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ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 4593–4602
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Carbohydrate-containing N-heterocyclic carbene complexes

Friederike Tewes, Andreas Schlecker, Klaus Harms, Frank Glorius *

Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Straße, 35032 Marburg, Germany

Received 22 March 2007; received in revised form 1 May 2007; accepted 1 May 2007
Available online 8 May 2007

Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Novel carbohydrate bearing imidazolium salts have been synthesized and used for the in situ generation of the corresponding N-heterocyclic carbenes. These compounds were successfully used as catalysts of the conjugate umpolung of cinnamaldehyde to form γ-butyrolactones. In addition, silver and palladium complexes of these N-heterocyclic carbenes were synthesized and structurally characterized.

Keywords: N-Heterocyclic carbenes; Carbohydrates; Palladium complex; Silver complex; Catalysis

1. Introduction

Carbohydrates are the most abundant biological molecules on earth, and fill numerous roles in organisms, such as the storage and transport of energy and structural components [1]. Additionally, carbohydrates and their derivatives play a major role in signalling and recognition processes, being crucial for the functioning of the immune system, fertilization, pathogenesis, blood clotting, and development. As a consequence, a great structural variety of molecules with multiple stereocenters exists and many of them are readily available, rendering them ideally suited for synthetic applications. Therefore, carbohydrates represent not only popular building blocks for the synthesis of biologically active compounds [2], but are also employed as chiral auxiliaries in asymmetric synthesis [3]. However, only a limited number of examples of the successful application of carbohydrates in ligands for transition metal catalysis or as organocatalysts has been reported [4]. The ability of carbohydrates to function as sites for molecular recognition by hydrogen bonding [5] as well as increasing the water solubility due to multiple hydroxyl groups render them very attractive as ligands and catalysts.

Since their first isolation [6], N-heterocyclic carbenes (NHCs) have become versatile neutral ligands for catalysis [7]. Among the applications are many cross-coupling reactions, the majority of which are palladium-catalyzed, like Heck reactions [8], Suzuki–Miyaura [9], Stille [7a,10] or Sonogashira cross-coupling reactions [11] and ruthenium-catalyzed metathesis reactions [12]. The use of NHCs as organocatalysts in transesterification [13] or umpolung reactions [14] is also rapidly increasing and thereby enriching the tools of organic chemistry. Their electron-richness, the often observed extraordinary stability of the corresponding metal complexes and the unique shape make these ligands very attractive and exceed the often employed "phosphine mimic" analogy. Steric and electronic properties can be varied independently, although especially the latter one, caused by introduction of different heteroatoms and heterocycles, has not been sufficiently explored to date.

Herein, we report the preparation of NHC precursors bearing a carbohydrate moiety starting from D-glucose and D-galactose and the preparation of metal NHC complexes thereof [15,16].

* Corresponding author. Tel.: +49 6421 2825562; fax: +49 6421 2825629.
E-mail address: glorius@chemie.uni-marburg.de (F. Glorius).

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doi:10.1016/j.jorganchem.2007.05.007

2. Results and discussion

The most popular route to NHCs is the deprotonation of the corresponding azolium salts (e.g. imidazolium, triazolium, tetrazolium, pyrazolium, benzimidazolium, oxazolium or thiazolium) with the help of suitable bases. Whereas in organocatalysis, mostly imidazolium, triazolium and thiazolium derived NHC are employed successfully, imidazolium and imidazolinium derived NHC are by far the most important NHC as ligands for transition metal catalysis. For the synthesis of imidazolium salts many different routes have been developed, however, the alkylation of imidazoles with suitable electrophiles is probably the most efficient entry [17]. Therefore, we envisioned attack of an imidazole at the suitably substituted anomeric position of a carbohydrate to be an efficient route for the synthesis of carbohydrate derived NHCs **1** (Scheme 1) or biscarbohydrate substituted ones [18]. As an additional advantage, many different stereoisomers and different ''protection'' groups on the hydroxyl termini of the carbohydrate moiety can be employed, thus allowing a valuable finetuning of the properties of these ligands.

Along these lines, differently protected pyranoses **2** and **3** bearing a bromide leaving group at the anomeric position were readily prepared from D-glucose and D-galactose [19]. Since bis-mesityl substituted NHCs IMes and SIMes are the NHCs most often employed in catalysis, mesityl imidazole was selected as the nucleophile of choice to react with **2** or **3**. Treatment of mesityl imidazole with galactose derived bromide **2** activated by silver triflate resulted in the formation of the corresponding imidazolium salt in 42% yield. In this process, only the β-anomer was obtained (Scheme 2). A ready distinction between α- and β-anomer by ^{1}H NMR was not possible. Nevertheless, crystals suitable for X-ray structural analysis were obtained by diffusion of pentane into a saturated solution of imidazolium triflate **4** in CH_2Cl_2, evidencing the β-stereochemistry (Fig. 1 and Table 1). Compound **4** crystallizes in the form of colorless plates in a monoclinical unit cell.

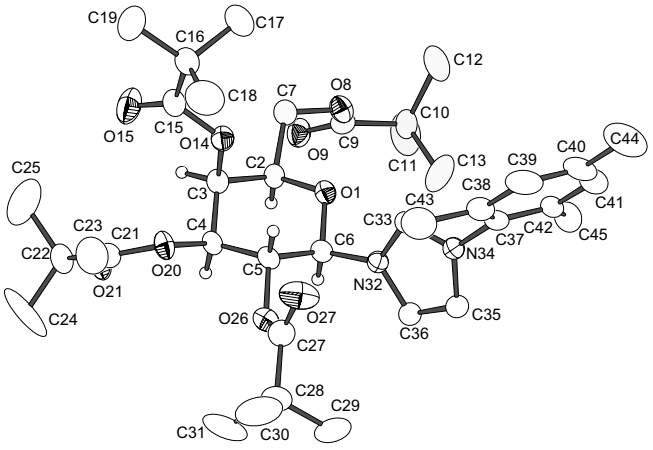
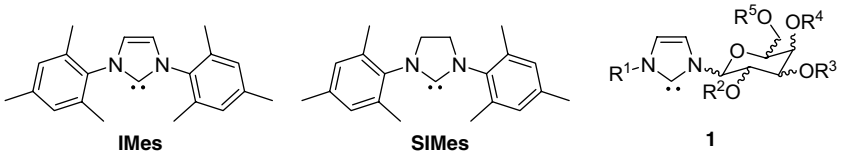


Fig. 1. ORTEP drawing of **4** (thermal ellipsoids set at 30% probability) showing the absolute configuration. Most hydrogen atoms, second positions of disorder and the anion are omitted for clarity.

