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Bimacrocyclic concave N-heterocyclic carbenes (NHCs): Synthesis, structure and application in catalyses

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Imidazolinium moieties have been incorporated into bimacrocycles to generate precursors for concave N-heterocyclic carbenes (NHCs). Starting from 2-nitroresorcinol and alkenols, symmetric concave imidazolinium salts **1** were obtained. Bimacrocyclisation was achieved via ring-closing metathesis (RCM). In an analogous fashion, axially chiral concave imidazolinium salts **2** were obtained using a naphthalene bridgehead devoid of local C_2-symmetry. The concave NHCs derived from the symmetric precursors **1** were used as nucleophilic catalysts for the synthesis of γ-butyrolactones and as ligands for transition metal catalysts. Copper complex **18** was used as a catalyst for the cyclopropanation of styrene and indene with ethyl diazoacetate (EDA). Palladium complex **24** was used as a catalyst for the Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions.

Keywords: bimacrocycles; N-heterocyclic carbenes; organocatalysis; transition metal complexes

Introduction

In 1958, Breslow (*1*) elucidated the nature of the 'active aldehyde' in thiamine-dependent biochemical transformations (reviews on thiamine-dependent enzymes: (*2*)) and suggested nucleophilic catalysis. He postulated that by deprotonation of thiamine's thiazolium unit in position 2, a betaine was formed, which acted as the nucleophile. Due to the electronegativity of the nitrogen atom, the drawing of a mesomeric carbene structure is also reasonable (Figure 1). Starting from imidazolium (*3*), imidazolinium (*4*) and other azolium ions, related carbenes have been made accessible, and they have been named N-heterocyclic carbenes (NHCs).

These NHCs exhibit excellent catalytic activity in metal-free organocatalysis, including umpolung and condensation of carbonyl compounds (*5*) and transesterification reactions (*6*). Metal complexes of NHCs have first been reported by Wanzlick and Schönherr (*7*) and Öfele (*8*) in 1968, but it was after the isolation of a stable crystalline carbene by Arduengo in 1991 (*3a*) that the coordination chemistry of NHCs (*9*) and their use in organocatalysis (*10*) has become an emerging field of research. As ligands, the nucleophilic NHCs are strong two-electron σ-donors, displaying similar ligand properties as trialkylphosphines (*11*). In comparison to related phosphine complexes, NHC metal complexes have been shown to possess increased stability and catalytic activity in numerous reactions, the second generation of Grubbs' catalyst for olefin metathesis being a prominent example (*12*). Besides their unique electronic properties, the steric demand of the NHCs is an important factor in cross-coupling reactions, and the use of NHC ligands has greatly expanded the scope of respective palladium-catalysed reactions (*13*). Besides some frequently used NHC ligands, bulky NHCs have been synthesised for challenging Suzuki–Miyaura (*14*) or Sonogashira (*15*) cross-coupling reactions. Also, quite a few examples of chiral NHCs exist in the literature (*16*).

In enzymes, the thiamine unit is located in the cavity of an enzyme. Its geometry and chirality is responsible for the selectivity of the enzymatic reaction. In principle, an NHC or its precursor can also be embedded in a suitable shielding, which, in return, shall be responsible for enhanced selectivities in the reactions catalysed by the NHC. Applying the concept of concave reagents (*17*), we envisaged imidazolinium salts as precursors to concave NHCs and developed a synthetic route to bimacrocyclic symmetric imidazolinium salts **1** (*18*) and axially chiral derivatives **2** (*19*) (Figure 2).

