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Expanding the Scope of Chelating Triazolylidenes: Mesoionic Carbenes from the 1,5-"Click"-Regioisomer and Catalytic Synthesis of Secondary Amines from Nitroarenes

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Abstract: Chelating 1,2,3-triazolylidenes have been established as privileged ligands in homogeneous catalysis. We present herein a new approach towards chelating 1,2,3-triazolylidene ligands based on the 1,5-regioisomer of the corresponding triazole, which can be obtained through simple click chemistry. The new ligands are compared to their 1,4-regioisomeric counterparts through coordination to the ruthenium *p*-cymene fragment. The complexes are characterized structurally and spectroscopically and are employed as (pre)catalysts in the reductive condensation of nitroarenes and primary alcohols to yield secondary amines. The activity of chelating mesoionic carbene ligands obtained from the two different regioisomers of the triazoles are compared and contrasted in catalysis. The performance of the ruthenium complexes with mesoionic carbenes could be improved through the choice of the employed base and reaction conditions, giving rise to the most effective systems thus far. The results presented here prove the utility of chelating mesoionic carbenes as an extremely potent class of ligands for the synthesis of secondary amines from nitroarenes.

Introduction

One of the most utilized reactions in contemporary chemistry is the copper-catalyzed [3+2] cycloaddition between azides and alkynes (CuAAC) yielding 1,2,3-triazoles.[1] This reaction is the best known example of a "click" reaction. The ease of performing this reaction, in combination with the huge substrate scope, is the main reasons for its popularity in chemistry today. 1,2,3-Triazoles have gained considerable attention in the last years in coordination chemistry.[2] One prominent use of triazoles in coordination/organometallic chemistry is the methylation of triazoles to obtain 1,2,3-triazolium salts, which can be used as precursors to generate mesoionic carbenes.[3] Metal complexes of 1,2,3-triazole-derived mesoionic carbenes (so called 1,2,3-triazolylidenes) have shown remarkable properties[4] and unique catalytic potential towards various transformations in the last years.[5,6] However, if one reconsiders the uncatalyzed version of the cycloaddition reaction between alkynes and azides, there are two regioisomers possible, the 1,4-regioisomer and the 1,5-regioisomer. (Scheme 1).[7]

Even though many effective protocols have emerged to obtain the 1,5-regioisomer selectively,[8] these triazoles have been rather neglected in the literature to date. We have recently published a first approach for the synthesis of 1,5-triazole-derived mesoionic carbenes and shown that their palladium complexes are efficient (pre)catalysts for Suzuki–Miyaura-type cross coupling reactions of aryl bromides and aryl chlorides with boronic acids.[9] One of the advantages we pointed out in that contribution is that, in contrast to the 1,4-regioisomer, the methylation (or functionalization) of the triazole to the triazolium salt occurs in the α-position to the carbene-carbon atom.[9] This offers great opportunities for the steric and electronic fine tuning of such carbenes, as well as the introduction of functional groups that interfere with methylation reactions (e.g., pyridines).[9]

Having tested the utility of chelating mesoionic carbenes derived from the 1,4-regioisomer of the click reaction as ligands in various catalytic transformations, and in particular transfer hydrogenation reactions,[10] we were interested in expanding the scope of chelating mesoionic carbenes derived from the 1,5-regioisomers. Additionally, we aimed to compare and contrast the two related ligand classes in a challenging catalytic reaction to generate useful chemical products from readily available starting materials.

The formation of carbon–nitrogen bonds is one of the most important reactions in organic synthesis.[11] The traditional route for C–N bond formation involves the condensation of amines with aldehydes or ketones, in the presence of Lewis acid catalysts, to form imines first, which can then be reduced. Other routes use the oxidation of amines.[12] In terms of metal-catalyzed reactions, one of the most prominent routes for this reaction is the "borrowing hydrogen" concept.[13] In such a reaction, an alcohol and an amine are coupled to give the corresponding *N*-alkylated product. This route thus provides an efficient catalytic way to synthesize secondary amines.

An innovative approach for the synthesis of secondary amines from readily available starting materials was first introduced by the group of Akiko Uno in 1966, in which nitroben-

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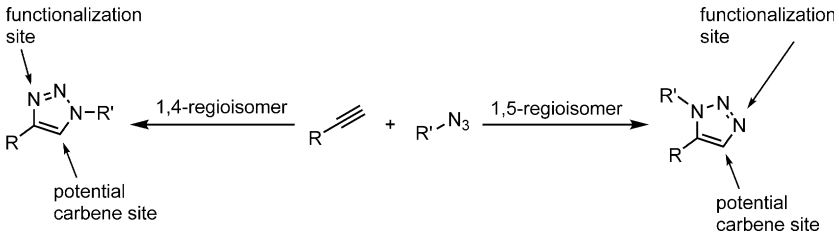


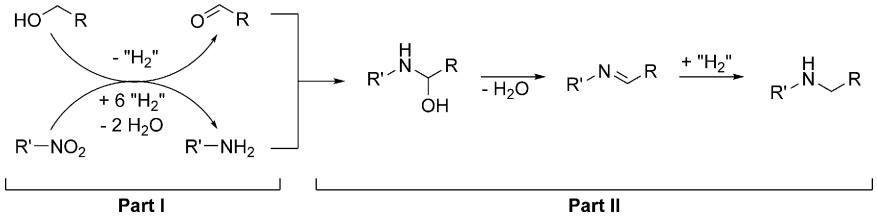
Scheme 1. The two possible regioisomers obtained in the [3+2] cycloaddition reaction between organic azides and alkynes.

zene and benzyl alcohol were reacted in the presence of potassium hydroxide under extreme conditions of 250 to 280 °C.[12a] This reaction, although ingenious, is stoichiometric, and suffers from low product yield and harsh reaction conditions. In the last years, ruthenium-based systems have been reported as efficient catalysts for this reaction.[14] In the catalytic reaction, the concepts of catalytic transfer hydrogenation to reduce nitroarenes[15] is combined with the borrowing hydrogen process. Thus, the nitroarenes are first reduced to the corresponding anilines using a primary alcohol as hydrogen source (Scheme 2, Part 1). During this transformation, the primary alcohol is converted into the aldehyde, which subsequently reacts with the anilines formed to yield imines. These imines can then be reduced in a final transfer hydrogenation step to the corresponding secondary amines (Scheme 2, Part 2). By using the catalytic protocol, nitrobenzenes and benzyl alcohols could be converted into secondary amines with high selectivities and yield.[14] Metal complexes of N-heterocyclic carbene based ligands were also used for the aforementioned catalytic transformation. However, the heterobimetallic Ir^{III}/Au^{I} or Pd^{II}/Ir^{III} complexes used for that purpose delivered the unreduced imine as the main product (Scheme 2).[16]