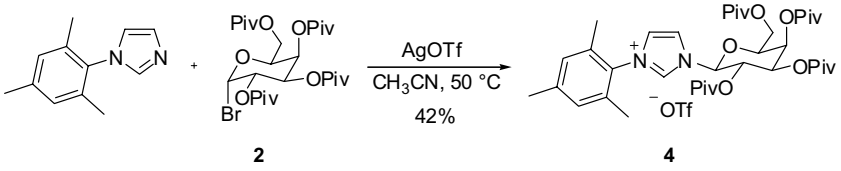
In addition, glucose derived bromide **3** was treated with mesityl imidazole under different conditions. Using silver nitrate, a mixture of anomers **5a** was obtained in 72% yield (Scheme 3). However, switching to silver triflate resulted once again in the isolation of the pure β-anomer **5b**. Besides the possibility to employ different stereoisomers and a variety of different end groups on the hydroxyl termini, a deprotection with KCN resulted in the formation of imidazolium salts **6a** and **6b** with free hydroxyl groups in fair

Table 1
Selected bond lengths and angles of **4**

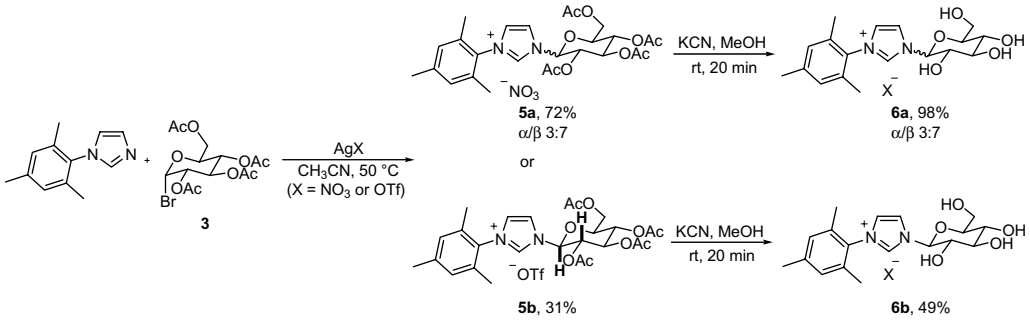
Bond	Distance [Å]	Angle	[°]
C6–N32	1.451(4)	N32–C6–O1	105.4(2)
C33–N32	1.355(3)	N34–C33–N32	107.4(3)
C33–N34	1.322(3)		
C35–C36	1.340(4)		
C35–N34	1.394(3)		
C36–N32	1.373(4)		
C37–N34	1.448(4)		



Scheme 1. Structural comparison of well-known IMes and SIMes with carbohydrate-containing NHC **1**.



Scheme 2. Formation of galactose derived imidazolium salt **4**.



Scheme 3. Formation of a set of glucose derived imidazolium salts **5** and **6** [20].

to excellent yields. The anomer ratio and purity remained unchanged. As a result, this simple method allows the formation of a large set of imidazolium salts with a great variety of properties.

The configuration at the anomeric position for compounds **5** and **6** was determined using ^{1}H NMR spectroscopy. The size of vicinal couplings is dependent of the angle of torsion between the vicinal C–H bonds. The determination of the configuration will be described for **5b**. The proton at the anomeric position results in a doublet at 6.48 ppm, the coupling constant ^3J being 8.4 Hz. This is indicative of a diaxial relationship of these two hydrogens and thus a β-configurated sugar as indicated in Scheme 3.

With these imidazolium salts in hand, we investigated the formation and isolation of the corresponding NHCs. However, using different deprotonation protocols we did not succeed with the isolation of carbohydrate derived NHC. Nevertheless, treatment of **4** or **5b** with a weak base like DBU resulted in the formation of the NHCs that subsequently reacted with elemental sulfur [21] to the imidazol-2-thions **7** and **8** in excellent yield (Scheme 4). Accordingly, treatment of a d_8-THF solution of **5a** with DBU resulted in the disappearance of the sharp ^{1}H NMR peaks of the imidazolium protons (mixture of anomers).

Since attempts to isolate NHC of type **1** failed, it was questionable, if these compounds could act as organocatalysts in umpolung reactions. We selected the conjugated umpolung of α,β-unsaturated aldehydes, a transformation recently independently developed by Bode et al. [14d–f] and us [14a–c] for the formation of γ-butyrolactones and related products. Cinnamaldehyde and α,α,α-trifluoroacetophenone were stirred in THF at ambient temperature together with a small amount of the carbohydrate-contain-

Table 2
Comparison of different catalysts in the formation of γ-butyrolactones

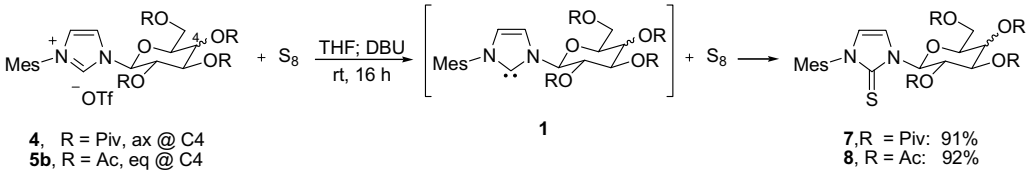
Entry	Catalyst	Amount cat. [mol%]	Yield [%]	**12a**:**12b**
1[a]	**IMes**	10	84	66:34
2[b]	**IMes**	10	78	50:50[d]
3[a]	**4**	10	81	73:27
4[a]	**5a**	10	79	84:16
5[b]	**5a**	5	93	63:37[d]
6[b,c]	**5a**	1	83	66:34[d]
7[a]	**5b**	10	83	76:24
8[a]	**6a**	10	79	83:17

[a] *Reaction conditions*: substrates **9** (0.5 mmol) and **10** (0.5 mmol), THF (3 ml), catalyst, DBU (60 mol%), r.t., 16 h. Yields determined by GC–MS using an internal standard.

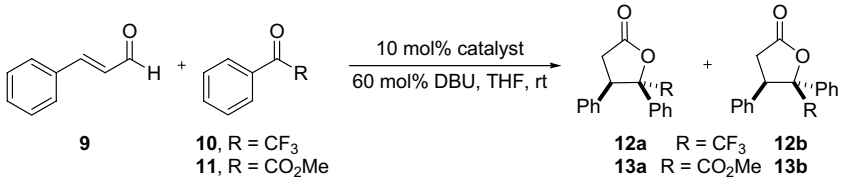
[b] *Reaction conditions*: substrates **9** (0.5 mmol) and **11** (0.5 mmol), THF (3 ml), catalyst, DBU (60 mol%), r.t., 16 h. Yields determined by GC–MS using an internal standard.

