Nickel(0) Complexes of N-Alkyl-Substituted N-Heterocyclic Carbenes and Their Use in the Catalytic Carbon−Carbon Bond Activation of Biphenylene

Thomas Schaub, Marc Backes, and Udo Radius*

Institut für Anorganische Chemie, Engesserstrasse Geb. 30.45, D-76131 Karlsruhe, Germany

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The reaction of $[Ni(COD)_2]$ with stable N-heterocyclic carbenes R_2Im (R_2Im = 1,3-di(R)imidazole-2-ylidene; R_2 = Me_2, $^nPr_2$, Me^iPr, $^iPr_2$) affords homoleptic $[Ni(Me_2Im)_3]$ (**1**) or dinuclear, COD-bridged complexes of the type $[Ni_2(R_2Im)_4(COD)]$ (R_2 = $^nPr_2$, **2**; Me^iPr, **3**; $^iPr_2$, **4**). Compounds **1**−**4** are suitable precursors for the synthesis of $[Ni(R_2Im)_2]$-containing complexes in solution, exemplified by the reaction with CO under atmospheric pressure, with equimolar amounts of diphenyl acetylene or with biphenylene to give carbonyl complexes $[Ni(R_2Im)_2(CO)_2]$ (R_2 = Me_2, **5**; $^nPr_2$, **6**; Me^iPr, **7**; $^iPr_2$, **8**), diphenyl acetylene complexes $[Ni(R_2Im)_2(\eta^2\text{-}C_2Ph_2)]$ (R_2 = Me_2, **9**; $^nPr_2$, **10**; Me^iPr, **11**; $^iPr_2$, **12**), and biphenylene complexes $[Ni(R_2Im)_2(2,2'\text{-biphenyl})]$ (R_2 = Me_2, **13**; $^nPr_2$, **14**; Me^iPr, **15**; $^iPr_2$, **16**). Furthermore, the reaction of **4** with 3-hexyne or 2-butyne afforded $[Ni(^iPr_2Im)_2(\eta^2\text{-}C_2R_2)]$ (R = Me, **18**; Et, **19**) in good yields. The compounds **1**, **11**, **13**, **17**, and **18** have been structurally characterized. Complexes **13**−**16** are the products of a stoichiometric carbon−carbon activation of biphenylene, and compounds **1**−**4** (as well as **9**−**12**) are efficient catalysts for the insertion of diphenyl acetylene into the C−C bond of biphenylene, a process in which the C−C activation of biphenylene is incorporated into a catalytic cycle. The reaction rate of the formation of 9,10-di(phenyl)phenanthrene depends on the nature of the carbene ligand of the catalyst; the highest was observed for $[Ni_2(^iPr_2Im)_4(COD)]$ (**4**).

Introduction

In the last 50 years, N-heterocyclic carbenes (NHCs; imidazol-2-ylidenes, Im) have evolved from intermediates whose existence could be demonstrated by kinetic and trapping studies in the 1960s[1] to stabilized forms currently being studied in many research groups.[2] During the past decade there has been considerable interest in N-heterocyclic carbenes (NHC) as spectator ligands in organometallic chemistry, particularly as alternatives to phosphine ligands in the field of homogeneous catalysis.[3] NHCs stabilize highly reactive organometallic species,[4] and many of these carbene complexes show high catalytic activities in many metal-mediated organic transformations, for example, in ruthenium-mediated olefin metathesis,[5] iridium-catalyzed hydrogenation and hydrogen transfer,[6] platinum-catalyzed hydrosilylation,[7] and palladium-catalyzed C−C coupling reactions.[8]

A number of studies have suggested that nucleophilic carbenes have ligating properties similar to electron-rich trialkylphosphines, and the strong σ-donor nature of the ligands often results in more stable catalysts than analogous phosphine-based systems.[9] Furthermore, NHC-type ligands usually possess greater thermal stability compared to alkylphosphines and are more stable with respect to oxidative degradation. Recent reports

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* To whom correspondence should be addressed. Fax: (Int) + 721-608-7021. E-mail: radius@aoc1.uni-karlsruhe.de.

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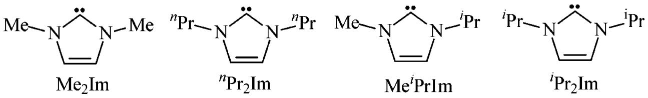
Scheme 1. N-Heterocyclic Carbenes Used in this Study



render in situ-generated aryl-substituted Mes_2Im (R_2Im = 1,3-di(R)imidazole-2-ylidene; Mes = 2,4,6-$Me_3C_6H_2$) and Dip_2Im (Dip = 2,6-$^iPr_2C_6H_4$) stabilized nickel(0) complexes as precatalysts for catalytic transformations such as C−C and C−N coupling reactions, dehalogenation, and transfer hydrogenation reactions.[10,11] Studies on isolated, NHC-stabilized nickel(0) complexes, however, are scarce so far, and no nickel-containing intermediates have been characterized, isolated, or synthesized by means of stoichiometric organometallic transformations during the above-mentioned investigations, which basically prevents a deeper understanding of the system at work. Recently, we briefly described the synthesis of the dinuclear compound $[Ni_2(^iPr_2Im)_4(COD)]$ as a source of the $[Ni(^iPr_2Im)_2]$ complex fragment in stoichiometric and catalytic transformations and first studies on the reactivity of this complex in C−F and C−C activation reactions.[12] In this contribution we give a detailed account of the synthesis and reactivity of some alkyl-substituted NHC complexes containing the $[Ni(R_2Im)_2]$ (R = Me, ^{n}Pr, ^{i}Pr) moiety and compare the behavior of these complexes in the catalytic conversion of biphenylene and diphenyl acetylene to 9,10-di(phenyl)phenanthrene.

Results and Discussion

Although NHC nickel complexes are among the first NHC metal compounds that have been synthesized starting from isolated N-heterocyclic carbenes,[10a,13] precursors similar to nickel(0) bis(phosphine) complexes are still rare. Known examples of structurally characterized, well-defined NHC nickel(0) complexes include NHC adducts of nickel carbonyls and homoleptic two-coordinated nickel(0) biscarbene complexes employing NHCs with aryl substitutents at the nitrogen atom.[10,11] Since we have been interested in complexes that exhibit a high basicity at the metal atom and first quantum chemical investigations rendered alkyl-substituted NHCs as better σ-donating ligands compared to their aryl-substituted counterparts, we studied the reaction behavior of stable, alkyl-substituted NHCs with respect to various nickel compounds, especially the Ni(0) precursor $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene). Starting from $[Ni(COD)_2]$ and sterically demanding carbene ligands, 2-fold coordinated, homoleptic complexes $[Ni(Mes_2Im)_2]$[10a] and $[Ni(Dip_2Im)_2]$[10d] have been synthesized by the groups of Arduengo and Herrmann, respectively. Cloke et al. reported the synthesis of $[Ni(^tBu_2Im)_2]$ in 10% yield via co-condensation reaction of nickel vapor and 1,3-di(*tert*-butyl)imidazole-2-ylidene,[10c] which is of limited use for a preparation of this complex in a large scale. The reaction of $^tBu_2Im$ with $[Ni(COD)_2]$, however, demonstrates the limitations of a preparations of complexes $[Ni(R_2Im)_2]$ in solution starting from $[Ni(COD)_2]$ and the stable NHC. As reported by Cloke and co-workers recently,[10g] the attempted conventional synthesis via reaction of $^tBu_2Im$ with $[Ni(COD)_2]$ proceeds under N−C-cleavage of one of the *tert*-butyl substituents to yield different mono(NHC)-stabilized complexes as main reaction products; the desired compound $[Ni(^tBu_2Im)_2]$ was only formed in traces. In the case of the isopropyl-substituted carbene, however, we have found that the reaction with $[Ni(COD)_2]$ proceeds smoothly under formation of the dinuclear complex $[Ni_2(^iPr_2Im)_4(COD)]$ (**4**) as the main product. This is a clear indication that the outcome of the reaction of NHCs with $[Ni(COD)_2]$ critically depends on the steric demand of the nitrogen substituent at the carbene ligand. A similar effect is observed with homoleptic nickel phosphine complexes. Coordinatively unsaturated, trigonal nickel phosphine complexes can be isolated with bulky phosphines, while less hindered phosphines afford the four-coordinate tetrahedral complexes. Therefore, we reacted differently substituted imidazole-2-ylidenes Me_2Im, $^nPr_2Im$, and $^iPr_2Im$ as well as the unsymmetrically substituted 1-methyl-3-isopropylimidazole-2-ylidene Me^iPrIm with $[Ni(COD)_2]$. The carbenes have been synthesized from the corresponding imidazolium salts by standard deprotonation techniques and can be purified and isolated in good yields. The isopropyl-substituted carbene was synthesized similarly to a procedure published by Erker et al. earlier,[14] whereas a protocol for the preparation of the *n*-propyl- and the methyl-isopropyl-substituted derivative was not given before. We provide details of these preparations in the Supporting Information. The propyl-substituted carbenes are yellow liquids at room temperature and can be stored at −40 °C for some time.

As shown in Scheme 2, $[Ni(COD)_2]$ reacts cleanly with all imidazolylidenes under investigation. Whereas the reactions of the propyl-substituted carbenes result in formation of cyclooctadiene-bridged dinuclear complexes of the type $[Ni_2(R_2Im)_4(COD)]$, the methyl-substituted carbene reacts smoothly with $[Ni(COD)_2]$ to afford a mononuclear, 3-fold-substituted compound, $[Ni(Me_2Im)_3]$, independent of the amount of carbene employed. Using 2 equiv of the carbene, unreacted $[Ni(COD)_2]$ remains in addition to **1** in the reaction mixture. The proton NMR spectrum of **1** reveals two singlets at 3.57 ppm (for the imidazole-2-ylidene methyl groups) and at 6.31 ppm (for the imidazole-2-ylidene olefinic protons), indicating a highly symmetric species of the type $[Ni(Me_2Im)_3]$ or $[Ni(Me_2Im)_4]$ in solution. Analytical data and mass spectroscopy of the red complex then confirmed the composition $[Ni(Me_2Im)_3]$ of the diamagnetic reaction product. Crystals of **1** suitable for X-ray diffraction have been obtained from a 1:1 mixture of hexane and toluene at −30 °C. Complex **1** crystallizes in the space

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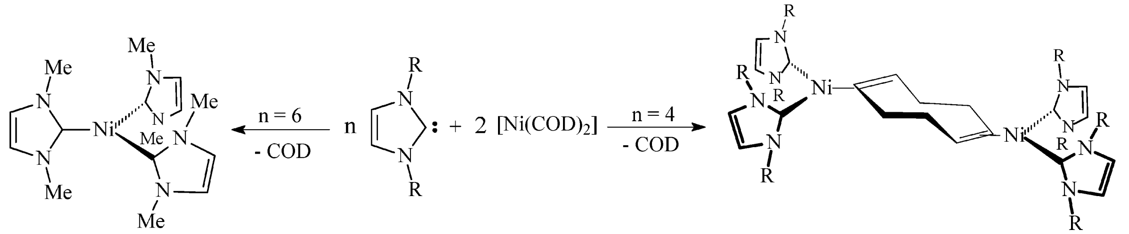
Scheme 2. Reaction of [Ni(COD)$_2$] with Me$_2$Im, ^{n}Pr$_2$Im, ^{i}Pr$_2$Im, and Me^{i}PrIm



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R$_2$= ^{n}Pr$_2$ **2**; Me^{i}Pr **3**; ^{i}Pr$_2$ **4**

group $P\bar{1}$ with one molecule in the asymmetric unit. The molecular structure of **1** along with important bond lengths and bond angles is given in Figure 1.

