxidations through metal−ligand cooperativity during proton transfer.[42,50,51,77−84] The ruthenium and iridium complexes **3**−**5** were therefore probed as precatalysts for the base-free oxidation of benzyl alcohol (Table 1). Catalytic experiments were performed at 5 mol % catalyst loading in 1,2-dichlorobenzene (1,2-DCB) at 150 °C in an open system.[39,42] The results indicate only minute reactivity differences between the different catalysts (entries 1−6; Figure S1 and Table S1). Complexes **3a** and **3b** perform similarly to related trz-Ru complexes but with only moderate activity compared to the most active systems that display full conversion within 16 h (entries 1 and 2).[38,39,41,69] Complexes **4** and **5** also do not show any improved activity in comparison to other trz-Ir systems (full conversion in 16 h),[37] suggesting a

Table 1. Base-Free Oxidation of Benzyl Alcohol to Benzaldehyde[a]



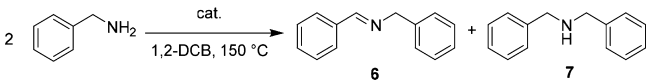
		conv/%	
entry	catalyst	5 h	24 h
1	**3a**	36	51
2	**3b**	32	53
3	**4a**	27	53
4	**4b**	23	57
5	**5a**	19	52
6	**5b**	29	69

[a]General conditions: benzyl alcohol (0.25 mmol), [Ru] or [Ir] (0.012 mmol, 5 mol %), 1,2-DCB, 150 °C. Conversions determined by ^{1}H NMR integration (trimethoxybenzene as the internal standard), averaged over two runs.

detrimental effect of the bulky carbohydrate wingtip group. The presence of free versus protected carbohydrate units does not affect the activity with the glucose derivative (cf. entries 3 and 5), while deprotected galactose wingtip groups show slightly higher activity compared to the acyl-protected analogue (69% vs 57% conversion after 24 h, entries 4 and 6). Possibly, the presence of large amounts of substrate ROH groups reduces the relevance of the ligand OH units, and, therefore, the carbohydrate only exerts steric constraints.[85]

Catalytic Oxidation of Benzylamine. Acceptorless amine oxidation through the self-condensation of amines, also referred to as transamination, offers a relatively simple procedure for the formation of imines and secondary and tertiary amines, with NH_3 as the only side product.[86−90] As a further probe for the catalytic potential of the carbohydrate-functionalized complexes, the oxidative homocoupling of benzylamine was investigated (Table 2 and Figure S2). In general, the complexes were all markedly more active toward amine oxidation than alcohol oxidation (full vs 20% conversion after 5 h). For example, complex **5a** reaches a turnover frequency of about 1 h^{-1} for alcohol oxidation and 16 h^{-1} in amine oxidation

Table 2. Oxidative Homocoupling of Benzylamine[a]



entry	catalyst	mol %	time (h)	conv (%)	**6**/**7**	yield (%)[b]
1	**3a**	1	5	94	100/−	61
2	**3b**	1	5	75	100/−	64
3	**4a**	5	1/5	44/94	83/17	90
4	**4b**	5	1/5	19/86	78/22	77
5	**5a**	5	1/5	78/> 95	86/14	>95
6	**5b**	5	1/5	71/>95	83/17	>95
7	**5a**	1	5	53	81/19	49
8	**5b**	1	5	51	80/20	48
9	$[Ru(cym)Cl_2]_2$	0.5	5	62	100/−	
10	$[Ir(Cp^*)Cl_2]_2$	2.5	5	<5	−/−	

[a]General conditions: benzylamine (1.25 or 0.25 mmol), [Ru] or [Ir] (0.012 mmol), 1,2-DCB, 150 °C. Conversions and yields were determined by ^{1}H NMR integration (hexamethylbenzene as the internal standard), averaged over at least two runs. [b]Spectroscopic yields are reported at 5 h.

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(determined after 1 h of reaction; see also Table S2). In contrast to the oxidation of benzyl alcohol, various trends in the activity can be deduced from amine oxidation catalysis. The activity of the ruthenium complexes **3a** and **3b** is markedly higher than that of the iridium analogues **4a** and **4b**, and high conversions were accomplished with only 1 mol % catalyst loading (cf. 5 mol % for the iridium complexes; entries 1 and 2 vs entries 3 and 4). The impact of the triazolylidene ligand is particularly pronounced in the iridium complexes because $[Ir(Cp^*)Cl_2]_2$ is essentially inactive and no products were detected under the applied standard conditions (entry 10). This effect is less marked in the ruthenium complexes, although we note a considerable rate enhancement imparted by the carbene ligand in complexes **3a** and **3b** in comparison to the simple ruthenium salt $[Ru(p\text{-cymene})Cl_2]_2$ (entries 1 and 2 vs entry 9). The beneficial role of the carbohydrate functionality is underpinned compared with an iridium complex related to **5** yet containing a chelating pyridyl instead of a carbohydrate substituent. With this complex and under essentially identical conditions, amine dehydrogenation requires about twice the time to reach completion, and the selectivity is much lower (almost 1:1 imine vs amine).[91] Likewise, related trz-Ru complexes with nonchelating substituents (alkyl and aryl) require substantially longer reaction times to reach high conversion, even when used at 5 mol % catalyst loading (cf. 1 mol % here).[41,69]