[c] 1.0 mmol **11**, 36 h.

[d] Products **13** were obtained.



Scheme 4. In situ formation of N-heterocyclic carbenes and trapping with elemental sulfur.



Scheme 5. Organocatalyzed formation of γ-butyrolactones by conjugate umpolung [14b].

Table 3
Selected geometrical parameters for **15** (Å, °)

First molecule[a]		Second molecule[a,b]	
Pd1–C1	1.990(10)	Pd2–C201	2.036(9)
Pd1–C101	1.977(10)	Pd2–C301	2.040(10)
Pd1–Cl1	2.298(2)	Pd2–Cl3	2.319(2)
Pd1–Cl2	2.316(2)	Pd2–Cl4	2.312(2)
C101–Pd1–C1	176.7(3)	C201–Pd1–C301	178.9(3)
C101–Pd1–Cl1	89.4(2)	C201–Pd2–Cl3	89.7(2)
C1–Pd1–Cl1	93.6(3)	C301–Pd2–Cl3	89.2(2)
C101–Pd1–Cl2	89.5(2)	C201–Pd2–Cl4	90.2(2)
C1–Pd1–Cl2	87.4(3)	C301–Pd2–Cl4	90.9(2)
Cl1–Pd1–Cl2	175.55(10)	Cl3–Pd2–Cl4	179.88(11)
C1–N1	1.361(12)	C201–N201	1.254(12)
C101–N101	1.409(10)	C301–N301	1.356(12)
C1–N2	1.400(12)	C201–N202	1.375(12)
C101–N102	1.393(12)	C301–N302	1.342(11)
N2–C13	1.476(10)	N202–C213	1.440(12)
N102–C113	1.379(11)	N302–C313	1.479(13)
C13–O14	1.400(10)	C213–O214	1.422(10)
C113–O114	1.467(11)	C313–O314	1.426(14)
C13–C18	1.502(14)	C213–C218	1.545(14)
C113–C118	1.511(14)	C313–C318	1.474(14)
C1–N2–C13	123.9(7)	C201–N202–C213	127.4(8)
C101–N102–C113	117.4(7)	C301–N302–C313	125.1(9)
N2–C13–O14	104.0(7)	N202–C213–O214	110.8(7)
N102–C113–O114	106.6(6)	N302–C313–O314	106.1(8)
N2–C13–C18	113.7(7)	N202–C213–C218	113.5(8)
N102–C113–C118	111.4(7)	N302–C313–C318	113.2(8)

[a] These data may not be fully reliable due to correlation of the parameters during twin refinement. However, the origin of some marked differences (e.g. C1–N1 vs. C201–N201 or N102–C113 vs. N302–C313) is not clear at date. For clarity, comparable bonds of the two independent complexes of the unit cell are placed side by side in the table above.

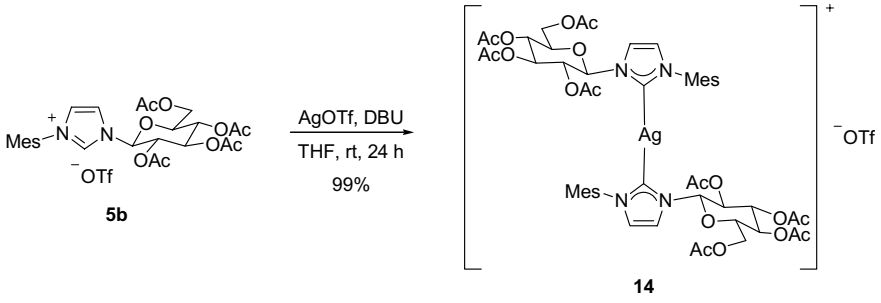
[b] There are two independent palladium complexes in the asymmetric unit.

ing imidazolium salt under investigation and a sixfold excess of DBU (Scheme 5). Remarkably, all NHC tested resulted in good yields of the desired lactone products, again indicating the intermediacy of carbene like compounds (Table 2). Moreover, in comparison to IMes as catalyst the ratio of regioisomers was greatly improved up to 83:17 in favor of the kinetic product **9a** (entries 4 and 8). Phenyl glyoxylate was another substrate successfully employed under these conditions. Reduction of the amount of catalyst down to 1 mol% still resulted in good yield and selectivity (entry 6). It is important to note that these results represent the best stereoselectivities obtained in this umpolung reaction for these substrate combinations to date. However, it is still unclear, if the counter anion or the configuration of the anomeric position significantly influence the outcome of these transformations (see Table 3).

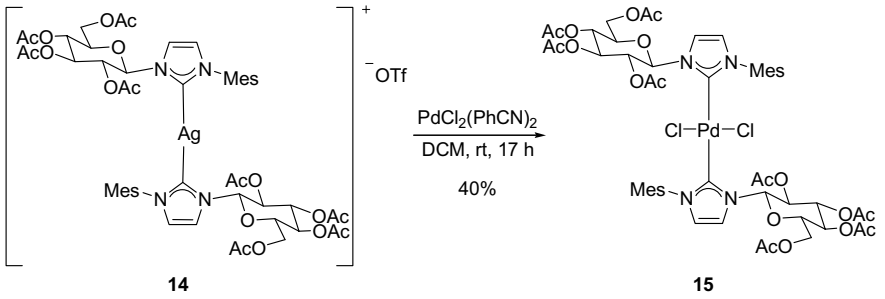
As mentioned in Section 1, palladium complexes of NHC are especially interesting and have a myriad of applications. However, many attempts to form palladium complexes of the carbohydrate derived NHC **1** by deprotonation of the imidazolium salts and addition of suitable metal complexes failed. Silver NHC complexes contain rather labile Ag–C bonds with a strong ionic character and have therefore often been employed to transfer their NHC ligands to other metals like Au(I), Cu(I), Rh(I), Pd(II) or Ni(II) [22]. Gratefully, treatment of a THF solution of imidazolium salt **5b** with silver triflate and DBU resulted in the formation of bis(NHC)silver(I)-complex **14** in an excellent yield of 99% (Scheme 6).

Simple stirring of silver complex **14** with a palladium (II) benzonitrile complex resulted in the formation of bis(NHC)palladium(II)-complex **15**. After chromatographic purification and crystallization, the product was obtained in the form of colorless crystals and in a yield of 40% (Scheme 7).

