Case Study of N-iPr versus N-Mes Substituted NHC Ligands in Nickel Chemistry: The Coordination and Cyclotrimerization of Alkynes at [Ni(NHC)₂]

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Dedicated to Professor Dr. Holger Braunschweig on the occasion of his 60th birthday

Abstract: A case study on the effect of the employment of two different NHC ligands in complexes [Ni(NHC)₂] (NHC = Pr(NHC)₂ 1Me, Mes(NHC)₂ 2) and their behavior towards alkynes is reported. The reaction of a mixture of [Ni(Pr(NHC)₂)(μ-(η⁵-H₂C=CC₃Me)COD)] B/ [Ni(Pr(NHC)₂)(μ-(η⁵-COD)) B² or [Ni(Mes(NHC)₂) 2, respectively, with alkynes afforded complexes [Ni(NHC)₂(η⁵-alkyne)] (NHC = Pr(NHC)₂, alkyl = MeC₆H₄, C₃H₅, PhC₆H₄, MeC₆H₃, H₃C₆H₄, 4, PhC₆H₄, PrC₆H₄, 5, MeOCC₆H₄CCOMe, 6, Me₃SiC₆H₅, 7, PhC₆H₄, 8, H₃C₆H₄, 9, H₃C₆C₈H₁₄, 10, H₃C₆C₈(p-Tol), 11, H₃C₆C₈(4-Bu-C₆H₄), 12, H₃C₆C₈Me₂, 13, NH-C₆H₄Me = Mes(NHC)₂, 14, Mes(NHC)₂Me, 15, PhC₆H₄, 16, H₃C₆C₈(4-Bu-C₆H₄), 17, H₃C₆C₈Me₂, 18). Unusual rearrangement products 11a and 12a were identified for the complexes of the terminal alkynes H₃C₆C₈(p-Tol) and H₃C₆C₈(4-Bu-C₆H₄), 11 and 12, which were formed by addition of a C−H bond of one of the NHC N′-Pr methyl groups to the C≡C triple bond of the coordinated alkylene. Complex 2 catalyzes the cyclotrimerization of 2-butyne, 4-octyne, diphenylacetylene, dimethyl acetylenedicarboxylate, 1-pentyne, phenylacetylene and methyl propiolate at ambient conditions, whereas 1Me is not a good catalyst. The reaction of 2 with 2-butylene was monitored in some detail, which led to a mechanistic proposal for the cyclotrimerization at [Ni(NHC)₂]. DFT calculations reveal that the differences between 1Me and 2 for alkylene cyclotrimerization lie in the energy profile of the initiation steps, which is very shallow for 2, and each step is associated with only a moderate energy change. The higher stability of 3 compared to 14 is attributed to a better electron transfer from the NHC to the metal to the alkylene ligand for the N-alkyl substituted NHC, to enhanced Ni-alkylene back-bonding due to a smaller C₆H₄(Ni)−C₆H₄(Ni) bite angle, and to less steric repulsion of the smaller NHC Pr(NHC)₂ bite angle.

Introduction

Transition-metal-catalyzed [2 + 2 + 2] cycloaddition reactions are elegant, atom-efficient and group tolerant processes which involve the formation of several C−C bonds in a single step.[1] These reactions offer the convenient access to a wide variety of carbocycles and heterocycles, mostly aromatic, starting from simple and inexpensive substrates.[1] After Reppe et al. provided their pioneering report on the first cyclopolymerization of acetylene using a mixture of NiBr₂ and CaC₂ as the precatalyst,[2] many different unsaturated substrates such as alkynes, diynes, alkenes, imines, isocyanates, isothiocyanates and CO₂ were transformed in cycloaddition reactions to yield highly substituted derivatives of benzenes, pyridines, pyridones, pyrones, thiopyridines and cyclohexanes. Since then, catalytic systems such as NiBr₂/dppe in the presence of Zn powder or [Ni(COD)]₂-based systems have been applied to many substrates.[1b,1c] Nickel complexes of N-heterocyclic carbenes (NHCs) were also explored in cycloaddition reactions in the last two decades, mainly by Louie[3a,b] and Montgomery[3a,b] and co-workers. The Louie group commonly employed an in situ prepared catalyst system using [Ni(COD)]₂ as a nickel source and two equivalents of a sterically bulky and electron rich NHC ligand such as Dipp,Im (1,3-bis(2,6-di-isopropylphenyl)-imidazolin-2-ylidine) or Dipp,Im² (1,3-bis(2,6-di-isopropylphenyl)-imidazolidin-2-ylidine), that supposedly forms complexes of the type [Ni(NHC)₂] or [Ni(NHC)] as the pre-catalyst. These catalyst systems are highly efficient in the cyclization of different carbohydrates such as diynes or alkynes with ketones, aldehydes, nitriles, isocyanates and other substrates.[3a,b,5] For example, the cycloaddition of alkynes or diynes with isocyanates to afford 2-pyridones and pyrimidinediones is highly efficient and occurs with a high degree of chemoselectivity if a 1:1 mixture of [Ni(COD)]₂/Dipp,Im² was used as catalyst.[3] For this Ni/NHC-catalyst system, alkylene cyclotrimerization was largely
inhibited. However, differences in reactivity, yield, and selectivity have been observed in these Ni/NHC-catalyzed cycloaddition reactions depending on the NHG ligand applied. The influence of the electronic and steric properties of the NHG ligand employed, for example DippIm vs. DippIm\textsuperscript{12} vs. MesIm (= 1,3-dimethylimidazolin-2-ylidine), to different cyclization reactions seems currently not to be completely understood.\textsuperscript{27} However, Montgomery et al. demonstrated that stereo-electronic properties of NHG ligands play a crucial role for the regioselectivity observed for related nickel catalyzed allene hydrosilylation and reductive coupling reactions of aldehydes and alkynes.\textsuperscript{28,29} The regioselectivity of the latter is supposedly controlled by steric repulsion between the NHG ligand and the alkynyl substituents in the first, rate determining oxidative addition step.\textsuperscript{30}

We reported earlier that complexes [Ni\textsubscript{i}(NHC\textsubscript{i})(μ-(η\textsuperscript{2}-π)}}\textsuperscript{[COD]}) of alkyl substituted NHGs such as Pr\textsubscript{i}Im (= 1,3-di-iso-propyl-imidazolin-2-ylidine) or Pr\textsubscript{i}Im, which act as a source of [Ni(NHC\textsubscript{i})], are efficient catalysts for the insertion of diphenyl acetylene into the C–C bond of biphenylene leading to 9,10-diphenylphenanthrene.\textsuperscript{31} The reaction rate of the formation of 9,10-diphenylphenanthrene depends on the steric demand of the NHG employed, giving the highest rates for the sterically most hindered NHG used. However, alkynyl cyclooligomerization was suppressed at the reaction conditions employed (60–80 °C) for diphenyl acetylene, but excess of other alkynes (3-hexyne or 2-butyne) afforded traces of the cyclooligomerization product. As we are currently interested to evaluate the differences in the reactivity of complexes [Ni(NHC\textsubscript{i})\textsubscript{2}] of NHGs of different size,\textsuperscript{32} we decided to (re)evaluate the reactivity of complexes [Ni(NHC\textsubscript{i})\textsubscript{2}] with alkynes in some detail.