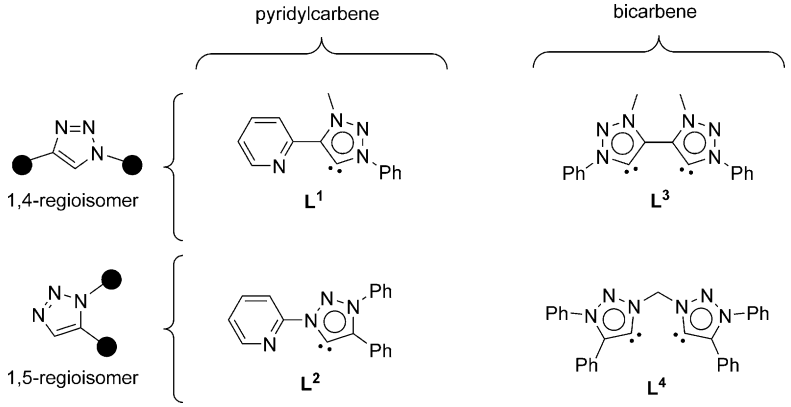
Recently, we have reported on the use of metal complexes of mesoionic carbenes for the catalytic transfer hydrogenation of nitroarenes to yield aniline and azobenzene depending on the conditions and catalysts applied to this reaction.[10d] Based on our previous results that showed that ruthenium complexes of chelating mesoionic carbenes were highly efficient catalysts for transfer hydrogenation reactions, we were interested in combining that catalytic capacity with the hydrogen-borrowing concept to develop catalytic synthetic routes for secondary amines starting from readily available starting materials such as nitroarenes and benzyl alcohols.

Herein, we present the synthesis of the new ligands $\mathbf{L^2}$ and $\mathbf{L^4}$ by using the 1,5-regioisomer of the triazoles, and compare them to their 1,4-regioisomer derived counterparts, $\mathbf{L^1}$ and $\mathbf{L^3}$ (Scheme 3).

Half sandwich complexes of the type [Ru(Cym)Cl(**L**)](PF_6) [with Cym = *p*-cymene and **L** = $\mathbf{L^1}$ (for Ru-**1**), $\mathbf{L^2}$ (for Ru-**2**), $\mathbf{L^3}$ (for Ru-**3**), and $\mathbf{L^4}$ (for Ru-**4**)] are presented for all ligands and



Scheme 2. Reductive coupling of nitroarenes and primary alcohols towards secondary amines.



Scheme 3. Ligands used in this work.

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their structural and spectroscopic properties are investigated. Furthermore, the catalytic properties of such complexes are explored in the condensative transfer hydrogenation of nitroarenes with primary alcohols for the synthesis of secondary amines.

Results and Discussion

Synthesis and Crystal Structures

The triazolium salt H**L**^{1}[OTf] from the 1,4-regioisomers were synthesized by following reported routes.[5p] To obtain the triazolium salt H_2**L**^{3}[BF_4]$_2$, the corresponding 1,4-regioisomer of the bitriazole was first synthesized by following a reported procedure,[17] followed by a methylation using Meerwein's salt at room temperature similar to previously reported conditions.[9]

For the synthesis of the 1,5-triazole-derived carbene, the 1,5-diphenyl-substituted triazole precursor **T1** was synthesized by following a metal-free procedure.[8a] To obtain the chelating ligand H**L**^{2}[BF_4], we exploited the fact that nucleophilic substitution on pyridines readily occurs at high temperatures, as has been shown with similar imidazolylidene systems before.[18] On heating 2-bromopyridine with the 1,5-triazole precursor **T1** at 160 °C for two days and subsequent aqueous anion exchange, we isolated the desired triazolium salt H**L**^{2}[BF_4] in reasonable yields (Scheme 4, right). However, trying to incorporate a picolyl group by using picolyl bromide always resulted in the formation of the desired product together with various inseparable side products. It is known that, in selected cases, a pyridine nitrogen can be alkylated more easily than the triazole nitrogen;[5a] therefore, we believe that the picolyl bromide most likely alkylates itself (Scheme 4, left).

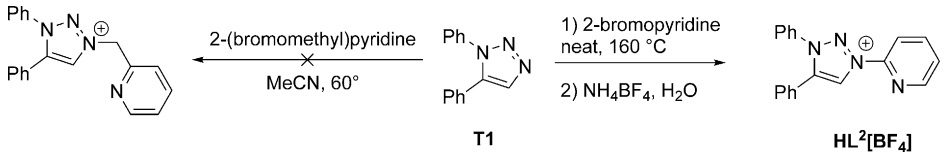
To obtain the triazolium salt H_2**L**^{4}[OTf]$_2$, we first reacted diiodomethane with silver triflate under exclusion of light to generate ditriflatomethane in situ, which was then reacted with the 1,5-triazole precursor **T1** to give the desired bis-triazolium salt H_2**L**^{4}[OTf]$_2$ (Scheme 5, right). It has to be mentioned here that the prior activation of the diiodomethane with silver triflate is desirable, because the direct reaction of the 1,5-triazole **T1** with diiodomethane results in the formation of mixtures of the desired triazolium salt H_2**L**^{4}[I]$_2$ and what we believe to be the mono-substituted iodomethylene triazolium salt H**L**^{5}[I] (Scheme 5, left).

The identity and purity of all ligands were established by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. All ligands display the characteristic low-field signal for the triazole-5*H* in their ^{1}H NMR spectra, unambiguously proving the formation of the desired triazolium salts. In case of H_2**L**^{4}[OTf]$_2$, the identity was further confirmed by the occurrence of the methylene protons of the bridging CH_2 group at $\delta = 8.08$ ppm (see experimental section).

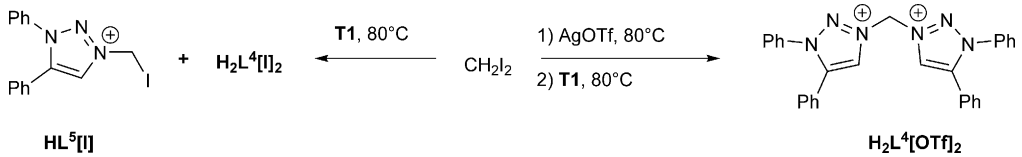
After establishing the ligands described above, piano-stool type ruthenium cymene complexes Ru-**1**–**4** were synthesized (Scheme 6).

The synthesis of Ru-**1** was performed as reported previously.[5] Complexes Ru-**2**–**4** were all synthesized by following a transmetallation protocol previously reported by our group.[10d] Formation of the desired complexes was indicated by the absence of the low-field signal of the triazole-5*H* in the ^{1}H NMR spectra of the corresponding complexes. Furthermore, on complexation of the ligand **L**^{4}, the methylene protons in the proton NMR spectra split into two signals. By coordination of **L**^{4} to the ruthenium center, the two methylene protons become chemically inequivalent and this results in the observation of two pseudo doublets for the two methylene protons at $\delta = 7.23$ ppm and $\delta = 6.51$ ppm, both integrating for only one proton ($J_{AB} = 13.6$ Hz). Formation of the desired complexes was further established by ^{13}C NMR spectroscopy showing the carbene-*C* signals at $\delta = 170.5$, 178.3, and 164.3 ppm for Ru-**2**, Ru-**3**, and Ru-**4**, respectively; thereby being in the same range as for comparable ruthenium-triazolylidene complexes (see Experimental Section and the Supporting Information).[5n,10d] In addition, mass spectrometric measurements displayed the molecular peaks for the cationic parts of the complexes.