The ^{1}H NMR of complex **15** shows only one set of NHC signals indicating a rather symmetric structure. For obtaining more information, colorless single crystals suitable for X-ray structural analysis were obtained by slow diffusion of pentane into a saturated solution of the complex in CH_2Cl_2 at ambient temperature (Figs. 2 and 3). Two independent palladium complexes were obtained in the unit cell. In this complex **15**, palladium is coordinated square planar and the NHC ligands are arranged in a *trans* fashion on the palladium and are bound through the C2-position of the heterocyclic ring. In the two independent palladium complexes of the unit cell, the planes of the two NHC ligands are only slightly tilted against each other by 17.1(6)° and 37.0(6)°, in each case one sugar moiety and one mesityl ring facing each other. Finally, this unequivocally shows that the carbene **5b** exists as the β-anomer.



Scheme 6. Formation of bis(NHC)silver(I)-complex (**14**).



Scheme 7. Formation of the bis(NHC)palladium(II)-complex (**15**).

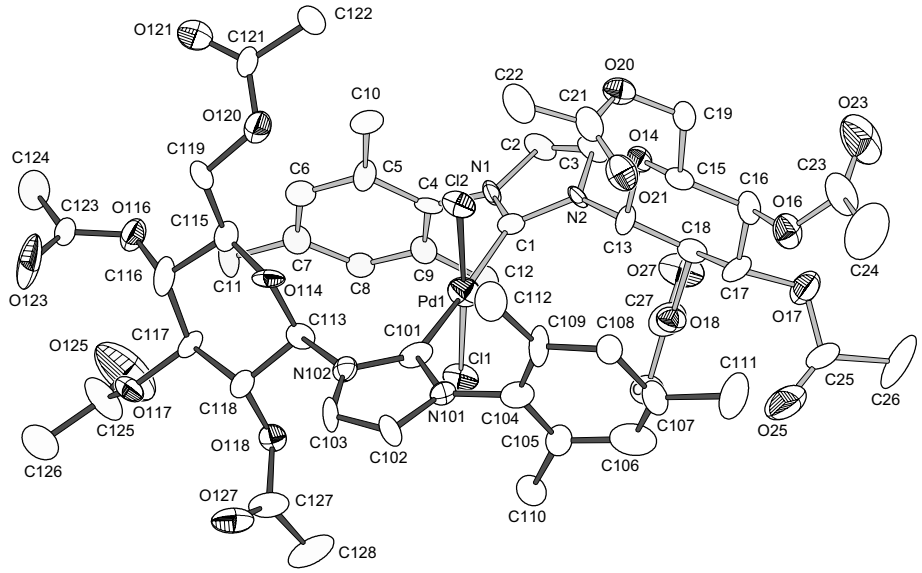


Fig. 2. ORTEP drawing of the first of the two independent Pd complexes **15** showing the absolute configuration (thermal ellipsoids set at 30% probability). Hydrogen atoms, second positions of disorder and solvent molecules are omitted for clarity.

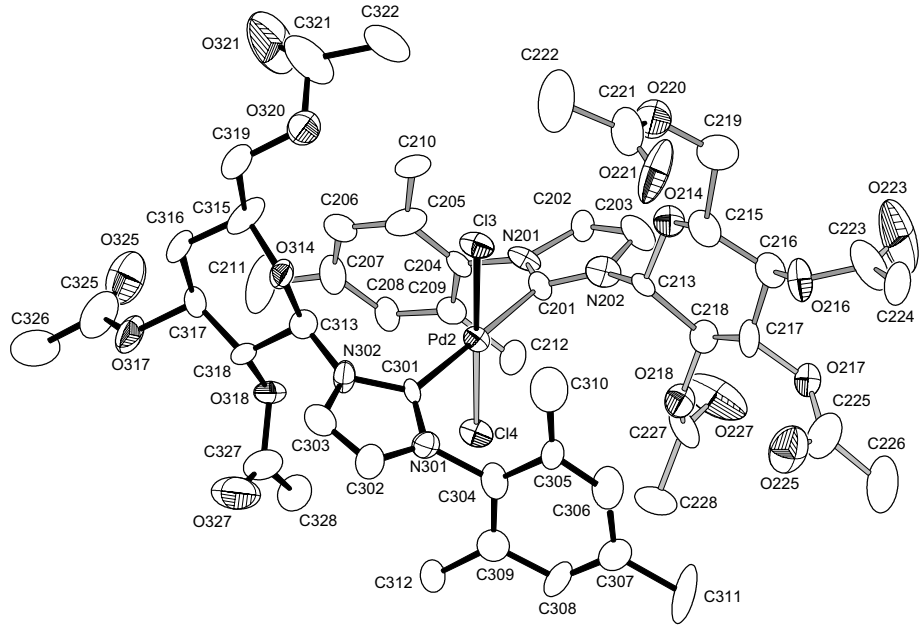


Fig. 3. ORTEP drawing of the second of the two independent Pd complexes **15** showing the absolute configuration (thermal ellipsoids set at 30% probability). Hydrogen atoms, second positions of disorder and solvent molecules are omitted for clarity.

3. Summary

We have developed a new class of readily available carbohydrate-containing N-heterocyclic carbene ligands. The characteristic properties of carbohydrates, e.g. many different stereoisomers being available in enantiomerically pure form, allowing a variety of substituents, providing multiple points of interaction as hydrogen bond donor or acceptor, render this class of compounds to be very promising. As has been shown, the free NHC can be prepared in situ, trapped or used as organocatalyst with improved selectivities in the formation of some γ-butyrolactones. Furthermore, silver and palladium complexes were formed in good yield and the palladium complex was structurally characterized by X-ray analysis. The application of these compounds in catalysis and especially asymmetric catalysis is under investigation.

4. Experimental

4.1. General

Chemicals were purchased in commercially available qualities puriss., p.a. or purum from Fluka, Aldrich, Acros, Lancaster and Merck and were used without further purification. Solvents toluene and CH_2Cl_2 were of technical quality and were distilled and dried over CaH_2. Solvents for extractions and column chromatography were of technical quality and were distilled prior to use. Molecular sieves (4 Å) were activated by microwave irradiation (3×3 min). For flash chromatography, Merck silica gel 60 (230–400 mesh) was used. NMR spectra were recorded on a ARX 300 or DRX 400 spectrometer (Bruker) in $CDCl_3$; chemical shifts (δ) are given in parts per million relative to tetramethylsilane, and coupling constants (J) are given in Hertz. For IR, a Bruker IFS 88 was used; wavenumbers (ν) are given in cm^{-1}. For MS [electron ionization (EI)], a Varian CH7 (70 eV) was used, and for highresolution MS (HRMS), a Finnigan LTQ FT or TSQ 700 was used.

2,3,4,6-Tetra-*O*-pivaloyl-β-D-galactopyranosyl-bromide (**2**) [23] and 2,3,4,5-tetra-*O*-acetyl-D-glucopyranosylbromide (**3**) [24] were prepared according to the literature procedures.