The product selectivity is strongly influenced by the type of metal center. Only imine **6** was observed when the ruthenium complexes were used as precatalysts, while the analogous iridium complexes formed both imine **6** and the secondary amine **7**. This product selectivity implies that ruthenium complexes directly release hydrogen gas before entering a subsequent catalytic cycle, while iridium complexes are capable of storing hydrogen and reusing it in a hydrogen-borrowing-type reaction.[92−94] Also, in all runs, benzaldehyde started to appear gradually once the conversion of benzylamine was complete. This side reaction was independent of the catalyst used and was therefore attributed to the gradual hydrolysis of imine **6**. A comparison of complexes **3a** and **4a** (entries 1 and 3) with **3b** and **4b** (entries 2 and 4) indicates that the glucose substituent imparts slightly higher activity than the galactose substituent for both ruthenium- and iridium-catalyzed reactions. Complexes **3a** and **3b** (entries 1 and 2) also reveal poor spectroscopic yields in comparison to complexes **4** and **5** (entries 3−8). The lower yield was tentatively attributed to overoxidation of the substrate to nitriles or hydrolysis of the product at early stages and subsequent overoxidation to acids.[95,96] Finally, complexes **3** are slightly more active than other trz-Ru compounds, which achieve only 72−83% conversion under comparable conditions (albeit in toluene, not 1,2-DCB).[41,69]

Notably, deprotection of the carbohydrate leads to a considerable increase in the catalytic activity (entries 3 and 4 vs entries 5 and 6; Figure 2). The glucose-functionalized complex **5a** achieved 78% conversion in 1 h, whereas the acetylated analogue reached only 44% (cf. entry 3 vs entry 5). The difference is even larger for the galactose-substituted systems, with the protected complex converting only 19% of the substrate, while the deprotected complex is 3 times more active (71%; entry 4 vs entry 6). The selectivity is not affected by the deprotection and remains at an approximate 5:1 ratio of imine versus secondary amine. Lowering the catalyst loading and using **5a** and **5b** at 1 mol % led to appreciable conversions;

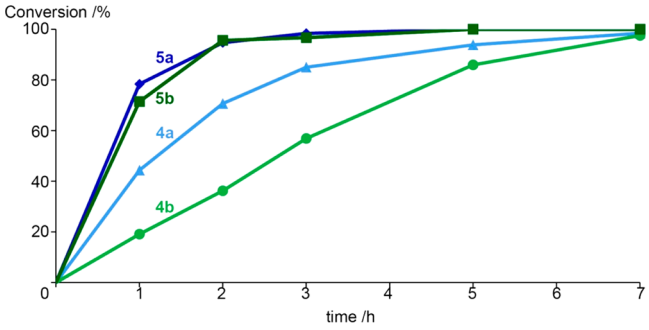

Figure 2. Comparison of the conversion of benzylamine by precatalysts **4** and **5**. General conditions: benzylamine (0.25 mmol), [Ir] (0.012 mmol, 5 mol %), 1,2-CB, 150 °C. Conversions were determined by ^{1}H NMR integration (hexamethylbenzene as the internal standard), averaged over at least two runs.

however, rates were much slower and reached only about 50% after 5 h, corresponding to 50 TON. The increased reactivity of complexes **5** with deprotected rather than acetylated carbohydrate wingtip groups is presumably due to the ability of the hydroxyl groups to promote substrate bonding and activation through hydrogen bonding or even complete hydrogen transfer.[50,51,78−82,85] In any case, the increased activity suggests a beneficial role of unprotected carbohydrates as functional sites on NHC-containing catalysts for amine oxidation.

Mixed Catalytic Oxidation of Benzyl Alcohol and Benzylamine. Because alcohol oxidation is about 1 order of magnitude slower than amine oxidation, we were interested in further investigating these reactivity differences of complexes **3**−**5** and therefore performed catalytic reactions using a mixture of benzyl alcohol and benzylamine (Tables 3 and S3). As observed in oxidation reactions with pure amines (cf. Tables 1 and 2), ruthenium complexes **3a** and **3b** displayed high selectivity for amine oxidation. Upon exposure to a mixture of amine and alcohol substrates, dehydrogenation of benzyl alcohol to benzaldehyde was only observed once oxidation of the amine was complete. Furthermore, the catalytic activity and selectivity toward the imine product was not significantly altered in comparison to amine oxidation in the absence of benzyl alcohol (Table 3, entries 1 and 2, compared to Table 2, entries 1 and 2, Figure S3). This outcome suggests a stronger bonding of the amine substrate to the Ru center in comparison to the alcohol substrate.