Single crystals of Ru-**2** and Ru-**3** could be obtained by slow diffusion of *n*-hexane into a diluted solution of the respective complex in dichloromethane at room temperature. X-ray diffraction studies show that Ru-**2** crystallizes in the monoclinic space group *C*2/*c*, and Ru-**3** in $P2_1/n$. By slow diffusion of *n*-hexane into a concentrated solution of Ru-**4** in dichloromethane at 8 °C, we were able to obtain single crystals of Ru-**4** as a dichloromethane solvate that was suitable for X-ray diffrac-



Scheme 4. Reaction conditions leading to the formation of H**L**^{2}[BF_4].



Scheme 5. Reaction yielding H_2**L**^{4}[OTf]$_2$ (right) and side product formation for the unactivated reaction without the use of silver(I) triflate (left).

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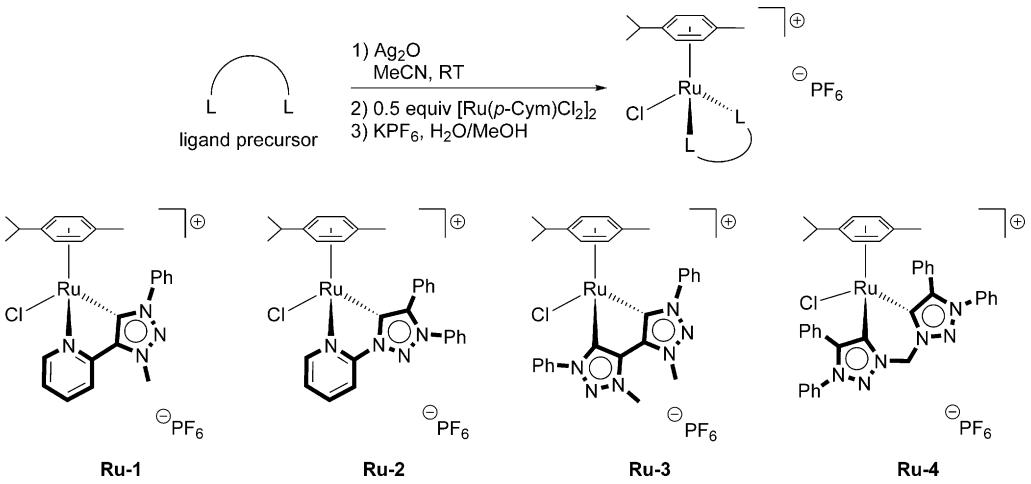

Scheme 6. Complexes Ru-**2**–**4** synthesized during this work.

tion studies. Complex Ru-**4** crystallizes in the triclinic space group $P\bar{1}$ as a dichloromethane solvate. All complexes exhibit a typical piano-stool geometry (Figure 1).

The *para*-cymene ligand is bound in a η^6-mode showing a distance of 1.710(1), 1.724(1), and 1.725(1) Å between the centroid of the cymene ligand and the ruthenium center for Ru-**2**, Ru-**3**, and Ru-**4**, respectively.

All complexes exhibit a C1–Ru1 or C2–Ru1 distance between 2.03 and 2.05 Å for the Ru–C(triazolylidene) (Table S1 in the Supporting Information) and are therefore in the same range as comparable triazolylidene complexes with chelating triazolylidenes.[10d] The pyridyl moiety in Ru-**2** exhibits a bond length of 2.113(3) Å for N2–Ru1. Comparison of the bond lengths within the triazolylidene rings shows a delocalized bonding situation within the ring systems. The angles on the carbene centers C1 and C2 are slightly reduced compared with those of free triazolium salts. Overall, the bond lengths and angles for Ru-**3** are similar to the diisopropylphenyl analogue, which was reported by us in 2013.[10d] The structure of Ru-**3** is also similar to the structure of a ruthenium complex with a bi-triazole-2-ylidene reported previously.[19]

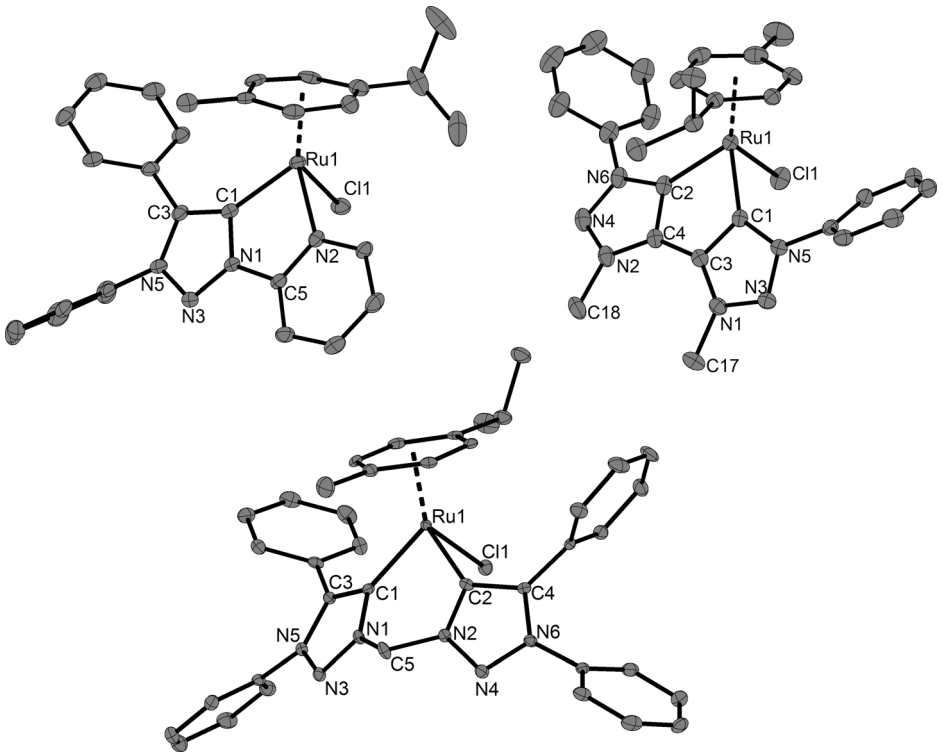

Figure 1. ORTEP representation of Ru-**2** (upper left), Ru-**3** (upper right), and Ru-**4**·CH_2Cl_2 (bottom). Hydrogen atoms, solvent molecules and counter ions are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

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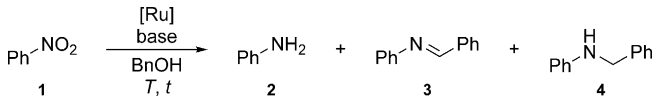
In the case of Ru-**4**, the two triazolylidene units are bridged by the C5 methylene linker, which displays single bonds to the ring nitrogen atoms. The N1-C5-N2 bond angle is 109.0(2)°, displaying a nearly perfect sp^3 hybridization of the linker. The two triazolylidene units are tilted by 32.3(2)° with respect to each other. The dihedral angles between the *N*-phenyl rings and the triazolylidene rings are 42.2(3)° and 60.9(2)°, whereas the *C*-phenyl rings are tilted by 56.8(2)° and 74.4(3)° towards the triazole planes. Further crystallographic details for Ru-**2**–**4** are given in the Supporting Information (Tables S1 and S2).

Catalysis

We next turned out attention to the use of the synthesized complexes as precatalysts for the conversion of nitroarenes and benzyl alcohols into secondary amines. In doing so, we were interested in comparing the activity of these new catalysts to ruthenium-cymene based catalysts containing N-heterocyclic carbenes[16] as well as other ligands.[14] Furthermore, we were interested in comparing the catalytic performance of a 1,4- versus a 1,5-disubstituted-triazole-derived triazolylidene ligand.