As the work presented so far point to a decisive role of the sterics of the NHG ligand, we decided to reduce the steric demand of the N-aryl substituted NHG on going from Dipp to Mes substituted NHG and to increase the steric demand of the N-alkyl substituted NHG by backbone methylation. It has been demonstrated previously that backbone substitution at the C4 and CS position of the imidazole framework, for example by methylation, greatly effects the stereo-electronics of the NHG ligands as repulsion between the C4-CS methyl group and the N-organic substituent leads to smaller C\textsubscript{aromatic}-N-C\textsubscript{substituent} bite-angles.\textsuperscript{33,34} Thus, the NHGs we use for this study are Mes\textsubscript{i}Im and \textsuperscript{1}Pr\textsubscript{i}Im\textsuperscript{35} (= 1,3-di-iso-propyl-4,5-dimethylimidazolin-2-ylidine).

**Results and Discussion**

The reaction pathways and the results of key-processes in transition metal chemistry and catalysis, such as oxidative addition, reductive elimination, migratory insertion, transmetalation, and α-hydride elimination, depend decisively on the sterics of the (NHC) co-ligands used and on the degree of electron transfer from the metal to the substrates and thus to the nature, sterics and number of co-ligands.\textsuperscript{36} We recently investigated differences in the reactivity of the NHG-stabilized nickel(0) complexes [Ni\textsubscript{i}(Pr\textsubscript{i}Im)(μ-(η\textsuperscript{2}-π)}}\textsuperscript{[COD]}) A\textsuperscript{15} as a source of [Ni(Pr\textsubscript{i}Im)]\textsubscript{1} and [Ni(Mes\textsubscript{i}Im)]\textsubscript{2} in some detail.\textsuperscript{11} In course of our work on C–F bond activation and catalytic defluoroborylation of polyfluoroarenes using the complexes A\textsuperscript{16} and 2,\textsuperscript{15} we provided evidence from experiment and theory that, depending on the NHG ligand used, the insertion of [Ni(NHC\textsubscript{i})\textsubscript{2}] into the C–F bond of hexafluorobenzene proceeds via a concerted oxidative addition pathway for the small NHG Pr\textsubscript{i}Im and via a radical pathway for the more bulky NHG Mes\textsubscript{i}Im. Additionally, we found for both mechanisms a competitive NHG-assisted reaction pathway which seems to be of general importance in transition metal NHG chemistry.\textsuperscript{14,15} Furthermore, we provided a detailed study on the steric influence of NHGs of different size on the stabilization of nickel π-complexes, such as cycloaddition reactions depending on the NHG ligand applied, for nickel(0) complexes [Ni\textsubscript{i}(NHC\textsubscript{i})(μ-(η\textsuperscript{2}-π)}}\textsuperscript{[COD]}) A\textsuperscript{i}, i.e., [Ni(Pr\textsubscript{i}Im)]\textsubscript{1} and [Ni(Mes\textsubscript{i}Im)]\textsubscript{2} with different olefines, aldehydes and ketones, which led to the formation of complexes of the type [Ni(NHCG)(η\textsuperscript{2}-CR=C=CR)]\textsubscript{i}, [Ni(NHC\textsubscript{i})(η\textsuperscript{2}-O=CHR)] and [Ni(NHC\textsubscript{i})(η\textsuperscript{2}-O=C=CR)]. Whereas A readily formed alkene complexes with olefins of different size, complex 2 reacted only with the smallest olefin ethylene or with activated acceptor olefins such as acrylates. Thus, the NHG nitrogen substituent influences the reactivity for steric reasons. However, these studies also pointed at the fact that substrate binding and electron transfer in bis-NHC nickel complexes can be fine-tuned very well beyond the accessibility of the metal center by steric protection and complex stability with respect to co-ligand or NHG dissociation.

A subtle influence of sterics to the electronic behavior of [Ni(NHC\textsubscript{i})\textsubscript{2}] lies in the C\textsubscript{aromatic}-N-C\textsubscript{substituent} bite-angle the NHG ligands will adopt in the final product and in the propensity of the complexes [Ni(NHC\textsubscript{i})\textsubscript{2}] to get involved into radical electron transfer processes.\textsuperscript{17} Herein we want to expand this study on the reactivity of NHG-stabilized nickel complexes towards simple alkynes using [Ni(Mes\textsubscript{i}Im)]\textsubscript{2} and suitable sources of [Ni(Pr\textsubscript{i}Im)]\textsubscript{36} \textsuperscript{1}. As mentioned above, we reported some alkynyl complexes [Ni(Pr\textsubscript{i}Im)(μ-(η\textsuperscript{2}-π)}}\textsuperscript{[COD]}) A\textsubscript{i} as a by-product in various amounts (up to approximately 40%). As B and B' typically show identical reactivity with respect to alkynes (the same was observed previously for A and its mononuclear counterpart [Ni(Pr\textsubscript{i}Im)(η\textsuperscript{2}-COD)]) we did not further purify the mixture for the following reactions.

Dinuclear B and mononuclear B' can be distinguished easily in their \textsuperscript{1}H and \textsuperscript{13}C(\textsuperscript{1}H) NMR spectra. The resonances of the NHG ligand of B were detected as a broad doublet at 1.42 ppm for the iso-propyl methyl protons, a singlet at 1.88 ppm for the backbone methyl protons and a septet at 6.03 ppm for the iso-propyl methine protons, whereas sharp resonances were found for the NHG ligand of complex B' at 1.33 ppm (d), 1.86 ppm (s) and 5.90 ppm (sept.). In the \textsuperscript{13}C(\textsuperscript{1}H) NMR spectra the resonances
for the carbene carbon atoms were detected in close proximity at 206.5 ppm (B) and 205.4 ppm (B'). Complex B was structurally characterized (Figure 1), it adopts in the solid state a distorted pseudo-square planar geometry at both nickel atoms. The complex is isostuctural to [Ni((Pr)Im)$_2$]$_2$(η$^3$-COOD) A$^{1,14a}$ and both complexes have almost identical Ni–C$_{carbene}$ distances (B: 1.9117(19) Å and 1.9122(19) Å; A: 1.906(3) Å and 1.904(3) Å) and similar C$_{carbene}$-Ni–C$_{carbene}$ angles (B: 138.36(8)°; A: 142.55(14)°).

