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Eight-Membered-Ring Diaminocarbenes Bearing Naphthalene Moiety in the Backbone: DFT Studies, Synthesis of Amidinium Salts, Generation of Free Carbene, Metal Complexes, and Solvent-free Copper Catalyzed Azide-Alkyne cycloaddition (CuAAC) reaction

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Abstract

New type of eight-membered ring N-heterocyclic carbenes bearing rigid naphthalene moiety in the backbone are reported for the first time. Stereoelectronic properties of 4,5-dihydro-1Hnaphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene (NaphtDHD) and smaller ring NHCs were theoretically studied at DFT level. Amidinium salts are prepared from corresponding amidines and dibromides. Free carbene NaphtDHD-Dipp (Dipp = 2,6-diisopropylphenyl) was generated in solution by treatment of the corresponding salt with LiHMDS. It is stable in solution at low temperatures, while decompose rapidly at room temperature. Silver(I) and copper(I) complexes were synthesized and structurally characterized in the solid state. Copper(I) complex [(NaphtDHD-Mes)CuBr] (Mes = mesityl, 2,4,6-trimethylphenyl) exhibits high catalytic activity in alkyne-azide cycloaddition (CuAAC) reaction under solvent-free conditions. Published on 09 February 2017. Downloaded by University of South Dakota on 09/02/2017 10:45:26.

Introduction

N-heterocyclic carbenes (NHC) are widely used as supporting ligands in organometallic chemistry and catalysis.¹ Their steric and electronic properties can be tuned using variation of substituents, number of nitrogen atoms attached to the ylidene carbon, nature of a backbone of the heterocycle.² First stable carbene, isolated by Arduengo and co-workers in the solid state in 1991, bears imidazolium core (**A**).³ Later, a wide variety of structural classes of carbenes was reported: imidazolinium carbenes (**B**),⁴ carbenes bearing one nitrogen atom at the ylidene center derived from aliphatic (**C**),⁵ and aromatic (**D**⁶ and **E**⁷) heterocycles, NHCs stabilized by the remote nitrogen atoms in the substituents (**F**)⁸ or in the aromatic ring (**G**).⁹ Many other classes of persistent and stable carbenes are extensively reviewed in the recent literature.¹⁰



Simple and efficient approach for tuning of carbene properties is the variation of a ring size of the NHC. Six- (**H**) and seven-membered (**I**) ring diaminocarbenes are commonly referred to as expanded-ring carbenes (er-NHCs). er-NHCs surpass their five-membered ring counterparts in stereoelectronic properties. These ligands are stronger donors and their steric bulk can be tuned in a wider range. er-NHCs were successfully used in a number of catalytic applications.¹¹ To exemplify, we were able to show that palladium complexes of six-membered ring carbenes are highly efficient in Suzuki cross-coupling of heteroaryl halides in water,¹² and Buchwald-Hartwig arylation of anilines under solvent-free conditions.¹³ Seven-membered ring carbenes exhibit steric and electronic properties sufficient for effective stabilization of cationic gold species, which are highly active catalysts in addition of nitrogen nucleophiles to aryl acetylenes.¹⁴

Recently Cavell et al. reported on the first synthesis of the eight-membered ring carbene bearing aliphatic backbone (**J**).¹⁵ The key features of the new type diazocanylidenes are high steric encumbrance around metal atom in the complexes (%V_{bur} up to 49.1 in Ag complexes),¹⁶ and strong donor properties ($v_{av} = 2024.5 \text{ cm}^{-1}$ in [Rh(NHC)(CO)₂Cl] complex).^{2, 17}

Following the trend of expansion of the ring size in NHCs and addition of various fragments in the backbone we performed theoretical and experimental studies of a new type of the eight-

membered ring carbene bearing rigid naphthalene moiety 4,5-dihydro-1H-naphtho[1,8ef][1,3]diazocin-3(2H)-ylidene (NaphtDHD). In this contribution we report on the comparative DFT studies of NaphtDHD and smaller ring NHCs, generation of a free carbene, synthesis of silver(I) and copper(I) complexes, utilization of copper(I) complexes in solvent-free alkyne-azide cycloaddition (CuAAC) reaction.



NaphtDHD

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Results and discussion

DFT calculations

Prior to experimental work, we compared the properties of the eight-membered ring carbene with smaller ring counterparts using DFT calculations. Recently, we developed a set of calculated parameters that is useful for characterization of carbenes as ligands in metal complexes.¹⁸ This set includes parameters that characterize donor properties of carbenes, steric properties, stability of free carbenes and their metal complexes.

Structure optimizations and calculations of electronic parameters of a series of diaminocarbenes and their rhodium [Rh(NHC)(CO)₂Cl] complexes were calculated at DFT level. Although, silver and copper complexes were prepared experimentally, we have chosen rhodium carbonyl complexes to calculate Tolman electronic parameter (TEP).¹⁹ The calculated parameters are collected in tables 1 and 2. Here we will discuss the comparison of carbenes' properties in brief. A detailed theoretical study will be published elsewhere. It should be noted, that all but one considered carbenes have aliphatic backbones. Only NaphtDHD-Mes bears aromatic naphthalene moiety. Firstly, we will discuss aliphatic carbenes. Then, we will discuss the peculiarities of NaphtDHD-Mes.

Table 1

Upon the expansion of the carbene ring from five to eight, the values of N-C_{carb}-N valence angles at the ylidene carbon increase from 106.0° up to 121.9° (Table 1). This leads to changes in hybridization of the ylidene carbon atom orbitals. The input of *p*-orbital into sp^x orbital corresponding to ylidene lone electron pair increases. Thus, the HOMO energies rise from -4.67 eV to -4.21 eV. Simultaneously, HOMO-LUMO gap (HLG), singlet-triplet energy gap E_{ST} , carbene stabilization energy (CSE) gradually decrease. This means that expanded ring carbenes are softer ligands, while are more reactive towards insertion into C-H bonds, multiple bonds and etc.^{1a} Thus, isolation of free expanded ring carbenes is more complicated than of five-membered ring NHCs.