Synthesis of NHC precursors 1 and 2

Symmetric NHC precursors 1

Several strategies are conceivable to construct a concave bimacrocycle **1**, which contains an imidazolinium moiety as a precursor for NHC. All strategies must provide (i) access to the trisubstituted aryl bridgeheads, (ii) a bimacrocyclisation strategy and (iii) a suitable synthesis of the heterocycle. We have selected ruthenium-catalysed metathesis for the ring closure to the bimacrocycle because such bimacrocyclisations have proven to be very successful for the synthesis of a number of concave

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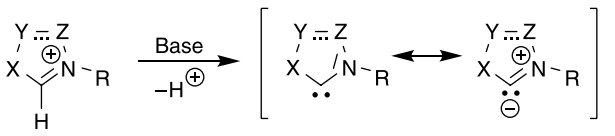

Figure 1. Heterocyclic azolium ions are the precursors for NHCs, which are also drawn in their mesomeric betaine form. Examples: thiazolium, X = S, Y = Z = CR′; imidazolium, X = NR″, Y = Z = CR′; imidazolinium, X = NR″, Y = Z = CR'_2; triazolium, X = NR″, Y = N, Z = CR′.

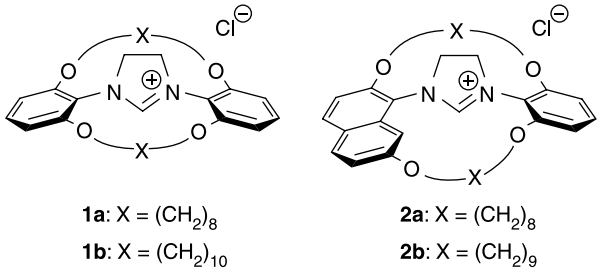

Figure 2. Symmetric NHC precursors **1** and axially chiral NHC precursors **2**.

reagents (*20*). Thus, a precursor was demanded which contains the aryl bridgeheads and the heterocycle. Prominent strategies for the synthesis of imidazolinium salts start from anilines, which are condensed with a C_2 and a C_1 unit ending up in the heterocycle as carbon atoms 4 and 5, and carbon atom 2, respectively (*4b*, *21*).

Thus, the first task was to synthesise the bis-*ortho*-substituted anilines **4**. In a two-step reaction, **4a** and **4b** could be obtained from commercially available 2-nitroresorcinol (**3**). The reaction sequence first uses the Mitsunobu coupling of the phenol OH groups of **3** and ω-alkenols. The resulting nitroarenes can then be reduced to the anilines **4** by tin(II) chloride (Figure 3).

Next, two equivalents of the anilines **4** were connected by oxalyl chloride to give respective diamides. After reduction with lithium aluminium hydride, the resulting diamines were reacted with triethyl orthoformiate and ammonium chloride to give imidazolinium salts **5**. After ring-closing metathesis (RCM) using Grubbs' catalyst, followed by hydrogenation of the newly formed double bonds, the bimacrocyclic concave imidazolinium salts **1** were obtained (*18*). Deprotonation of **1a** led to the formation of a bimacrocyclic NHC that was characterised as its thiocarboxylate (reaction of the NHC with carbon disulphide). The bimacrocyclic structures of **1a** (*18*) and **1b** (*22*) were proven by single-crystal X-ray analysis (Figure 4).

Axially chiral NHC precursors 2

The synthetic strategy for the formation of axially chiral imidazolinium salts **2** was adopted from the route leading to non-chiral **1**. But instead of using two symmetric phenyl bridgeheads, one naphthalene bridgehead devoid of local C_2-symmetry was incorporated into the macrocycle to create axial chirality. 2,7-Dihydroxy-1-nitronaphthalene (**6**) was used as the starting material, and the axially chiral salts **2** were obtained in racemic form (Figure 5) (*19*). For **2b**, an X-ray structural analysis was carried out (Figure 6) and the crystal contained both enantiomers.