In contrast, iridium complexes **4** and **5** were less selective and converted benzylamine and benzyl alcohol simultaneously, albeit the alcohol in a much lower rate than the amine (Table 3, entries 3−7). Interestingly, the conversion of both substrates is slightly enhanced when using the mixture. This effect is most pronounced with complex **4b**, which converted benzylamine completely within 5 h when starting from the substrate mixture (Table 3, entry 4), while the oxidation of benzylamine in the absence of benzyl alcohol at 5 h was only 86% (Table 2, entry 4). Similarly, benzyl alcohol conversion reached 33% during the mixed oxidation at 5 h (Table 3, entry 4), compared to 23% conversion in the absence of benzylamine (Table 1, entry 4). The same effect was observed for complex **4a** and for complexes **5a** and **5b** containing the triazolylidene with deprotected carbohydrate groups (entries 3−7). For example, conversion of benzyl alcohol with the deprotected carbohydrate system **5a** doubled in the presence of benzylamine (39% vs 19%). These data indicate that catalyst activation from the iridium complexes preferably takes place from the amine,

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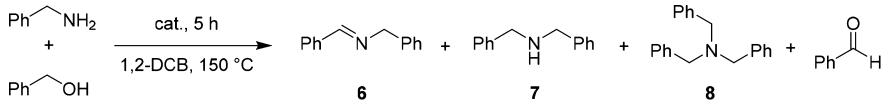
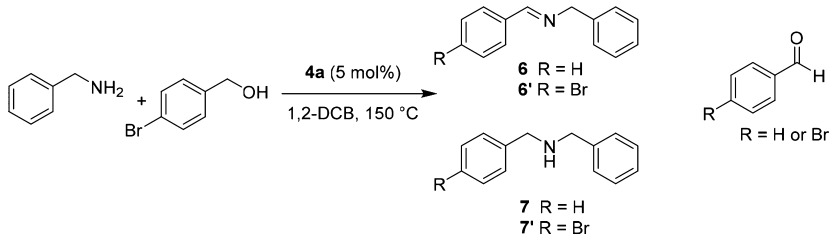
Table 3. Mixed Substrate Oxidation Catalysis



			conv (%)		
entry	catalyst	mol %	benzylamine	benzyl alcohol	6/7/8
1	**3a**	1	84		100/–/–
2	**3b**	1	90		100/–/–
3	**4a**	5	>95	43	42/58/–
4	**4b**	5	>95	33	50/50/–
5	**5a**	5	>95	39	37/59/4
6	**5a**	1	65	15	46/54/–
7	**5b**	1	71	15	44/56/–

[a]General conditions: benzylamine (1.25 or 0.25 mmol), benzyl alcohol (1.25 or 0.25 mmol), [Ru] or [Ir] (0.012 mmol) 1,2-DCB, 150 °C. Conversions were determined by ^{1}H NMR integration (hexamethylbenzene as the internal standard), averaged over at least two runs.

Scheme 2. Imine Products Formed during Catalytic Homocoupling of 4-Bromobenzylamine with Benzyl Alcohol



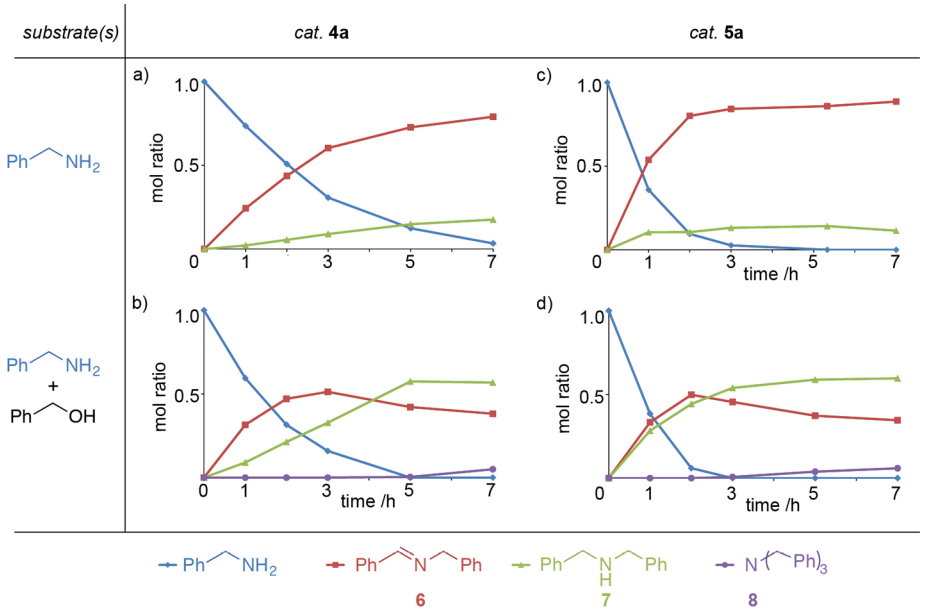


Figure 3. Catalytic profile expressed as the mole ratio for the oxidation of benzylamine (a) with catalyst **4a** (5 mol %), (b) with benzyl alcohol and catalyst **4a** (5 mol %), (c) with catalyst **5a** (5 mol %), and (d) with benzyl alcohol and catalyst **5a** (5 mol %). Conversion of benzyl alcohol was omitted for clarity.

although once formed, it is active toward both amine and alcohol oxidation. Alternatively, the amine may act as a base and facilitate alcohol deprotonation within the metal coordination sphere, thereby accelerating catalytic conversion. Moreover, when using complexes **4** or **5** as catalyst precursors, trace amounts of tribenzylamine **8** were observed at extended reaction times when the conversion of benzylamine was complete (ca. 6% after 7 h). Formation of the tertiary amine **8** is most likely a product of the reaction of **7** with benzaldehyde, which is formed from the oxidation of benzyl alcohol, a reaction that is only favorable once the more reactive primary benzylamine is consumed.