Complex **1** is one of the few structurally characterized homoleptic nickel(0) complexes in which three σ-donor ligands surround the nickel atom in a trigonal planar arrangement. In the case of phosphine compounds, crystallographic studies have confirmed the formation of trigonal planar [Ni(PPh$_3$)$_3$], [15] and West et al. reported the formation and crystallographic characterization of two homoleptic [Ni(silylene)$_3$] complexes. [16] The Ni$-$C$_{\text{Carbene}}$ distances in the range 1.860(2)$-$1.888(2) Å are significantly longer compared to the distances found in the structurally characterized, homoleptic 2-fold-coordinated compounds [Ni(Mes$_2$Im)$_2$] (1.827(6)$-$1.830(6) Å)[10a] and [Ni(tBu$_2$-Im)$_2$] (1.874(2) Å),[10b] which is in accordance with the expectations resulting from simple electronic and steric factors, but slightly shorter compared to those found for [Ni$_2$(^{i}Pr$_2$Im)$_4$-(COD)][12] (1.904(3) and 1.906(3) Å). The coordination polyhedron at the nickel atom is marginally distorted from an ideal trigonal planar coordination. The C$-$Ni$-$C angles of 121.83-(9)°, 122.65(9)°, and 115,52(9)° deviate slightly from 120°, but the sum of these angles is 360°. The nickel atom is exactly aligned in the plane spanned by the carbene carbon atoms C(1), C(6), and C(11). DFT calculations on the full model of the compound reveal a regular trigonal planar coordination as the global minimum of the compound, and we attribute the distortion of **1** in the solid state to packing forces.

Whereas 1,3-di(methyl)imidazole-2-ylidene (Me$_2$Im) reacts with [Ni(COD)$_2$] to yield a 3-fold homoleptic coordinated complex, imidazole-2-ylidenes with sterically more demanding groups such as ^{n}Pr$_2$Im or ^{i}Pr$_2$Im afford dinuclear, COD-bridged complexes of the type [Ni$_2$(R$_2$Im)$_4$(COD)] (R$_2$ = ^{n}Pr$_2$, **2**; Me^{i}Pr, **3**; ^{i}Pr$_2$, **4**). As reported for the isopropyl-substituted complex **4** earlier,[12] these complexes can be isolated in the form of yellow, air- and moisture-sensitive solids, which decompose at higher temperatures in solution as well as in the solid state. In some instances, minor amounts (up to 5% for R$_2$ = ^{n}Pr and ^{i}Pr$_2$ and up to 15% for R$_2$ = Me^{i}Pr based on proton NMR spectroscopy) of complexes of higher symmetry were observed as side products. The proton NMR spectra of these side products are in accordance with mononuclear compounds of the type [Ni-(R$_2$Im)$_2$(η^4-COD)], for which the cyclooctadiene ligand gives rise to three sets of resonances at approximately 2.40 and 4.45 ppm. Expectably, the signal pattern of the COD ligand in the dinuclear complexes is more complex. Aside from the set of signals typically found for the coordinated carbene ligands, unresolved multiplets in the region between 2.10 and 2.90 ppm for the bridging COD ligand are typically detected in the proton NMR spectrum. A ^{1}H$-^1$H-COSY NMR spectrum of complex **4**, which clearly reveals the cross-peaks expected for the COD protons at 2.21, 2.42, and 2.89 ppm, is depicted in Figure 2. Only one isomer was detected from the reaction of the asymmetrically substituted carbene Me^{i}PrIm with [Ni(COD)$_2$], which clearly indicates unhindered rotation around the Ni$-$C axis.

The different structures obtained from the reaction of the carbenes with [Ni(COD)$_2$] clearly reflect the differing steric bulkiness of the carbene ligands. The reaction with methyl-substituted carbene, large enough to prevent tetrasubstitution, affords a trigonal planar complex, whereas the usage of bulky aryl-substituted carbenes leads to homoleptic, two-coordinated complexes. Dinuclear, COD-bridged complexes are obtained from carbenes with intermediate steric bulkiness, large enough to prevent three-substitution but too small in steric hindrance to stabilize a two-coordinated structure. Complexes **1**$-$**4** do not exchange carbene ligands on the NMR time scale. Compound **4**, for example, does not react even with an excess of ^{n}Pr$_2$Im to give either a mixed substituted complex of the type [Ni$_2$(^{n}Pr$_2$Im)$_x$-

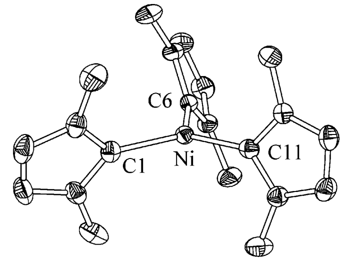

Figure 1. ORTEP diagram of the molecular structure of [Ni(Me$_2$-Im)$_3$] (**1**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)$-$C(1) 1.888(2), Ni(1)$-$C(6) 1.870(2), Ni-(1)$-$C(11) 1.860(2), C(6)$-$Ni(1)$-$C(11) 121.83(9), C(1)$-$Ni(1)$-$C(11) 122.65(9), C(1)$-$Ni(1)$-$C(6) 115.52(9).

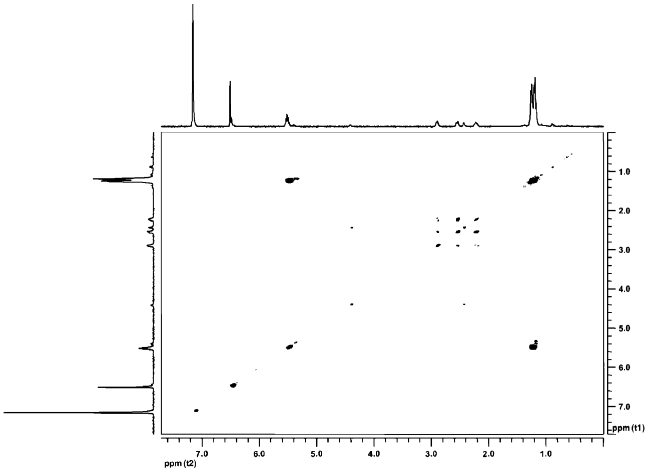

Figure 2. ^{1}H$-^1$H-COSY NMR spectrum of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)], **4**.

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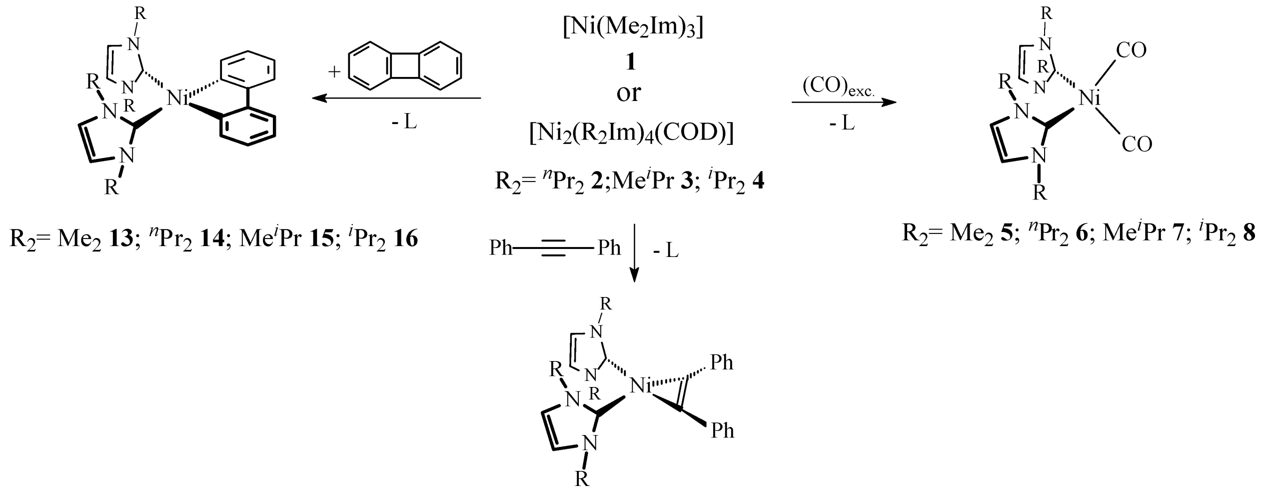
Scheme 3. Reactions of $[Ni(Me_2Im)_3]$ (1) and $[Ni_2(R_2Im)_4(COD)]$ (R_2 = $^nPr_2$, 2; Me^iPr, 3; $^iPr_2$, 4) with CO, Diphenyl Acetylene, and Biphenylene



R_2= Me_2 **13**; $^nPr_2$ **14**; Me^iPr **15**; $^iPr_2$ **16**

R_2= Me_2 **5**; $^nPr_2$ **6**; Me^iPr **7**; $^iPr_2$ **8**

R_2= Me_2 **9**; $^nPr_2$ **10**; Me^iPr **11**; $^iPr_2$ **12**

Table 1. Frequencies of the CO Stretch of Symmetry A_1 and B_1 for Selected Nickel Carbonyl Complexes of the Type $[NiL_2(CO)_2]$[a]

complex	A_1 [cm^{-1}]	B_2[cm^{-1}]
$[Ni(^iPr_2Im)_2(CO)_2]$, **8**	1927	1847
$[Ni(^nPr_2Im)_2(CO)_2]$, **6**	1935	1851
$[Ni(Me^iPrIm)_2(CO)_2]$, **7**	1939	1855
$[Ni(Me_2Im)_2(CO)_2]$, **5**	1940	1851
$[Ni(bipy)(CO)_2]$[17a]	1950	1861
$[Ni(bdepe)(CO)_2]$[17a]	1984	1920
$[Ni(P^iPr_3)_2(CO)_2]$[17b]	1984	1922
$[Ni(PMe_3)_2(CO)_2]$[17b]	1990	1926
$[Ni(PPh_3)_2(CO)_2]$[17b]	1994	1936

[a] Abbreviations used: bipy, 2,2′-bipyridyl; bdepe, 1,2-bis(diethylphosphino)ethane.

$(^iPr_2Im)_{4-x}(COD)]$ or a 3-fold-substituted complex $[Ni(^nPr_2Im)(^iPr_2Im)_2]$. Similarly, the reaction of $[Ni(COD)_2]$ with 3 equiv of $^iPr_2Im$ leads to formation of complex **4** and not to a three-coordinated $[Ni(^iPr_2Im)_3]$.

Compounds **1**−**4** are suitable precursors for the synthesis of $[Ni(R_2Im)_2]$-containing complexes in solution (see Scheme 3). These compounds react smoothly at room temperature with CO under atmospheric pressure and with equimolar amounts of diphenyl acetylene or biphenylene to yield carbonyl complexes $[Ni(R_2Im)_2(CO)_2]$ (R = Me, **5**; ^nPr, **6**; Me^iPr, **7**; ^iPr, **8**), diphenyl acetylene complexes $[Ni(R_2Im)_2(\eta^2\text{-}C_2Ph_2)]$ (R_2 = Me_2, **9**; $^nPr_2$, **10**; Me^iPr, **11**; $^iPr_2$, **12**), and biphenylene complexes $[Ni(R_2Im)_2(2,2'\text{-biphenyl})]$ (R_2 = Me_2, **13**; $^nPr_2$, **14**; Me^iPr, **15**; $^iPr_2$, **16**) in good to excellent yields. These complexes were characterized by ^1H NMR, ^{13}C NMR, IR, and mass spectroscopy as well as elemental analysis.