To apply the bimacrocycles **2** to enantioselective processes, the enantiomers need to be separated. As an interconversion of the enantiomers can occur by a simple rotation of the imidazolinium ring with respect to the two

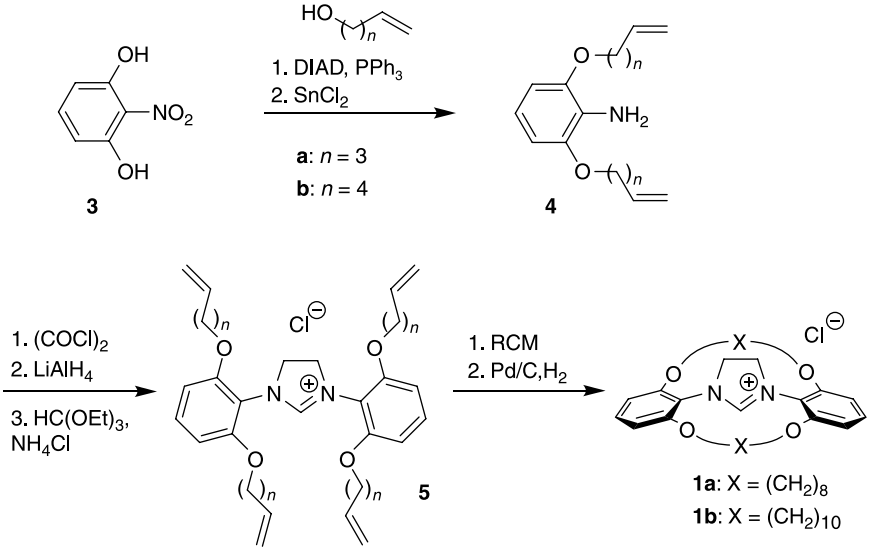

Figure 3. Synthesis of symmetric bimacrocyclic imidazolinium chlorides **1**.

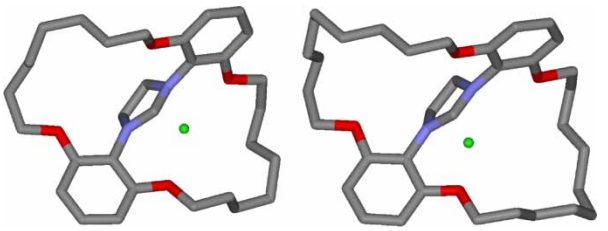

Figure 4. Comparison of the crystal structures of **1a** (left) and **1b** (right). Hydrogen atoms and solvent molecules are omitted for clarity.

bridgeheads, the question of the configurational stability of **2** had to be examined. This was done using helically chiral anions as stereodynamical probes. Association of enantiopure hexacoordinated phosphorus anions Δ-TRISPHAT **7** (*23*) or Λ-BINPHAT **8** (*24*) (Figure 7) with racemic **2** led to the formation of diastereomeric ion pairs that were examined by ^{1}H NMR (*19*).

While Δ-TRISPHAT **7** induced only a small separation of the NMR signals, Λ-BINPHAT **8** was more effective as a chiral NMR solvating agent. The integration of the separated signals indicated an imbalance in the diastereomeric population (for the diastereomeric ion pair prepared from **2b** and **8**, the diastereomeric excess (d.e.) was 15% in CD_2Cl_2 at room temperature). This imbalance was supposed to result from supramolecular diastereoselective interactions that may occur only with configurationally *labile* species (*Pfeiffer* effect (*25*)), causing the predominance of one diastereomeric ion pair in solution and being a good probe for the lack of configurational stability of the cation (*26*). As the stereoselective recognition among chiral ions is most pronounced in low polarity solvents (*27*), the maximum diastereoselectivity with salts made of configurationally *labile* cations is achieved in low polar solvents and varies with modifications of the solvent polarity. The examination of the aforementioned diastereomeric mixture in deuterated solvents of different polarities indeed supported the configurational lability of **2b** ($CDCl_3$: $\varepsilon = 4.89$, d.e. = 40%; $C_2D_2Cl_4$: $\varepsilon = 8.42$, d.e. = 17%; CD_2Cl_2: $\varepsilon = 9.02$, d.e. = 15%; $C_2D_4Cl_2$: $\varepsilon = 10.74$, d.e. = 10%). Virtually identical results were obtained for the diastereomeric salts of the smaller bimacrocycle **2a**.