To start our catalytic studies, an initial screening was carried out using the *N*-alkylation of nitrobenzene towards *N*-benzylaniline as the benchmark reaction (Scheme 7), using 3 mol% of the catalyst and 0.6 equivalents of KO*t*Bu in benzyl alcohol at 120 °C. The results are summarized in Table 1.



Scheme 7. Reductive coupling of nitrobenzene and benzyl alcohol.

Table 1. First survey to determine most active (pre)catalyst for optimization.

Entry	Complex	Mole fraction [%][a]			
		1	**2**	**3**	**4**
1	Ru-**1**	0	0	>99	0
2	Ru-**2**	0	0	>99	0
3	Ru-**3**	0	0	89	11
4	Ru-**4**	0	0	>99	0

[a] Reaction conditions: KO*t*Bu (0.6 equiv), benzyl alcohol (1 mL), toluene (1 mL), nitrobenzene (0.2 mmol), catalyst (3 mol%), 120 °C, 24 h; mixture composition determined based on GC-MS analysis using hexadecane as internal standard.

These results pointed out that Ru-**3** is likely the most potent (pre)catalyst in this series; therefore, for further optimizations, Ru-**3** was employed. We then reduced the amount of benzyl alcohol to 10 equivalents with regard to the nitrobenzene to minimize the twofold *N*-alkylation resulting in tertiary amines. Screening of different potassium-based bases revealed a strong influence of base on the product distribution: inorganic bases as well as potassium *tert*-butanolate (Table 2, entries 1–3) led to *N*-benzalaniline (**3**) as the main product. By using a solution of potassium *tert*-amylate (1.7 M in toluene), the desired *N*-benzylaniline (**4**) was delivered in extremely high selectivity.

Table 2. Optimization regarding the employed base.

Entry	Base	Mole fraction [%][a]			
		1	**2**	**3**	**4**
1	KOH	0	0	90	10
2	K_2CO_3	0	11	73	17
3	KO*t*Bu	7	19	65	9
4	KO*t*Amyl	0	0	0	>99

[a] Reaction conditions: base (0.6 equiv), benzyl alcohol (2.0 mmol), nitrobenzene (0.2 mmol), Ru-**3** (3 mol%), 120 °C 24 h; mixture composition determined based on GC-MS using hexadecane as internal standard.

We ascribe this vast difference to two different effects: the solubility of the whole system and especially of the base is increased, and a pre-activation of the catalyst occurs via the base, given that mixing the base and ruthenium complexes results in a strong change of color (see the Supporting Information). Adding toluene to the reactions with other bases had no influence on the product formation. Furthermore, we reduced the catalyst loading, reaction temperature and reaction time (Table 3). Reducing the reaction time to 7 h still gave excellent yields without loss in selectivity (entry 3), whereas a reaction over 24 h resulted in a slightly lower yield (entry 1). The formation of the twofold *N*-alkylated product over longer periods is a possibility.[14a] Unfortunately, we were not able to detect the twofold *N*-alkylated product by GC, and hence we cannot rule out the operation of other side reactions of the mono-*N*-alkylated products with components present in the catalytic reaction mixture. Decreasing the reaction temperature to 100 °C (entry 4) still gave reasonable yields over 12 h. Furthermore, we could reduce the catalyst loading to 1 mol% and still get yields of over 90% after 12 h (entry 5). Lowering both temperature and catalyst loading (entry 6) as well as reducing the reaction time to 3 h (entry 8), resulted in moderate yields.

Table 3. Optimization towards temperature and catalyst loading.[a]

Entry	Cat. loading [mol%]	*T* [°C]	*t* [h]	Yield [%][b]
1	3	120	24	85
2	3	120	12	95
3	3	120	7	92
4	3	100	12	78
5	1	120	12	92
6	1	100	12	75
7	4	120	3	73[c]

[a] Reaction conditions: Ru-**3** (3 mol%), KO*t*Amyl (0.6 equiv), benzyl alcohol (2.0 mmol), nitrobenzene (0.2 mmol). [b] Yield of *N*-Benzylaniline determined based on GC-MS analysis using internal standard. [c] Aniline and *N*-benzalaniline were also observed.

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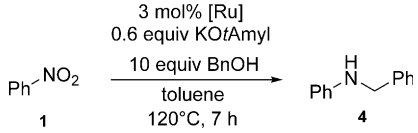
From these results, we decided that the reaction conditions utilized in Table 3, entry 3 are the most convenient for laboratory applications, and these conditions were used to re-evaluate the ruthenium complexes Ru-**1**–**4** under these optimized conditions (Scheme 8, Table 4).



Scheme 8. Optimized conditions for benchmark reaction.

Table 4. Comparison of complexes Ru-**1**–**4** under optimized conditions.[a]

Entry	(Pre)catalyst	Yield [%][b]
1	Ru-**1**	85
2	Ru-**2**	92
3	Ru-**3**	95
4	Ru-**4**	70
5	$[Ru(p\text{-Cym})Cl_2]_2$ (1.5 mol%)	40
6	no catalyst	30[c]

[a] Reaction conditions: KO*t*Amyl (0.6 equiv), benzyl alcohol (2.0 mmol), nitrobenzene (0.2 mmol), catalyst (3 mol%), 120 °C, 7 h. [b] Yield of *N*-benzylaniline determined based on GC-MS analysis using hexadecane as internal standard. [c] Azobenzene observed as side product.

All catalysts exhibit good to excellent yields under these conditions towards the desired amine. The low yield with Ru-**4** (Table 4, entry 4) could be ascribed to the high acidity of the methylene bridge of the ligand. Although we cannot rule out the operation of steric effects, the low product yield with Ru-**4**, in comparison with Ru-**3**, which also has two phenyl substituents on the ligand backbone, likely indicates the aforementioned acidity of the methylene bridge as the reason for the lower activity of Ru-**4**. It is conceivable that the catalyst might not be stable over the course of the reaction in the presence of potassium *tert*-amylate. The ruthenium precursor without any ligands delivers only 40% product yield (entry 5) under the same conditions. This result shows the necessity of the MIC ligands for the high activity of these ruthenium catalysts.

Interestingly, product formation also occurs in the absence of ruthenium catalysts (Table 4, entry 6). Given that this could only be observed when potassium *tert*-amylate was used, this must be due to this particular base and is not completely surprising considering the work by Uno et al.[12a]

According to our proposed reaction pathway (Scheme 2), the reaction can be subdivided into the reduction of nitrobenzene to aniline (Scheme 2, Part I) and the condensation of aniline with benzaldehyde, followed by a final reduction step (Scheme 2, Part II). The progress of the reaction could be observed by tracking the composition of the reaction mixture by using GC-MS. During the first two hours of the reaction, there was almost no accumulation of aniline or *N*-benzalaniline, but there was an inversely proportional correlation between the consumption of nitrobenzene and the formation of *N*-benzylaniline up to four hours (Figure 2).