The reaction of a mixture of [Ni(Pr)$_2$(η$^1$-Me$_2$SiC$_3$)] and [Ni(Pr)$_2$(η$^2$-COD)] B with equimolar amounts of 2-butyne, 4-octyne, diphenylacetylene, dimethyl acetylenedicarboxylate, bis(trimethylsilyl)acetylene, 1-phenyl-1-propanone, 1-pentyne, phenylacetylene, p-tolualdehyde, 4-(tert-butyl)phenylacetylene and methyl propiolate selectively afforded the corresponding η$^3$-(C$_2$)-alkyne complexes [Ni(Pr)$_2$(η$^2$-MeOC(O)CMe$_2$)] 3, [Ni((Pr)Im)$_2$(η$^2$H$_2$C$_6$C$_5$H$_4$)] 4, [Ni((Pr)Im)$_2$(η$^2$-PhC=CH)] 5, [Ni((Pr)Im)$_2$(η$^2$MeOC(O)CCOO)Me] 6, [Ni((Pr)Im)$_2$(η$^2$-Me$_2$SiC$_3$)] 7, [Ni((Pr)Im)$_2$(η$^2$-PhC=CH)] 8, [Ni((Pr)Im)$_2$(η$^2$H$_2$C$_6$C$_5$H$_4$)] 9, [Ni((Pr)Im)$_2$(η$^2$-HC=CH)] 10, [Ni((Pr)Im)$_2$(η$^2$-H$_2$C$_6$C$_5$H$_4$)] 11, [Ni((Pr)Im)$_2$(η$^3$-C(4′-Bu-2-C$_6$H$_4$))] 12, and [Ni((Pr)Im)$_2$(η$^3$-HC=CCOO)Me] 13 (Scheme 1).

The complexes 3–13 were isolated as yellow or orange-red, air and moisture sensitive powders and were characterized using $^1$H NMR, $^{13}$C($^1$H) NMR and IR spectroscopy (see Supporting Information). The complexes were obtained as analytically pure material except for the complexes of the terminal alkyne 1-pentynyl and phenylacetylene, [Ni((Pr)Im)$_2$(η$^2$H$_2$C$_6$C$_5$H$_4$)] 9 and [Ni((Pr)Im)$_2$(η$^2$-HC=CH)] 10, which are only stable in solution and decompose upon removal of the solvent. The reactions of B/B' with alkynes proceeded in quantitative yield if performed on NMR scale; the yield of isolated 7, however, is rather low due to losses in the crystallization process to get analytically pure material. Important $^1$H and $^{13}$C($^1$H) NMR data for the compounds 3–13 are summarized in Table 1. In the $^1$H NMR and $^{13}$C($^1$H) NMR spectra the signals for the NHCl ligands were observed in the typical regions expected, and for the complexes 8–13 of unsymmetrical or terminal alkynes the set of NHCl resonances is doubled due to a lowering of the complexes’ symmetry. Each alkyne proton of 9–13 is shifted upon

![Figure 1](image-url)
coordination to nickel by 4.87–5.48 ppm to lower fields compared to the uncoordinated alkyne and was observed as a singlet in the range between 6.71 and 7.64 ppm. Strong backbonding from the metal atom to the ligand is also reflected in the $^{13}$C[1'H] NMR spectra of these complexes as a significant low-field coordination shift of 41.7–61.9 ppm occurs upon complexation.[16,18] The observed IR stretching vibrations of the alkyne triple bonds (1659–1785 cm$^{-1}$) in the complexes 3–13 are also significantly shifted to lower wavenumbers compared to the uncoordinated alkyne, which show typical stretching vibrations between 2100 cm$^{-1}$ and 2310 cm$^{-1}$, and thus reflect a lower bond order upon coordination to nickel.[19] The $\Delta$C=C coordination shift ($\Delta$C=C) of complex 5 (1754 cm$^{-1}$), for example, is $-469$ cm$^{-1}$ compared to uncoordinated diphenylacetylene (2223 cm$^{-1}$) and much larger compared to $\Delta$C=C reported for the corresponding phosphine complex ([PPh$_3$]Ni-(η$^2$-PhC≡CPh)) ($-419$ cm$^{-1}$).[20] Thus, these complexes may rather be described as metallacyclopropenes, according to the Dewar-Chatt-Duncanson model.[21]

Crystals of [Ni(Pr)Im$_{2}$]$_{2}$[η$^2$-MeC≡CMe]) 3, [Ni(Pr)Im$_{2}$][η$^2$-PhC≡CPh])$_{5}$ and [Ni(Pr)Im$_{2}$][η$^2$-MeSiC≡CSiMe$_{3}$])$_{7}$ suitable for X-ray analysis were obtained from saturated hexane or pentane solutions at $-30$ °C (Figure 2, Table 4, for selected bond lengths and angles see the Supporting Information Figures S2–S4). Each of the complexes adopt a distorted pseudo-square planar geometry, spanned by the two NHCs and the alkyne ligand. The Ni–C$_{NHC}$ distances lie in the range between 1.9097(14) and 1.9251(13) Å and are thus in line with Ni–C$_{NHC}$ distances reported previously for [Ni(MePrIm)$_{2}$][η$^2$-PhC≡CPh]) C (1.896(6)/1.915(4) Å) and [Ni(Pr)Im$_{2}$][η$^2$-MeC≡CMe]) D $(1.917(8)/1.934(7)$ Å).[22] The distances from nickel to the alkyne carbon atoms (Ni–C$_{alkyne}$ 1.8804(14)–1.9047(16) Å) are slightly shorter than the Ni–C$_{NHC}$ distances. The C≡C separation of the alkyne ligands (1.285(2) Å–1.304(3) Å; C: 1.310(6) Å, D: 1.286(13) Å) are remarkably enlarged compared to the uncoordinated alkyne.[23] The alkyne ligands are slightly twisted out of the C$_{carbon}^{-}\text{Ni}--\text{C}_{carbon}^{+}$ plane with twist angles between 7.90(8)° (5) and 9.27(12)° (7). This deviation from planarity is considerably larger compared to the values observed for C (1.76(19))° and D (1.96(26))° and we attribute this deviation to increased steric repulsion of the ligand Pr$_{2}$Im$_{3}$ with methyl substituents in the backbone compared to Pr$_{2}$Im and/or the MePrIm analogues.