These results proved that the barrier of rotation along the chiral axes in **2a** and **2b** is too small to allow their physical resolution at room temperature and the NHCs derived from **2** could not be applied to asymmetric catalysis. However, configurationally *stable* derivatives may be obtained by increasing the steric interactions along the chiral axes in order to enlarge the rotational barrier, e.g. by the incorporation of sterically demanding substituents into positions 4 and 5 of the imidazolinium ring.

Concave NHCs in nucleophilic organocatalysis

The mechanism for the thiamine-catalysed benzoin condensation was established by Breslow in 1958, and it is based on the umpolung of a carbonyl carbon atom by the deprotonated thiazolium salt (*1*). The scope of this reaction was expanded by Stetter in 1976 (*5a*), who reacted aldehydes with Michael acceptors in the presence of thiazolium salts and base, yielding 1,4-diketones, 4-ketoesters or 4-ketonitriles (Stetter reaction). Chiral NHCs have successfully been applied as a catalysts for asymmetric benzoin condensations and Stetter reactions, and thiazolium or triazolium salts are used as NHC precursors for these reactions (*5d*). In 2004, Glorius and Bode reported on the use of a sterically demanding imidazolium-derived NHC as a catalyst for the synthesis of γ-butyrolactones **13** from enals **9** and aldehydes **10** or ketones **11** (Figure 8). Either potassium *tert*-butoxide or DBU was used for the deprotonation of NHC precursor **12**, and the preferred formation of *like*-**13** was observed using the NHC derived from **12** as a catalyst (*5b,c*). However, in a recent publication (*28*), the use of some thiazolium-derived NHC catalysts has resulted in the predominant formation of *unlike*-**13**.

A reasonable mechanism was proposed for the reaction, involving the vinylogous umpolung of the β-carbon atom of the enal **9**, caused by the nucleophilic attack of the NHC on its carbonyl carbon atom. The proposed catalytic cycle was supported by the observation of postulated intermediates by ESI mass spectrometry (*29*). We have tested the concave NHCs derived from **1** as a catalyst for this reaction, expecting to effect the diastereoselectivity with the bimacrocyclic structures.

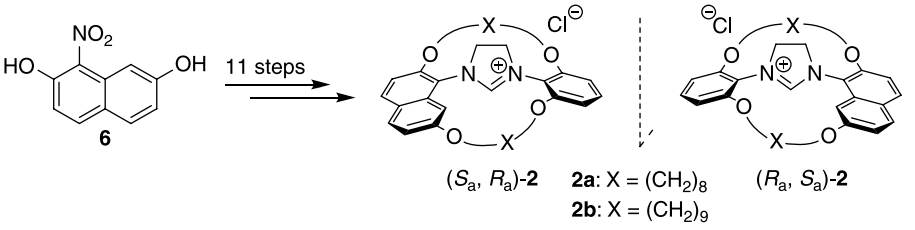

Figure 5. Synthesis of racemic axially chiral bimacrocyclic imidazolinium chlorides **2**.

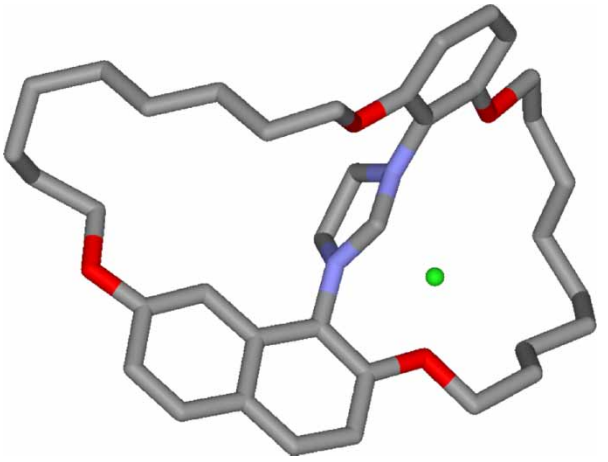

Figure 6. Crystal structure of **2b** [only the (S_a,R_a)-enantiomer is shown]. Hydrogen atoms are omitted for clarity.