An analysis of the CO stretching frequencies of the carbonyl complexes **5**−**8** and a comparison to the CO stretches of other known complexes of the type $[NiL_2(CO)_2]$ can serve as a measure of the basicity at the metal atom in these complexes. The values of the carbonyl stretching frequencies of **5**−**8** depend on the alkyl substituent at the nitrogen atom. The carbonyl stretching frequencies of the isopropyl-substituted complex **8** at 1847 and 1927 cm^{-1} are the lowest found in this series (see Table 1) and thus confirm the high metal basicity of the $[Ni(^iPr_2Im)_2]$ complex fragment as compared to other nickel(0) carbonyl complexes of the type $[NiL_2(CO)_2]$. At higher frequencies are the CO stretches of the *n*-propyl (1857 and 1935 cm^{-1}) and the methyl-substituted complex (1851 and 1940 cm^{-1}), suggesting increased donor capabilities of the carbene ligand in the order Me < ^nPr < ^iPr. The overall difference of the data found for alkyl-substituted NHC complexes, however, is relatively small.

The quantification of steric and electronic effects of ligands has a major impact on the development of new and improved ligands for catalysis. Compounds **5**−**8** are well suited to allow a direct comparison of N-heterocyclic carbenes in these complexes with steric or electronic properties of phosphine ligands. The comparison of the CO stretches clearly reveals the better σ-donating capabilities of the alkyl-substituted NHC ligands. On the other hand, the steric demand of the ^nPr- and ^iPr-substituted NHC ligands is in a range similar to the demand of bulky phosphines. Thus, these ligands provide enough steric hindrance to stabilize the metal atom but keep it readily accessible for substrates and further reactions. The widely used aryl-substituted ligands such as Dip_2Im and Mes_2Im are much bulkier and protect the metal atom more efficiently. By way of example, for the reaction of $[Ni(CO)_4]$ with NHCs it is known that 1,3-di(methyl)imidazole-2-ylidene forms the bis(NHC) complex $[Ni(Me_2Im)_2(CO)_2]$,[13] whereas the reaction with sterically more demanding carbene ligands affords four-coordinate mono(NHC) complexes $[Ni(R_2Im)(CO)_3]$ (R = Mes, Dip, cyclohexyl), and the usage of very bulky NHC ligands (R = ^tBu, adamantyl) leads to isolation of unsaturated three-coordinate mono(NHC) carbonyl nickel complexes $[Ni(R_2Im)(CO)_2]$.[18]

Most examples of C−C bond cleavage by transition metal complexes have been stoichiometric, mostly relying on ring strain, prearomaticity, or intramolecular addition in which a C−C bond is in close proximity to the metal atom of the complex.[19] Catalytic C−C bond activation and functionalization is much less common, but it has been shown in some cases that biphenylene is an appropriate substrate for this process.[20−22]

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The insertion of a reactive [L_nM] fragment into the central C−C bond of biphenylene generates a [L_nM(2,2′-biphenyl)] complex with two strong M−aryl bonds, which is thermodynamically feasible. Eisch et al. reported the formation of 9,10-di(phenyl)-phenanthrene by heating of [$(Et_3P)_2Ni$(2,2′-biphenyl)] in the presence of diphenyl acetylene,[20] and Jones et al. published the catalytic formation of 9,10-di(phenyl)phenanthrene by heating a mixture of diphenyl acetylene and biphenylene in the presence of a catalyst precursor such as [$Ni(PPh_3)_2(\eta^2\text{-}C_2Ph_2)$], [$Ni(^iPr_2P-C_2H_4-P^iPr_2)(\eta^2\text{-}C_2Ph_2)$] ($^iPr_2P-C_2H_4-P^iPr_2$ = dippe) or [$Ni(^iPr_2P-C_2H_4-NMe_2)(\eta^2\text{-}C_2Ph_2)$] ($^iPr_2P-C_2H_4-NMe_2$ = PN).[21] The bis-phosphino-substituted complexes [$Ni(dippe)(\eta^2\text{-}C_2Ph_2)$] and [$Ni(PPh_3)_2(\eta^2\text{-}C_2Ph_2)$] produced only small amounts of 9,10-di(phenyl)phenanthrene (2.5% conversion after 40 h at 110 °C using 12.5% of the dippe complex).[21] In these systems, however, the rate reported increases dramatically to a turnover frequency of 3 TO/h (10% catalyst, 70 °C) if molecular oxygen (6 mol %) is present in the reaction mixture. In these cases oxygen was presumably required to remove the bis-phosphino ligand from the metal center and to generate a reactive Ni(0) species. The nickel complex [$Ni(PN)(\eta^2\text{-}C_2Ph_2)$], stabilized with a bidentate hybrid ligand, also turned out to be an effective catalyst for the C−C bond activation in biphenylene. In the presence of 8.3 mol % of this complex, a mixture of biphenylene and diphenyl acetylene was quantitatively converted into 9,10-di(phenyl)phenanthrene within 22.5 h at 70 °C (approximately 0.5 TO/h). For a comparison of the catalytic activity of the carbene-stabilized complexes with the above-mentioned phosphine complexes as well as for a comparison of the catalytic behavior of nickel complexes stabilized with differently substituted alkyl imidazolylidene ligands, we investigated the catalytic conversion of biphenylene and diphenyl acetylene to 9,10-di(phenyl)phenanthrene in some detail.

Complexes **1**−**4** react at room temperature smoothly with equimolar amounts of diphenyl acetylene or biphenylene to afford either the diphenyl acetylene complexes [$Ni(R_2Im)_2(\eta^2\text{-}C_2Ph_2)$] ($R_2$ = Me_2, **9**; $^nPr_2$, **10**; Me^iPr, **11**; $^iPr_2$, **12**) or the products of an insertion of the [$Ni(R_2Im)_2$] complex fragment into the 2,2′ bond of biphenylene, [$Ni(R_2Im)$(2,2′-biphenyl)] (R = Me, **13**; ^nPr, **14**; Me^iPr, **15**; ^iPr, **16**) (see Scheme 3).

The carbon NMR spectra of complexes **9** to **12** reveal significantly shifted resonances of the acetylene carbon atoms and are in all cases in accordance with alkyne complexes with a high degree of π back-bonding into the carbon−carbon multiple bond. The molecular structure of complex **11** is shown in Figure 3. The nickel atom in **11** is coordinated with two imidazolylidene and an alkyne ligand. The $Ni-C_{carben}$ distances of 1.896(6) and 1.915(4) Å are similar to those found for **1**, whereas the $C_{carben}-Ni-C_{carben}$ angle of 109.27(19)° significantly deviates.

The solid-state structure of **13** (Figure 4) shows a distorted square planar complex with a pseudo-2-fold axis bisecting the two carbene ligands and the biphenyl moiety. The distortion from planarity is best defined by a twist angle of 14.0° between the planes through the atoms Ni, C(1), C(6) and Ni, C(11), C(12). Alternatively, the carbon atoms C(1) and C(6) of the carbene ligands lie 0.407 Å above and below the best plane of the almost planar biphenylene moiety. The bond angles at the nickel atom lie in a range between 83.9(2)° and 93.8(2)°.

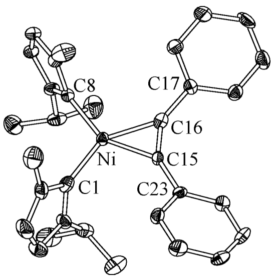

Figure 3. ORTEP diagram of the molecular structure of [$Ni(Me^iPr_2Im)_2(\eta^2\text{-}C_2Ph_2)$] (**11**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni−C(1) 1.896(6), Ni−C(8) 1.915(4), Ni−C(15) 1.882(5), Ni−C(16) 1.890(4), C(1)−Ni−C(8) 109.27(19), C(1)−Ni−C(15) 101.89(15), C(1)−Ni−C(16) 142.54(19), C(8)−Ni−C(15) 148.8(2), C(8)−Ni−C(16) 108.17(18), C(15)−Ni−C(16) 40.65(19), C(15)−C(16)−C(17) 144.5(4), C(15)−C(16)−Ni 69.3(3), C(16)−C(15)−Ni 70.0(3), C(23)−C(15)−Ni 143.1(4), C(17)−C(16)−Ni 146.0(3).

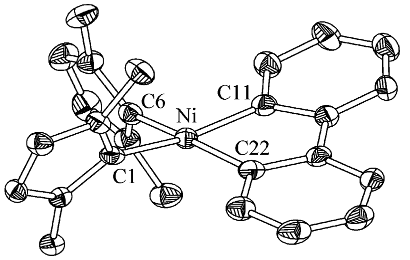

Figure 4. ORTEP diagram of the molecular structure of [$Ni(Me_2Im)$(2,2′-biphenyl)] (**13**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni−C(1) 1.911(4), Ni−C(6) 1.898(4), Ni−C(11) 1.935(4), Ni−C(22) 1.940(4), C(1)−Ni−C(6) 93.66(17), C(1)−Ni−C(11) 167.39(18), C(1)−Ni−C(22) 93.28(16), C(6)−Ni−C(11) 90.62(17), C(6)−Ni−C(22) 170.81(18), C(11)−Ni−C(22) 83.86(16), C(11)−C(12)−Ni 129.1(3), C(11)−C(16)−Ni 115.3(3), C(17)−C(22)−Ni 114.6(3), C(21)−C(22)−Ni 128.5(3).

DFT calculations on the reaction profile of this insertion reaction performed on the reduced model [$Ni_2(H_2Im)_4(COD)$] indicate a thermodynamic preference for the insertion of the nickel biscarbene moiety into the strained 2,2′ bond of biphenylene (Figure 5). According to these calculations, the transfer of the nickel biscarbene complex fragment from the COD complex to biphenylene is exothermic (−30 kJ/mol) and should result in a complex in which this fragment is $\eta^4(C_4)$ coordinated to the four-membered ring of biphenylene. Alternative structures of complexes with precoordinated biphenylene, for example a coordination of the arene ring, are at least 21.7 kJ/mol higher in energy, as shown for an intermediate with $\eta^2(C_6)$-coordinated biphenylene in Figure 5. These intermediates are local minima on the energy surface, but so far we were not able to detect a likely η^4(C4) intermediate spectroscopically. The reaction product of the insertion of the [$Ni(H_2Im)_2$] complex fragment into the 2,2′ bond of biphenylene is 83.0 kJ/mol lower in energy as compared to the η^4(C4) intermediate, whereas the reaction products of a possible C−H activation reaction lie 97.8 and 110.4 kJ/mol, respectively, higher in energy. Thus, the C−C cleavage reactions of biphenylene using the nickel complexes **1**−**4** have a strong thermodynamic driving force, and we were

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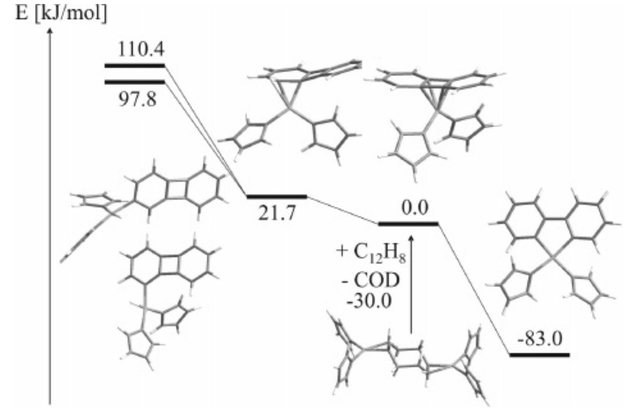
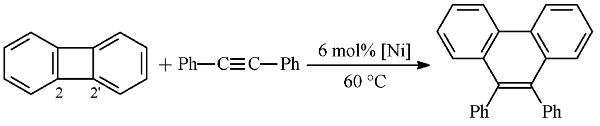


Figure 5. DFT calculations on the reaction of $[Ni_2(H_2Im)_4(COD)]$ with biphenylene: C−H versus C−C activation.