The calculated measure of NHCs' basicity is proton affinity (PA). Expansion of the ring leads to strong increase of the basicity. The difference in calculated PA for five- and eight-membered ring carbenes is 10.8 kcal mol⁻¹. This corresponds to the increase of gas phase basicity by eight orders of magnitude. Indeed, generation of free expanded ring carbenes are only possible using very strong and non-nucleophilic bases such as LiHMDS. While bases, such as alkoxides and hydrides, suitable for generation of five membered ring carbenes, are inapplicable.^{15a, 20}

Upon expansion of the ring, substituents at nitrogen atoms are pushed towards the metal in the complexes, thus making carbenes more bulky (Table 2).² Calculated V_{bur}^{16} for

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[Rh(NHC)(CO)₂Cl] increase from 23.3% to 28.1%. Since metal fragment is pushed away from the ylidene carbon, the metal-carbon bond $R(C_{carb}$ -Rh) slightly increase from 2.10 Å to 2.15 Å. Elongation of the metal-carbon bond and increase of HOMO energy are competitive factors governing the value of metal-ligand interaction energy. Thus, E_{int} increase when going from five- to six- and seven-membered ring carbenes, while decrease for eight-membered ring carbene. The decomposition energy *D* gradually decreases in the row from 55.9 down to 50.9 kcal mol⁻¹. This fact is very important to note. Previously, we claimed that the expansion of the ring in carbene leads to increase in HOMO and, correspondingly, to increase of metal-ligand bond energy.¹⁸ This turned out to be true for carbenes bearing small substituents, but false for carbenes bearing bulky aryls. It is well known that steric properties of ligands are the key for many catalytic applications.²¹ Thus, when designing a new carbene ligand one might consider its' bulkiness since overcrowding the ylidene carbon might destabilize the resulting metal complex.

Table 2

Tolman electron parameter (TEP) is a commonly accepted yardstick for comparison of the overall ligand donor properties.¹⁹ The lower the value of the average wavenumber $v_{av}(CO)$ for symmetric and asymmetric CO stretching vibrations, the stronger donor is the ligand attached to the metal atom. Thus, for five-membered ring carbene calculated TEP is 2000 cm⁻¹. It gradually decreases upon expansion of the ring to 1992 cm⁻¹. Such difference in TEP corresponds to a significant increase of donor strength of the expanded ring carbenes.²

Since NaphtDHD-Mes bears naphthalene moiety in the backbone, its properties differs significantly from those of HHD-Mes, bearing aliphatic backbone. The valence angle at the ylidene carbon is smaller by 1.4°. Evidently, this is due to shorter C-C bonds of the sp^2 hybridized carbon atoms of the naphthalene moiety and rigid fixation of the benzyl carbons in the plane of the naphthalene ring. The calculated E_{HOMO} energy in NaphtDHD-Mes (-4.21 eV) is significantly lower than for HHD-Mes (-4.09 eV). The value of -4.21 eV is close to the value, calculated for sixmembered ring carbone THD-Mes (-4.23 eV). It can be supposed, that this is due to two factors: shrinking of N-C_{carb}-N valence angle, and corresponding decrease of the input of the *p*-orbital into sp^x orbital corresponding to ylidene lone electron pair, and acceptor properties of benzylic carbon atoms attached to nitrogens of the N-C_{carb}-N moiety.

Calculated HLG for NaphtDHD-Mes is only 1.93 eV, much lower that for NHCs bearing aliphatic backbone. Evidently, this due to participation of low-lying π -orbitals of the naphthalene ring in the carbene LUMO (see plots of the frontier orbitals in supplementary information). Thus, NaphtDHD type carbenes are softer ligands for transition metal complexes, than aliphatic backbone NHCs. Notably, the E_{ST} value is the lowest among all carbenes studied here. Lowest predicted Published on 09 February 2017. Downloaded by University of South Dakota on 09/02/2017 10:45:26

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values of HLG and E_{ST} leads to the assumption that NaphtDHD might lack stability as a free carbene for isolation in the solid state (see experimental part below) comparing to other NHCs. However, the calculated carbene stabilization energy (CSE), 97.8 kcal mol⁻¹, is higher than for any of the expanded ring carbenes. The calculated value of PA, 287.7 kcal mol⁻¹, lies in between eight-and seven-membered ring carbenes.

Ligand properties of NaphtDHD-Mes are close to its aliphatic eight-membered ring counterpart HHD-Mes (Table 2). Although, NaphtDHD-Mes is less bulky, $V_{bur} = 27.6\%$, it is a stronger donor, $v_{av}(CO) = 1991$ cm⁻¹. Energies *D* and E_{int} in the complexes [Rh(NHC)(CO)₂Cl] are virtually the same for both carbenes.

Thus, based on the DFT calculations, one might propose that eight-membered ring carbene bearing naphthalene moiety in the backbone is a feasible target for synthesis. Combination of NaphtDHD ligand properties (steric encumbrance, ligand softness, strong donor properties, and the rigidity of the carbene backbone) promise rich reactivity and interesting catalytic applications.

Synthesis of amidinium salts and generation of carbenes

Eight-membered ring amidinium salts, bearing naphthalene moiety in the backbone, were synthesized by condensation of formamidines (3) and 1,8-bis-(bromomethyl)-naphthalene (2) (Scheme 1). This strategy was initially introduced by Bertrand *et al.*²² and further developed in our group for the synthesis if six- and seven-membered ring amidinium salts.²³ Corresponding dibromide can be easily prepared starting from commercially available 1,8-naphthalic anhydride.²⁴

Scheme 1

Preparation of amidinium salts bearing naphthalene moiety in the backbone.



1,8-Naphthalic anhydride can be reduced to 1,8-naphthalenedimethanol (1) using two methods: interaction with lithium aluminum hydride in THF,²⁴ and a mixture of sodium borohydride with bromine in 1,2-dimethoxyethane (1,2-DME).²⁵ Yields of diol are 84% and 61%, correspondingly. Treatment of the obtained diol with PBr₃ in 1,4-dioxane afforded dibromide (2) in 94% yield.²⁶

Amidinium salts (**4a**, **4b**) were obtained by interaction of the dibromide with corresponding amidines (**3a**, **3b**) in presence of Hünig's base (N,N-diisopropylethylamine, DIPEA) in DMF. Corresponding salts were obtained in excellent yields, 87% and 88%, respectively for Mes and Dipp derivatives.²²

We performed the attempts to isolate a free carbene. Previously, Cavell et al. have shown that deprotonation of amidinium salts is more efficient and high yielding when tetrafluoroborates are used instead of bromides.^{20b} Presumably, this is due to the fact that in bromides the anion is bonded to the amidinium proton through a hydrogen bond (see X-ray sections below). Tetrafluoroborate has lower coordination ability, and, thus, does not hinder the deprotonation of amidinium salt by bulky base. Thus, we converted amidinium bromides into tetrafluoroborates by treatment of salts with sodium tetrafluoroborate in acetone at room temperature (Scheme 2). Notably, amidinium bromides are poorly soluble in acetone. Upon addition of sodium tetrafluoroborate to a suspension of amidinium bromide, the mixture gradually homogenized, and became a clear solution when reaction finished. Amidinium tetrafluoroborates are white non-hygroscopic solids, isolated in virtually quantitative yields, 97% and 98%, correspondingly for Mes and Dipp derivatives.