4.2. Characterizations of imidazolium salts, imidazol-2-thions and metal NHC complexes as well as procedures for the organocatalyzed reactions

4.2.1. 1-(2,3,4,6-Tetra-O-pivaloyl-D-galactopyranosyl)-3-(2,4,6- trimethyl-phenyl)-3H-imidazolium triflate (*4*)

To a solution of silver triflate (0.43 g, 1.69 mmol) in acetonitrile (7 ml) were added 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosyl-bromide (**2**, 0.98 g, 1.69 mmol) and mesityl imidazole (0.28 g, 1.52 mmol). The reaction mixture was stirred for 6 d at 50 °C. All insoluble parts were filtered off over Celite, and then the remaining solution was concentrated under reduced pressure. The resulting solid was dissolved in DCM and the solution was stirred over $Na_2CO_3$for 1 h. After filtration the solvent was removed under reduced pressure and the resulting solid was washed severall times (7×10 mL) with pentane to give an off-white solid. Yield: 0.53 g (41%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ (s, 9H, $C(CH_3)_3$), 1.11 (s, 9H, $C(CH_3)_3$), 1.14 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 2.01 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.04 (dd, 1H, $J = 11.1$ Hz, $J = 7.2$ Hz, CH_2), 4.19 (dd, 1H, $J = 11.1$ Hz, $J = 6.9$ Hz, CH_2), 4.56 (t, 1H, $J = 7.2$ Hz, C*H*-CH_2), 5.46 (m, 2H, $CH_{carbohydrate}$), 5.60 (s, 1H, $CH_{carbohydrate}$), 6.64 (m, 1H, N–CH–O), 7.02 (s, 2H, CH_{aromat}), 7.33 (s, 1H, =CH), 7.82 (s, 1H, =CH), 9.52 (s, 1H, N=CH–N); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.2$, 21.0, 26.9, 27.0, 27.1, 27.2, 38.6, 38.7, 38.9, 39.1, 60.2, 66.4, 68.4, 70.5, 74.3, 84.7, 120.7, 124.2, 129.5, 129.9, 130.0, 130.2, 133.4, 134.2, 137.6, 141.9, 176.2, 176.3, 177.7; IR (KBr) $\nu = 639$, 1031, 1157, 1279, 1482, 1741, 2978; HRMS (ESI-pos., MeOH) m/z: 685.4061 (calculated: 685.4059) $[C_{38}H_{57}N_2O_9]^+$. Colorless crystals, suitable for the X-ray diffraction, were obtained from diffusion of pentane into a solution of DCM.

4.2.2. Data for the X-ray structural analysis of imidazolium salt *4*

$C_{38}H_{57}N_2O_9$, CF_3O_3S, $M_r = 834.93$ g mol^{-1} colorless plates, size $0.27 \times 0.15 \times 0.03$ mm^3, monoclinic, space group $P2_1$, $a = 9.601(2)$, $b = 10.632(2)$, $c = 22.461(5)$ Å, $\beta = 98.882(18)°$, $V = 2265.1(9)$ Å^3, $T = -100$ °C, $Z = 2$, $\rho_{calc} = 1.224$ mg m^{-3}, $\mu = 1.41$ cm^{-1}, semi-empirical absorption correction from equivalent reflections, $F(000) = 888$, 17,838 reflections in h (−11/11), k (−12/12), l (−26/26), measured in the range $1.84° < \Theta < 25.00°$, completeness $\Theta_{max} = 100\%$, 7980 independent reflections, $R_{int} = 0.0868$, 4156 reflections with $I > 2.0\,\sigma(I)$, 585 parameters, 1 restraints, $R_1 = 0.0400$, $wR_{2all} = 0590$, GOF = 0.776, largest difference peak and hole 0.14 and −0.14 e/Å^3, Flack parameter 0.08(7). Two of the four *t*-butyl groups are disordered.

4.2.3. 1-(2,3,4,5-Tetra-O-acetyl-D-glucopyranosyl)-3-(mesityl)- 3H-imidazolium nitrate (*5a*)

To a solution of 2,3,4,5-tetra-*O*-acetyl-D-glucopyranosylbromide (**3**, 2.00 g, 4.88 mmol) in acetonitrile (20 ml) were added silver nitrate (0.83 g, 4.88 mmol) and mesityl imidazole (0.82 g, 4.41 mmol). The reaction mixture was stirred at 50 °C for 18 h. All insoluble parts removed by filtration through Celite, and then the solution was concentrated under reduced pressure. The resulting solid was dissolved in DCM and stirred over Na_2CO_3 for 30 min. After filtration the product was recrystallized several times from DCM/MTBE to give a yellow solid. Both anomeres were formed in a ratio β:$\alpha = 7$:3. Yield: 1.82 g (72%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.11$–1.97 (m, 18H, CH_3), 2.34 (s, 3H, CH_3), 4.18 (dd, 0.7H, $J = 12.6$ Hz, $J = 1.9$ Hz, $CH_{carbohydrate}$), 4.28–4.23

(m, 0.7H, $CH_{carbohydrate}$), 4.40–4.34 (m, 1H, $CH_{carbohydrate}$), 4.56–4.46 (m, 0.6H, $CH_{carbohydrate}$), 5.03–5.00 (m, 0.3H, $CH_{carbohydrate}$), 5.31–5.23 (m, 1.7H, $CH_{carbohydrate}$), 5.50 (t, 0.7H, $J = 9.4$ Hz, $CH_{carbohydrate}$), 5.55 (dd, 0.3H, $J = 4.3$ Hz, $J = 2.8$ Hz, $CH_{carbohydrate}$), 6.65 (d, 0.7H, $J = 9.65$ Hz, $CH_{carbohydrate}$), 6.99 (m, 2H, CH_{aromat}), 7.07 (d, 0.3H, $J = 2.7$ Hz, $CH_{carbohydrate}$), 7.25 (t, 0.7H, $J = 1.7$ Hz, =CH), 7.27 (t, 0.3H, $J = 1.5$ Hz, =CH), 7.82 (t, 0.7H, $J = 1.7$ Hz, =CH), 7.95 (s, 0.3H, =CH), 10.03 (s, 0.3H, α-anomer, N=CH–N), 10.33 (s, 0.7H, β-anomer, N=CH–N); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.9$, 17.2, 17.2, 17.4, 20.2, 20.4, 20.5, 20.6, 20.6, 21.0, 61.2, 61.3, 66.8, 67.5, 67.6, 71.1, 72.3, 74.6, 75.2, 84.5, 120.1, 124.0, 129.9, 130.0, 130.3, 130.6, 133.8, 134.2, 139.2, 139.2, 141.7, 169.2, 169.2, 169.5, 169.6, 170.0, 170.4, 170.5; IR (KBr) $\nu = 580$, 601, 672, 754, 830, 858, 911, 962, 1039, 1108, 1146, 1220, 1373, 1434, 1549, 1609, 1754, 2988, 3084, 3467; HRMS (ESI-pos., MeOH) *m/z*: 517.2182 (calculated: 517.2181) $[C_{26}H_{33}N_2O_9]^+$.