Many of the complexes 3–13 are unstable upon heating and the result of thermal exposure in solution depends on the alkyne ligand coordinated. While [Ni(Pr)Im$_{2}$][η$^2$-PhC≡CPh]) 5 and [Ni(Pr)Im$_{2}$][η$^2$-MeOOC$\text{C}\text{C}O$CMe$]$ 6 are stable in solution at 100 °C for days, complexes [Ni(Pr)Im$_{2}$][η$^2$-MeC≡CMe]) 3 and [Ni(Pr)Im$_{2}$][η$^2$-HC≡CPh]) 10 decompose already at room temperature, but much more rapidly upon heating with formation of so far unidentified products. Although we could not identify many of the decomposition products, for the thermal decomposition of the terminal alkyne complexes [Ni(Pr)Im$_{2}$][η$^2$-HC≡C(p-Tol)]) 11 and [Ni(Pr)Im$_{2}$][η$^2$-HC≡C(4'-Bu-C$_{6}$H$_{4}$)]) 12 we characterized the rearrangement products 11a and 12a (Scheme 2 and Figure 3) after heating of benzene or toluene solutions of these complexes to 60 °C for 72 h. In addition to 11a or 12a other, so far unidentified side-products were formed. However, the complexes 11a and 12a result from an interesting addition of a C–H bond of one of the NHC $\text{N}$-iso-propyl substituent methyl groups across the C≡C triple bond of the coordinated alkyne (Scheme 2).

We reported recently that NHC ligands are no good spectator ligands in cobalt NHC half sandwich alkyne chemistry and that they react in the coordination sphere of cobalt with terminal alkyne under coupling of the NHC and the alkyne ligand.[22a] Related decomposition pathways involving coordinated alkyne and NHC ligands are also known.[23] For the alkyne complexes of [Ni(NHC)$_{2}$] we did not observe this kind of NHC alkyne coupling so far, but the complexes 11a and 12a were formed via an intramolecular C–C coupling reaction of the NHC N-substituent. Formally, a hydrogen atom is transferred from the nearest $\text{N}$-iso-propyl methyl group of the NHC ligand to the coordinated alkyne carbon atom. The terminal alkyne carbon thus couples with the iso-propyl methyl carbon with formation of a 6-membered metallacycle and reduction of the C≡C triple bond to an $\eta^1$-(C,C)-coordinated alkyne.

![Figure 2](image-url)
Red crystals of compound 11a were isolated for a complete characterization of this complex including X-ray analysis, while 12a was only characterized in situ via the characteristic $^1$H NMR resonances in the NMR spectrum (see Figure 3, for the full NMR spectra see Supporting Information Figures S34–S40). In each case, the resonances of the olefinic protons of 11a and 12a were detected as a doublet at 3.85 ppm (C=C=CHR) for the proton at C$^1$ (see Scheme 2 and Figure 3) and a doublet of doublets of doublets at 2.91 ppm for the proton at C$^2$. The two diaster- eotopic protons of the CH$_2$ group at C$^3$ give rise to two separate resonances at 2.64 ppm (ddd) and 2.78 ppm (ddd), while the former iPr methine proton was detected as a broad multiplet at 3.99 ppm. The three remaining iso-propyl methine protons of the NHC ligands give rise to three partially overlapping and broadened septets in the range between 5.30 ppm and 5.90 ppm. In the $^{13}$C(H) NMR spectrum of complex 11a the resonances of the olefinic carbon atoms are shifted towards higher fields compared to complex 11 and were detected at 34.1 ppm (C$^2$) and 51.9 ppm (C$^3$). The signals for the C$^1$ carbon atom and the former iso-propyl methine carbon C$^4$ were observed at 40.2 and 54.1 ppm, respectively. The carbene carbon atom resonance of the NHC ligand involved in the metallacycle is also shifted to higher fields at 191.7 ppm, whereas the resonance of the unaffected NHC carbon atom was found at 204.5 ppm.

Crystals of 11a suitable for X-ray diffraction were obtained from storing a saturated solution of the complex in hexane at $-30^\circ$C (Figure 4). Complex 11a adopts a distorted pseudo-square planar geometry in the solid state. The distance Ni1–C6 of 1.9072(15) Å and Ni1–C7 of 1.9140(15) Å to the NHC ligand carbon atoms are unexceptional and lie in the same range as observed for the alkynic complexes 3, 5 and 7. The distances of the nickel center to the olefin carbon atoms of 1.9945(14) Å (Ni1–C1) and 1.9321(14) Å (Ni1–C2) are larger compared to the Ni-C$_{alkyne}$ distances observed for the alkynic complexes, but in...
Scheme 3 sketches two reasonable reaction pathways for the rearrangement of [Ni(Pr2Im)4(C=C–p-Tol)] to product 11a. The first pathway (i) involves the rearrangement of the terminal alkyne ligand to a nickel vinylidene complex along the typical hydrido alkyne route, which occurs with insertion of nickel into the C–H bond of the coordinated terminal alkyne ligand and subsequent hydride rearrangement to the β-C atom. Insertion of the vinylidene into the NHC methyl C–H bond would lead then to complex 11a. Another likely pathway (ii) involves a concerted or nickel mediated addition of the NHC methyl C–H bond across the C=C triple bond of the coordinated alkyne. DFT calculations (BP86/def2-TZVP(Ni)/def2-SVP(C,N,H)) reveal first of all that the rearrangement with the resulting complex 11a energetic (maroon).

As it is known that [Ni(NHC)]2 catalysts for cyclooligomerization reactions were prepared in situ from [Ni(COD)2] and a bulky and electron rich NHC ligand such as DippIm, DippIm2+ or Mes2Im, we reacted isolated [Ni(Mes2Im)]2 with alkynes. Initial NMR experiments revealed that complex 2 catalyzes 2-butyne quantitatively and therefore we investigated the catalytic activity and stereoselectivity of complex 2 in cyclooligomerization reactions using different internal and terminal alkynes (see Table 2). NMR spectra of the reactions of 2-butylene, 4-octyne, diphenylacetylene, dimethyl acetylenedicarboxylate, 1-pentene, phenylacetylene and methyl propiolate with 5 mol% of [Ni(Mes2Im)]2 in C6D6 at 60 °C were recorded and the consumption of the alkynes was monitored. The catalyst was then removed by filtration over a pad of silica gel and the products were analyzed using 1H and 13C([H]) NMR spectroscopy as well as GC/MS. In all cases the cyclooligomerization of internal alkynes proceeded in quantitative yield on NMR scale (isolated yields were only determined for the preparation of hexaphenylbenzene, in this case the TON is 30) and no formation of side-products was detected, with exception of the cyclooligomerization of 1-pentene, where traces of tetramerization products were observed (see Supporting Information). The reactions with terminal alkynes did not show any specific stereoselectivity and afforded mixtures of the 1,2,4- and 1,3,5-stereoisomers. The exact determination of the product ratio via integration of the 1H NMR spectrum was only possible for the reaction of methyl propiolate due to overlapping NMR resonances for the products of the other alkynes. The use of internal alkynes yielded hexa-substituted benzene derivatives, and the cyclooligomerization of diphenylacetylene to give hexaphenylbenzene proceeded much faster compared to the cyclooligomerization of other alkynes (entry 3, Table 2). This reaction was finished after five minutes at room temperature using a small catalyst load of just 1 mol%. As the product is almost insoluble in CD2Cl2, it was isolated directly from the NMR tube as a colorless solid in 88% yield.