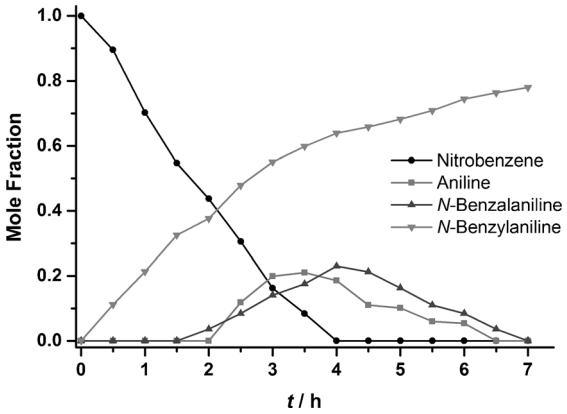
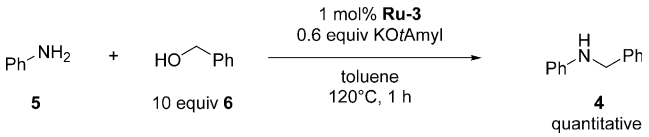


Figure 2. Composition of reaction mixture over time.

Between the first and second hour, we could also identify phenyl(phenylamino)methanol (Scheme 2, Part II) by mass spectrometry, which presented as a broad signal in the gas chromatogram. Accumulation of aniline and *N*-benzalaniline in the reaction mixture was observed after 2.5 and 3 h, respectively, probably due to reduced catalyst activity over time.

This would suggest that the reaction of aniline and benzaldehyde is fairly fast compared with the preceding reduction of nitrobenzene to aniline. To verify this assumption, aniline was reacted by using only 1 mol% catalyst loading of complex Ru-**3**; under these conditions, the secondary amine was formed quantitatively within one hour (Scheme 9 and the Supporting Information).



Scheme 9. Conversion of aniline under catalytic conditions. Determined based on GC-MS analysis by using hexadecane as internal standard.

We also got indications of the likely operation of the homogeneous pathway of the reaction by adding a drop of Hg according to the amalgam poisoning test; this did not result in decreased activity of the catalyst (see the Supporting Information, Section 4.3).

To screen whether our catalytic system would tolerate functional groups on the nitrobenzene, we converted the methoxy-substituted substrate **7** and the chloro-substituted **9** under the optimized conditions. Both nitro-compounds could be transformed in satisfying isolated yields (Scheme 10).

We were also able to use 4-nitroaniline (**11**) as a substrate in this reaction to obtain the di-amine-di-hydrochloride **12** without increasing the catalyst loading (Scheme 10). In this case, isolation of the product was achieved through formation of the corresponding hydrochloride to reduce the effort of purifi-

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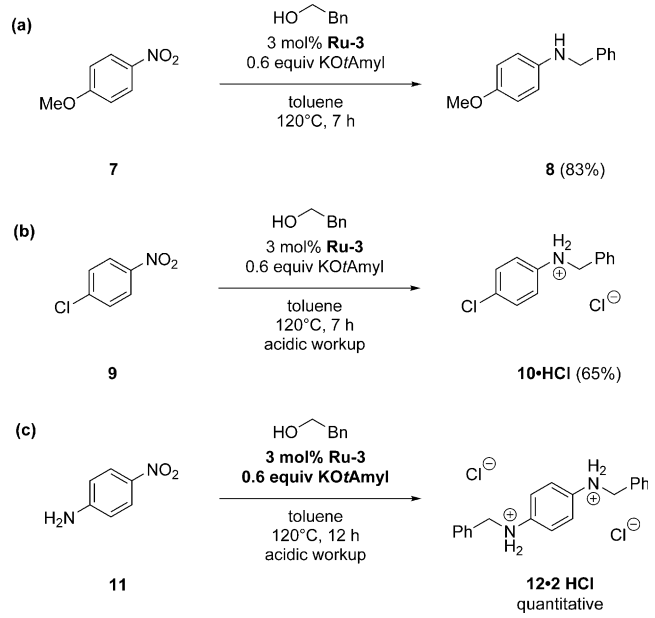
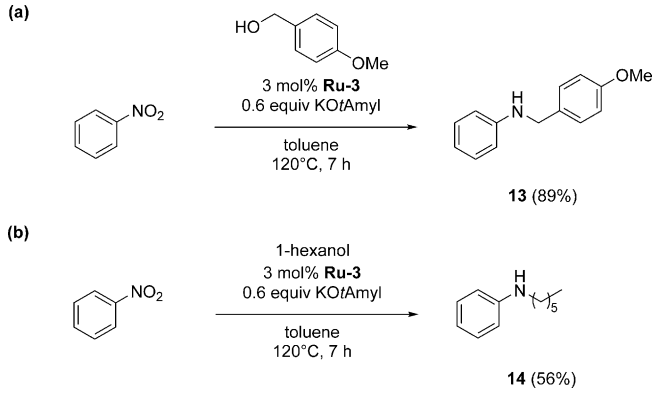


Scheme 10. Conversion of: a) 1-methoxy-4-nitrobenzene, b) 1-chloro-4-nitrobenzene (isolated as the corresponding hydrochloride), and c) 4-nitroaniline (isolated as the corresponding hydrochloride) under catalytic conditions. Yields refer to isolated products.

cation from a column to a simple precipitation. We found this to be a convenient way to save time during the work up.

To further investigate the scope of this reaction, two additional primary alcohols were tested in the reductive condensation of nitrobenzene (Scheme 11). The use of (4-methoxy)benzyl alcohol resulted in a smooth reaction with a satisfactory yield of 89%, whereas 1-hexanol gave in a reduced yield of 56%. This can be attributed to the lower reactivity of 1-hexanol to form the corresponding aldehyde compared with benzylic substrates, but we still find this to be a good example of the broad applicability of the present protocol.



Scheme 11. Conversion of: a) (4-methoxy)benzyl alcohol, and b) 1-hexanol under catalytic conditions. Yields refer to isolated products.

Thus, it is seen that, of the four complexes tested here, Ru-**3**, containing a bicarbene ligand derived from a 1,4-regioisomer of triazoles, delivers the best catalytic yield (Table 1 and Table 4). However, Ru-**2**, which contains a pyridyl-triazolylidene ligand derived from a 1,5-regioisomer of triazole, delivers comparable catalytic yield (Table 4). As noted above, the efficiency of Ru-**4** is probably lower because of the sensitivity of the methylene groups in the ligand backbone towards bases, which can lead to catalyst degradation. Hence, it is to be expected that functionalization of those methylene groups would lead to more efficient catalysts based on such ligands in the future. A comparison of the (pre)catalysts presented here with similar Ru-NHC complexes shows a much higher catalytic efficiency for the present complexes towards the formation of secondary amines.[16] Furthermore, to our knowledge, in overall terms, the (pre)catalysts presented here are capable of catalyzing the formation of secondary amines from nitroarenes and benzyl alcohols in shorter reactions times and under milder reaction conditions compared with the best reported catalysts for this transformation.[14]