interested to include this C−C activation reaction into catalytic cycles. Therefore, we focused on the performance of the compounds **1**−**4** in the catalytic insertion of internal alkynes into the C−C bond of biphenylene, a reaction that was previously investigated by Jones and co-workers for other nickel complexes.[21]

First investigations have shown that neither the NHC complexes **1**−**4** nor the alkyne compounds **9**−**12** catalyze oligomerization reactions of diphenyl acetylene on a reasonable time scale. The reaction of diphenyl acetylene with 0.1 equiv of $[Ni_2(^iPr_2Im)_4(COD)]$ (**4**) for 3 days in C_6D_6 at 80 °C afforded complex **12** and unreacted alkyne, and no oligomerization product such as hexaphenylbenzene was observed. Another major side reaction, the dimerization of biphenylene, is very slow compared to the catalytic insertion (see below). A catalytic reaction in which tetraphenylene and derivatives of tetraphenylene were formed from biphenylene derivatives was achieved previously by Vollhardt et al. using $[Ni(PMe_3)_2(COD)]$ as a catalyst.[23] The reaction of biphenylene with 7 mol % **4** in C_6D_6 at 80 °C gave after a period of 3 days the dimerization product tetraphenylene in 58% yield. For a comparative investigation of the influence of the NHC nitrogen alkyl substituent of the NHC ligand on the reaction rate of the insertion of diphenyl acetylene into the 2,2′ bond of biphenylene, we monitored this reaction catalyzed with **1**−**4** in detail. We used $[Ni(Me_2Im)_3]$ (**1**) and $[Ni_2(R_2Im)_4(COD)]$ ($R_2 = {}^nPr_2$, **2**; Me^iPr, **3**; $^iPr_2$, **4**) in concentrations of 6 mol % Ni as a catalyst, i.e., 6 mol % of the mononuclear compound and 3 mol % of the dinuclear complexes, in benzene at 60 °C (see eq 1).



(1)

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Time-dependent recorded ^1H NMR spectra in the region between 5.60 and 8.80 ppm for the reaction of biphenylene (characteristic resonances at 6.40 and 6.55 ppm) and diphenyl acetylene using complex $[Ni_2(^nPr_2Im)_4(COD)]$ (**2**) as a catalyst to give 9,10-di(phenyl)phenanthrene (characteristic resonances at 7.55 and 8.44 ppm) are depicted in Figure 6. The reaction is completed after 5 h at 60 °C in benzene. The analysis of this experiment leads to an average TON of 3.3 $mol^{-1}\ h^{-1}$ per nickel atom involved and to an initial rate of $1.46 \times 10^{-4} \pm 1.83 \times 10^{-6}\ s^{-1}$. To identify the reaction product unequivocally, crystals of the resulting colorless solid were grown from toluene, and its molecular structure is shown in Figure 7.

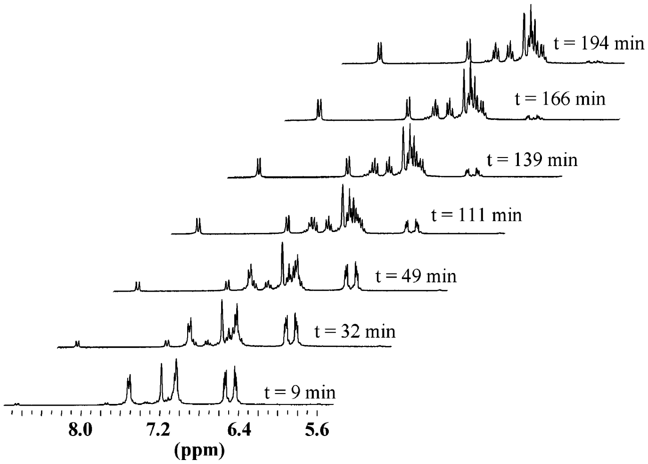

Figure 6. Reaction of biphenylene and diphenyl acetylene using complex $[Ni_2(^nPr_2Im)_4(COD)]$ (**2**) followed by ^1H NMR spectroscopy.

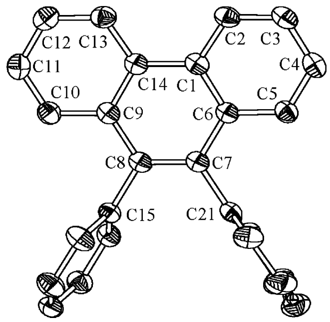

Figure 7. ORTEP diagram of the molecular structure of 9,10-di(phenyl)phenanthrene (**17**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å): C(1)−C(2) 1.411(3), C(1)−C(6) 1.422(3), C(1)−C(14) 1.458(3), C(2)−C(3) 1.373(3), C(3)−C(4) 1.387(3), C(4)−C(5) 1.372(3), C(5)−C(6) 1.413(3), C(6)−C(7) 1.446(3), C(7)−C(8) 1.370(3), C(7)−C(21) 1.499(3), C(8)−C(9) 1.449(3), C(8)−C(15) 1.492(3), C(9)−C(10) 1.410(3), C(9)−C(14) 1.419(3), C(10)−C(11) 1.371(3), C(11)−C(12) 1.394(3), C(12)−C(13) 1.367(3), C(13)−C(14) 1.411(3), C(15)−C(16) 1.390(3), C(15)−C(20) 1.390(3), C(16)−C(17) 1.386(3), C(17)−C(18) 1.375(3), C(18)−C(19) 1.373(3), C(19)−C(20) 1.382(3), C(21)−C(26) 1.388(3), C(21)−C(22) 1.389(3), C(22)−C(23) 1.386(3), C(23)−C(24) 1.373(3), C(24)−C(25) 1.373(3), C(25)−C(26) 1.381(3).

The reaction rate of the formation of 9,10-di(phenyl)phenanthrene critically depends on the nature of the carbene complex employed as a catalyst (see Figure 8). Whereas the usage of $[Ni_2(^nPr_2Im)_4(COD)]$ (**2**) (initial rate $1.46 \times 10^{-4} \pm 1.83 \times 10^{-6}\ s^{-1}$) and $[Ni_2(Me^iPrIm)_4(COD)]$ (**3**) (initial rate $1.67 \times 10^{-4} \pm 3.41 \times 10^{-6}\ s^{-1}$) afforded 9,10-di(phenyl)phenanthrene after approximately 300 min in quantitative yield (based on ^1H NMR spectroscopy), the usage of $[Ni_2(^iPr_2Im)_4(COD)]$ (**4**) gave higher reaction rates (initial rate $3.17 \times 10^{-3} \pm 2.95 \times 10^{-4}\ s^{-1}$). Using this catalyst, the reaction is completed within 19 min. On the other hand, reaction rates significantly decrease if the three-coordinated complex $[Ni(Me_2Im)_3]$ (**1**) was used. Employing the same conditions, the reaction between diphenyl acetylene and biphenylene gave only 58% phenanthrene after 3 days.

As compared to other well-defined nickel-containing catalysts for the insertion of internal alkynes into the 2,2′ bond of

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[23] Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200.

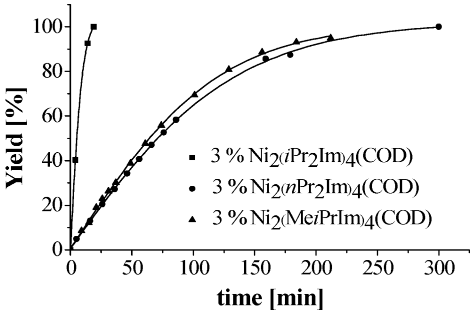

Figure 8. Dependence of the reaction rate of the formation of 9,10-di(phenyl)phrnathrene on the alkyl substituent R in the catalyst {$Ni_2(R_2Im)COD)$}.

biphenylene, our NHC-stabilized complexes seem to work very efficiently for the insertion of diphenyl acetylene into the 2,2′ bond of biphenylene. As mentioned above, the bis-phosphino-substituted complexes [Ni(dippe)(η^2-C_2Ph_2)] (dippe = iPr$_2$P−C$_2$H$_4$−PiPr$_2$) and [Ni(PPh$_3$)$_2$(η^2-C_2Ph_2)] produce only small amounts of 9,10-di(phenyl)phenanthrene (2.5% conversion after 40 h at 110 °C using 12.5% of the dippe complex), but the rate reported for these systems increases to a turnover frequency of 3 TO/h (10% catalyst, 70 °C) in the presence of molecular oxygen.[21a] In the presence of 8.3 mol % [Ni(^{i}Pr$_2$P−C$_2$H$_4$−NMe$_2$)(η^2-C_2Ph_2)] a mixture of biphenylene and diphenyl acetylene was quantitatively converted into 9,10-di(phenyl)-phenanthrene within 22.5 h at 70 °C (approximately 0.5 TO/h).[21c]

For all catalysts employed, we observe at higher catalyst loadings the diphenyl acetylene complexes, presumably the resting states of the catalysts, as the only metal-containing species in the reaction mixture. Details of the reaction mechanism are currently under investigation; we assume, however, that electronic as well as steric factors render complex **4** the best catalyst in this series.

Furthermore, we are currently investigating the catalytic insertion of other alkynes into the 2,2′ bond of biphenylene using [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**4**) as a catalyst. The reaction with 1 equiv of either 3-hexyne or 2-butyne at 80 °C overnight in the presence of 3% **4** leads to 9,10-di(ethyl)phenanthrene (in the case of 3-hexyne) or 9,10-di(methyl)phenanthrene (in the case of 2-butyne) in quantitative yields, based on the proton NMR spectroscopy. In contrast to our observations for the insertion of diphenyl acetylene, cyclooligomerizations of the alkyne are more likely. Using more than 1 equiv of the alkyne (3-hexyne or 2-butyne) in the reaction mixture, traces of the cyclooligomerization product were detected in the reaction mixture. Using an excess of the alkyne, we observe the quantitative formation of the insertion product and the cyclotrimerization product hexaethylbenzene or hexamethylbenzene. Similarly to the catalytic insertions of diphenyl acetylene, alkyne complexes of the type [Ni$_2$(^{i}Pr$_2$Im)$_4$(η^2-C_2R_2)] (R = Me, **18**; Et, **19**) can be detected in solution and have been synthesized for a proper characterization independently. The molecular structure of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C_2Me_2)] (**18**) is shown in Figure 9. The reaction of biphenylene with terminal alkynes such as phenyl acetylene and 1-hexyne with 3% [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**4**) at 80 °C does not afford any insertion product so far, but leaves unreacted biphenylene and some presently not further characterized species in the reaction mixture. The reaction of phenyl acetylene with [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**4**) leads to an η^2-coordinated alkyne complex, which can be characterized by proton and carbon NMR spectroscopy. This complex, however, seems to be stable only in solutions. Removal of the solvent gave a black oil consisting of mixtures of presently not further characterized compounds.