Different combinations of substrates **9** and **10** or **11** were examined, and lactones **13** could indeed be obtained using the concave NHCs derived from **1a** or **1b** by deprotonation with DBU (*22*). Unfortunately, the precatalysts **1** proved to be less effective in this reaction compared to **12**, and high loadings of **1** (25 mol%) were needed to produce reasonable amounts of products **13** with little stereoselectivity (*like*:*unlike* ≅ 1:1). While **1a** and **1b** showed the same reactivity and selectivity in most cases, an unexpected product was formed with precatalyst **1b** in the reaction of cinnamaldehyde (**9a**) with methyl 4-formyl-benzoate (**10a**). While **1a** afforded the expected lactone **13a**, a cyclic hemiacetal **14** was obtained as the main product with **1b** (Figure 9) (*22*).

An equilibrium between both anomeric forms (ratio 10:1) of **14** was observed in $CDCl_3$ at room temperature, with the hydroxyl and phenyl groups being oriented *trans* in the major anomer, as could be deduced from the NOESY spectrum. The relative stereochemistry at the quaternary carbon atom could not be assigned undoubtedly. A molecule related to **14** has been reported to be produced from cinnamaldehyde (**9a**), acetaldehyde and fermenting baker's yeast (*30*), and the reported NMR

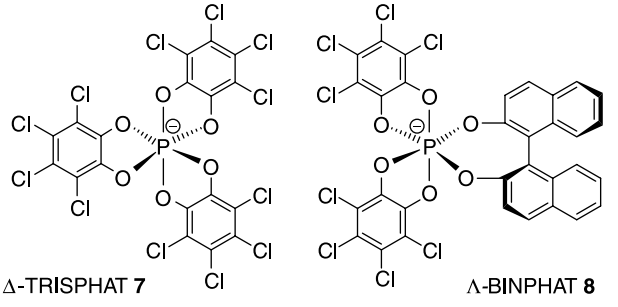

Figure 7. Helically chiral phosphorus anions.

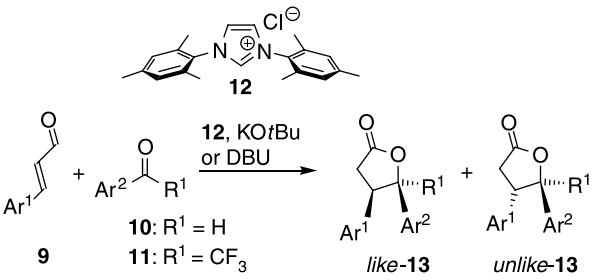

Figure 8. NHC-catalysed synthesis of γ-butyrolactones **13** (*5b,c*).

assignments support our structure elucidation (also regarding the anomers). In analogy to the mechanistic explanation of the enzymatic reaction, the isolation of **14** implies the formation of benzoin **16**, whose anion reacts with the Michael acceptor **9a**. The resulting hydroxy-aldehyde **15** undergoes ring closure to hemiacetal **14**, as revealed by the NMR spectra. Reasonable amounts of hemiacetal **14** were only obtained with precatalyst **1b**, and we suggest that these different reactivities result from the structural differences between **1a** and **1b** (Figure 4). The scope of this new reaction is currently under investigation in our laboratory.