The detection of benzaldehyde as a product of the reaction is remarkable because Schiff base reaction with residual amine is expected to enhance the ratio of the imine product. In an attempt to elucidate such reaction trajectories and to further detail the substrate specificity of the iridium complexes, reactions were performed using 4-bromobenzyl alcohol instead

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of benzyl alcohol (Scheme 2) in mixed oxidation together with benzylamine. In such a setup, coupling of the oxidized alcohol with the amine will produce an unsymmetrical monobrominated product **6′**, while homocoupling will give the standard unsubstituted imine **6**. Likewise, hydrolysis of the imine will produce benzaldehyde, and bromobenzaldehyde should form predominantly from direct alcohol oxidation.

When this mixed reaction was carried out with the iridium complex **4a**, a complex product mixture was obtained, indicative of the simultaneous oxidation of both benzylamine and benzyl alcohol. The imine **6** and mixed imine **6′** were observed in a 4:3 ratio after 1 h, and the amine products were present in almost the same ratio (**7**/**7′** was 3:2). The formation of substantial amounts of brominated products **6′** and **7′** confirms that the alcohol and amine oxidations occur concurrently. At extended reaction times, the formation of both benzaldehyde and bromobenzaldehyde is observed in a relative ratio of ca. 4:3. The quantity of benzaldehyde was minor after 7 h and more significant after 24 h. This increasing amount of benzaldehyde, together with the fact that the brominated versus bromine-free aldehyde ratio is identical with the ratio observed in the imine products, strongly suggests that the aldehydes are formed by hydrolysis of the Schiff base **6** and not by selective oxidation of the bromobenzyl alcohol.

A comparison of the iridium-catalyzed amine oxidation in the presence or absence of benzyl alcohol also reveals a significant alteration of the imine/amine product ratio. In runs with pure amine substrate, the imine **6** was the predominant substrate (ca. 5:1 ratio of imine vs amine), whereas in runs in the presence of benzyl alcohol, the quantities of imine and amine were essentially equal (Table 2, entries 3−8, vs Table 3, entries 3−7). Inspection of the reaction profiles for complexes **4a** and **5a** reveals that both complexes catalyze the formation of amine **7** at faster rates in the presence of benzyl alcohol (Figure 3b,d) than when only amine is available as the substrate (Figure 3a,c). This change of the conversion rate is independent of the carbohydrate system on the catalyst used and is observed whether the carbohydrate unit is deprotected or not. The increased formation of the saturated amine therefore suggests that the presence of benzyl alcohol facilitates hydrogen storage and transfer to the imine, while with only benzylamine as the substrate, hydrogen release is predominant.

As a consequence of this model, the low conversion of benzyl alcohol to benzaldehyde with iridium catalysts (Table 1, entries 3−6) may principally originate from efficient hydrogen storage and, hence, a reversible reaction, involving hydrogenation of the benzaldehyde product back to the benzyl alcohol substrate. Such hydrogen shuffling was probed by adding acetophenone (20 mol % relative to benzyl alcohol) to a catalytic run for the dehydrogenation of benzyl alcohol with the iridium complex **4a**. In this experiment, no hydrogenation of acetophenone was observed. It is thus unlikely that the dehydrogenation of aldehydes is reversible under the catalytic conditions employed. This conclusion is also supported by the fact that the alcohol oxidation is slow, while fast hydrogen shuttling should rapidly reach an equilibrium situation (see the reaction profiles for alcohol oxidation in Figure S1).

Previous mechanistic studies indicated that N-alkylation of alcohols generally requires the aldehyde and subsequently formed hemiaminal and imine intermediates to remain coordinated to the Ir center for hydrogenation (formation of the amine product **7** via hydrogen borrowing).[97−99] In contrast, homocoupling of amines involves release of the aldimine (benzylimine) and ensuing formation of the alkylated imine (**6**) outside the metal coordination sphere.[86−89,91] While in ruthenium chemistry, the high selectivity toward the imine product indicates easy dissociation of the imine from the coordination sphere, coordination is apparently stronger in the iridium complexes and, hence, leads to a mixture of imine and amine products. This trend may be superimposed by the high stability of iridium hydrides, which facilitates storage of hydrogen in the metal coordination sphere and, hence, increases the propensity for hydrogenation and formation of the saturated amine. We therefore suggest that the distinct product selectivity of iridium-catalyzed amine oxidation and its dependence on the presence or absence of benzyl alcohol is due to the divergent mechanisms for N-alkylation of alcohols (amine formation) versus amine homocoupling (imine formation).