Scheme 2

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Preparation of amidinium tetrafluoroborates.



We performed generation of a free carbene from [(NaphtDHD-Dipp)H]BF₄ (**5b**) using bulky lithium hexamethyldisilazide base (LiHMDS) in dry aprotic solvent.²⁷ To a solution of amidinium tetrafluoroborate in THF LiHMDS was slowly added. At room temperature, upon addition of a base, reaction mixture changed its color from transparent into green, then discolored instantly. The isolated products are a mixture of unidentifiable compounds. There were no signals found in ¹³C NMR spectrum in the 220 – 260 ppm region, characteristic for a carbene carbon atom. Typically, intense coloration is due to the formation of a conjugated π -system. We supposed that deprotonation could take place in less hindered benzylic position of a naphthalene moiety, giving rise to the formation of highly reactive azomethine ylide (Scheme 3).

Generation of a free carbene



At - 80°C, the obtained intense coloring of a solution lasts for a long period of time. To determine the deprotonation position, we added deuterated water as a scavenger. THF was evaporated from the reaction mixture, a dichloromethane was added. The mixture was dried over Na₂SO₄, solvent was evaporated, and the residues of a solvent were eliminated under high vacuum. The product was obtained in virtually quantitative yield. ¹H NMR of the product contains no signal at 7.48 ppm corresponding to starting [(NaphtDHD-Dipp)H]BF₄ salt (**5b**). In ¹³C{¹H} NMR signal of an amidinium carbon atom at 157.1 ppm disappears. Instead, a multiplet at 154.3 ppm appears with spin-spin coupling constant $J(^{2}D, ^{13}C) = 25.4$ Hz.

Formation of D_2 -2,4-bis(2,6-diisopropylphenyl)-2,3,4,5-tetrahydro-1H-naphtho[1,8ef][1,3]diazocin-3-ol (**6b**), bearing deuterium atom in 3-position corresponds to the formation of the carbene, rather than the ylide. However, it can be supposed that a carbene and an ylide might be in a dynamic equilibrium in the reaction mixture. Even small share of an ylide might lead to intense coloring, while the major share of a carbene leads to the formation of diazocin-3-ol in virtually quantitative yield.

Thus, we obtained solid proofs, that a free carbene bearing eight-membered ring and a naphthalene moiety in the backbone can be generated from the corresponding amidinium tetrafluoroborate by treatment with LiHMDS. The carbene is stable in the solution at low temperatures, while decompose rapidly at room temperature, thus preventing its isolation and structural characterization. It is worth mentioning, that Cavell and coworkers succeeded to isolate and structurally characterized first eight-membered ring carbene bearing aliphatic backbone.^{15a}

To rationalize the observed experimental data we went back to the results of DFT calculations. Lower stability of NaphtDHD than HHD can be attributed to lower HOMO-LUMO gap (HLG, see Table 1). Lower HLG leads to increased reactivity of a carbene towards intramolecular C-H activations and other side reactions.²⁸

It was also of interest to determine the nature of the green coloring of the reaction media upon generation of the carbene. We optimized the structure of the proposed ylide. To model absorption spectra of the carbene and the ylide, we performed TDDFT calculations. It was found, that for the carbene there are only two weak bands at 636 nm and 459 nm in the visible region.

Thus, calculations support that the free carbene NaphtDHD-Dipp should be colorless. Oppositely, for the ylide a number of intense absorption bands were predicted from calculations: 686 nm, 652 nm, 624 nm, 595 nm (red – orange region), and 490 nm (blue region). Exclusion of red and blue bands from the spectrum should lead to green coloring of the solution bearing ylide. Thus, based on the simulations of visible spectra of the carbene and the ylide, it can be supposed that the ylide exists, at least in some ratio, in the equilibrium with the carbene NaphtDHD-Dipp in the solution at low temperature.

Calculated total energy of the ylide is 1.9 kcal mol⁻¹ lower than for the corresponding carbene NaphtDHD-Dipp. Certainly, this calculated energy difference cannot be taken as a quantitative value of the relative stability of two isomers since calculations were performed in the gas phase, while the experiment was performed in the solution. However, it can be supposed, that the energies of both isomers are rather close in the reaction media and both isomers might be in dynamic equilibrium. It is known from the experiment, that upon scavenging with deuterated water, only carbene derived product is formed. Thus, we can conclude, that carbene is the major isomer in the real solution, while ylide is the minor one. Ylide derived product of scavenging with water is not traced in the NMR spectra, while ylide itself manifests its existence in the solution with the intense green coloring.

Synthesis of silver and copper complexes

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Silver(I) complexes of N-heterocyclic carbenes are synthetically useful. Due to low energy of a carbene-silver bond, these complexes can be easily transmetallated to obtain NHC complexes of other transition metals. The most convenient method of synthesis of silver(I) complexes is interaction of amidinium salt with silver(I) oxide in CH_2Cl_2 (Scheme 4).²⁷

Scheme 4



Preparation of silver(I) complexes

In our case, in CH_2Cl_2 the formation of silver(I) complexes proceeds with moderate yields (44% for **7a** and 40% for **7b**). We performed optimization of synthesis of silver(I) complexes (Table 3). The highest yield for [(NaphtDHD-Dipp)AgBr] (**7b**) was obtained in THF at 60°C. The

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obtained yield of [(NaphtDHD-Mes)AgBr] (7a) under optimized conditions is 80%. Previously only two examples of eight-membered ring NHC silver(I) complexes [(HHD-Mes)AgBr] and [(HHD-Xyl)AgBr] were reported by Cavell et al.^{15a}

Table 3

The obtained complexes are air- and light-stable colorless solids with melting points over 300°C. These complexes were characterized by ¹H and ¹³C NMR. The characteristic signal for the carbene silver(I) complexes is a doublet of doublets in the 200-220 ppm region. Appearance of such signal is due to spin-spin interaction of ¹³C with ¹⁰⁷Ag (spin 1/2, 51.84 %) and ¹⁰⁹Ag (spin 1/2, 48.16 %). Signals at 210.4 (J(¹⁰⁹Ag, ¹³C) = 267.7 Hz, J(¹⁰⁷Ag, ¹³C) = 226.7 Hz) and 211.8 (J(¹⁰⁹Ag, ¹³C) = 261.3 Hz, J(¹⁰⁷Ag, ¹³C) = 227.2 Hz) were found, correspondingly to Mes and Dipp substituted complexes.