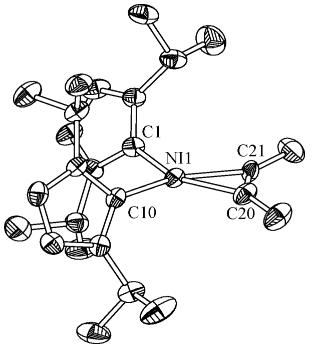

Figure 9. ORTEP diagram of the molecular structure of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C_2Me_2)] (**18**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Molecule 1: Ni(1)−C(1) 1.917(8), Ni(1)−C(10) 1.934(7), Ni(1)−C(21) 1.890(7), Ni(1)−C(20) 1.899(8), C(1)−Ni(1)−C(10) 100.4(3), C(1)−Ni(1)−C(20) 147.5(4), C(1)−Ni(1)−C(21) 107.8(4), C(10)−Ni(1)−C(20) 112.1(4), C(10)−Ni(1)−C(21) 151.7(4), C(20)−Ni(1)−C(21) 39.7(4); Molecule 2: Ni(2)−C(23) 1.890(8), Ni(2)−C(32) 1.906(8), Ni(2)−C(42) 1.859(8), Ni(2)−C(43) 1.865(8), C(23)−Ni(2)−C(32) 100.4(3), C(23)−Ni(2)−C(42) 151.6(4), C(23)−Ni(2)−C(43) 112.1(4), C(32)−Ni(2)−C(42) 108.0(4), C(32)−Ni(2)−C(43) 147.5(4), C(42)−Ni(2)−C(43) 39.6(4); Molecule 3: Ni(3)−C(45) 1.921(9), Ni(3)−C(54) 1.908(9), Ni(3)−C(64) 1.908(9), Ni(3)−C(65) 1.896(9), C(45)−Ni(3)−C(54) 100.3(4), C(45)−Ni(3)−C(64) 148.9(4), C(45)−Ni(3)−C(65) 109.4(4), C(54)−Ni(3)−C(64) 110.8(4), C(54)−Ni(3)−C(65) 150.3(4), C(64)−Ni(3)−C(65) 39.5(4); Molecule 4: Ni(4)−C(67) 1.927(9), Ni(4)−C(76) 1.899(9), Ni(4)−C(86) 1.890(9), Ni(4)−C(87) 1.862(9), C(86)−Ni(4)−C(87) 40.4(4), C(76)−Ni(4)−C(87) 149.3(4), C(76)−Ni(4)−C(86) 108.9(4), C(67)−Ni(4)−C(87) 109.3(4), C(67)−Ni(4)−C(86) 149.6(4), C(67)−Ni(4)−C(76) 101.5(4).

Conclusion

The reaction of [Ni(COD)$_2$] with NHCs critically depends on the steric demand of the nitrogen substituent of the carbene. Whereas Me$_2$Im reacts with [Ni(COD)$_2$] to yield the three-coordinated homoleptic complex [Ni(Me$_2$Im)$_3$] (**1**), imidazole-2-ylidenes with sterically slightly more demanding substituents such as ^{n}Pr$_2$Im or ^{i}Pr$_2$Im afford dinuclear, COD-bridged complexes of the type [Ni$_2$(R$_2$Im)$_4$(COD)] (R$_2$ = ^{n}Pr$_2$, **2**; Me^{i}Pr, **3**; ^{i}Pr$_2$ **4**). Twofold-coordinated, homoleptic complexes [Ni(Mes$_2$Im)$_2$], [Ni(Dip$_2$Im)$_2$], and [Ni(^{t}Bu$_2$Im)$_2$] have been reported earlier for bulky carbene ligands by the groups of Arduengo, Herrmann, and Cloke. The dinuclear, COD-bridged complexes can be isolated in the form of yellow, air- and moisture-sensitive solids and may serve as isolable synthons for the [Ni(R$_2$Im)$_2$] moiety. The transfer of these entities usually takes place under mild conditions in stoichiometric and catalytic transformations. The analysis of CO stretching frequencies of the complexes [Ni(R$_2$Im)$_2$(CO)$_2$] (R$_2$ = Me$_2$, **5**; ^{n}Pr$_2$, **6**, Me^{i}Pr, **7**; ^{i}Pr$_2$, **8**) and a comparison to the CO stretches of other known complexes of the type [NiL$_2$(CO)$_2$] underpin the high metal basicity of the NHC-stabilized complexes; in fact the stretching frequencies obtained for the isopropyl-substituted complex are to our knowledge the lowest observed so far for a complex of the type [NiL$_2$(CO)$_2$]. Complexes **1**−**4** react at room temperature smoothly with equimolar amounts of diphenyl acetylene or biphenylene to afford the diphenyl acetylene complexes [Ni(R$_2$Im)$_2$(η^2-C_2Ph_2)] (R$_2$ = Me$_2$, **9**; ^{n}Pr$_2$, **10**; Me^{i}Pr, **11**; ^{i}Pr$_2$, **12**) or the C−C activation products [Ni(R$_2$Im)$_2$(2,2′-biphenyl)] (R$_2$ = Me$_2$, **13**;

^{n}Pr$_2$, **14**; Me^{i}Pr, **15**; ^{i}Pr$_2$, **16**). Compounds **1**−**4** (as well as **9**−**12**) are efficient catalysts for the insertion of diphenyl acetylene into the C−C bond of biphenylene, a process in which the C−C activation of biphenylene is incorporated into a catalytic cycle. The reaction rate of the formation of 9,10-di(phenyl)phenanthrene depends on the nature of the carbene ligand of the catalyst; by far the highest reaction rates were observed for [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)], **4**. This NHC-stabilized complex is very efficient for the insertion of diphenyl acetylene into the 2,2′ bond of biphenylene and superior compared to other well-defined nickel-containing catalysts for this particular reaction. Currently we are exploring the synthetic and catalytic potential especially of complex **4** in other stoichiometric and catalytic processes.

Experimental Section

General Considerations. All reactions and subsequent manipulations involving organometallic reagents were performed under a nitrogen atmosphere using standard Schlenk techniques as reported previously.[24] Elemental analyses were performed in the microanalytical laboratory of the author's department. EI mass spectra were recorded on a Varian MAT 3830 (70 eV). NMR spectra were recorded on a Bruker AMX 300 and a Bruker AV 400 at 298 K. ^{13}C NMR spectra are broad-band proton-decoupled (^{13}C{^{1}H}). NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Coupling constants are quoted in hertz. Spectra are referenced internally to residual protio-solvent resonances (^{1}H: CDCl$_3$, 7.24 ppm; C$_6$D$_6$, 7.15 ppm) or natural-abundance carbon resonances (^{13}C: CDCl$_3$, 77.0 ppm; C$_6$D$_6$, 128.0 ppm). Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 and are reported in cm^{-1}. Biphenylene was prepared according to a published procedure.[25]

Synthesis of [Ni(Me$_2$Im)$_3$] (1). A solution of Me$_2$Im (1.41 g, 14.6 mmol) in 20 mL of toluene was added to a stirred suspension of [Ni(COD)$_2$] (1.30 g, 4.70 mmol) in 20 mL of toluene at −78 °C. The resulting deep red solution was stirred overnight and allowed to reach room temperature. The reaction mixture was filtered over a pad of Celite, and all volatile material of the mother liquor was removed in vacuo. The remaining red solid was suspended in 10 mL of hexane, and the product was filtered off, washed with 10 mL of hexane, and dried in vacuo to yield 1.10 g (67%) of a deep red solid. Crystals suitable for X-ray diffraction were obtained from hexane/toluene (1:1) solutions of [Ni(Me$_2$Im)$_3$] at −30 °C. Anal. Calcd (found) for C$_{15}$H$_{24}$N$_6$Ni [347.1 g/mol]: C 51.91 (51.85), H 6.97 (6.84), N 24.21 (23.80). EI/MS *m/z* (%): 250 (4) [(Me$_2$Im)$_2$Ni]$^+$, 96 (100) [Me$_2$Im]$^+$. IR ([cm^{-1}]): 351 (w), 465 (w), 544 (w), 639 (s), 672 (m), 693 (m), 749 (m), 794 (m), 1000 (m), 1050 (vs), 1218 (s), 1293 (s), 1333 (m), 1364 (m), 1385 (m), 1427 (m), 2913 (m, br), 3118 (w). ^{1}H NMR (C$_6$D$_6$): δ 3.57 (s, 18 H, C*H*$_3$), 6.31 (s, 6 H, NC*H*C*H*N). ^{13}C NMR (C$_6$D$_6$): δ 36.73 (*C*H$_3$), 117.53 (N*CC*N), 203.71 (N*C*N).

Synthesis of [Ni$_2$(^{n}Pr$_2$Im)$_4$(COD)] (2). A solution of ^{n}Pr$_2$Im (3.27 g, 21.5 mmol) in 50 mL of toluene was added to a stirred suspension of [Ni(COD)$_2$] (3.00 g, 10.9 mmol) in 50 mL of toluene at −78 °C. The solution was stirred overnight and allowed to reach room temperature. The reaction mixture was filtered over a pad of Celite, and all volatiles of the mother liquor were removed in vacuo. The remaining yellow solid was suspended in 50 mL of hexane, filtered off, washed with 30 mL of hexane, and dried in vacuo to yield 5.80 g (65%) of a yellow, air-sensitive powder. Anal. Calcd (found) for C$_{44}$H$_{76}$N$_8$Ni$_2$ [835.0.1 g/mol]: C 63.29 (63.88), H 9.17 (8.74), N 13.42 (13.16). EI/MS *m/z* (%): 362 (20) [(^{n}Pr$_2$Im)$_2$Ni]$^+$, 152 (100) [^{n}Pr$_2$Im)]$^+$, 108 (95) [COD]$^+$. IR ([cm^{-1}]): 378 (w), 551 (m), 659 (m), 671 (s), 696 (s), 747 (m), 771 (w), 795 (m), 840 (w), 865 (m), 900 (m), 925 (m), 1009 (m), 1047 (w), 1083 (s), 1105 (s), 1192 (s), 1217 (vs), 1280 (m), 1301 (m), 1322 (s), 1377 (vs), 1407 (s), 1454 (m), 1500 (s), 1566 (w), 1613 (w), 1676 (m), 2813 (m), 2872 (s), 2918 (s), 2960 (vs), 3121 (w). ^{1}H NMR (C$_6$D$_6$): δ 0.81 (t, 24 H, C*H*$_3$), 1.71 (m, 16 H, NCH$_2$C*H*$_2$), 2.19 (s, br, 4 H, COD-C*H*$_2$), 2.56 (d, 4 H, *J* = 10.5 Hz, COD-C*H*$_2$), 2.95 (d, 4 H, *J* = 7.1 Hz, COD-C*H*), 4.08 (m, 16 H, NC*H*$_2$), 6.39 (s, 8 H, NC*H*C*H*N). ^{13}C NMR (C$_6$D$_6$): δ 12.32 (*C*H$_3$), 25.94 (NCH$_2$*C*H$_2$), 39.40 (COD-*C*H$_2$), 52.63 (N*C*H$_2$), 55.59 (COD-*C*H), 118.18 (N*CC*N), 207.88 (N*C*N).

Synthesis of [Ni$_2$(Me^{i}PrIm)$_4$(COD)] (3). A solution of Me^{i}PrIm (1.29 g, 10.4 mmol) in 20 mL of THF was added at −78 °C to a stirred suspension of [Ni(COD)$_2$] (1.41 g, 10.9 mmol) in 40 mL of THF. The solution was stirred overnight and allowed to reach room temperature. The reaction mixture was filtered over a pad of Celite, and all volatiles of the mother liquor were removed in vacuo. The remaining yellow solid was suspended in 30 mL of hexane, and the product was filtered off, washed with 10 mL of hexane, and dried in vacuo to give 840 mg (45%) of a yellow, very air-sensitive powder. Anal. Calcd (found) for C$_{36}$H$_{60}$N$_8$Ni$_2$ [722.3 g/mol]: C 59.86 (59.97), H 8.37 (8.14), N 15.51 (15.65). EI/MS *m/z* (%): 306 (4) [(Me^{i}PrIm)$_2$Ni]$^+$, 124 (100) [Me^{i}PrIm]$^+$, 108 (60) [COD]$^+$. IR ([cm^{-1}]): 510 (w), 549 (w), 626 (w), 662 (m), 673 (s), 692 (w), 719 (w), 786 (m), 837 (w), 878 (w), 923 (w), 986 (w), 1005 (w), 1047 (m), 1070 (m), 1091 (w), 1127 (w), 1216 (s), 1242 (s), 1309 (m), 1388 (s), 1429 (m), 1566 (w), 2824 (m), 2896 (s), 2966 (m), 3069 (w), 3199 (w). ^{1}H NMR (C$_6$D$_6$): δ 1.18 (d, 24 H,$^3J_{\mathrm{HH}}$ = 6.6 Hz, ^{i}Pr-C*H*$_3$), 2.26 (m, br, 4 H, COD-C*H*$_3$), 2.58 (d, 4 H, *J* = 10.7 Hz, COD-C*H*$_3$), 3.01 (d, 4 H, *J* = 7.5 Hz, COD-C*H*), 3.50 (s, 12 H, N-C*H*$_3$), 5.48 (sept, 4 H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, ^{i}Pr-C*H*), 6.31 (d, 4 H, $^3J_{\mathrm{HH}}$ = 1.9 Hz, NC*H*CHN), 6.39 (d, 4 H, $^3J_{\mathrm{HH}}$ = 1.9 Hz, NCHC*H*N). ^{13}C NMR (C$_6$D$_6$): δ 24.26 (^{i}Pr-*C*H$_3$), 37.73 (N-*C*H$_3$), 39.39 (COD-*C*H$_2$), 51.19 (^{i}Pr-*C*H), 55.21 (COD-*C*H), 113.99 (N*C*CN), 120.23 (NC*C*N) 207.91 (N*C*N).