Conclusions

We were able to extend the synthetic diversity offered by the 1,5-regioisomer of the [3+2] cycloaddition product between azides and alkynes to generate new chelating mesoionic carbenes. Besides the synthesis of a new chelating pyridyl-triazolylidene ligand $\mathbf{L^2}$, we were also able to explore a new synthetic route for the synthesis of chelating bitriazolylidene ligands (such as $\mathbf{L^4}$). In addition to the introduction of the new ligands, we also presented the synthesis and characterization of their corresponding half-sandwich metal complexes using the ruthenium cymene metal fragment. We found that, in case of methylene-linked bitriazolylidene ligands, not only the absence of the triazolium-5*H* gives good indication for complex synthesis, but the protons of the methylene linker also act as probes because they become diastereotopic in the reaction product. In addition to the new complexes Ru-**2** and Ru-**4**, the corresponding complexes derived from the 1,4-regioisomer of triazoles are presented and, in case of complex Ru-**3**, characterized. The four complexes were then tested for their catalytic activity in the condensative reduction of nitroarenes by using primary alcohol as the hydrogen source, yielding secondary amines as the final product. Extremely short reaction times could be used by introducing potassium *tert*-amylate; to our knowledge, this protocol exceeds all other reported protocols for this reaction.[14]

These results once again demonstrate the diversity offered by triazolylidene ligands, and highlight the ease of synthetic procedures available to build interesting ligand systems and also to extend the multiple catalytic applications that metal complexes containing 1,2,3-triazolylidene ligands can facilitate. In future, we will explore the possibilities of generating new ligands (especially tripodal ligands) that can be achieved through the new approach of using 1,5-disubstituted triazoles as starting materials for mesoionic carbenes. Work focusing on these topics is being pursued in our laboratories. The use of the 1,5-disubstituted triazoles as precursors for mesoionic carbenes thus provides a valuable addition to this rapidly expanding ligand class.

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Experimental Section

Materials and physical methods

$[RuCymCl_2]_2$ was purchased from ABCR. All the reagents were used as supplied. HL^1[OTf] and Ru-**1** were synthesized by following reported procedures.[5o,p] All reactions were carried out by using standard Schlenk-line techniques under an inert atmosphere of nitrogen (Linde, HiQ Nitrogen 5.0, purity > 99.999%). Anhydrous solvents were obtained with a MBRAUN MB-SPS-800 solvent system. All solvents were degassed by using standard techniques prior to use. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded with a Jeol ECS 400 spectrometer or a JEOL ECZ 400R spectrometer at 20 °C. Chemical shifts are reported in ppm (relative to the TMS signal) with reference to the residual solvent peaks.[20] Multiplets are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and combinations thereof. Mass spectrometry was performed with an Agilent 6210 ESI-TOF. GC-MS analysis was performed with an Agilent 7820A GC System combined with an Agilent 5977E GC/MSD (Column: Agilent HP-5 ms UI, 30 m × 250 μm, 0.25 μm, p/n 190915–433UI, Method: 50 °C to 300 °C, heating rate 15 K min^{-1}, inlet temperature 300 °C). Purity of benzyl alcohol, nitrobenzene and hexadecane for catalysis experiments was checked by GC-MS analysis.

Synthesis of ligands

3,4-Diphenyl-1-(pyridin-2-yl)-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (HL^2[BF$_4$]): 1,5-Triazole **T1** (1.2 equiv, 3.0 mmol, 665 mg) was mixed with 2-bromopyridine (1 equiv, 2.5 mmol, 390 mg, 230 μL) in a screw-capped vial and the mixture was stirred and heated for 3 days at 160 °C. The mixture was subsequently cooled to RT, dissolved in dichloromethane (10 mL) and slowly added to diethyl ether (400 mL). The brown precipitate was collected by filtration and immediately dissolved in methanol (15 mL) and a large excess of ammonium tetrafluoroborate (2 g) was added. The mixture was stirred for 15 min and then diluted with water (250 mL) to cause precipitation of the desired solid. The product was recrystallized from dichloromethane/*n*-hexane (1:3) at −18 °C. The product was obtained as crystalline colorless plates. Yield: 521 mg (1.35 mmol, 54%); ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.23 (s, 1H; triazole-5H), 8.86–8.85 (m, 1H; py-*H*), 8.37–8.33 (m, 2H; py-*H*), 7.90–7.89 (m, 1H; py-*H*), 7.78–7.68 (m, 5H; Ph-*H*), 7.61–7.47 ppm (m, 5H; Ph-*H*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 150.4 (triazole-5*C*), 143.1, 135.8, 132.7, 131.8, 131.7, 130.8, 130.1, 127.8, 127.7, 126.9, 115.6 (all aryl-*C*); MS (ESI): *m/z* calcd for $[C_{19}H_{15}N_4]^+$: 299.1297; found: 299.1323.

1,1′-Diphenyl-3,3′-dimethyl-1*H*,1′*H*-[4,4′-bi(1,2,3-triazole)]-3,3′-diium ditetrafluoroborate (H$_2$L^3[BF$_4$]$_2$): Synthesized by following a reported procedure.[18] The corresponding bitriazole (1.0 equiv, 288 mg, 1.0 mmol) was dissolved in anhydrous dichloromethane (15 mL) and trimethyloxonium tetrafluoroborate (2.5 equiv, 372 mg, 2.5 mmol) was added. The mixture was stirred at RT for three days, then methanol (3 mL) was added and the mixture was stirred for 15 min before it was slowly poured into diethyl ether (400 mL). The white precipitate was filtered, washed with diethyl ether (100 mL) and dried to give the desired product as a white powder. Yield: 368 mg (0.75 mmol, 75%); ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.18 (s, 2H; triazole-5H), 8.12–8.10 (m, 4H; aryl-*H*), 7.85–7.83 (m, 6H; aryl-*H*), 4.58 ppm (s, 6H; N-CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 135.5 (triazole-5*C*), 132.4, 131.2, 130.6, 127.3, 122.0 (all aryl-*C*), 39.8 ppm (N-CH$_3$, overlay with solvent); MS (ESI): *m/z* calcd for $[C_{18}H_{18}N_6]^{2+}$: 159.0791; found: 159.0795.

3,3′-Methylenebis(1,5-diphenyl-1*H*-1,2,3-triazol-3-ium) ditriflate (H$_2$L^4[OTf]$_2$): Diiodomethane (1.0 equiv, 2.5 mmol, 665 mg, 0.2 mL) was dissolved in anhydrous *n*-hexane (10 mL) and silver(I) triflate (2.1 equiv, 5.25 mmol, 1.34 g) was added. The mixture was capped in a Schlenk flask under argon and heated to 70 °C shielded from light for 5 h. In the meantime, in a second Schlenk flask, 1,5-triazole **T1** (2.5 equiv, 6.25 mmol, 1.39 g) was suspended in anhydrous toluene (10 mL). When the reaction with silver triflate was complete, the mixture was directly filtered over Celite into the triazole-containing toluene solution. The Celite was washed once again with *n*-hexane (5 mL) and the resulting reaction mixture (toluene/*n*-hexane 1:1.5) was heated to reflux overnight. The reaction mixture was then cooled to RT and poured into diethyl ether (400 mL). The resulting colorless precipitate was collected by filtration and washed with diethyl ether (50–100 mL). The product was obtained as a colorless solid. Yield: 1.53 g (2.00 mmol, 81%); ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.69 (s, 2H; triazole-5*H*), 8.09 (s, 2H; N-C*H*$_2$-N), 7.82–7.79 (m, 2H; aryl-*H*), 7.77–7.73 (m 8H; aryl-*H*), 7.68–7.63 (m, 2H; aryl-*H*), 7.60–7.54 (m, 4H; aryl-*H*), 7.50–7.46 ppm (m, 4H; aryl-*H*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 145.6 (triazole-5*C*), 135.1, 133.3, 132.6, 132.1, 130.9, 129.9, 127.4, 123.3 (all aryl-*C*), 65.8 ppm (N-*C*H$_2$-N); MS (ESI): *m/z* calcd for $[C_{29}H_{24}N_6]^{2+}$: 228.1026; found 228.1044.