Previously we have shown that the most convenient way of synthesis of expanded ring NHC copper(I) complexes is transmetallation of silver(I) complexes with corresponding copper(I) salts. This approach is high yielding, very simple experimentally and easily reproducible (Scheme 5).^{23, 29} The obtained yields of copper complexes are high, 84% for **8a** and 83% for **8b**.

Scheme 5

Synthesis of [(NaphtDHD)CuBr].



Complexes are colorless crystalline solids stable in air. Melting points are over 300°C. Characteristic for ylidene carbon in NHC copper(I) complex is the signal in ¹³C NMR in 200-210 ppm region; 203.6 ppm and 204.7 ppm, respectively for Mes and Dipp derivatives. These complexes are the first examples of eight membered ring NHCs with copper(I). Moreover, reaction in scheme 7 is the first example of transmetallation in silver(I) complexes bearing eight-membered ring carbones.

X-ray structure studies

We were able to obtain X-ray quality crystals of Dipp-substituted salt and complexes [(NaphtDHD-Dipp)H]Br (**4b**), [(NaphtDHD-Dipp)AgBr] (**7b**), and [(NaphtDHD-Dipp)CuBr] (**8b**) (Figures 1-3, supporting information).

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Figure 1 Figure 2 Figure 3

Remarkably, all the three investigated compounds are isostructural, apparently, due to the rigid geometry of the bulk NaphtDHD-Dipp ligand. The central heterocyclic eight-membered fragment of this NHC ligand adopts the roof-like conformation with the fold angle on the C1...C5 line of 62.43(7), 61.89(10) and $62.04(8)^{\circ}$ for [(NaphtDHD-Dipp)H]Br (4b), [(NaphtDHD-Dipp)AgBr] (7b), and [(NaphtDHD-Dipp)CuBr] (8b), respectively. The idealized C_s (m) symmetry of these complexes is distorted. The two nitrogen atoms have the trigonal-planar configurations with the dihedral angle between the corresponding planes of 17.5(1), 17.0(2) and $18.3(1)^{\circ}$, respectively. Here it is important to note that the previously studied silver complexes [(HHD-Mes)AgBr] and [(HHD-Xyl)AgBr] show small values of the spatial twist of the N coordination planes. The N-C_{carb}-N angles (Figures 1-3) are large, and exceed 120° analogously to previously reported eight-membered ring carbenes.^{15a} With the attendant C_{dipp}-N-C_{carb} angles (117.0(2)/118.7(2), 115.1(2)/116.6(2) and 116.3(2)/114.6(2)°, respectively) being small, pushing the Dipp substituents toward the C_{carb} atom. As the result, the Ag and Cu atoms form the short contacts to the H atom of one of the Dipp ligands (Ag1...H20A 2.81 Å and Cu1...H23A 2.79 Å). The benzene rings of the Dipp substituents are roughly perpendicular to the carbene plane (87.74(7)/80.36(8), 84.79(10)/83.28(11) and 82.35(9)/85.72(8)° for [(NaphtDHD-Dipp)H]Br (4b), [(NaphtDHD-Dipp)AgBr] (7b), and [(NaphtDHD-Dipp)CuBr] (8b), respectively.

As it can be expected, the cation and anion in [(NaphtDHD-Dipp)H]Br (4b) are linked by the strong C_{carb} -H...Br hydrogen bond (Table 4, Figure 1). The solvate water molecule forms the hydrogen bonds of two different types – the O1–H1C...Br1 and O1–H1D... π (C27–C28). Further, the cation, anion and water molecule are bound by the C5–H5A...O1^{*a*} and C5–H5B...Br1^{*a*} intermolecular hydrogen bonds into the layers parallel to (100).

Table 4

The Ag–C_{carb} and Cu–C_{carb} distances (2.116(3) and 1.907(2) Å, respectively, figures 2 and 3) for [(NaphtDHD-Dipp)AgBr] (**7b**) and [(NaphtDHD-Dipp)CuBr] (**8b**) are close to those observed by us previously in the related complexes with the THP-Dipp and THD-Dipp ligands.²³ The C_{carb}–Ag–Br and C_{carb}–Cu–Br bond angles are practically linear (179.58(9) and 179.22(8)°, respectively). It is interesting to note that, in contrast to the [(THP-Dipp)CuBr] and [(THD-Dipp)CuBr] complexes, the C_{carb}–Cu–Br bond angle in [(NaphtDHD-Dipp)CuBr] (**8b**) does not indicate the significant deviation from linearity.

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Catalytic studies

In 2006 Nolan *et al.* reported on the efficient catalysis of alkyne-azide cycloaddition (CuAAC) reaction under solvent-free conditions using [(SIMes)CuBr] complex. A series of 1,4-disubstituted-1,2,3-triazoles were obtained in high yields under mild reaction conditions.³⁰ In 2010 Nolan *et al.* reported on utilization of [(IAd)CuI] as catalyst in the same solvent-free reaction. 1,2,3-Triazoles were obtained at room temperature in higher yields, shorter reaction times, and at low (down to 0.8 mol%) catalyst loadings.³¹

In continuation of our studies of metal mediated catalytic transformations under solvent-free conditions we performed tests of activity of a series of NHC copper(I) bromides in the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reaction.^{13, 14b, 32} Cycloaddition of benzyl azides with acetylenes is an efficient, high yielding method of synthesis of 1,2,3-triazoles. However, aryl azides³³ are more challenging substrates.³⁴ Thus, for comparative tests of the catalysts and optimization of the reaction conditions we have chosen cycloaddition of phenyl acetylene with *p*-tolyl azide (tables 5 and 6).

Table 5

As shown in table 5, Mes-substituted six- and eight-membered ring NHC complexes (THP-Mes)CuBr and (NaphtDHD-Mes)CuBr (8a) give virtually quantitative yields. NHCs bearing more bulky Dipp aryl groups give very low yields. We suppose that this is due to the steric overcrowding of the metal center.

For the most active precatalysts [(THP-Mes)CuBr] and [(NaphtDHD-Mes)CuBr] (**8a**) we performed a set of experiments to determine precatalysts loading suitable for efficient catalysis (Table 6). At 1 mol% loading both precatalysts give virtually quantitative yields. Upon decrease of precatalyst loading to 0.5 and 0.1 mol% the yield drops down only by a few percent. Only at 0.05 mol% loading the yields are below 80%. For [(NaphtDHD-Mes)CuBr] (**8a**) at 0.05 mol% loading we were able to obtain TON value of 1560, which is rather high result if comparing to previously reported data for solvent-free CuAAC reaction with aryl azides.³⁰⁻³¹

Table 6

To determine the scope and limitations of the developed catalytic system we performed testing of activity of [(NaphtDHD-Mes)CuBr] (8a) in cycloaddition of *p*-tolyl azide (Table 7) and benzyl azide (Table 8) with various terminal acetylenes. Utilization of [(NaphtDHD-Mes)CuBr] (8a) leads to highly efficient cycloaddition of *p*-tolyl azide and benzyl azide with aliphatic (table 7 entries 1-5; table 8, entries 1-5) as well as aromatic (table 7, entries 6-10; table 8, entries 6-12) acetylenes. The catalytic system tolerates functional groups in acetylenes (table 7, entries 2-4, 7-9;

table 8, entries 4, 5, 10-12). Only for bulky Mes substituted acetylene (table 7, entry 10; table 8, entry 9) the isolated yields were 78% and 80%, respectively for *p*-tolyl and benzyl azides.