CONCLUSIONS

We have used the triazole scaffold to introduce acetyl-protected carbohydrates to a carbene ligand moiety. Deprotection under acidic conditions was achieved on the complex, although only the Ir−C_{trz} bond is sufficiently robust to sustain the deprotection conditions, while the Ru−C_{trz} bond is cleaved and the complexes decompose. These iridium complexes are rare examples of carbene complexes containing unprotected sugar units. Most significantly, the catalytic amine oxidation activity of the Ir center is significantly enhanced when the carbohydrate is deprotected rather than acetyl-protected. Crossover experiments indicate that the presence of benzyl alcohol is changing the selectivity of amine oxidation (amine vs imine) for iridium catalysts, and this change is due to different mechanistic pathways (homocoupling vs hydrogen-borrowing mechanisms). The increased catalytic activity of the deprotected sugar complexes reveals the beneficial impact of the hydroxy functionalities on the catalytic performance. Current work is focusing on exploitation of the carbohydrate functionality on these iridium complexes for other (catalytic) applications, as well as alteration of the stereochemistry of the carbohydrate substituent to enhance its effect.

EXPERIMENTAL SECTION

General Procedures. Ag_2O was used after regeneration by heating to >160 °C under vacuum. Dry degassed solvents were obtained by filtering over columns of dried neutral aluminum oxide under a positive pressure of argon. Compounds **1a**,[55] **1b**,[100,101] **2a**,[55] **3a**,[55] and $[Ir(Cp^*)Cl_2]_2$[102] were synthesized using modified literature procedures. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on Bruker and Varian spectrometers operating at room temperature. Chemical shifts (δ in ppm; coupling constants J in Hz) were referenced to residual solvent resonances and are given downfield from $SiMe_4$. Elemental analysis and mass spectrometry were performed by the microanalytical services of University College Dublin and University of Bern.

Compound ***2b***. This compound was prepared using a modified literature procedure for **2a**. A suspension of 1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-phenyl-1*H*-1,2,3-triazole (1.0 g, 2.1 mmol) and trimethyloxonium tetrafluoroborate (0.44 g, 3.0 mmol) in dry CH_2Cl_2 (100 mL) was stirred for 2 days under a N_2 atmosphere. MeOH (5 mL) was added and the solution evaporated to dryness under reduced pressure. The crude product was dissolved in minimal CH_2Cl_2, and diethyl ether (Et_2O; 100 mL) and pentane (100 mL) were added, followed by cold storage to induce the precipitation of a white solid. This solid was dissolved in CH_2Cl_2 filtered over Celite and dried under reduced pressure. The product was obtained as a white solid (1.0 g, 1.7 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H, $C_{trz}H$),

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7.65−7.54 (m, 5H, $C_{Ar}H$), 6.26 (d, $^3J_{HH}$ = 9.1 Hz, 1H, H_{Gal}-1), 5.76 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H_{Gal}-2), 5.56 (d, J = 3.10 Hz, 1H, H_{Gal}-4), 5.34 (dd, $^3J_{HH}$ = 10.1 and 3.3 Hz, 1H, H_{Gal}-3), 4.48 (t, $^3J_{HH}$ = 6.2 Hz, 1H, H_{Gal}-5), 4.31 (s, 1H, NCH_3), 4.27−4.12 (m, 2H, H_{Gal}-6), 2.2, 2.07, 2.05, 2.02 (4s, 3H, C═OCH_3).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.6, 170.2, 170.0, 169.7 (4C═O), 144.1 ($C_{trz}C_{Ar}$), 132.4, 129.9, 129.7 ($3C_{Ar}$), 128.36 ($C_{trz}H$), 121.5 (C_{Ar}), 88.1 (C_{Gal}-1), 74.7 (C_{Gal}-5), 70.8 (C_{Gal}-3), 67.1 (C_{Gal}-2), 66.9 (C_{Gal}-4), 60.9 (C_{Gal}-6), 39.4 (NCH_3), 20.8, 20.7, 20.6, 20.6 (4C═OOCH_3). HRMS (ESI^+). Calcd for $C_{23}H_{28}N_3O_9$ ($[M - BF_4]^+$): m/z 490.1826. Found: m/z 490.1827

General Procedure for the Synthesis of Carbohydrate Triazolylidene Complexes 3 and 4. A suspension of triazolium salt **1** (1 equiv), NMe_4Cl (1 equiv), and Ag_2O (0.57 equiv) in MeCN (25 mL) was stirred for 24 h under the exclusion of light. The reaction mixture was filtered over Celite, and the volatiles were removed under reduced pressure. The resulting brown solid was suspended in CH_2Cl_2 (50 mL), $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2(Cp^*)]_2$ (0.38 equiv) was added, and the reaction mixture was stirred under the exclusion of light for 2 and 24 h, respectively. The reaction mixture was filtered through Celite, and volatiles were removed under reduced pressure. The crude product was purified by gradient column chromatography (SiO_2).