Concave NHC transition metal complexes

The bimacrocyclic NHC derived from **1a** was used as a ligand for transition metal ions, and eight concave NHC complexes **17**–**24** were obtained (Figure 10) (*31*). Complexes **17**, **18**, **19** and **24** were characterised by single-crystal X-ray analyses. Most of the complexes were synthesised by transmetalation from the NHC silver complex **17**, which is accessible in 86% yield by the reaction of **1a** with silver(I) oxide. The use of NHC silver complexes as carbene transfer reagents is a popular method for the synthesis of NHC metal complexes, avoiding the handling of the sensitive free carbenes (*32*). In contrast to the other complexes, palladium complex **19**

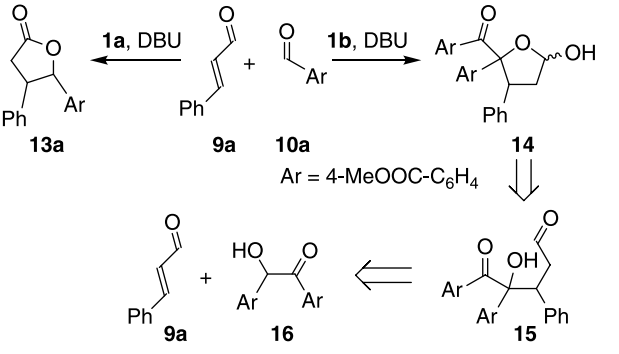

Figure 9. Reaction of cinnamaldehyde (**9a**) with methyl 4-formyl-benzoate (**10a**) using NHC precursor **1a** or **1b**.

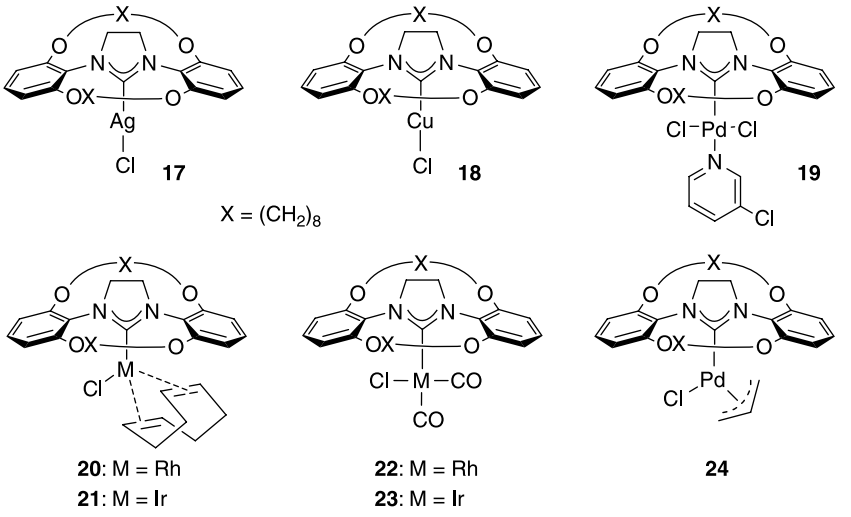

Figure 10. Concave NHC transition metal complexes.

was not accessible by transmetalation from silver complex **17** and could only be obtained in poor yield via the free carbene. The rhodium and iridium dicarbonyl complexes **22** and **23** were synthesised to investigate the electronic properties of the bimacrocyclic NHC ligand. The carbonyl stretching frequencies of respective complexes are a popular indirect measure of the ligands σ-donor strength (*33*). A low stretching frequency (wavenumber) of CO corresponds to strong σ-donation of the NHC. By using a linear fit procedure (*33c*), the CO stretching frequencies of Ir(I)–NHC can be used to estimate Tolman's electronic parameter (TEP) (*34*), which is well documented for various phosphines. The CO stretching frequencies and the TEP values of respective NHC complexes fall in a narrow range, and the NHCs are more electron donating than the most donating phosphines. Compared to frequently used NHCs, our new ligand was found to be significantly more electron donating (*31a*).

Copper complex **18** proved to be reactive as a catalyst for the cyclopropanation of styrene (**25**) and indene (**27**) with ethyl diazoacetate (EDA), but the diastereoselectivity was only slightly affected by the concave NHC ligand (Figure 11). Silver complex **17** was also tested as a catalyst for this reaction, but only very low EDA consumption was observed as complex **17** decomposed under the reaction conditions (*31a*).