In the course of the syntheses of **3**, the compound **[Ni(Me^{i}PrIm)$_2$(COD)]** was detected in various amounts (up to 15%) as a side product. ^{1}H NMR (C$_6$D$_6$): 1.13 (d, 12 H, $^3J_{\mathrm{HH}}$ = 6.8 Hz, ^{i}Pr-CH$_3$), 2.43 (s, 8 H, COD-C*H*$_2$), 3.48 (s, 6 H, N-C*H*$_3$), 4.44 (s, 4 H, COD-C*H*), 5.37 (sept, 2 H, $^3J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-C*H*), 6.31 (d, 2 H, $^3J_{\mathrm{HH}}$ = 1.9 Hz, NC*H*CHN), 6.37 (d, 2 H, $^3J_{\mathrm{HH}}$ = 1.9 Hz, NCHC*H*N).

Synthesis of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (4). A solution of 1,3-diisopropylimidazol-2-ylidene (12.2 mL, 80.3 mmol) in 50 mL of THF was cooled to −78 °C and added at this temperature to a solution of [Ni(COD)$_2$] (11.0 g, 40.0 mmol) in 300 mL of THF. The temperature of the reaction mixture was raised to room temperature overnight. Insoluble material was filtered off, and all volatile material of the filtrate was removed in vacuo. The yellow residue was suspended in 100 mL of hexane, filtered off, washed twice with 30 mL of hexane, and dried in vacuo. Yield: 14.7 g (87%) of a yellow powder. Anal. Calcd (found) for C$_{44}$H$_{76}$N$_8$Ni$_2$ [834.5 g/mol]: C 63.33 (63.56), H 9.18 (9.09), N 13.34 (12.99). EI/MS *m/z* (%): 362.2 (24) [(^{i}Pr$_2$Im)$_2$Ni]$^+$, 320.1 (8) [(^{i}Pr$_2$Im)$_2$Ni-Pr]$^+$. IR ([cm^{-1}]): 3216 (w), 2964 (s), 2925 (s), 2814 (m), 1659 (w), 1599 (w), 1466 (m), 1410 (s), 1393 (s), 1366 (m), 1279 (m), 1259 (s), 1217 (vs), 1130 (m), 1085 (w), 1006 (m), 982 (m), 925 (w), 875 (w), 793 (m), 673 (s), 549 (m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 1.19 (d, 48 H, $^3J_{\mathrm{HH}}$ = 6.8 Hz, ^{i}Pr-C*H*$_3$), 2.21 (m, 4 H, COD-C*H*$_2$), 2.42 (d, 4 H, *J* = 10.5 Hz, COD-C*H*$_2$), 2.89 (d, 4 H, *J* = 7.2 Hz, COD-C*H*), 5.51 (sept, 8 H, $^3J_{\mathrm{HH}}$ = 6.8 Hz ^{i}Pr-C*H*), 6.50 (s, 8 H, NC*H*C*H*N). ^{13}C NMR (C$_6$D$_6$): δ 23.81 (^{i}Pr-*C*H$_3$), 23.98 (^{i}Pr-*C*H$_3$), 31.96 (COD-*C*H$_2$), 33.52 (COD-*C*H$_2$), 38.57 (COD-*C*H), 50.58 (^{i}Pr-*C*H), 50.69 (^{i}Pr-*C*H), 54.57 (COD-*C*H), 113.93 (N*C*CN), 114.29 (N*C*CN), 204.19 (N*C*N), 205.28 (N*C*N).

In the course of the synthesis of **4**, the compound **[Ni(^{i}Pr$_2$Im)$_2$(COD)]** was detected in various amounts (up to 5%) as a side product. ^{1}H NMR (C$_6$D$_6$): 1.18 (d, 24 H, $^3J_{\mathrm{HH}}$ = 6.8 Hz, ^{i}Pr-C*H*$_3$),

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2.42 (s, 8 H, COD-CH_2), 4.41 (s, 4 H, COD-CH), 5.40 (sept, 4 H, $^3J_{HH} = 6.8$ Hz, ^{i}Pr-CH), 6.48 (s, 4 H, NCHCHN).

Synthesis of [Ni(Me$_2$Im)$_2$(CO)$_2$] (5). Carbon monoxide was passed through a solution of [Ni(Me$_2$Im)$_3$] (300 mg, 0.86 mmol) in 30 mL of toluene at room temperature until the color changed from deep red to yellow. Traces of insoluble material were filtered off, and all volatile material of the filtrate was removed in vacuo. The remaining solid was suspended in 5 mL of hexane, and the product was filtered off and washed twice with 5 mL of hexane to yield 160 mg (61%) of [Ni(Me$_2$Im)$_2$(CO)$_2$] as a yellow powder. Anal. Calcd (found) for $C_{12}H_{16}N_4O_2Ni$ [307.0 g/mol]: C 46.95 (46.31), H 5.25 (4.82), N 18.25 (18.04). EI/MS *m*/*z* (%): 306 (8) [M]$^+$, 278 (40) [(Me$_2$Im)$_2$Ni(CO)]$^+$, 250 (100) [(Me$_2$Im)$_2$Ni]$^+$. IR ([cm^{-1}]): 326 (w), 454 (w), 507 (w), 651 (m), 665 (m), 705 (s), 716 (s), 747 (m), 814 (w), 1072 (m), 1101 (m), 1223 (s), 1362 (m), 1394 (m), 1446 (m), 1529 (w), 1569 (w), 1599 (w), 1628 (w), 1665 (w), 1851 (vs, ν_{CO}), 1940 (vs, ν_{CO}), 2941 (m), 3132 (w). ^{1}H NMR (C$_6$D$_6$): δ 3.23 (s, 12 H, CH_3), 6.24 (s, 4 H, NCHCHN). ^{13}C NMR (C$_6$D$_6$): δ 37.74 (CH$_3$), 120.27 (NCCN), 199.78 (NCN), 205.76 (CO).

Synthesis of [Ni(^{n}Pr$_2$Im)$_2$(CO)$_2$] (6). Carbon monoxide was passed through a solution of [Ni$_2$(^{n}Pr$_2$Im)$_4$(COD)] (363 mg, 0.47 mmol) in 30 mL of toluene at room temperature. All volatile material was removed in vacuo to afford 354 mg (90%) of [Ni(^{n}Pr$_2$Im)$_2$(CO)$_2$] as a yellow powder. EI/MS *m*/*z* (%): 390 (10) [(^{n}Pr$_2$Im)$_2$Ni(CO)]$^+$, 362 (100) [(^{n}Pr$_2$Im)$_2$Ni]$^+$. IR ([cm^{-1}]): 454 (w), 476 (w), 508 (w), 652 (m), 665 (m), 705 (s), 717 (s), 747 (w), 813 (w), 1001 (w), 1071 (m), 1111 (m), 1223 (s), 1298 (w), 1347 (m), 1362 (m), 1394 (m), 1446 (s), 1529 (w), 1851 (vs, ν_{CO}), 1935 (vs, ν_{CO}), 2942 (s), 3129 (m). ^{1}H NMR (C$_6$D$_6$): δ 0.75 (t, 12 H, CH_3), 1.54 (m, 8 H, NCH$_2$CH_2), 3.86 (t, 8 H, NCH_2), 6.34 (s, 4 H, NCHCHN). ^{13}C NMR (C$_6$D$_6$): δ 12.02 (CH$_3$), 25.13 (NCH$_2$$CH_2$), 53.11 (N$CH_2$), 120.00 (N$CC$N), 199.64 (N$C$N), 206.22 (CO).

Synthesis of [Ni(Me^{i}Pr$_2$Im)$_2$(CO)$_2$] (7). Carbon monoxide was passed through a solution of [Ni$_2$(Me^{i}PrIm)$_4$(COD)] (300 mg, 0.42 mmol) in 30 mL of THF at room temperature. All volatile material was removed in vacuo, and the residue was suspensed in hexane, filtered off, and dried in vacuo to afford 180 mg (59%) of [Ni(Me^{i}PrIm)$_2$(CO)$_2$]. EI/MS *m*/*z* (%): 334 (5) [(Me^{i}PrIm)$_2$Ni(CO)]$^+$, 306 (49) [(Me^{i}PrIm)$_2$Ni], 210 (7) [(Me^{i}PrIm)Ni(CO)]$^+$. IR ([cm^{-1}]): 472 (w), 517 (w), 624 (w), 668 (w), 681 (w), 718 (m), 800 (s), 877 (w), 993 (m), 1023 (m), 1080 (s), 1216 (s), 1261 (s), 1328 (m), 1369 (m), 1394 (m), 1437 (m), 1463 (m), 1630 (w), 1855 (vs, ν_{CO}), 1939 (vs, ν_{CO}), 2972 (s), 3120 (m), 3158 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.01 (s, 24 H, $^3J_{HH} = 6.9$ Hz, ^{i}Pr-CH_3), 3.29 (s, 6 H, N-CH_3), 5.23 (sept, 2 H, $^3J_{HH} = 6.9$ Hz, ^{i}Pr-CH), 6.24 (d, 2 H, $^3J_{HH} = 2.0$ Hz, NCHCHN), 6.37 (d, 2 H, $^3J_{HH} = 2.0$ Hz, NCHCHN). ^{13}C NMR (C$_6$D$_6$): δ 23.52 (^{i}Pr-CH$_3$), 38.42 (N-CH$_3$), 52.02 (^{i}Pr-CH), 115.52 (NCCN), 121.68 (NCCN), 199.46 (NCN), 206.18 (CO).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(CO)$_2$] (8). Carbon monoxide was passed through a solution of [Ni$_2$(^{n}Pr$_2$Im)$_4$(COD)] (363 mg, 0.42 mmol) in 30 mL of toluene at room temperature. All volatile material was removed in vacuo to afford 310 mg (88%) of a yellow powder. Anal. Calcd (found) for $C_{20}H_{32}N_4NiO_2$ [419.2 g/mol]: C 57.31 (56.94), H 7.69 (7.65), N 13.37 (12.95). IR ([cm^{-1}]): 473 (w), 507 (w), 572 (w), 672 (s), 712 (s), 725 (m), 800 (w), 882 (m), 989 (s), 1016 (m), 1079 (m), 1134 (m), 1216 (vs), 1248 (m), 1285 (s), 1367 (s), 1398 (s), 1415 (s), 1466 (m), 1847 (vs, ν_{CO}), 1927 (vs, ν_{CO}), 2872 (m), 2931 (m), 2979 (s), 3107 (w), 3142 (w), 3173 (w). ^{1}H NMR (C$_6$D$_6$): δ 1.05 (d, 24 H, $^2J_{HH} = 6.8$ Hz, CH_3), 5.39 (sept, 4 H, $^5J_{HH} = 6.8$ Hz, ^{i}Pr-CH), 6.49 (s, 4 H, NCHCHN). ^{13}C NMR (C$_6$D$_6$): δ 23.63 (^{i}Pr-CH$_3$), 51.68 (^{i}Pr-CH), 116.19 (NCCN), 198.01 (CO), 205.80 (NCN).