*Complex **3b**.* As per the general method, triazolium salt **2b** (81.3 mg, 0.14 mmol), NMe_4Cl (16 mg, 0.14 mmol), Ag_2O (21 mg, 0.091 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (32.6 mg, 0.053 mmol) and subsequent purification by column chromatography (SiO_2; CH_2Cl_2, then 9:1 CH_2Cl_2/acetone, and then 2:1 CH_2Cl_2/acetone) yielded complex **3b** as a red-brown solid (57.1 mg, 0.072 mmol, 71%) ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69−7.61 (m, 2H, H_{Ar}), 7.55−7.45 (m, 3H, H_{Ar}), 7.23 (d, $^3J_{HH}$ = 9.2 Hz, 1H, H_{Gal}-1), 6.08 (app. t, 1H, H_{Gal}-2), 5.55 (app. d, 1H, H_{Gal}-4), 5.25 (dd, $^3J_{HH}$ = 10.2 and 3.4 Hz, 1H, H_{Gal}-3), 5.22−5.19 (m, 2H, H_{cym}), 4.86 (d, $^3J_{HH}$ = 5.9 Hz, 1H, H_{cym}), 4.83 (d, $^3J_{HH}$ = 6.2 Hz, 1H, H_{cym}), 4.38−4.32 (m, 1H, H_{Gal}-5), 4.28−4.21, 4.17−4.10 (2m, 1H, H_{Gal}-6), 3.83 (s, 3H, NCH_3), 2.66−2.52 (m, 1H, $CHMe_2$), 2.20, 2.05, 2.00, 1.99 (4s, 3H, $C(O)CH_3$), 1.85 (s, 3H, $C_{cym}CH_3$), 1.18, 1.14 (2d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 170.4, 170.3, 169.9, 169.5 (4C═O), 165.8 (C_{trz}−Ru), 148.4 ($C_{trz}C$), 132.2 ($C_{Ar}H$), 130.4 ($C_{trz}C_{Ar}$), 128.4, 128.3, ($2C_{Ar}H$), 105.9 ($C_{cym}CH$), 97.3 ($C_{cym}CH_3$), 87.2 (C_{Gal}-1), 86.2, 85.9, 84.0, 83.0 ($4C_{cym}H$), 73.6 (C_{Gal}-5), 71.9 (C_{Gal}-3), 68.4 (C_{Gal}-2), 67.5 (C_{Gal}-4), 61.4 (C_{Gal}-6), 37.9 (NCH_3), 30.7 ($CHMe_2$), 22.9, 22.5 ($2CHCH_3$), 21.2, 20.9, 20.9, 20.7 ($4C(O)CH_3$), 18.4 ($C_{cym}CH_3$). HRMS (ESI^+). Calcd for $C_{33}H_{41}ClN_3O_9Ru$ ($[M - Cl]^+$): m/z 760.1575. Found: m/z 760.1576. Anal. Calcd for $C_{33}H_{41}Cl_2N_3O_9Ru\cdot H_2O$: C, 48.71; H, 5.33; N, 5.16. Found: C, 48.98; H, 5.12; N, 5.28.

*Complex **4a**.* According to the general method, the reaction of **2a** (325 mg, 0.56 mmol), NMe_4Cl (61 mg, 0.56 mmol), Ag_2O (75 mg, 0.32 mmol), and $[IrCl_2(Cp^*)]$ (170 mg, 0.21 mmol), followed by purification by column chromatography (SiO_2; CH_2Cl_2, then 9:1 CH_2Cl_2/acetone, and then 9:1 CH_2Cl_2/MeOH or 20:1−2:1 CH_2Cl_2/acetone gradient), yielded the title product as an orange solid (0.321 g, 0.36 mmol, 86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.73 (br s, 2H, H_{Ar}), 7.50−7.43 (m, 3H, H_{Ar}), 6.80 (br s, 1H, H_{Glc}-1), 5.99 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H_{Glc}-2), 5.40−5.22 (m, 2H, H_{Glc}), 4.39−4.24 (m, 2H, H_{Glc}-6 and H_{Glc}), 4.24−4.16 (m, 1H, H_{Glc}-6), 3.81 (s, 3H, NCH_3), 2.08, 2.05, 2.03, 1.97 (4s, 3H, $C(O)CH_3$), 1.39 (s, 15H, $CpCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 170.9, 170.2, 169.6, 168.8 (4C═O), 149.5, 149.1 ($2C_{trz}$), 132.8, 130.3, 128.3, 127.2, ($4C_{Ar}$), 88.8 (C_{Cp}), 86.5 (C_{Glc}-1), 74.4 ($2C_{Glc}$), 71.1 (C_{Glc}-2), 68.1, 61.7 ($2C_{Glc}$), 38.1 (NCH_3), 21.1, 21.0 ($2C(O)CH_3$), 20.8 ($2C(O)CH_3$), 8.8 ($CpCH_3$). HRMS (ESI^+). Calcd for $C_{33}H_{42}ClIrN_3O_9$ ($[M - Cl]^+$): m/z 852.2239. Found: m/z 852.2217. Anal. Calcd for $C_{33}H_{42}Cl_2IrN_3O_9$: C, 44.64; H, 4.77; N, 4.73. Found: C, 44.63; H, 4.55; N, 4.59.