To gain further insight into the mechanistic details of the catalysis we analyzed the reaction of 2 with 2-butylene. Therefore, we initially performed the reaction of 2 with a slight excess of
Addition of the alkyne led to an immediate color change from reaction mixture by NMR spectroscopy after five minutes at room temperature. The analysis of the deep violet, which is the color of hexamethylenbenzene, was observed. The presence of uncoordinated carbene in the solution indicates that complex E might be a mono-NHC complex [{Mes$_2$Im}(η$^6$-C$_6$Me$_6$)] E, stabilized by hexamethylenbenzene. A similar arene-stabilized complex has been reported previously by Ogoshi et al.$^{[2]}$ for a larger NHC, i.e., [{Dipp$_2$Im}(η$^6$-C$_6$H$_4$Me$_2$)]. Despite of several attempts, we were not able to isolate this complex. Furthermore, the absence of 2-butyne after five minutes at room temperature indicates that oligomerization proceeds very fast and quantitatively. To learn more details about this process, especially at which temperature the catalysis sets in, we additionally performed a variable temperature NMR experiment of the reaction from −40 °C to +60 °C in steps of 10 °C (see Figure 5a). At −40 °C, the reaction mixture had a bright yellow color and the NMR spectrum showed the formation of the alkyne complex [Ni(Mes$_2$Im)$_2$(η$^4$-MeC$\equiv$Me)] 14 (see below), similar as observed for complex B'/B with the smaller NHC ligand. Resonances of the trimerization product, free Mes$_2$Im as well as the signals of complex E were already detected at temperatures of 0–10 °C. Integration of the resonances was consistent with the formation of a mono-NHC arene complex [{Mes$_2$Im}Ni(η$^6$-C$_6$Me$_6$)]. After raising the temperature to 40 °C, the alkyne was completely consumed, the resonance of hexamethylenbenzene increased and both, the NHS Mes$_2$Im as well as the complex [{Mes$_2$Im}Ni(η$^6$-C$_6$Me$_6$)] E, were detected. Finally, at 60 °C, the recovery of complex 2 and the decrease of the resonances of the uncoordinated NHS and the mono-NHC complex E occurred. We also performed the reaction of [Ni(Pr$_2$Im)$_2$](η$^4$-MeC$\equiv$Me)] 3 with an excess of 2-butyne, to see if it is also suitable for the catalytic trimerization. In contrast to complex 2 no cyclization was observed after 20 h at room temperature, but heating the reaction mixture to higher temperatures of 80 °C and above led to slow transformation of 2-butyne to hexamethylenbenzene.

We also tried to isolate some of the possible intermediates [Ni(Mes$_2$Im)$_2$(η$^4$-R'C$\equiv$CR)], [Ni(Mes$_2$Im)$_2$(η$^4$-R'C$\equiv$CR)$_2$] (for R' = R = Me: F) or [(Mes$_2$Im)Ni(η$^6$-C$_6$R$_6$)] (for R = Me: E) of the catalysis from reactions of 2 with stoichiometric amounts, i.e., 1, 2, or 3 equivalents, of alkyne. However, all attempts to isolate complexes [Ni(Mes$_2$Im)$_2$(η$^4$-R'C$\equiv$CR)] and [(Mes$_2$Im)Ni(η$^6$-C$_6$R$_6$)] failed so far, but some complexes of the type [Ni(Mes$_2$Im)$_2$(η$^4$-R'C$\equiv$CR)$_2$] were obtained in pure form. The complexes with η$^2$-(C$_C$)-coordinated alkyne [Ni(Mes$_2$Im)$_2$(η$^2$-MeC$\equiv$CMe)] 14, [Ni(Mes$_2$Im)$_2$(η$^2$-MeOOC$\equiv$C$\equiv$OCMe)] 15, [Ni(Mes$_2$Im)$_2$(η$^2$-PhC$\equiv$CMe)] 16, [Ni(Mes$_2$Im)$_2$(η$^2$-HC$\equiv$C(4'-Bu-C$_6$H$_2$))] 17 and [Ni(Mes$_2$Im)$_2$(η$^2$-HC$\equiv$COCMe)] 18 precipitated as yellow to brown powders if the reactions were carried out at 0 °C in pentane or hexane, which made their isolation possible. These complexes are, once isolated, stable at room temperature in the solid state (see Scheme 4). The complexes 14 to 18 were fully characterized including elemental analysis and single crystal X-ray structures for 14, 15, 16 and 17. However, due to significant line broadening and signal overlap at room temperature or 0 °C, NMR spectroscopy of 14, 16 and 17 was performed at −80 °C.

In general, the stability of complexes [Ni(Mes$_2$Im)$_2$(η$^2$-R'C$\equiv$CR)] depend on the steric demand of the alkyne used, but also on the electronic properties of the alkyne ligand. As

### Table 2. Scope of the catalytic cyclotrimerization of alkynes with [Ni-(Mes$_2$Im)$_2$].

| Entry | Substrate | Products$^{[a]}$ | t [h] |
|-------|-----------|-----------------|------|
| 1     | 2-Butyne  | ![Structure](image1) | 3    |
| 2     | Phenylacetylene | ![Structure](image2) | 3    |
| 3     | Diphenylacetylene | ![Structure](image3) | 5 min|
| 4     | 1-Pentyne | ![Structure](image4) | 4    |
| 5     | 4-Octyne  | ![Structure](image5) | 48   |
| 6     | Methyl propiolate | ![Structure](image6) | 4    |
| 7     | Dimethyl acetylenedicarboxylate | ![Structure](image7) | 3    |