Table 7 Table 8

Table 9 exemplifies the broad spectrum of utilization of [(NaphtDHD-Mes)CuBr] (8a) in cycloadditions of various acetylenes and organic azides. Volatile acetylenes bearing propyl, *tert*-butyl, trimethylsilyl groups are efficiently added to azides at room temperature (entries 1-9). High yields over 80% were obtained in the reactions of various aryl (entries 2, 4, 5, 7, 9, 11, 12) and benzyl azides (entries 1, 3, 6, 8, 10).

Table 9

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Conclusions

In conclusion, we developed a new type of expanded ring NHC NaphtDHD bearing eightmembered ring and a naphtyl moiety in the backbone.

Properties of a new type of carbenes were compared to smaller ring (5, 6, and 7) NHCs. According to DFT calculations, NaphtDHD-Mes is a bulky carbene bearing a rigid backbone. It exhibits strong donor properties as ligand in transition metal complexes.

A free NaphtDHD-Dipp carbene was generated in solution from the corresponding amidinium salt under treatment of a strong base LiHMDS. It is stable at low temperatures, while decompose rapidly at room temperature. Formation of a free carbene was confirmed by scavenging with deuterated water.

Silver(I) complexes of NaphtDHD-Mes and NaphtDHD-Dipp were synthesized by treatment of corresponding amidinium salts with Ag₂O. Copper(I) complexes were obtained via transmetallation of silver(I) complexes with copper(I) salts. Structures of amidinium salts and metal complexes in the solid state were determined by X-ray crystallography.

We performed comparative study of catalytic activity of 5-, 6-, 7-, and 8-membered ring NHC copper(I) complexes in Huisgen cycloaddition of organic azides with terminal acetylenes under solvent-free conditions. A highly efficient catalytic system based on [(NaphtDHD-Mes)CuBr] (8a) complex was developed. Cycloaddition of various aryl and benzyl azides with various aliphatic and aromatic terminal acetylenes proceeds in high to quantitative yields. The developed catalytic system is suitable for substrates bearing functional groups.

This report is another successful example of utilization of expanded ring carbenes in synthesis of transition metal complexes and catalysis of important organic transformations. er-NHCs and their complexes are synthetically accessible. Variation of the ring size gives simple access for tuning of stereoelectronic properties of NHCs in a wide range. This enabled us to develop a new type of catalyst operative under solvent-free conditions.

Acknowledgements

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Experimental

Calculation procedures

All calculations were conducted at the DFT level using the PBE functional.³⁵ Valence electrons were treated using a TZ2P basis set. Innermost electrons of Rh, Cl, C, N, O atoms were emulated using effective core potentials ECP-SBKJC.³⁶ All stationary points, except those corresponding to complex fragments, were characterized as minima by calculations of normal modes of vibrations. All calculations were made using PRIRODA program.³⁷ Graphical representation of molecular orbitals were made using MOLEKEL 4.3.³⁸ For detailed explanation of the meaning of calculated parameters E_{ST} , CSE, PA, *D*, E_{int} , V_{bur} see reference.¹⁸

General procedure for preparation of amidinium salts.

N,N-Diisopropylethylamine (0.142 g, 1.1 mmol, 1.1 eq) was added to mixture of appropriate N,N'-diarylformamidine (1 mmol, 1 eq) and 0.314 g (1 mmol, 1 eq) of 1,8bis(bromomethyl)naphthalene (**2**) in 5 ml of dry DMF. Reaction mixture was heated at 125°C for 3 h. After cooling to r.t., water (50 ml) was added and resulting mixture was extracted with CH_2Cl_2 (3x25 ml), organic phase was washed with saturated solution of K_2CO_3 and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude solid was recrystallized from toluene or hexane-dichloromethane mixture, filtered and dried in vacuum.

2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4a)



Yield 87%. White microcrystalline solid. Mp = 275-276°C

¹H NMR (600 MHz, Chloroform-d) δ 8.10 (d, J = 16.5 Hz, 2H), 7.94 (d, J = 7.0 Hz, 2H), 7.39 (dd, J = 8.2, 7.0 Hz, 2H), 7.33 (s, 1H), 7.19 (d, J = 7.0 Hz, 2H), 6.99 (s, 2H), 6.76 (s, 2H), 4.48 (d, J = 16.3 Hz, 2H), 2.65 (s, 6H), 2.24 (s, 6H), 1.39 (s, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 154.9, 140.5, 140.2, 135.9, 135.7, 132.9, 132.3, 132.0, 131.5, 130.9, 130.7, 129.7, 126.0, 60.0, 21.0, 19.4, 17.8.

E.A. found (calcd.), %: C 72.60 (72.51), H 6.42 (6.48), N 5.37 (5.46).

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2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4b)



Yield 88%. White microcrystalline solid. Mp = 333-335°C

¹H NMR (600 MHz, DMSO-d6) δ 8.94 (s, 1H), 8.16 (dd, J = 8.1, 1.5 Hz, 2H), 7.61 (dd, J = 7.1, 1.5 Hz, 2H), 7.57 (dd, J = 8.1, 6.9 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.25 (dd, J = 7.5, 1.7 Hz, 2H), 7.20 (d, J = 16.5 Hz, 2H), 4.67 (d, J = 16.2 Hz, 2H), 2.26 – 3.30 (m, J = 6.8 Hz, 2H), 2.01 (p, J = 6.7 Hz, 2H), 1.49 (d, J = 6.7 Hz, 6H), 1.28 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.8 Hz, 6H), 0.71 (d, J = 6.6 Hz, 6H).

¹³C{¹H} NMR (151 MHz, DMSO-d6) δ 157.1, 145.1, 144.1, 139.3, 135.2, 133.0, 131.4, 130.4, 130.2, 130.2, 125.9, 125.3, 124.8, 58.8, 28.6, 28.0, 25.2, 24.7, 24.2, 23.7.