Palladium complex **24**, accessible in 85% yield via transmetalation with allyl palladium chloride dimer from silver complex **17**, was successfully applied as a catalyst for the Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions (Figure 12) (*31b*). While the use of aryl chlorides as coupling partners is nowadays established in the latter case (*35*), the Mizoroki–Heck olefination of unactivated aryl chlorides is not trivial and mainly bromides and activated chlorides are successfully used in the reaction (*36*). The olefinations were performed in tetrabutylammonium bromide as an ionic liquid at 140°C (16 h reaction time). Using 1 mol% of catalyst **24**, good results were obtained in the reaction of activated and electronically neutral aryl bromides **29** with styrene (**25**), and also hindered 2-bromo-toluene afforded 72% of the coupling product. Unfortunately, a decrease in yield was

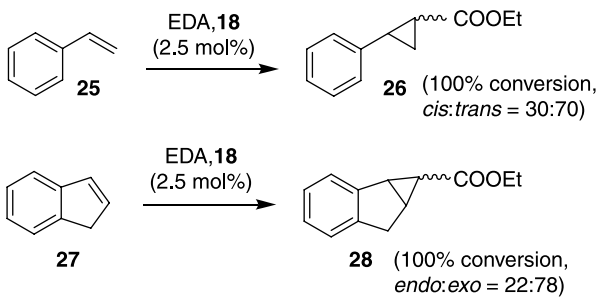

Figure 11. Cyclopropanation of styrene (**25**) and indene (**27**) with EDA using catalyst **18**.

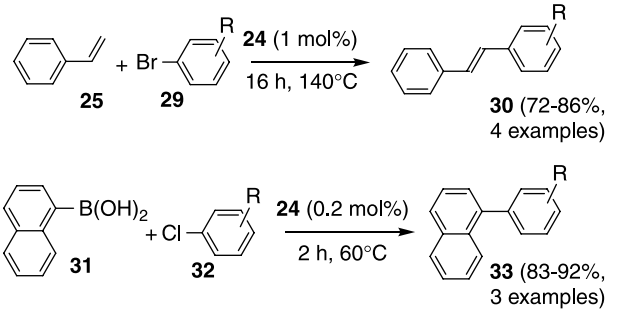

Figure 12. Mizoroki–Heck and Suzuki–Miyaura reactions using catalyst **24**.

observed when analogous aryl chlorides **32** were used as the coupling partners. In contrast to these results, high yields were obtained in the Suzuki–Miyaura reaction of aryl chlorides **32** with 1-naphthalene-boronic acid (*31*) at low catalyst loading in short reaction times (0.2 mol% **24**, 2 h at 60°C).

Also, axially chiral biaryls could be produced via Suzuki–Miyaura reactions using catalyst **24** (however, in racemic form). As the catalytic activity of the complexes **18** and **24** shows promise, we are currently investigating the feasibility to obtain configurationally *stable*, axially chiral NHC complexes derived from the *labile* NHC precursors **2** (*19*) for asymmetric catalysis. We suggest that a tightly bound metal ion should increase the steric interactions along the chiral axes, resulting in resolvable chiral NHC complexes. Experiments in this vein are under way.

Conclusion

Concave imidazolinium ions **1** and **2** can readily be obtained as precursors to concave NHCs. These NHCs are active as nucleophilic catalysts and they can be used as ligands for transition metal catalysts. While stereoselectivities still have to be improved, a hitherto not observed hemiacetal **14** could be produced using one specific precatalyst (**1b**). As the catalytic activity of the concave NHCs and that of respective transition metal complexes shows promise, we are currently focusing on chiral modifications of the bimacrocyclic NHCs for asymmetric catalysis. In order to yield configurationally *stable* axially chiral imidazolinium salts, *labile* cations **2** will have to be further modified. Alternatively, configurationally *stable* axially chiral NHC complexes might be obtained from the *labile* NHC precursors **2**.

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