4.2.4. 1-(2,3,4,6-Tetra-O-acetyl-D-glucopyranosyl)-3-(2,4,6- trimethyl-phenyl)-3H-imidazolium triflate (**5b**)

To a solution of silver triflate (2.5 g, 9.72 mmol) in acetonitrile (40 ml) were added 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylbromide (4.0 g, 9.72 mmol) and mesityl imidazole (1.63 g, 8.75 mmol). The reaction mixture was stirred for 16 h at 50 °C. The resulting solid was removed by filtration through Celite. After evaporation of the solvent under reduced pressure the resulting solid was recrystallized several times from DCM/MTBE to give a brown solid. Yield: 1.82 g (31%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.10$–1.97 (m, 18 H, CH_3), 2.35 (s, 3H, CH_3), 4.18 (d, 1H, $J = 12$ Hz, CH_2), 4.30 (m, 1H, $CH_{carbohydrate}$), 4.39 (m, 1H, CH_2), 5.27 (t, 2H, $J = 9.3$ Hz, $CH_{carbohydrate}$), 5.50 (t, 1H, $J = 9.3$ Hz, $CH_{carbohydrate}$), 6.48 (d, 1H, $J = 8.4$ Hz, N–CH–O), 7.03 (s, 2H, CH_{aromat}), 7.25 (s, 1H, =CH), 7.83 (s, 1H, =CH), 9.51 (s, 1H N=CH–N); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.9$, 17.3, 20.2, 20.4, 20.5, 20.6, 21.1, 61.2, 67.4, 71.3, 72.3, 75.2, 84.5, 120.6, 124.1, 129.9, 130.1, 133.6, 134.2, 137.5, 142.0, 169.2, 169.7, 170.0, 170.4; IR (KBr): 1031, 1159, 1225, 1373, 1755, 2925, 3453; HRMS (ESI-pos., MeOH) *m/z*: 517.2180 (calculated: 517.2181) $[C_{26}H_{33}N_2O_9]^+$.

4.2.5. 1-(D-Glucopyranosyl)-3-(2,4,6-trimethyl-phenyl)-3H-imidazolium salt (**6a**) [20]

To a solution of 1-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)-3-(2,4,6-trimethyl-phenyl)-3H-imidazolium nitrate (0.55 g, 0.95 mmol) in methanol (1.5 ml) was added dry KCN (30.8 mg, 0.47 mmol). The reaction mixture was stirred at room temperature for 20 min. Then the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (DCM/MeOH = 9:1) to give a yellow oil. Both anomers were formed in a ratio $\beta{:}\alpha = 7{:}3$. Yield: 380 mg (98%); ^{1}H NMR (300 MHz, DMSO): $\delta = 2.01$ (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.16 (d, 0.7H, $J = 5.4$ Hz, $CH_{carbohydrate}$), 3.29 (m, 1 H), 3.51 (m, 3H), 3.76 (m, 1H), 3.92 (m, 0.3H, $CH_{carbohydrate}$), 4.12 (q, 0.3H, $J = 5.1$ Hz, $CH_{carbohydrate}$), 4.72 (m, 1H), 5.32 (m, 1H), 5.47 (m, 3H), 5.93 (d, 0.7H, $J = 5.7$ Hz, $CH_{carbohydrate}$), 6.21 (d, 0.3H, $J = 4.8$ Hz, $CH_{carbohydrate}$), 6.31 (d, 0.3H, $J = 5.4$ Hz, $CH_{carbohydrate}$), 7.16 (s, 2H, CH_{aromat}), 8.04 (s, 1H, =CH), 8.15 (s, 0.3H, =CH), 8.27 (s, 0.7H, =CH), 9.56 (s, 0.3H, N=CH–N), 9.70 (s, 0.7H, N=CH–N); ^{13}C NMR (75 MHz, DMSO): $\delta = 16.7$, 16.8, 20.5, 60.5, 69.0, 72.9, 76.1, 77.1, 80.2, 87.3, 121.3, 124.2, 129.1, 129.2, 131.0, 134.1, 136.8, 140.3; IR (Film) $\nu = 621$, 763, 825, 859, 898, 1005, 1026, 1051, 1105, 1208, 1372, 1486, 1549, 1608, 1653, 1779, 2126, 2253, 2921, 3340; HRMS (ESI-pos., MeOH)*m/z*: 349.1753 (calculated: 349.1758) $[C_{18}H_{25}NO_2]^+$.

4.2.6. 1-(D-Glucopyranosyl)-3-(2,4,6-trimethyl-phenyl)-3H-imidazolium salt (**6b**) [20]

To a solution of 1-(2,3,4,5-tetra-*O*-acetyl-D-glucopyranosyl)-3-(2,4,6-trimethyl- phenyl)-3H-imidazolium triflate (240 mg, 0.36 mmol) in methanol (6 ml) was added dry KCN (11.7 mg, 0.18 mmol). The reaction mixture was stirred at room temperature for 90 min. Then the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (DCM/MeOH = 9:1) to give a colorless oil. Yield: 88 mg (49%); ^{1}H NMR (300 MHz, *d*-DMSO): $\delta = 2.01$ (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.55-3.25 (m, 5H, OH, $CH_{carbohydrate}$), 3.77 (dd, 1H, $J = 10.1$ Hz,$J = 5.3$ Hz, $CH_{carbohydrate}$), 4.68 (t, 1H, $J = 6.0$ Hz, $CH_{carbohydrate}$), 5.30 (d, 1H, $J = 5.5$ Hz, $CH_{carbohydrate}$), 5.50–5.45 (m, 2H, $CH_{carbohydrate}$), 5.90 (d, 1H, $J = 5.5$ Hz, $CH_{carbohydrate}$), 7.16 (s, 2H, CH_{aromat}), 8.03 (t, 1H, $J = 1.7$ Hz, =CH), 8.26 (t, 1H, $J = 1.7$ Hz, =CH), 9.69 (t, 1H, $J = 1.4$ Hz, N=CH–N); ^{13}C NMR (75 MHz, *d*-DMSO): $\delta = 16.7$, 16.8, 20.5, 60.5, 69.0, 72.9, 76.1, 80.2, 87.3, 121.3, 124.1, 129.2, 130.9, 134.1, 136.8, 140.3; IR (KBr) $\nu = 517$, 575, 639, 766, 827, 859, 898, 1031, 1104, 1164, 1227, 1278, 1383, 1447, 1486, 1552, 1632, 2261, 2952, 3399; HRMS (ESI-pos., MeOH) *m/z*: 349.1757 (calculated: 349.1758) $[C_{18}H_{25}NO_2]^+$.