Synthesis of [Ni(Me$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] (9). A mixture of [Ni(Me$_2$Im)$_3$] (346 mg, 1.00 mmol) and diphenyl acetylene (178 mg, 1.00 mmol) was dissolved in 20 mL of toluene at room temperature and stirred overnight. Afterward, all volatile material was removed in vacuo, and the remaining red solid was suspended in 15 mL of hexane. The product was filtered off and dried in vacuo to yield 197 mg (46%) of [Ni(Me$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] as a deep red solid. Anal. Calcd (found) for $C_{24}H_{26}N_4Ni$ [429.2]: C 67.16 (66.84), H 6.11 (6.19), N 13.05 (12.89). EI/MS *m*/*z* (%): 428 (10) [M]$^+$, 250 (87) [(Im^{Me})$_2$Ni]$^+$. IR ([cm^{-1}]): 464 (w), 513 (w), 555 (w), 599 (m), 626 (w), 659 (m), 676 (m), 694 (s), 717 (m), 731 (m), 759 (s), 804 (m), 907 (w), 997 (m), 1022 (m), 1075 (s), 1112 (s), 1150 (w), 1165 (w), 1222 (s), 1260 (m), 1344 (s), 1366 (s), 1393 (m), 1438 (m), 1479 (s), 1523 (w), 1585 (s), 1666 (w), 1737 (m), 1758 (m), 1871 (w), 2931 (m), 2999 (m), 3067 (m), 3101 (w), 3120 (m), 3153 (w). ^{1}H NMR (C$_6$D$_6$): δ 3.35 (s, 12 H, CH_3), 6.21 (s, 4 H, NCHCHN), 7.02 (m, 2H, aryl-H_p), 7.23 (m, 4 H, aryl-H_m), 7.61 (d, 4 H, aryl-H_o). ^{13}C NMR (C$_6$D$_6$): δ 36.88 (CH$_3$), 119.84 (NCCN), 123.99 (aryl-C_p), 128.27 (aryl-C_m), 128.65 (aryl-C$_o$) 138.68 ($C{\equiv}C$), 139.17 (aryl-C_i), 204.15 (NCN).

Synthesis of [Ni(^{n}Pr$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] (10). A mixture of [Ni$_2$(^{n}Pr$_2$Im)$_4$(COD)] (363 mg, 0.47 mmol) and diphenyl acetylene (178 mg, 1.00 mmol) was dissolved in 20 mL of toluene and stirred overnight. During this time a deep red solution formed, which was filtered over a pad of Celite. All volatile material of the mother liquor was removed in vacuo, and the remaining red solid was suspended in 10 mL of hexane. The product was filtered off, washed with 10 mL of hexane, and dried in vacuo to give 320 mg (63%) of [Ni(^{n}Pr$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] as a purple solid. Anal. Calcd (found) for $C_{32}H_{42}N_4Ni$ [541.4 g/mol]: C 70.99 (70.79), H 7.82 (7.58), N 10.35 (10.08). EI/MS *m*/*z* (%): 540 (15) [M]$^+$. IR ([cm^{-1}]): 499 (w), 555 (w), 599 (m), 628 (m), 669 (m), 681 (s), 691 (s), 705 (m), 721 (m), 757 (s), 804 (m), 866 (m), 895 (m), 996 (m), 1022 (m), 1048 (m), 1064 (m), 1076 (m), 1112 (m), 1190 (m), 1227 (s), 1245 (w), 1272 (m), 1327 (m), 1354 (s), 1389 (s), 1410 (m), 1436 (m), 1454 (m), 1542 (s), 1735 (m), 1755 (m), 1804 (w). 1875 (w), 1938 (w), 2873 (s), 2931 (s), 2962 (s), 3002 (w), 3018 (w), 3050 (w), 3068 (m). ^{1}H NMR (C$_6$D$_6$): δ 0.66 (t, 12 H, CH_3), 1.56 (m, 8 H, CH_2), 4.02 (t, 8 H, NCH_2), 6.43 (s, 8 H, NCHCHN), 7.00 (m, 2 H, aryl-H_p), 7.19 (m, 4 H, aryl-H_m), 7.54 (d, 4 H, aryl-H_o). ^{13}C NMR (C$_6$D$_6$): δ 11.38 (CH$_3$), 24.10 (CH$_2$), 51.95 (NCH$_2$), 118.59 (NCCN), 123.90 (aryl-C_p), 128.09 (aryl-C_m), 128.69 (aryl-C$_o$) 138.46 ($C{\equiv}C$), 138.87 (aryl-C_i), 202.85 (NCN).

Synthesis of [Ni(Me^{i}PrIm)$_2$(η^2-C$_2$Ph$_2$)] (11). A mixture of [Ni$_2$(Me^{i}PrIm)$_4$(COD)] (361 mg, 0.50 mmol) and diphenyl acetylene (178 mg, 1.00 mmol) was dissolved in 20 mL of toluene and stirred overnight. During this time a deep red solution formed, which was filtered over a pad of Celite. All volatile material of the mother liquor was removed in vacuo, and the remaining red solid was suspended in 10 mL of hexane. The product was filtered off, washed with 10 mL of hexane, and dried in vacuo to give 315 mg (62%) of [Ni(Me^{i}PrIm)$_2$(η^2-C$_2$Ph$_2$)] in the form of a deep red solid. Crystals suitable for X-ray diffraction were obtained from saturated diethyl ether solutions of [Ni(Me^{i}PrIm)$_2$(η^2-C$_2$Ph$_2$)] at −40 °C. Anal. Calcd (found) for $C_{28}H_{34}N_4Ni$ [485.3 g/mol]: C 69.30 (68.97), H 7.06 (6.88), N 11.54 (11.84). EI/MS *m*/*z* (%): 484 (2) [M − H]$^+$, 306 (100) [(Me^{i}PrIm)$_2$Ni]$^+$. IR ([cm^{-1}]): 412 (w), 506 (w), 557 (w), 595 (m), 627 (m), 682 (s), 693 (m), 719 (m), 740 (m), 763 (m), 819 (m), 993 (w), 1024 (w), 1078 (w), 1094 (w), 1105 (w), 1129 (w), 1167 (w), 1214 (s), 1256 (m), 1273 (w), 1322 (m), 1366 (w), 1394 (s), 1434 (m), 1478 (m), 1505 (w), 1536 (w), 1584 (m), 1639 (w), 1730 (w), 1755 (m, $\nu_{C\equiv C}$), 2868 (m), 2930 (m), 2966 (s), 3066 (w), 3126 (m), 3150 (w). ^{1}H NMR (C$_6$D$_6$): δ 0.99 (d, 12 H, $^3J_{HH} = 6.9$ Hz, ^{i}Pr-CH$_3$), 3.48 (s, 6 H, N-CH_3), 5.36 (sept, 2 H, $^3J_{HH} = 6.9$ Hz, ^{i}Pr-CH), 6.33 (d, 2 H, $^3J_{HH} = 1.9$ Hz, NCHCHN), 6.41 (d, 2 H, $^3J_{HH} = 1.9$ Hz, NCHCHN), 7.02 (m, 2H, aryl-H_p), 7.22 (m, 4 H, aryl-H_m), 7.60 (d, 4 H, aryl-H_o). ^{13}C NMR (C$_6$D$_6$): δ 23.79 (^{i}Pr-CH$_3$), 37.66 (N-CH$_3$), 51.90 (^{i}Pr-CH),

115.24 (N*C*CN), 121.15 (NC*C*N), 124.73 (aryl-C_p), 129.03 (aryl-C_m), 129.48 (aryl-C_o), 139.37 ($C\equiv C$), 139.75 (aryl-C_i), 203.58 (N*C*N).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] (12). A mixture of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (417 mg, 0.50 mmol) and diphenyl acetylene (178 mg, 1.00 mmol) was dissolved in toluene (20 mL) and stirred overnight. Undissolved components were filtered over a pad of Celite, and all volatiles of the filtrate were removed in vacuo to afford 310 mg (57%) of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] as a deep red powder. Anal. Calcd (found) for $C_{32}H_{42}N_4Ni$ [541.4 g/mol]: C 70.99 (70.97), H 7.82 (7.70), N 10.35 (9.56). EI/MS *m*/*z* (%): 540 (1) $[M - H]^+$,362.1 (15) [(^{i}Pr$_2$Im)$_2$Ni − H]$^+$. IR ([cm^{-1}]): 556 (m), 668 (m), 697 (m), 763 (e), 911 (w), 1006 (w), 1013 (w), 1128 (w), 1214 (vs), 1258 (m), 1274 (m), 1395 (m), 1413 (m), 1472 (m), 1490 (m), 1576 (m), 1741 (m, $\nu_{C\equiv C}$), 2866 (m), 2932 (m), 2966 (m), 3049 (w). ^{1}H NMR (400 MHz, C_6D_6): δ 1.03 (d, 24 H, CH_3), 5.53 (sept, 4 H, ^{i}Pr-C*H*), 6.55 (s, 4 H, NC*H*C*H*N), 7.02 (m, 2H, aryl-H_p), 7.19 (m, 4 H, aryl-H_m), 7.61 (d, 4 H, aryl-H_o). ^{13}C NMR (100 MHz, C_6D_6): δ 23.92 (CH$_3$), 51.78 (^{i}Pr-*C*H), 115.78 (N*CC*N), 124.60 (aryl-C_p), 129.50 (aryl-C_m), 132.60 (aryl-C_o) 139.26 ($C\equiv C$), 139.69 (aryl-C_i), 201.49 (N*C*N).

Synthesis of [Ni(Me$_2$Im)$_2$(2,2′-biphenylene)] (13). [Ni(Me$_2$Im)$_3$] (347 mg, 1.00 mmol) and biphenylene (152 mg, 1.00 mmol) were dissolved in toluene (20 mL) and stirred overnight. During this time a bright yellow solid was formed, which was filtered off, washed with 20 mL of hexane, and dried in vacuo to yield 340 mg (84%) of [Ni(Me$_2$Im)$_2$(2,2′-biphenylene)] as a bright yellow solid. Crystals suitable for X-ray diffraction can be obtained from saturated solutions of **13** in CH_2Cl_2 at −40 °C. Anal. Calcd (found) for $C_{22}H_{24}N_4Ni$ [403.2 g/mol]: C 65.54 (65.23), H 6.00 (6.14), N 13.89 (13.55). EI/MS *m*/*z* (%): 402 (37) $[M]^+$. IR ([cm^{-1}]): 411 (m), 455 (m), 480 (m), 494 (m), 616 (m), 677 (s), 699 (s), 727 (s), 744 (s), 816 (w), 856 (w), 994 (m), 1008 (m), 1018 (m), 1074 (m), 1120 (m), 1152 (w), 1220 (s), 1264 (m), 1309 (w), 1365 (m), 1379 (m), 1393 (m), 1417 (m), 1451 (s), 1530 (w), 1572 (w), 1642 (w), 1666 (w), 1711 (w), 1892 (w), 2942 (m), 2973 (m), 3010 (m), 3036 (s), 3103 (m), 3123 (m), 3156 (w). ^{1}H NMR (CD_2Cl_2): δ 3.85 (s, 12 H, N-CH_3), 5.86 (m, 2 H, aryl-H_m), 6.50 (m, 2 H, aryl-H_p), 6.81 (m, 2 H, aryl-H_m), 6.94 (s, 4 H, NC*H*C*H*N), 7.18 (m, 2 H, aryl-H_o). ^{13}C NMR (CD_2Cl_2): δ 37.85 (N-CH$_3$), 117.85 (aryl-C_p), 121.75 (N*CC*N), 123.29 (aryl-C_m), 125.18 (aryl-C_m), 138.48 (aryl-C_o), 160.03 (aryl-C_o), 172.12 (aryl-C_i), 194.99 (N*C*N).