[Note: $^{[a]}$ Reaction conditions: [Ni(Mes$_2$Im)$_2$] 2 (5 mol%), alkyne (1.0 equiv.), C$_6$D$_6$ (0.6 mL), 60 °C, 20 h. Products after total consumption of the substrates, checked by NMR and GC/MS. Product ratios were determined by $^1$H NMR integration, if possible. [b] [Ni(Mes$_2$Im)$_2$] 2 (1 mol%), rt, 5 minutes. [c] Yield of isolated material after workup.]
observed previously for olefin complexes,[11] the steric bulk of the NHC ligand Mes$_2$Im of complex 2 limits the coordination of a third ligand to the nickel atom, which is in stark contrast to the behavior of complexes 1/1M. Alkynes with electron-withdrawing substituents increase π-backboning from the nickel atom to the alkyne and increase the stability of the alkyne complex in solution at room temperature. As noticed above, alkyl and/or aryl substituted alkynes lead to decomposition of the alkyne complexes with extrusion of one NHC ligand at temperatures slightly above 0 °C. Unlike the complexes 3–13, the NMR spectra of the compounds 14–18 reveal remarkably broadened resonances for the bulkier NHC ligand Mes$_2$Im due to hindered rotation, as it was previously reported by us for similar π-complexes with ketone or aldehyde ligands.[11b] Even the low temperature NMR spectra of 14, 16 and 17 revealed some signal broadening. Nevertheless, all characteristic resonances were assigned and the integration of the resonances is consistent with the presence of one alkyne ligand per two NHC ligands in complexes of the type [Ni(Mes$_2$Im)$_2$][η$_2$-alkyne]].

Table 3. $^{13}$C($^1$H) NMR and $^1$H NMR shifts (ppm) of the alkyne carbon and terminal alkyne hydrogen atoms as well as IR C≡C stretching vibrations (cm$^{-1}$) of the complexes 14–18 (Δδ = $^{13}$C($^1$H) NMR shift of the alkyne carbon atoms; Δδ$_{^1}$H = $^1$H NMR shift of the terminal alkyne hydrogen atoms; Δν$_{C≡C}$ = $^{13}$C($^1$H) NMR shift of the NHC carbene carbon atoms, $\nu_{C≡C}$ = IR stretching vibration of the alkyne triple bond).

| Compound | $\delta_{^1}$H | $\delta_{^13}$C | $\Delta$δ$_{^1}$H | $\Delta$δ$_{^13}$C | $\nu_{C≡C}$ (cm$^{-1}$) |
|----------|----------------|----------------|------------------|------------------|----------------------|
| 14       | 118.6$^{[a]}$  | 44.2           | –                | 207.0$^{[a]}$    | 1808                 |
| 15       | 136.7          | 61.8           | –                | 198.2            | 1713                 |
| 16       | 123.9$^{[a]}$  | 44.1           | –                | 205.8$^{[a]}$    | 1756                 |
| 17       | 122.8$^{[a]}$  | 45.8           | 6.1$^{[a]}$      | 202.2$^{[a]}$    | 1701                 |
| 18       | 131.5$^{[a]}$  | 47.5           | –                | 206.5$^{[a]}$    |                     |
| 19       | 134.6          | 58.6           | 6.94             | 4.78             | 201.8                |
| 20       | 136.6          | 61.6           | –                | 202.4            |                     |

[a] THF-$d_8$ – 80 °C.

Figure 5. a) Time-resolved $^1$H NMR spectrum of the reaction of [Ni(Mes$_2$Im)$_2$] 2 with 2-butyne (4 equiv.; C$_6$D$_6$); b) Variable temperature $^1$H NMR spectrum of the reaction of [Ni(Mes$_2$Im)$_2$] 2 with 2-butyne (4 equiv.; thf-$d_8$).
Molecular structures of \([\text{Ni(Mes}_2\text{Im})_2\eta^3\text{MeC} \equiv \text{CMe}]\) 5 and [Ni(Pr$_3$Im)$_2\eta^3\text{MeSiC} \equiv \text{CSiMe}]_2\) 7 are given in Table 4. All complexes adopt a distorted pseudo-square planar geometry, spanned by two NHCs and the alkynyl ligand. All molecular structures reveal much larger C$_{\text{NHC}}$–N$_{\text{NHC}}$ bite angles of 122.24(6)$^\circ$ (14), 118.47(12)$^\circ$ (15), 118.5(2)$^\circ$ (16) and 124.59(14)$^\circ$ (17) compared to the Pr$_3$Im and Pr$_3$Im$_2$Ni complexes of the N-alkyl substituted carbenes (C: 109.27(19)$^\circ$, D: 100.4(3)$^\circ$; 3: 102.42(6)$^\circ$; 5: 110.66(8)$^\circ$; 7: 114.54(6)$^\circ$), which is associated with the increased steric demand of the bulkier NHC Mes$_2$Im. The C–C distances of the alkynyl ligands of the complexes 14 (1.280(2) Å) and 17 (1.277(5) Å) are slightly shorter compared to the complexes with the small carbenes (1.285(2) Å (3)–1.310(6) Å (C)), which is consistent with decreased $\pi$-backbonding.

NMR experiments as well as the isolation of the NHC nickel alkynyl complexes point to a mechanism for the NHC Ni mediated alkynyl trimerization as depicted in Scheme 5 for the trimerization of 2-butyne. The first step of the catalytic cycle is the coordination of the alkynyl to deep-purple [Ni(Mes$_2$Im)$_2$] 2 to yield bright yellow [Ni(Mes$_2$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$ 14, a step which occurs at low temperatures. In a second step, another alkynyl molecule coordinates to the nickel atom to replace one of the NHC ligands with formation of the bis(alkyne) complex [Ni(Mes$_2$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$ 14 F. We have no evidence currently for the formation of F, but Louie et al.$^{[25]}$ and Cavell et al.$^{[26]}$ reported previously the synthesis of comparable mono-NHC stabilized nickel olefin complexes of the type ([NHCNi(η-$^3$CR$_2$)$_2$] using bulky NHC ligands such as Mes$_2$Im or Dipp$_2$Im. As we never detected intermediate F, we assume that the following reaction step, the addition of another equivalent alkynyl to F with cyclization of the alkynes to give [Mes$_2$ImNi(η-$^3$CR$_2$)$_2$] E, is very fast. Complex E was detected by NMR spectroscopy but defined all efforts at isolation. As the complexes 2 or 14 were never observed during catalysis, we propose that the formation of 2 and 14 are the initial steps to prepare the catalytically active species [Ni(Mes$_2$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$ 14 F (“Initiation” in Scheme 5, highlighted in red) and that the effective catalytic process occurs as a shuttle between the complexes F and E (“Propagation” in Scheme 5). At the end of the catalysis, the NHC ligand re-coordinates to the nickel atom of E with elimination of the aromatic trimerization product and recovery of complex 2 (“Termination” in Scheme 5, highlighted in violet). This last step only occurs if the concentration of alkynyl is very low, otherwise [Ni(Mes$_2$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$ F will be formed directly to close the catalytic cycle. As our NMR studies on the reaction of 2 with a slight excess of 2-butyne clearly reveal is this last step associated with the highest barrier.