4.2.7. 1-(2,3,4,6-Tetra-O-pivaloyl-D-galactopyranosyl)-3-(2,4,6- trimethylphenyl)-1,3-dihydro-imidazol-2-thione (**7**)

To a solution of 1-(2,3,4,6-tetra-*O*-pivaloyl-D-galactopyranosyl)-3-(2,4,6-trimethyl-phenyl)-3H-imidazolium triflate (25 mg, 0.03 mmol) and elemental sulfur (2 mg, 0.07 mmol) in 1 ml THF was added DBU (9 mg, 0.06 mmol). The reaction mixture was stirred at room temperature for 16 h. Afterwards the reaction was quenched with water (2 ml) and the aqueous phase was extracted with DCM (4 × 5 ml). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to give a brown solid. Yield: 19.6 mg (91%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.09$ (s, 9H, $C(CH_3)_3$), 1.14 (s, 9H, $C(CH_3)_3$), 1.16 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.99 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.31 (s,

3H, CH_3), 4.03 (dd, 1H, $J = 10.8$ Hz, $J = 6.9$ Hz, $CH_{carbohydrate}$), 4.19 (dd, 1H, $J = 10.8$ Hz, $J = 6.6$ Hz, $CH_{carbohydrate}$), 4.28 (t, 1H, $J = 6.6$ Hz, $CH_{carbohydrate}$), 5.39 (dd, 1H, $J = 9.9$ Hz, $J = 3.0$ Hz, $CH_{carbohydrate}$), 5.54 (d, 1H, $J = 2.7$ Hz, $CH_{carbohydrate}$), 5.63 (t, 1H, $J = 9.6$ Hz, $CH_{carbohydrate}$), 6.35 (d, 1H, $J = 9.6$ Hz, $CH_{carbohydrate}$), 6.62 (d, 1H, $J = 2.4$ Hz, =CH), 6.96 (s, 1H, CH_{aromat}), 6.97 (s, 1H, CH_{aromat}), 7.01 (d, 1H, $J = 2.4$ Hz, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.9$, 18.0, 21.1, 27.06, 27.08, 27.1, 27.3, 38.7, 38.8, 39.1, 60.7, 66.8, 67.4, 71.5, 73.6, 82.8, 114.6, 128.1, 129.1, 129.4, 133.2, 135.2, 135.9, 139.4, 165.7, 176.5, 176.9, 177.1, 177.8; IR (KBr) $\nu = 751$, 1129, 1208, 1234, 1281, 1741, 2975; HRMS (ESI-pos., MeOH) m/z: 739.3616 (calculated:739.3599) $[C_{38}H_{56}N_2O_9SNa]^+$.

4.2.8. 1-(2,3,4,6-Tetra-O-acetyl-D-glycopyranosyl)-3-(2,4,6- trimethylphenyl)-1,3-dihydro-imidazol-2-thione (8)

To a solution of 1-(2,3,4,5-tetra-*O*-acetyl-D-glucopyranosyl)-3-(2,4,6-trimethyl- phenyl)-3H-imidazolium triflate (**56b**) (50.0 mg, 0.075 mmol) and elemental sulfur (5.76 mg, 0.18 mmol) in 3 ml THF was added DBU (22.5 μl, 0.15 mmol) The reaction mixture was stirred at room temperature for 17 h. Afterwards the reaction was quenched with water (5 ml) and the aqueous phase was extracted with MTBE (2 × 5 ml). The combined organic phases were concentrated under reduced pressure to give a brown oil. Yield: 38 mg (92%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.96$ (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.05 (s, 3H), 2.06 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.03–3.97 (m, 1H, $CH_{carbohydrate}$), 4.16 (dd, 1H, $J = 12.6$ Hz, $J = 2.0$ Hz, $CH_{carbohydrate}$), 4.34 (dd, 1H, $J = 12.6$ Hz, $J = 4.6$ Hz, $CH_{carbohydrate}$), 5.23 (t, 1H, $J = 9.6$ Hz, $CH_{carbohydrate}$), 5.28 (t, 1H, $J = 9.5$ Hz, $CH_{carbohydrate}$), 5.48 (t, 1H, $J = 9.5$ Hz, $CH_{carbohydrate}$), 6.29 (d, 1H, $J = 9.3$ Hz, $CH_{carbohydrate}$), 6.63 (d, 1H, $J = 2.6$ Hz, =CH), 6.97 (s, 2H, CH_{aromat}), 7.02 (d, 1H, $J = 2.6$ Hz, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.5$, 17.9, 20.5, 20.5, 20.6, 20.7, 21.1, 61 .6, 66.0, 71.0, 72.7, 74.8, 82.7, 114.6, 118.5, 129.2, 129.3, 133.0, 135.4, 135.7, 139.4, 164.5, 169.4, 169.6, 169.6, 170.5; IR (KBr): $\nu = 3480$, 3138, 2954, 1752, 1610, 1573, 1491, 1419, 1375, 1340, 1231, 1095, 1064, 1038, 912, 854, 710, 756, 680, 599; HRMS (ESI-pos., MeOH) m/z: 571.1725 (calculated: 571.1721) $[C_{26}H_{32}N_2O_9SNa]^+$.

4.3. Organocatalyzed reactions

4.3.1. Experimental procedure for the conjugate umpolung to give 12

The catalyst (0.05 mmol, 0.1 equiv.) was dissolved in THF (3 ml). Cinnamaldehyde (63 μl, 0.5 mmol, 1.0 equiv.) and α,α,α-trifluoroacetophenone (70 μl, 0.5 mmol, 1.0 equiv.) were added followed by DBU (45 μl, 0.3 mmol, 0.6 equiv.). The reaction mixture was stirred at r.t. for 16 h. Methanol (0.5 ml) and dodecane (20 μl, internal standard) were added via syringe and a sample was taken for GC–MS analysis. An authentic sample of the products **12a** and **12b** [14b] was used to identify the product peaks and to calibrate the GC–MS. Isolation of the products as well as their stereochemical assignment was previously described [14b].