*Complex **4b**.* As per the general method, the triazolium salt **2b** (325 mg, 0.56 mmol), NMe_4Cl (61 mg, 0.56 mmol), Ag_2O (75 mg, 0.32 mmol), and $[IrCl_2(Cp^*)]_2$ (170 mg, 0.21 mmol, 86%) afforded complex **4b**, following column chromatography (SiO_2; CH_2Cl_2, then 9:1 CH_2Cl_2/acetone, and then 9:1 CH_2Cl_2/MeOH or 20:1−2:1 CH_2Cl_2/acetone gradient), as an orange solid (321 mg, 0.36 mmol, 86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.73 (br s, 2H, H_{Ar}), 7.52−7.42 (m, 3H, H_{Ar}), 6.98 (br s, 1H, H_{Gal}-1), 6.13 (t, $^3J_{HH}$ = 9.7 Hz, 1H, H_{Gal}-2), 5.55 (app. d, 1H, H_{Gal}-4), 5.22 (app. d, 1H, H_{Gal}-3), 4.39 (br s, 1H, H_{Gal}-5), 4.29−4.20, 4.19−4.09 (2m, 1H, H_{Gal}-6), 3.84 (s, 3H, NCH_3), 2.22, 2.04, 2.00, 2.00 (4s, 3H, C═$COCH_3$), 1.38 (s, 15H, $CpCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 170.5, 170.4, 169.9 (4C═O), 149.5, 148.8 ($2C_{trz}$), 132.9, 130.3, 128.3, 127.2 ($4C_{Ar}$), 88.7 (C_{Cp}), 87.0 (C_{Gal}-1), 73.5 (C_{Gal}-5), 72.2 (C_{Gal}-3), 68.4 (C_{Gal}-2), 67.5 (C_{Gal}-4), 61.3 (C_{Gal}-6), 38.2 (NCH_3), 21.3, 21.0, 20.9, 20.7 ($4C(O)CH_3$), 8.76 ($CpCH_3$). HRMS (ESI^+). Calcd for $C_{33}H_{42}ClIrN_3O_9$ ($[M - Cl]^+$): m/z 852.2239. Found: m/z 852.2230. Anal. Calcd for $C_{33}H_{42}Cl_2IrN_3O_9$: C, 44.64; H, 4.77; N, 4.73. Found: C, 44.87; H, 4.32; N, 5.33.

General Procedure for Carboyhdrate Deprotection and Formation of Complexes 5. Complex **4** (100 mg, 0.11 mmol) was stirred in methanolic HCl (0.5 M, 2.5 mL, 1.3 mmol) for 2 days. Precipitation was induced by the addition of Et_2O (50 mL) and pentane (50 mL), followed by cooling to −20 °C. The solvent was decanted and the precipitate washed with pentane (100 mL) and dried in vacuo, yielding the product as a yellow solid.

*Complex **5a**.* The general method from **4a** was used. Yield: 67.3 mg (0.094 mmol, 83%). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.62−7.33 (m, 5H, H_{Ar}), 6.07 (d, $^3J_{HH}$ = 4.4 Hz, 1H, OH_{Glc}-2), 5.58 (d, $^3J_{HH}$ = 9.2 Hz, 1H, H_{Glc}-1), 5.44 (d, $^3J_{HH}$ = 4.8 Hz, 1H, OH_{Glc}), 5.20 (d, $^3J_{HH}$ = 5.7 Hz, 1H, OH_{Glc}), 4.53 (t, $^3J_{HH}$ = 5.4 Hz, 1H, OH_{Glc}-6), 4.07 (td, $^3J_{HH}$= 9.2 and 4.4 Hz, 1H, H_{Glc}-2), 3.85 (s, 3H, NCH_3), 3.68−3.51 (m, 3H, H_{Glc}-6 and H_{Glc}), 3.48−3.34 (m, 2H, H_{Glc}), 1.60 (s, 15H, $CpCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2SO$): δ 149.0 ($C_{trz}C$), 135.4 ($C_{trz}Ir$), 132.1 ($C_{trz}C_{Ar}$) 129.8, 127.4, 126.9 ($3C_{Ar}H$), 95.9 (C_{Cp}), 88.7 (C_{Glc}-1), 78.9 (C_{Glc}), 76.6(C_{Glc}-3), 72.9 (C_{Glc}-2), 69.1 (C_{Glc}), 60.0 (C_{Glc}-6), 38.3 (NCH_3), 8.2 ($CpCH_3$). HRMS (ESI^+). Calcd for $C_{25}H_{34}ClIrN_3O_5$ ($[M - Cl]^+$): m/z 684.1811. Found: m/z 684.1811 Anal. Calcd for $C_{25}H_{34}Cl_2IrN_3O_5$: C, 41.72; H, 4.76; N, 5.84. Found: C, 41.23; H, 4.30; N, 6.34.