![Figure 6. Molecular structures of [Ni(Mes$_2$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$ 14 (top left), [Ni(Mes$_2$Im)$_2\eta^3\text{MeOCC} \equiv \text{COOMe}]$ 15 (top right), [Ni(Mes$_2$Im)$_2\eta^3\text{PhC} \equiv \text{CMe}]$ 16 (bottom left) and [Ni(Mes$_2$Im)$_2\eta^3\text{HC} \equiv ([4^\prime\text{BuC} \equiv \text{H}_2])$ 17 (bottom right) in the solid state (ellipsoids set at 50% probability level). The hydrogen atoms and a hexane molecule (17) were omitted for clarity.](image)

Table 4. Comparison of important bond lengths and bond angles of [Ni(Me$_3$Im)$_2\eta^3\text{PhC} \equiv \text{CPh}]$ 5 and [Ni(Ph$_3$Im)$_2\eta^3\text{MeC} \equiv \text{CMe}]$. All molecular structures reveal much larger C$_{\text{NHC}}$–N$_{\text{NHC}}$ bite angles of 122.24(6)$^\circ$ (14), 118.47(12)$^\circ$ (15), 118.5(2)$^\circ$ (16) and 124.59(14)$^\circ$ (17) compared to the Pr$_3$Im and Pr$_3$Im$_2$Ni complexes of the N-alkyl substituted carbenes (C: 109.27(19)$^\circ$, D: 100.4(3)$^\circ$; 3: 102.42(6)$^\circ$; 5: 110.66(8)$^\circ$; 7: 114.54(6)$^\circ$), which is associated with the increased steric demand of the bulkier NHC Mes$_2$Im. The C–C distances of the alkynyl ligands of the complexes 14 (1.280(2) Å) and 17 (1.277(5) Å) are slightly shorter compared to the complexes with the small carbenes (1.285(2) Å (3)–1.310(6) Å (C)), which is consistent with decreased $\pi$-backbonding.

![Scheme 5. Proposed mechanism of the NHC nickel-catalyzed cyclotrimerization of 2-butyne.](image)
So what is the difference between [Ni(Pr$_2$Im)$_2$] and [Ni(Me$_2$Im)$_2$] in the behavior towards alkynes? All three compounds form alkyne complexes, but only the complexes of the sterically more encumbered Mes$_2$Im ligand enter the catalytic cycle at ambient temperatures. To answer this question, DFT calculations (BP86//def2-TZVP(Ni)/def2-SVP(C,N,H)) have been performed on the initiation steps of the cyclotrimerization of 2-butyne with [Ni(NHC)$_2$] (NHC = Pr$_2$Im$_{18}$, Mes$_2$Im, Fe$_2$Im; see Scheme 5). The results of these computations are given in Figure 7.

A comparison of the energy profile of the cyclotrimerization initiation steps of 2-butyne with [Ni(Pr$_2$Im)$_{18}$] (red) and [Ni(Mes$_2$Im)$_2$] (green) reveals that the profile is very shallow for 2 and each step is associated with a moderate energy change. The formation of the alkyne complexes [Ni(Pr$_2$Im)$_{18}$](η$^2$-MeC≡CMe)] and [Ni(Mes$_2$Im)$_2$(η$^2$-MeC≡CMe)] requires $+126.6$ kJ/mol for the Pr$_2$Im$_{18}$ complex, whereas for the Mes$_2$Im complex only $+49$ kJ/mol are needed. The attachment of another alkyne to [Ni(NHC)(η$^2$-MeC≡CMe)] is exothermic in both cases, $-41.3$ kJ/mol for the formation of [Ni(Mes$_2$Im)(η$^2$-MeC≡CMe)$_2$] and $-83.1$ kJ/mol for [Ni(Pr$_2$Im)$_{18}$](η$^2$-MeC≡CMe)$_2$]. Thus, the potential surface of the nickel complex [Ni(Mes$_2$Im)$_2$] with both, low energy gain for alkyne addition and low energy loss for NHC dissociation, is nicely suited for catalysis, whereas for [Ni(Pr$_2$Im)$_{18}$] the alkyne complex seems to be too stable for further ligand loss (either alkyne or NHC) to enter a catalytic cycle at ambient temperatures.

As there is a distinct difference in the coordination of alkyne, specifically 2-butyne, to [Ni(Pr$_2$Im)$_{18}$] (red) and [Ni(Mes$_2$Im)$_2$] (green) it is interesting to track down the differences. Both ligands are different in their stereo-electronic features. For this purpose the steric demand of the NHCs Pr$_2$Im, Pr$_2$Im$_{18}$ and Mes$_2$Im expressed by their $\%V_{bur}$ ("percent buried volume") was re-evaluated on the basis of DFT geometry optimized structures (BP86//def2-TZVP(all)) of (NHC$_2$Ni(CO)$_2$). With the aid of the Web application SambVca,
As the molecular structure is known for all three complexes it should be noted here that the experimentally determined C=C bond lengths in principle do not provide a good basis for this discussion, as the differences lie within the experimental error of the structure determination (3σ). However, the trend observed here is as expected, i.e., that the C=C bond length of the alkyne ligand of the MesIm complex [Ni(MesIm),(η^2-MeC≡CMe)] 14 is the shortest while those of the complexes D and 3 are longer due to enhanced electron donation to the alkyne: 1.280(2) (14) < 1.285(2) (D) < 1.286(13) (3). This order of the net donor properties is also reflected in the observed coordination shifts of the alkyne carbon atoms (ΔδC [ppm] = 44.2 (14) < 47.2 (3) < 47.5 (D)) and even more pronounced in the coordination shifts of the η^1C=C stretching vibrations (ΔδC=C [cm^-1] = 425 (14) < 448 (3) < 455 (D)) (cf. Tables 1 and 3).