4.3.2. Experimental procedure for the conjugate umpolung to give 13

The catalyst **5a** (28 mg, 0.05 mmol, 0.1 equiv.) was dissolved in THF (3 ml). Cinnamaldehyde (63 μl, 0.5 mmol, 1.0 equiv.) and methylbenzoylformate (71 μl, 0.5 mmol, 1.0 equiv.) were added followed by DBU (45 μl, 0.3 mmol, 0.6 equiv.). The reaction mixture was stirred at r.t. for 16 h. Methanol (0.5 ml) and dodecane (20 μl, internal standard) were added via syringe and a sample was taken for GC/MS analysis. An authentic sample of the products **13a** and **13b** [14b] was used to identify the product peaks and to calibrate the GC/MS. Isolation of the products as well as their stereochemical assignment was previously described [14b].

4.3.3. Bis(NHC)silver(I)-complex 14

To a solution of silver triflate (35 mg, 0.14 mmol) in 2.5 ml THF were added 1-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)-3-(2,4,6-trimethyl-phenyl)-3H-imidazolium triflate (0.2 g, 0.3 mmol) and DBU (91 mg, 0.6 mmol). The reaction mixture was stirred in the dark for 24 h at ambient temperature. The solvent was removed under reduced pressure. The resulting solid was resolved in DCM (7 ml) and washed with water (2 × 10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give a black solid. Yield: 175 mg (99%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.53$ (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 2.04–1.99 (m, 24H, CH_3), 2.35 (s, 6H, CH_3), 4.21 (d, 2H, $J = 12.0$ Hz, $CH_{carbohydrate}$), 4.45 (m, 4H, $CH_{carbohydrate}$), 5.29 (m, 4H, $CH_{carbohydrate}$), 5.47 (t, 2H, $J = 9.6$ Hz, $CH_{carbohydrate}$), 6.08 (d, 2H, $J = 9.0$ Hz, $CH_{carbohydrate}$), 6.87 (s, 2H, CH_{aromat}), 6.90 (s, 2H, CH_{aromat}), 6.94 (s, 2H, =CH), 7.54 (s, 2H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.9$, 17.7, 19.9, 20.6, 20.7, 21.0, 61.4, 67.6, 71.9, 74.3, 86.3, 120.0, 122.9, 129.2, 129.5, 134.5, 135.3, 135.5, 139.3, 168.8, 169.6, 169.7, 170.4; IR (KBr) $\nu = 601$, 638, 919, 1031, 1101, 1153, 1226, 1372, 1433, 1491, 1645, 1755, 2962, 3136, 3449; HRMS (ESI-pos., MeOH) m/z: 1141.3258 (calculated:1141.3258) $[C_{52}H_{64}AgN_4O_{18}]^+$.

4.3.4. Bis(NHC)palladium(II)-complex 15

To a solution of bis(benzonitrile)palladium(II)dichloride (16 mg, 0.04 mmol) in DCM (2 ml) was added the silver complex **14** (56 mg, 0.04 mmol). The reaction mixture was stirred in the dark for 17 h at ambient temperature. All insoluble parts were removed by filtration through Celite and the filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography (DCM/MeOH = 19:1) to give a colorless solid. Yield: 20 mg (40%); R_f: 0.96 (DCM/MeOH = 19:1, NEt_3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.73$ (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 2.12 (s,6H, CH_3), 2.37 (s, 6H, CH_3), 2.42 (s, 6H,

CH_3), 3.75 (m, 2H, $CH_{carbohydrate}$), 4.16 (d, 2H, $J = 12.5$ Hz, $CH_{carbohydrate}$), 4.37 (dd, 2H, $J = 12.5$ Hz, $J = 4.3$ Hz, $CH_{carbohydrate}$), 5.39–5.17 (m, 6H, $CH_{carbohydrate}$), 6.45 (d, 2H, $J = 9.2$ Hz, $CH_{carbohydrate}$), 6.78 (d, 2H, $J = 1.8$ Hz, =CH), 7.01 (s, 2H, CH_{aromat}), 7.16 (s, 2H, CH_{aromat}), 7.21 (d, 2H, $J = 1.8$ Hz, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.5$, 19.3, 20.4, 20.5, 20.6, 20.7, 20.8, 61.4, 68.2, 70.1, 73.2, 74.6, 86.3, 118.0, 123.7, 128.9, 129.1, 135.6, 135.7, 136.7, 138.7, 169.6, 169.7, 170.0, 170.7, 172.8; IR (KBr) $\nu = 1038$, 1066, 1099, 1230, 1375, 1427, 1755, 2956, 3138, 3426; HRMS (ESI-pos., MeOH) m/z: 1233.2556 (calculated: 1233.2524) $[C_{52}H_{64}Cl_2N_4O_{18}PdNa]^+$. Colorless crystals, suitable for the X-ray diffraction, were obtained from diffusion of pentane into a solution of DCM.

4.3.5. Data for the X-ray structural analysis of bis(NHC)palladium(II) complex 15

$2(C_{52}H_{64}Cl_2N_4O_{18}Pd)$, $3(CH_2Cl_2)$, $M_r = 2675.52$ g mol^{-1} colorless needles, size $0.21 \times 0.15 \times 0.06$ mm^3, monoclinic, space group $P2_1$, $a = 10.8657(3)$, $b = 19.6474(6)$, $c = 30.8477(11)$ Å, $\beta = 90.026(3)°$, $V = 6585.5(4)$ Å^3, $T = -100$ °C, $Z = 2$, $\rho_{calc} = 1.349$ mg m^{-3}, $\mu = 5.51$ cm^{-1}, empirical absorption correction, $F(000) = 2764$, 42927 reflections in h (−12/12), k (−23/23), l (−36/36), measured in the range $1.32° < \Theta < 25.00°$, completeness $\Theta_{max} = 100\%$, 23,189 independent reflections, $R_{int} = 0.0504$, 16748 reflections with $I > 2.0\sigma(I)$, 1522 parameters, 101 restraints, $R_1 = 0.0487$, $wR_{2all} = 0.0868$, GOF = 0.891, largest difference peak and hole 0.48 and −0.58 e/Å^3, Flack parameter 0.01(2). The crystal was twinned (matrix −1 0 0 0 −1 0 0 0 1 with BASF 0.5). Therefore, the metric of the unit cell and the symmetry of the reflection intensities almost perfectly fit the orthorhombic case. One side chain shows positional disorder. More large anisotropic displacement parameters indicate additional disorder that has not been resolved.

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie (Dozentenstipendium), Lilly Germany (Lilly Lecture Award) and the BASF AG (BASF Catalysis Award) as well as donations by Bayer A.G., Heraeus and Degussa are gratefully acknowledged. The research of F.G. was also supported by the Alfried Krupp Prize for Young University Teachers of the Alfried Krupp von Bohlen und Halbach Foundation.

Appendix A. Supplementary material

CCDC 641068 and 641069 contain the supplementary crystallographic data for **4** and **15**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.007.

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