E.A. found (calcd.), %: C 73.97 (74.35), H 7.52 (7.59), N 4.51 (4.69).

2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5a)



Solution of sodium tetrafluoroborate (0.367 g, 3.3 mmol) in 50 ml of water was added to solution of 1.69 g (3.3 mmol) 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 40 ml of acetone. Acetone was slowly evaporated in vacuum from homogenous solution; precipitate was filtered and dried in vacuum over P_4O_{10} . Yield 1.67 g (97%).

¹H NMR (600 MHz, Chloroform-d) δ 7.99 (d, J = 7.9 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.36 (s, 1H), 7.28 – 7.21 (m, 4H), 7.05 (s, 2H), 6.81 (s, 2H), 4.55 (d, J = 16.4 Hz, 2H), 2.60 (s, 6H), 2.29 (s, 6H), 1.43 (s, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 155.7, 140.6, 136.0, 133.0, 132.6, 131.7, 131.8, 131.1, 130.0, 126.3, 59.0, 21.0, 18.3, 17.8.

IR (v/cm⁻¹): 2954 (w), 2919 (w), 2859 (w), 2360 (vw), 1652 (vs), 1506 (w), 1477 (m), 1452 (m), 1386 (m), 1359 (m), 1315 (w), 1189 (m), 1135 (m), 1049 (vs), 1024 (vs), 985 (m), 950 (m), 906 (m), 860 (m), 812 (m), 773 (m), 681 (m).

2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5b)



Solution of sodium tetrafluoroborate (0.367 g, 3.3 mmol) in 50 ml of water was added to solution of 2.0 g (3.3 mmol) 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 50 ml of acetone. Acetone was slowly evaporated in vacuum from homogenous solution; precipitate was filtered and dried in vacuum over P_4O_{10} . Yield 1.98 g (98%).

¹H NMR (600 MHz, Chloroform-d) δ 8.00 (d, J = 7.0 Hz, 2H), 7.49 – 7.40 (m, 5H), 7.34 (dd, J = 7.8, 1.5 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.25 (d, J = 16.0 Hz, 2H), 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 4.57 (d, J = 16.4 Hz, 2H), 3.50 (p, J = 6.6 Hz, 2H), 2.07 (p, J = 6.7 Hz, 2H), 1.52 (d, J = 6.6 Hz, 6H), 1.29 (d, J = 6.7 Hz, 6H), 0.85 (d, J = 6.9 Hz, 6H), 0.76 (d, J = 6.6 Hz, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 154.8, 146.7, 144.3, 139.3, 133.0, 132.0, 131.2, 130.3, 126.2, 126.0, 125.2, 60.3, 29.1, 28.4, 26.1, 25.2, 24.7, 24.4.

 D_2 -2,4-bis(2,6-diisopropylphenyl)-2,3,4,5-tetrahydro-1H-naphtho[1,8-ef][1,3]diazocin-3-ol (6b)



To a solution of 200 mg (0.3 mmol) of (E)-2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1Hnaphtho[1,8-ef][1,3]diazocinium tetrafluroborate (**5b**) in 15 ml of dry, degassed THF was added a solution of 55 mg (0.3 mmol) of LiHMDS in 15 ml THF at -80°C. Reaction mixture color changed from transparent to dark green. Reaction mixture was stirred for 30 min at -80°C, 2 ml of D₂O was added in one portion and reaction mixture was allowed to warm to room temperature. All volatiles were removed on rotary evaporator and the residue was dissolved in 20 ml of CH₂Cl₂, dried over anhydrous Na₂SO₄ and evaporated to dryness. Drying in vacuum to constant weight gave 168 mg (95%) of white solid. Published on 09 February 2017. Downloaded by University of South Dakota on 09/02/2017 10:45:26

¹H NMR (600 MHz, Chloroform-d) δ 7.99 (dd, J = 8.3, 1.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.33 (dd, J = 7.8, 1.6 Hz, 2H), 7.29 (dd, J = 7.1, 1.3 Hz, 2H), 7.22 (d, J = 16.7 Hz, 2H), 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 4.55 (d, J = 16.3 Hz, 2H), 3.48 (p, J = 6.7 Hz, 2H), 2.05 (p, J = 6.8 Hz, 2H), 1.50 (d, J = 6.7 Hz, 6H), 1.27 (d, J = 6.7 Hz, 6H), 0.84 (d, J = 6.9 Hz, 6H), 0.75 (d, J = 6.5 Hz, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 154.3 (td, J = 30.0, 3.8 Hz), 146.5, 144.3, 139.2, 132.9, 132.0, 131.1, 130.5, 130.1, 126.1, 125.9, 125.2, 67.8, 67.8, 60.2, 29.0, 28.4, 26.0, 25.6, 25.1, 24.6, 24.3.

General procedure for preparation of silver complexes

A screw-cap vial equipped with a magnetic stir bar was charged with 0.232 g (1 mmol, 1 eq) of Ag₂O, 2 ml of solvent followed by 1 mmol of corresponding amidinium salt. Reaction mixture was stirred for 24 h at room temperature or at 60°C, filtered through celite and carefully diluted with equal volume of methanol. Precipitate was filtered and dried in vacuum.

(2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7a)



Reaction of 45.1 mg (0.195 mmol) of Ag_2O and 100 mg (0.195 mmol) of 2,4-dimesityl-4,5dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 2 ml of dry CH₂Cl₂ gave 53 mg (44%) of product as colorless needles.

Reaction of 45.1 mg (0.195 mmol) of Ag_2O and 100 mg (0.195 mmol) of 2,4-dimesityl-4,5dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 2 ml of dry THF gave 96 mg (80 %) of product as colorless needles. Mp = 220-221°C

¹H NMR (600 MHz, Chloroform-d) δ 7.95 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.0 Hz, 2H), 6.98 (s, 2H), 6.79 (s, 2H), 6.44 (d, J = 16.0 Hz, 2H), 4.45 (d, J = 15.9 Hz, 2H), 2.42 (s, 6H), 2.26 (s, 6H), 1.44 (s, 6H).

 13 C{¹H} NMR (151 MHz, Chloroform-d) δ 210.4 (dd, J(109 Ag, 13 C) = 267.7 Hz, J(107 Ag, 13 C) = 226.7 Hz), 146.5, 137.9, 135.4, 134.1, 133.8, 133.0, 131.4, 130.7, 130.2, 130.2, 126.0, 57.2, 57.1, 21.1, 18.6, 18.3.

IR (v/cm⁻¹): 3029 (w), 2969 (w), 2914 (w), 1740 (m), 1498 (vs), 1471 (s), 1358 (m), 1306 (m), 1284 (w), 1190 (w), 1031 (w), 993 (w), 854 (w), 820 (m), 773 (m), 678 (w). **E.A.** found (calcd.), %: C 59.77 (60.02), H 5.17 (5.20), N 4.43 (4.52).