*Complex **5b**.* The general method from **4b** was used. Yield: 66 mg (0.092 mmol, 82%). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.54−7.37 (m, 5H, H_{Ar}), 5.88 (d, $^3J_{HH}$ = 5.9 Hz, 1H, OH_{Gal}-2), 5.51 (d, $^3J_{HH}$ = 9.3, 1H, H_{Gal}-1), 5.21 (d, $^3J_{HH}$ = 5.6, 1H, OH_{Gal}-3), 4.90 (d, $^3J_{HH}$ = 3.9 Hz, 1H, OH_{Gal}-4), 4.63 (t, $^3J_{HH}$ = 5.5 Hz, 1H, OH_{Gal}-6), 4.47 (td, $^3J_{HH}$ = 9.3 and 4.4 Hz, 1H, H_{Gal}-2), 3.96−3.86 (m, 1H, H_{Gal}-4), 3.84−3.80 (m, 1H, H_{Gal}-5), 3.84 (s, 3H, NCH_3), 3.63−3.55 (m, 1H, H_{Gal}-6), 3.53−3.41 (m, 2H, H_{Gal}-3 and H_{Gal}-6), 1.60 (s, 15H, $CpCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2SO$): δ 148.8 ($C_{trz}C$), 135.1 ($C_{trz}Ir$), 132.2($C_{trz}C_{Ar}$), 129.7, 127.3, 127.0 ($3C_{Ar}H$), 95.8 (C_{Cp}), 89.4 (C_{Gal}-1), 77.4 (C_{Gal}-5), 73.5 (C_{Gal}-3), 69.8 (C_{Gal}-2), 67.3 (C_{Gal}-4), 59.0 (C_{Gal}-6), 38.2 (NCH_3), 8.2 ($CpCH_3$). HRMS (ESI^+). Calcd for $C_{25}H_{34}ClIrN_3O_5$ ($[M - Cl]^+$): m/z 684.1811. Found: m/z 684.1793.

General Considerations for Catalytic Oxidation. One-neck, 10 mL round-bottomed flasks fitted with reflux condensers were used for all catalytic runs, and reactions were heated in an oil bath at 150 °C. For all oxidation reactions 1,2-DCB was used as the solvent (5 mL for runs with ruthenium complexes; 2 mL for runs with iridium complexes). The reaction progress was monitored by dissolving aliquots (0.1 mL) of the reaction mixture in $CDCl_3$ (0.6 mL) and analysis by ^1H NMR spectroscopy through a comparison to the commercial samples and literature values.[103] Conversions and yields were determined relative to the internal standard.

Procedure for the Base-Free Oxidation of Alcohols or Amines (5 mol % Catalyst Loading). A mixture of trimethoxybenzene (9.4 mg, 0.056 mmol) and benzyl alcohol (26 μL, 0.25 mmol), or hexamethylbenzene (2 mg, 0.012 mmol) and benzylamine (27 μL, 0.25 mmol) in 1,2-DCB, with the corresponding metal complex (0.012 mmol) was heated for the time indicated.

Procedure for the Catalytic Oxidation of Amines (1 mol % Catalyst Loading). A mixture of hexamethylbenzene (34 mg, 0.21 mmol, for ruthenium catalysts and 10 mg, 0.062 mmol, for iridium catalysts), 1,2-DCB, benzylamine (135 μL, 1.2 mmol), and a metal complex (0.012 mmol) were heated for the time indicated.

Procedure for the Mixed Catalytic Oxidation of Alcohols and Amines (5 mol % Catalyst Loading). A mixture of hexamethylbenzene (2 mg, 0.012 mmol), benzyl alcohol (26 μL, 0.25 mmol),

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benzylamine (27 μL, 0.25 mmol), and a metal complex (0.012 mmol) were heated for the time indicated.

Procedure for the Mixed Catalytic Oxidation of Alcohols and Amines (1 mol % Catalyst Loading). A mixture of hexamethylbenzene (34 mg, 0.21 mmol, for ruthenium catalysts and 10 mg, 0.062 mmol, for iridium catalysts), 1,2-DCB, benzyl alcohol (130 μL, 1.3 mmol), benzylamine (135 μL, 1.2 mmol), and a metal complex (0.012 mmol) were heated for the time indicated.

Crystal Structure Determination. All measurements were made on an Oxford Diffraction SuperNova area-detector diffractometer using mirror-optics-monochromated Mo Kα radiation (λ = 0.71073 Å) and Al-filtered. Data reduction was performed using the *CrysAlisPro* program.[104,105] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multiscan method using *SCALE3 ABSPACK* in *CrysAlisPro*[104] was applied. The structure was solved by direct methods using *SHELXT*,[106] which revealed the positions of all non-H atoms of the title compound. The non-H atoms were refined anisotropically. All H atoms were placed in geometrically calculated positions and refined using a riding model. Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7*[107] program. Further crystallographic details are compiled in Table S4. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as the supplementary publication number 1560689.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01899.

Data pertaining to catalytic conversions, crystallographic details, and NMR spectra of new compounds (PDF)

Accession Codes

CCDC 1560689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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