Synthesis of the complexes

In a 100 mL-Schlenk flask, the corresponding ligand precursor (2.0 equiv, 0.2 mmol) was mixed with basic silver(I) oxide (7.0 equiv, 0.7 mmol, 163 mg) and a chloride source, potassium chloride (20 equiv, 2.0 mmol, 155 mg), and was dissolved in anhydrous acetonitrile (10 mL). The mixture was stirred under the exclusion of light for 2 days, then the black suspension was filtered and all solvents were removed under high vacuum. The resulting white-yellowish solid was then dissolved in dichloromethane (15 mL) and $[Ru(p\text{-}Cym)Cl_2]_2$ (1.0 equiv, 0.1 mmol, 60 mg) was added and the mixture stirred for 2 days under the exclusion of light. The precipitated silver(I) chloride was filtered through a pad of Celite and all volatiles were removed. The crude product was then dissolved in methanol (5 mL). KPF_6 (8.0 equiv, 0.8 mmol, 147 mg) was added and the solution was stirred for another 20 min before water (80 mL) was slowly added to cause precipitation of the desired complex. The yellow solids were filtered and dried under air. The complexes were obtained as powders in moderate yields of 56% and higher.

[Ru(Cym)Cl(L^2)](PF$_6$) (Ru-2): Synthesized from HL^2[BF$_4$] (2.0 equiv, 0.20 mmol, 77 mg). Yield: 110 mg (0.15 mmol, 77%); orange solid; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.61 (d, *J* = 5.6 Hz, 1H; py-*H*), 8.49–8.47 (m, 2H; py-*H*), 7.86 (m, 1H; py-*H*), 7.75–7.61 (m, 10H; aryl-*H*), 5.84 (d, *J* = 6.2 Hz, 1H; Cym-*H*), 5.75 (d, *J* = 6.2 Hz, 1H; Cym-*H*), 5.68 (d, *J* = 6.1 Hz, 1H; Cym-*H*), 5.21 (d, *J* = 6.0 Hz, 1H; Cym-*H*), 2.56 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 2.09 (s, 3H; C*H*$_3$), 1.03 (d, *J* = 6.9 Hz, 3H; CH(C*H*$_3$)$_2$), 0.98 ppm (d, *J* = 7.0 Hz, 3H; CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (176 MHz, [D$_6$]acetone): δ = 171.6 (carbene-*C*), 158.4, 143.1, 132. 7, 131.8, 131.7, 130.8, 130.1, 127.8, 127.73, 126.9, 115.6 (all aryl-*C*), 91.6, 88.1, 87.1, 84.2 (Cym-*C*), 31.9 (CH(CH$_3$)$_2$), 22.7 (CH$_3$), 22.0, 19.0 ppm (CH(CH$_3$)$_2$); MS (ESI): *m/z* calcd for $[C_{29}H_{28}N_4ClRu]^+$: 569.1046; found: 569.1090.

[Ru(Cym)Cl(L^3)](PF$_6$) (Ru-3): Synthesized from H$_2$L^3[BF$_4$]$_2$ (2.0 equiv, 0.2 mmol, 98 mg). Yield: 82 mg (0.11 mmol, 56%); yellow solid. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.15–8.09 (m, 4H; aryl-*H*), 7.83–7.77 (m, 6H; aryl-*H*), 4.9–4.87 (m, 8H; N-C*H*$_3$ and 2 × Cym-*H*), 4.83 (d, *J* = 6.0 Hz, 2H; Cym-*H*), 1.94 (s, 3H; C*H*$_3$), 0.64 ppm (d, *J* = 7.2 Hz, 6H; C*H*(CH$_3$)$_2$ not observed due to solvent overlay); ^{13}C{^{1}H} NMR

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(700 MHz, CD_2Cl_2): $\delta = 178.3$ (carbene-*C*), 139.0, 138.3, 131.1, 129.7, 125.8 (all aryl-*C*), 90.5, 87.4 (Cym-*C*), 40.0 (N-CH_3), 31.3 ($CH(CH_3)_2$), 22.1 (CH_3), 18.3 ppm ($CH(CH_3)_2$); MS (ESI): *m/z* calcd for $[C_{28}H_{30}N_6ClRu]^+$: 587.1264; found: 587.1256.

[Ru(Cym)Cl(L^4)][PF_6] (Ru-4): Synthesized from $H_2L^4[OTf]_2$ (2.0 equiv, 0.20 mmol, 150 mg). Yield: 131 mg (0.15 mmol, 75%); green solid. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.80–7.75$ (m, 4H; Aryl-*H*), 7.51–7.40 (m, 16H; Aryl-*H*), 7.23 (d, $J = 13.6$ Hz, 1H; N-CH_2-N), 6.51 (d, $J = 13.6$ Hz, 1H; N-CH_2-N), 4.89 (d, $J = 6.0$ Hz, 2H; Cym-*H*), 4.70 (d, $J = 6.0$ Hz, 2H; Cym-*H*), 2.13 (hept, $J = 7.2$ Hz, 1H; $CH(CH_3)_2$), 1.67 (s, 3H; CH_3), 0.84 ppm (d, $J = 7.2$ Hz, 6H; $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (700 MHz, CD_2Cl_2): $\delta = 164.3$ (carbene-*C*), 149.0, 135.1, 131.9, 131.0, 130.2, 129.6, 128.6, 127.9, 125.5 (all aryl-*C*), 90.7, 86.7 (Cym-*C*), 66.3 (N-CH_2-C), 31.3 ($CH(CH_3)_2$), 22.5 (CH_3), 18.4 ppm ($CH(CH_3)_2$); MS (ESI): *m/z* cacld for $[C_{39}H_{36}N_6ClRu]^+$: 725.1733; found: 725.1741.

Catalysis

General setup: In a typical reaction, the substrate (1.0 equiv, 0.2 mmol) was added to a 25 mL-Schlenk flask filled with the respective catalyst (1–3 mol%), base (0.6 equiv), and hexadecane (1.0 equiv, 0.2 mmol, 50 μL) as internal standard, and the respective alcohol (10 equiv, 2.0 mmol). The mixture was then heated to 100–120 °C for the indicated time.

Optimized reactions: In a 25 mL-Schlenk flask, the respective complex (3 mol%, 6 μmol) was dissolved in benzyl alcohol (10 equiv, 2.0 mmol, 0.2 mL). Potassium *tert*-amylate (0.6 equiv, 0.12 mmol, 1.7 M in toluene) and hexadecane as internal standard (1.0 equiv, 0.2 mmol, 50 μL) were added and the mixture was stirred for 5 min at RT before nitrobenzene (1.0 equiv, 0.2 mmol, 20 μL) was also added to the flask. The mixture was heated to 120 °C for 7 h. Samples for GC-MS analysis were taken directly from the mixture and filtered over a short pad of silica using ethyl acetate as eluent.