(2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)ylidene)silver(I) bromide (7b)



Reaction of 38.8 mg (0.167 mmol) of Ag₂O and 100 mg (0.167 mmol) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 2 ml of dry dichloromethane gave 47.1 mg (40%) of product as white solid.

Reaction of 38.8 mg (0.167 mmol) of Ag₂O and 100 mg (0.167 mmol) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 2 ml of dry THF gave 100 mg (85%) of product as white solid. Mp = 290° C

¹H NMR (600 MHz, Chloroform-d) δ 7.97 (dd, J = 8.3, 1.3 Hz, 2H), 7.46 (dd, J = 8.2, 6.9 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.10 (dd, J = 7.7, 1.5 Hz, 2H), 6.44 (d, J = 15.9 Hz, 2H), 4.58 (d, J = 15.9 Hz, 2H), 3.30 (hept, J = 6.9 Hz, 2H), 2.30 (hept, J = 6.7 Hz, 2H), 1.47 (d, J = 6.9 Hz, 6H), 1.41 (d, J = 6.8 Hz, 6H), 1.02 (d, J = 6.8 Hz, 6H), 0.68 (d, J = 6.7 Hz, 6H).

 13 C{¹H} NMR (151 MHz, Chloroform-d) δ 211.8 (dd, J(109 Ag, 13 C) = 261.3 Hz, J(107 Ag, 13 C) = 227.2 Hz), 145.3, 145.2, 145.1, 131.8, 131.0, 129.5, 125.9, 125.4, 125.3, 58.9, 58.8, 29.4, 28.1, 26.3, 25.4, 25.0, 24.1.

IR (v/cm⁻¹): 2962 (vs), 2923 (m), 2863 (m), 1589 (w), 1496 (s), 1456 (m), 1381 (m), 1356 (m), 1300 (m), 1178 (m), 1051 (m), 812 (m), 796 (m), 765 (m).

E.A. found (calcd.), %: C 63.26 (63.08), H 6.35 (6.29), N 3.70 (3.98).

General procedure for preparation of copper complexes.

A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol (1 eq) of corresponding silver complex, 1 mmol of copper halide and 2 ml of dichloromethane. Reaction mixture was stirred for 24 h at room temperature, filtered through celite and evaporated to dryness. Resulting solid was recrystallized from dichloromethane-diethyl ether mixture.

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(2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (8a)



Yield 84%. White microcrystalline solid. Mp = 295° C.

¹H NMR (600 MHz, Chloroform-d) δ 7.95 (dd, J = 8.3, 1.3 Hz, 2H), 7.43 (dd, J = 8.2, 7.0 Hz, 2H), 7.20 (dd, J = 7.0, 1.3 Hz, 2H), 6.98 (s, 2H), 6.80 (s, 2H), 6.43 (d, J = 15.9 Hz, 2H), 4.39 (d, J = 15.9 Hz, 2H), 2.44 (s, 6H), 2.27 (s, 6H), 1.50 (s, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 203.6, 145.3, 137.8, 135.5, 134.3, 134.0, 133.3, 131.4, 131.3, 130.7, 130.1, 125.9, 57.3, 21.1, 18.7, 18.5.

IR (v/cm⁻¹): 3025 (w), 2979 (m), 2946 (w), 2913 (w), 1740 (w), 1600 (w), 1504 (vs), 1471 (s), 1432 (m), 1351 (m), 1303 (s), 1187 (m), 1031 (m), 1002 (m), 852 (m), 819 (m), 771 (s), 682 (m).

E.A. found (calcd.), %: C 62.71 (63.08), H 6.13 (6.29), N 3.71 (3.98).

(2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)ylidene)copper(I) bromide (**8b**)



Yield 83%. White microcrystalline solid. Mp = 312° C.

¹H NMR (600 MHz, Chloroform-d) δ 7.96 (dd, J = 8.3, 1.3 Hz, 2H), 7.45 (dd, J = 8.2, 6.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.10 (dd, J = 7.7, 1.5 Hz, 2H), 6.43 (d, J = 15.9 Hz, 2H), 4.52 (d, J = 15.9 Hz, 2H), 3.31 (p, J = 6.8 Hz, 2H), 2.31 (p, J = 6.8 Hz, 2H), 1.47 (d, J = 6.9 Hz, 6H), 1.43 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.9 Hz, 6H), 0.69 (d, J = 6.7 Hz, 6H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 204.7, 145.5, 145.3, 144.0, 135.4, 132.1, 131.7, 131.5, 130.9, 129.3, 125.9, 125.2, 125.1, 59.0, 29.4, 28.2, 26.2, 25.2, 25.0, 24.1.

IR (v/cm⁻¹): 2958 (s), 2925 (m), 2865 (w), 1654 (vs), 1504 (w), 1462 (m), 1446 (m), 1388 (m), 1365 (m), 1321 (m), 1267 (m), 1184 (m), 1166 (m), 1056 (m), 813 (s), 790 (m), 771 (m), 727 (s).

E.A. found (calcd.), %: C 62.61 (63.08), H 6.13 (6.29), N 3.71 (3.98).

General procedure for solvent free cycloaddition

A screw-cap vial equipped with a magnetic stir bar was charged with organic azide (1.0 mmol, 1 eq), terminal acetylene (1.03 mmol, 1.03 eq) and 1 mol% of (NHC)CuBr. The reaction mixture was stirred at ambient temperature overnight (unoptimized). The reaction mixture was dissolved in 10 ml of dichloromethane and filtered through a pad (4.5 cm) of silica gel. Concentration of containing product fractions in vacuum afforded 1,4-disubstitued 1,2,3-triazole. Isolated yields are average of two runs.

Tables

Table 1

Calculated parameters of free carbenes: valence angle at the ylidene carbon atom ($\angle N$ -C_{carb}-N),

HOMO energy (E_{HOMO}), HOMO–LUMO gap (HLG), singlet–triplet energy gap (E_{ST}), carbene

stabilization energy (CSE), proton affinity (PA). (Valence angle in °, E_{HOMO} , HLG in eV; E_{ST} , CSE, PA in kcal mol⁻¹)^{a,b}



NHC	∠N-C _{carb} -N	E _{HOMO}	HLG	E _{ST}	CSE	PA
SIMes	106.0	-4 67	3 55	78 3	102.2	277.2
Silvies	100.0	-4.07	5.55	70.5	102.2	211.2
THP-Mes	115.6	-4.23	3.27	73.2	97.3	285.6
THD-Mes	118.2	-4.07	3.12	67.5	95.2	287.2
HHD-Mes	121.9	-4.09	3.09	67.7	96.1	288.0
NaphtDHD-Mes	120.5	-4.21	1.93	61.3	97.8	287.7

^a Here and below: Mes – mesityl, 2,4,6-trimethylphenyl, Dipp – 2,6-diisopropylphenyl, SI – saturated imidazolin-2-ylidene, THP – tetrahydropyrimidin-2-ylidene, THD – tetrahydrodiazepin-2-ylidene, HHD – hexahydrodiazocin-2-ylidene, NaphtDHD – dihydronaphtodiazocin-2-ylidene.