Different degrees of C=C bond activation of the alkyne ligands of [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3 and [Ni(MesIm),(η^2-MeC≡CMe)] 14 was also confirmed by DFT calculations, either using the C=C distances (3: 1.304 Å, 14: 1.297 Å), the calculated charges on the alkyne carbon atoms (e.g., NBO-charges: 3: -0.245, 14: -0.225), calculated (uncorrected) C=C stretching frequencies (3: 1876 cm^-1; 14: 1876 cm^-1) or the C=C Wiberg bond indices (3: 1.809, 14: 1.835). A detailed analysis also reveals that alkene activation (i.e., the strength of the π-backbond) is indirectly influenced by the steric demand of the NHC ligand in so far, as the complexes [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3 and [Ni(MesIm),(η^2-MeC≡CMe)] 14 adopt different angles C_Ni–C–C. It is well known that a decrease of the bite angle L–M–L (i.e., C=C_Ni–C=C) in d^8-[ML₂] (L = neutral 2VE donor ligand) and related complexes is connected with a more favorable π-backbonding in complexes d^8-[ML₂(alkyne)] and thus an increase of the net charge donation from the metal center to the π-ligand. The bite angles of the complexes [Ni(NHC),(η^2-MeC≡CMe)] decrease in the order 122.24(6)° (14) > 102.42(6)° (3) > 100.4(3)° (D). To evaluate the contribution of the different bite angles we optimized the geometry of [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3 with the fixed angle of geometry optimized [Ni(MesIm),(η^2-MeC≡CMe)] 14 (angle C=C₆–Ni–C=C₆ 123.60°, exp.:122.24(6)°). The potential for a change of the C=C₆–Ni–C=C₆ angle is very shallow, as the most stable combinations of structures [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3 differ by a mere 2.8 kJ/mol. However, the parameters evaluated above for the alkyne ligand of 3 and 14 adopt for the complex of the constrained geometry complex values within those computed for 3 and 14, for example 1.301 Å for the C=C distance (3: 1.304 Å, 14: 1.297 Å), -0.233 for the NBO-charges on the alkyne carbon atoms (3: -0.245, 14: -0.225), and 1852 cm^-1 for the C=C stretching frequencies (3: 1852 cm^-1; 14: 1876 cm^-1).

In total, we attribute the much higher stability of [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3 with respect to [Ni(MesIm),(η^2-MeC≡CMe)] 14 to three main reasons: (i) electron transfer from the NHC to the metal to the alkyne ligand is higher for the N-alkyl compared to the N-aryl substituted NHC ligands in [Ni(NHC),(η^2-MeC≡CMe)] due to different electron donor/acceptor properties of the NHC ligand. (ii) Electron transfer from the metal center to the alkyne ligand is enhanced for the N-alkyl compared to the N-aryl substituted NHC ligands due to their different steric size, as smaller NHC ligands (such as PrIm or PrIm) can adopt smaller C=C–C=C bite angles, which leads to increased π-backdonation to the alkyne. (iii) Ligand dissociation is facilitated for the complex of the sterically more encumbered NHC ligand, i.e., [Ni(MesIm),(η^2-MeC≡CMe)] 14 loses the NHC ligand more readily than [Ni(PrIm)₃],(η^2-MeC≡CMe)] D and [Ni(PrIm)₃],(η^2-MeC≡CMe)] 3. All these factors lead to a significantly enhanced stability of the alkyne complexes of the N-aryl substituted NHCs and are thus the reason why these complexes are not catalytically active for alkyne oligomerization at ambient temperatures.

**Conclusion**

A case study on the effect of two different NHC ligands in complexes [Ni(NHC)₂] (NHC = PrIm, MesIm 2) is reported; it presents some details to demonstrate how small differences in the stereo-electronic features of closely related ligands can significantly alter the reactivity pattern. The reaction of (suitable precursors of) both complexes with alkynes afforded Ï^2(C=C)alkyne complexes [Ni(NHC),(η^2-alkyne)] (3–18), although the number of complexes available for [Ni(MesIm)] 3 is limited to small alkynes and good acceptor alkynes. Many of the [Ni(PrIm)₃] complexes 3–13 are unstable upon heating, leading to various, in many cases unidentified decomposition products. However, for the thermal reaction of the complexes [Ni(PrIm)₃],(η^2-HC≡C(p-Tol))] 11 and [Ni(PrIm)₃],(η^2-HC≡C(4′-Bu-C₆H₄))] 12 the isomers 11a and 12a were identified. DFT calculations, as well as deuteration experiments, were in accordance with the formation of 11a and 12a via a concerted or nickel-mediated C–H addition of a NHC methyl C–H bond across the C≡C triple bond of the coordinated alkyne.

Complex 2 cyclotrimerizes alkynes at ambient conditions, which is in contrast to the behavior found for 18th or 1. NMR exploration of the reaction of 2 with 2-butyne gave evidence for the formation of the complexes ([MesIm]Ni(η^2-C₂Me₆)] 14 and [Ni(MesIm),(η^2-MeC≡CMe)] 14 as intermediates of the reaction. A mechanism for the NHC-nickel catalyzed cyclotrimerization of 2-butyne was proposed, which involves coordination of the alkyne to [Ni(MesIm)] 2 to yield [Ni(MesIm),(η^2-MeC≡CMe)] 14 and [Ni(MesIm),(η^2-MeC≡CMe)] F with loss of one NHC ligand as the initiation step of the catalysis. The efficient steps of the catalytic cycle involve addition of 2-butyne to [Ni(MesIm),(η^2-MeC≡CMe)] F with cyclization to yield [MesIm]Ni(η^2-C₂Me₆)] E and re-formation of F with aren release. The re-coordination of the NHC ligand to the nickel atom of E with elimination of the aromatic trimerization product and recovery of complex 2 at the end of the catalysis is the termination of the catalytic cycle.

This study demonstrates for the example of bis-NHC nickel alkyne complexes and their reactivity how valuable NHCs are in the fine-tuning of substrate binding, electron transfer and reactivity. Although the differences in the TEP of both NHCs under investigation is small, the differences in the electron transfer of the complexes [Ni(NHC)₂] to a coordinated substrate are quite impressive. The increase of the steric demand of the
NHC lead, of course, to a different accessibility of the metal center (steric protection) and to different complex stabilities as co-ligand/NHC dissociation is facilitated for the bulkier ligand. But we also demonstrate here that steric properties of the NHC significantly influence the donor properties of \([\text{M(NHC)}_2]\)-moieties by the \(\text{C}_{\text{NHC}}-\text{M}-\text{C}_{\text{NHC}}\) bite-angle NHC ligands of different size can adopt in the final product. Furthermore, we have shown previously[1,13,14] that simple electron-transfer processes are possible if the substrate cannot bind to a (sterically encumbered) complex \([\text{M(NHC)}_2]\) and that thus radical processes dominate its reactivity and catalysis. We anticipate that, as shown herein, further tuning of the NHC stereo-electronics, keeping \([\text{M(NHC)}_2]\) units intact, will lead to the (further) design of catalysts which enter different reaction channels for similar (or even same) starting materials.

Crystallographic details

Crystal data collection and processing parameters are given in the Supporting Information. Deposition Numbers 2100093 (15), 2100094 (5), 2100095 (14), 2100096 (3), 2100097 (B), 2100098 (17), 2100099 (11a), 2100100 (16), and 2100101 (7) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkyne complexes · cyclooligomerization · cyclotrimerization · N-heterocyclic carbenes · nickel complexes

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