***N*-Benzylaniline (4)**: Obtained from nitrobenzene (0.20 mmol, 20 μL) after 7 h reaction time after column chromatography (SiO_2, *n*-hexane/ethyl acetate 95:5). Yield: 34.4 mg (0.19 mmol 94%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.38–7.32$ (m, 4H; aryl-*H*), 7.29–7.25 (m, 1H; aryl-*H*), 7.20–7.15 (m, 2H; aryl-*H*), 6.71 (t, $J = 7.33$ Hz, 1H; aryl-*H*), 6.64 (d, $J = 7.5$ Hz, 2H; aryl-*H*), 4.33 (s, 2H; benzyl-*H*), 4.02 ppm (br. s, 1H; amine-*H*); GC-MS (EI): *m/z* (%): 77.1, 91.1, 122.1, 196.1, 213.2.[14d]

***N*-Benzyl-4-methoxyaniline (8)**: Obtained from 1-nitro-4-methoxybenzene (0.20 mmol, 42.6 mg) after 7 h reaction time after column chromatography (SiO_2, *n*-hexane/ethyl acetate 95:5). Yield: 38.5 mg (0.17 mmol, 83%); yellow oil; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.28$ (m, 5H; aryl-*H*), 6.81 (d, $J = 16.0$ Hz, 2H; aryl-H), 6.63 (d, $J = 15.9$ Hz, 2H; aryl-*H*), 4.31 (s, 2H; benzyl-*H*), 3.76 ppm (s, 3H; CH_3).[14d]

***N*-Benzyl-4-chloroaniline hydrochloride (10·HCl)**: Obtained from 1-nitro-4-chlorobenzene (0.20 mmol, 31.2 mg) as a white solid after 7 h reaction time. The crude product was dissolved in ethanol and ethereal HCl was added dropwise until the product was completely precipitated. The solid was then washed with diethyl ether and dried to give the product. ^1H NMR (400 MHz, D_2O): $\delta = 7.51–7.38$, 7.30–7.23, 4.83 (s, 2H, overlay with solvent signal), 4.60 ppm (s, 2H, NH_2). Solubility was too low for ^{13}C NMR spectroscopy. MS (ESI): *m/z* calc. for $[C_{13}H_{13}ClN]^+$: 218.0731; found: 218.0719.

1,4-Di-(*N*-benzylamino)benzene dihydrochloride (12·2HCl): Obtained from 4-nitroaniline (0.20 mmol, 27.6 mg) after 12 h reaction time. The crude product was dissolved in ethanol and ethereal HCl was added dropwise until the product was completely precipitated. The solid was then washed with diethyl ether and dried to give the product. Yield: 66.2 mg (0.18 mmol, 92%); colorless solid; ^1H NMR (400 MHz, D_2O): $\delta = 7.41–7.35$ (m, 8H; aryl-*H*), 7.31–7.29 (m, 2H; aryl-*H*), 7.25 (dd, $J = 7.8$, 1.6 Hz, 4H; aryl-*H*), 7.10 (s, 4H; benzyl-*H*), 4.51 (s, 4H; ammonium-*H*). Solubility was too low for ^{13}C NMR spectroscopy. MS (ESI): *m/z* calc. for $[C_{20}H_{22}N_2]^{2+}$: 145.0886; found: 145.0895.

***N*-(4-Methoxybenzyl)aniline (13)**: Obtained from (4-methoxy)benzyl alcohol (2.0 mmol, 0.25 mL) after 7 h reaction time after column chromatography (SiO_2, *n*-hexane/ethyl acetate, 95:5). Yield: 37.9 mg (0.18 mmol, 89%); colorless solid; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.31–7.30$ (m, 2H; aryl-*H*), 7.23–7.18 (m, 2H; aryl-*H*), 6.92–6.89 (m, 2H; aryl-*H*), 6.74 (tt, $J = 7.3$, 1.2 Hz, 1H; aryl-*H*), 6.68–6.64 (m, 2H; aryl-*H*), 4.27 (s, 2H; benzyl-*H*), 3.96 (br. s, 1H; amine-*H*), 3.82 (s, 3H; CH_3).[21]

***N*-Hexylaniline (14)**: Obtained from 1-hexanol (2.0 mmol, 0.25 mL) after 7 h reaction time after column chromatography (SiO_2, *n*-hexane/ethyl acetate, 95:5). Yield: 19.8 mg (0.11 mmol, 56%); colorless oil; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.19–7.15$ (m, 2H; aryl-*H*), 6.69 (tt, $J = 7.3$, 1.1 Hz, 1H; aryl-*H*), 6.62–6.59 (m, 2H; aryl-*H*), 3.59 (br. s, 1H; amine-H), 3.10 (t, $J = 7.2$ Hz, 2H; alkyl-*H*), 1.65–1.56 (m, 2H; alkyl-*H*), 1.44–1.26 (m, 6H; alkyl-*H*), 0.90 ppm (t, $J = 7.2$ Hz, 3H; alkyl-*H*).[22]

X-ray crystallography

X-ray quality crystals of Ru-**2** and Ru-**3** were obtained by layering diluted solutions in dichloromethane with *n*-hexane at RT. X-ray quality crystals of Ru-**4** were obtained by layering concentrated solutions in dichloromethane with *n*-hexane at 8 °C. X-ray data of Ru-**2** were collected with a Bruker Smart AXS. Data were collected at 140(2) K using graphite-monochromated Mo Kα radiation ($\lambda_\alpha = 0.71073$ Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard "omega scan techniques", and were scaled and reduced by using Saint+ software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2. X-ray data of Ru-**3** and Ru-**4** were collected with a Bruker D8 Venture system at 100(2) K using graphite-monochromated MoKα radiation ($\lambda_\alpha = 0.71073$ Å). The strategy for the data collection was evaluated by using APEX2. The data were collected by using "omega + phi scan techniques", and were scaled and reduced by using APEX2 and SADABS software. The structures were solved by intrinsic phasing using APEX2 and refined by full matrix least-squares using SHELXL-2014/7, refining on F^2. Non-hydrogen atoms were refined anisotropically.[23] CCDC 1012084 (Ru-**2**), 1020050 (Ru-**3**), and 1442699 (Ru-**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: regioselectivity · carbene ligands · carbenes · click chemistry · ruthenium

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FULL PAPER

Ligand Design

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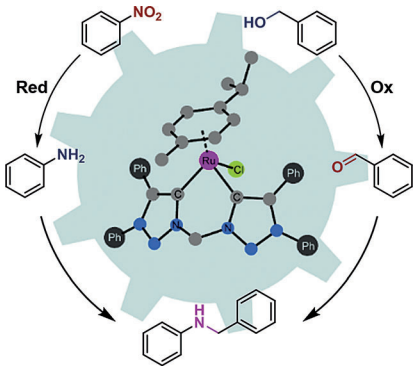
Expanding the Scope of Chelating Triazolylidenes: Mesoionic Carbenes from the 1,5-"Click"-Regioisomer and Catalytic Synthesis of Secondary Amines from Nitroarenes



Ru getting into gear: The use of the 1,5-regiomer of the azide–alkyne cycloaddition reaction for the development of chelating mesoionic carbene ligands is reported (see scheme). The corresponding ruthenium complexes are shown to be extremely potent catalysts for the synthesis of secondary amines.

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