^b Detailed explanation of the calculation parameters are given in the supplementary information.

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Table 2

Calculated parameters of the complexes [Rh(NHC)(CO)₂Cl] (interatomic distances R(C–Rh) in Å, ligand dissociation energies D and carbene–metal interaction energies E_{int} in kcal mol⁻¹, CO average

stretching frequencies $v_{av}(CO)$ in cm⁻¹, buried volume V_{bur} in %).

In dissociation energies D and carbene–inetar interaction energies E_{int} in Real more, CO average

NHC	R(C _{carb} -Rh)	D	$E_{\rm int}$	v _{av} (CO)	

NHC	R(C _{carb} -Kn)	D	$\boldsymbol{L}_{\text{int}}$	V _{av} (CO)	v bur
SIMes	2.10	55.9	64.7	2000	23.3
THP-Mes	2.13	55.4	65.7	1994	25.8
THD-Mes	2.13	53.9	65.9	1993	26.9
HHD-Mes	2.15	50.9	63.2	1992	28.7
NaphtDHD-Mes	2.14	49.9	63.2	1991	27.6

Table 3

Optimization of the synthesis of (NaphtDHD-Dipp)AgBr (7b)

Entry	Solvent	Yield, %
1	DMSO	No reaction
2	CH ₃ CN	57
3	1, 2-D CE	67
4	THF	85
5	CH ₃ OH	Decomposed
6	1, 2-DM E	Decomposed

Table 4

D*-HA*	d(D-H)	d(HA)	d(DA)	∠(D-HA)
	1.00	2.65	2 (15 (2)	170 5
C3-H3Br1	1.00	2.65	3.645(2)	1/8.5
C5–H5AO1a	0.99	2.52	3.292(4)	134.4
C5–H5BBr1a	0.99	2.78	3.680(2)	150.6
O1-H1CBr1	0.96	2.41	3.362(3)	172.2
O1-H1DC27	0.94	2.89	3.772(4)	156.4
O1-H1DC28	0.94	2.63	3.534(4)	161.4

Hydrogen bonds for [(Naph-8-Dipp)H]Br (4b) [Å and °].

* D – proton donor; A – proton acceptor;

Symmetry transformations used to generate equivalent atoms: ${}^{a}x$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$

Table 5

Catalytic activity of (NHC)CuBr complexes.^a



Complex	Yield (%)	Complex	Yield (%)
[(SIMes)CuBr]	90	[(SIPr)CuBr]	4
[(THP-Mes)CuBr]	>99	[(THP-Dipp)CuBr]	5
[(THD-Mes)CuBr]	33	[(THD-Dipp)CuBr]	1
[(NaphtDHD-Mes)CuBr] (8a)	>99	[(NaphtDHD-Dipp)CuBr] (8b)	2

p-Tolyl azide (1.0 mmol, 1 eq), phenyl acetylene (1.03 mmol, 1.03 eq), 1 mol% (NHC)CuBr.

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Table 6

Optimization of the catalyst loading.^a



Precatalyst, mol%	Yield, %			
	(THP-Mes)CuBr	(NaphtDHD-Mes)CuBr (8a)		
1	>99	>99		
0,5	98	97		
0,1	95	94		
0.05	70	78		

^a *p*-Tolyl azide (1.0 mmol, 1 eq), phenyl acetylene (1.03 mmol, 1.03 eq), n mol% (NHC)CuBr.

Table 7



^a *p*-Tolyl azide (1.0 mmol, 1 eq), acetylene (1.03 mmol, 1.03 eq), 1 mol% (NaphtDHD-Mes)CuBr (**8a**).

Table 8

Cycloaddition of benzyl azide with various acetylenes mediated by (NaphtDHD-Mes)CuBr (8a).^a



а

Benzyl azide (1.0 mmol, 1 eq), acetylene (1.03 mmol, 1.03 eq), 1 mol% (NaphtDHD-Mes)CuBr (8a).

Table 9

Cycloaddition of various azides with various acetylenes mediated by (NaphtDHD-Mes)CuBr (8a).^a



^a Azide (1.0 mmol, 1 eq), acetylene (1.03 mmol, 1.03 eq), 1 mol% (NaphtDHD-Mes)CuBr (8a).

Figures

Figure 1

Molecular structure of complex [(NaphtDHD-Dipp)H]Br • ³/₄H₂O (40% ellipsoids). Dashed lines indicate the intermolecular O–H...Br and O–H...π(C27–C28) hydrogen bonds. Selected geometrical parameters (Å and deg.): C1–N2 1.493(3), N2–C3 1.320(3), C3–N4 1.316(3), N4–C5 1.487(3), N2–C1–C11A 115.2(2), C1–N2–C3 126.7(2), N2–C3–N4 127.2(2), C3–N4–C5 125.5(2), N4–C5–C5A 113.9(2).



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Figure 2

Molecular structure of complex (NaphtDHD-Dipp)AgBr (**7b**) (40% ellipsoids). Selected geometrical parameters (Å and deg.): Ag1–Br1 2.4229(4), Ag1–C3 2.116(3), C1–N2 1.495(4), N2–C3 1.343(4), C3–N4 1.331(4), N4–C5 1.483(4), Br1–Ag1–C3 179.58(9), N2–C1–C11A 115.8(2), C1–N2–C3 129.5(3), N2–C3–N4 122.1(3), C3–N4–C5 127.5(2), N4–C5–C5A

114.2(3).



Figure 3

Molecular structure of complex (NaphtDHD-Dipp)CuBr (**8b**) (40% ellipsoids). Selected geometrical parameters (Å and deg.): Cu1–Br1 2.2288(5), Cu1–C3 1.907(2), C1–N2 1.491(3), N2–C3 1.334(3), C3–N4 1.347(3), N4–C5 1.486(3), Br1–Cu1–C3 179.22(8), N2–C1–C11A 113.7(2), C1–N2–C3 128.1(2), N2–C3–N4 120.7(2), C3–N4–C5 130.7(2), N4–C5–C5A



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