Synthesis of [Ni(^{n}Pr$_2$Im)$_2$(2,2′-biphenylene)] (14). [Ni$_2$(^{n}Pr$_2$Im)$_4$(COD)] (420 mg, 0.50 mmol) and biphenylene (152 mg, 1.00 mmol) were dissolved in toluene (20 mL) and stirred overnight. Undissolved components were removed by filtration through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The remaining orange solid was suspended in 20 mL of hexane and the undissolved product was filtered off and dried in vacuo to afford 320 mg (62%) of [Ni(^{n}Pr$_2$Im)$_2$(2,2′-biphenylene)] as an orange solid. EI/MS *m*/*z* (%): 514 (15) $[M]^+$, 362 (25) [Ni(^{n}Pr$_2$Im)$_2$]$^+$. IR ([cm^{-1}]): 393 (w), 416 (w), 484 (m), 615 (m), 683 (s), 699 (s), 735 (vs), 753 (m), 770 (w), 802 (m), 831 (w), 901 (m), 995 (m), 1008 (m), 1017 (m), 1045 (w), 1080 (m), 1107 (m), 1126 (m), 1148 (w), 1202 (s), 1231 (vs), 1275 (w), 1304 (m), 1413 (s), 1454 (s), 1566 (m), 1659 (w), 1786 (w), 1819 (w), 1855 (w), 1887 (w), 1918 (w), 2872 (s), 2930 (s), 2966 (vs), 3035 (s), 3100 (m), 3125 (m), 3148 (w). ^{1}H NMR (C_6D_6): δ 0.58 (t, 12 H, $^3J_{HH}$ = 7.5 Hz, CH_3), 1.53 (m, 8 H, CH_2CH$_3$), 3.78 (m, 4 H, N-CH_2), 4.26 (m, 4 H, N-CH_2), 6.22 (m, 2 H, aryl-H_m), 6.33 (s, 4 H, NC*H*C*H*N), 7.00 (m, 2 H, aryl-H_p), 7.19 (m, 2 H, aryl-H_m), 7.68 (m, 2 H, aryl-H_o). ^{13}C NMR (C_6D_6): δ 12.07 (CH$_3$), 24.30 (CH$_2$CH$_3$), 52.91 (N-CH$_2$), 119.42 (aryl-C_p), 120.08 (N*CC*N), 124.60 (aryl-C_m), 125.57 (aryl-C_m), 140.20 (aryl-C_o), 161.62 (aryl-C_o), 173.25 (aryl-C_i), 196.34 (N*C*N).

Synthesis of [Ni(Me^{i}PrIm)$_2$(2,2′-biphenylene)] (15). [Ni$_2$(Me^{i}PrIm)$_4$(COD)] (361 mg, 0.50 mmol) and biphenylene (152 mg, 1.00 mmol) were dissolved in toluene (20 mL) and stirred overnight. During this time a bright yellow solid was formed, which was filtered off, washed with 20 mL of hexane, and dried in vacuo to yield 420 mg (91%) of [Ni(Me^{i}PrIm)$_2$(2,2′-biphenylene)] as a bright yellow solid. Anal. Calcd (found) for $C_{26}H_{32}N_4Ni$ [459.3 g/mol]: C 68.00 (67.57), H 7.02 (6.67), N 12.20 (12.54). EI/MS *m*/*z* (%): 458 (61) $[M]^+$, 306 (100) [(Me^{i}PrIm)$_2$Ni]$^+$, 182 (48) [(Me^{i}PrIm)Ni]$^+$. IR ([cm^{-1}]): 412 (w), 475 (w), 515 (w), 685 (m), 697 (m), 727 (s), 810 (w), 881 (w), 1000 (m), 1020 (m), 1081 (m), 1110 (w), 1133 (w), 1209 (vs), 1274 (w), 1341 (m), 1368 (m), 1393 (s), 1438 (s), 1521 (w), 1571 (w), 2870 (w), 2933 (m), 2970 (s), 3038 (s), 3099 (w), 3129 (w). ^{1}H NMR (CD_2Cl_2): δ 0.82 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr-CH_3), 1.38 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr-CH_3), 3.92 (s, 6 H, N-CH_3), 5.08 (sept, 2 H, $^3J_{HH}$ = 6.6 Hz, NC*H*C*H*N), 5.91 (m, 2 H, aryl-H_m), 6.51 (m, 2 H, aryl-H_p), 6.76 (m, 2 H, aryl-H_m), 6.89 (d, 2 H, $^3J_{HH}$ = 1.9 Hz, NC*H*CHN), 6.98 (d, 2 H, $^3J_{HH}$ = 1.9 Hz, NCHC*H*N) 7.13 (m, 2 H, aryl-H_o). ^{13}C NMR (CD_2Cl_2): δ 22.41 (^{i}Pr-CH_3), 23.54 (^{i}Pr-CH_3), 38.04 (N-CH_3), 51.68 (^{i}Pr-C*H*), 115.74 (aryl-C_p), 117.73 (N*C*CN), 117.81 (NC*C*N), 122.58 (aryl-C_m), 123.16 (aryl-C_m), 139.02 (aryl-C_o), 160.01 (aryl-C_o), 172.48 (aryl-C_i), 193.00 (N*C*N).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(2,2′-biphenylene)] (16). [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (420 mg, 0.50 mmol) and biphenylene (152 mg, 1.00 mmol) were dissolved in toluene (20 mL) and stirred overnight. Undissolved components were filtered off over a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The remaining orange solid was washed with small portions of hexane and dried in vacuo to afford 400 mg (78%) of an orange powder. Anal. Calcd (found) for $C_{30}H_{40}N_4Ni$ [515.4 g/mol]: C 69.92 (69.34), H 7.82 (7.95), N 10.87 (11.21). EI/MS *m*/*z* (%): 362 (49) [Ni(^{i}Pr$_2$Im)$_2$]$^+$. IR ([cm^{-1}]): 575 (w), 669 (m), 676 (m), 692 (m), 708 (m), 735 (s), 878 (w), 991 (m), 1018 (m), 1107 (m), 1131 (m), 1216 (vs), 1258 (w), 1294 (m), 1369 (m), 1390 (s), 1407 (s), 1417 (s), 1467 (m), 1570 (m), 2871 (m), 2929 (s), 2971 (vs), 3034 (s), 3098 (m), 3130 (w), 3159 (m). ^{1}H NMR (C_6D_6): δ 0.70 (d, 12 H, CH_3), 1.14 (d, 12 H, CH_3), 5.43 (sept, 4 H, ^{i}Pr-C*H*), 6.37 (d, 2 H, aryl-H_m) 6.39 (s, 4 H, NC*H*C*H*N), 6.97 (m, 2 H, aryl-H_p), 7.18 (m, 2 H, aryl-H_m), 7.70 (m, 2 H, aryl-H_o). ^{13}C{^{1}H} NMR (C_6D_6): δ 23.26 (^{i}Pr-CH$_3$), 23.86 (^{i}Pr-CH$_3$), 52.07 (^{i}Pr-*C*H), 116.76 (N*CC*N), 119.30 (aryl-C_p), 124.52 (aryl-C_m), 125.31 (aryl-C_m), 141.05 (aryl-C_o), 161.61 (aryl-C_o), 173.51 (aryl-C_i), 193.47 (N*C*N).

NMR Experiments for the Catalytic Conversion of Biphenylene and Diphenyl Acetylene to 9,10-Di(phenyl)phenanthrene in the Presence of 1−4. In a NMR tube, 36.0 mg (0.20 mmol) of diphenyl acetylene, 30.4 mg (0.20 mmol) of biphenylene, and 0.006 mmol of compounds **2**−**4** (0.012 mmol of compound **1**) were dissolved in 1 mL of deuterobenzene and immediately transferred into the NMR spectrometer with a preheated (60 °C) probehead. The course of the reaction was monitored by proton NMR spectroscopy.

Synthesis of 9,10-Di(phenyl)phenanthrene (17) from Biphenylene. Biphenylene (456 mg, 3.00 mmol), diphenyl acetylene (543 mg, 3.00 mmol), and [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (60 mg, 0.08 mmol) were dissolved in 40 mL of toluene and stirred overnight at 80 °C. NaOH (4 N, 30 mL) was added to the reaction mixture. The organic layer was separated, dried over Na_2SO_4, and filtered. All volatiles of the organic layer were removed in vacuo, and the product was washed twice with water and dried to yield 910 mg (91%) of 9,10-di(phenyl)phenanthrene. Crystals suitable for X-ray diffraction can be obtained by cooling a saturated solution of **17** in toluene to −40 °C. Anal. Calcd (found) for $C_{26}H_{18}$ [330.4 g/mol]: C 94.51 (94.16), H 5.49 (5.68). ^{1}H NMR (C_6D_6, 400 MHz): δ 6.94 (m, 2 H, aryl-$H_{2,7}$), 6.98−7.13 (m, 10 H, aryl-H_{phenyl}), 7.41 (m, 2 H, aryl-$H_{3,6}$), 7.55 (m, 2 H, aryl-$H_{1,8}$), 8.74 (m, 2 H, aryl-$H_{4,5}$). ^{13}C NMR (C_6D_6): δ 139.17 (aryl-C_i), 136.70 (aryl-C_i), 131.55 (aryl-C_i),

Table 2. X-ray Data Collection and Processing Parameters

	[Ni(Me_2Im)$_3$] (**1**)	[Ni(Me^iPr_2Im)$_2$(η^2-C_2Ph_2)] (**11**)	[Ni(Me_2Im)-(2,2′-biph)] (**13**)	phenanthrene (**17**)	[Ni($^iPr_2Im$)$_2$(η^2-C_2Me_2)] (**18**)
formula	$C_{15}H_{24}N_6Ni$	$C_{28}H_{34}N_4Ni$	$C_{23}H_{26}Cl_2N_4Ni$	$C_{26}H_{18}$	$C_{22}H_{38}N_4Ni$
fw	347.11	485.30	488.09	330.40	417.27
cryst syst	triclinic	orthorhombic	monoclinic	tetragonal	triclinic
space group	$P\bar{1}$	$Pna2_1$	$P2_1/c$	I_1/n	$P\bar{1}$
a/Å	8.2976(9)	19.5585(10)	11.706(2)	26.8026(13)	15.974(3)
b/Å	9.9888(12)	13.4766(6)	9.935(2)		16.264(3)
c/Å	12.2401(15)	9.7786(13)	19.644(4)	9.9436(5)	21.793(4)
α/deg	102.199(14)				98.42(3)
β/deg	105.149(14)		91.30(3)		91.06(3)
γ/deg	110.023(14)				90.03(3)
V/Å^3	867.98(18)	2577.5(4)	2284.0(8)	7143.3(6)	5600(2)
Z	2	4	4	16	8
μ/mm^{-1}	1.123	0.775	1.101	0.069	0.704
total no./no. indep reflns	8516/3151	8979/4194	10 321/4314	25 160/3470	33 563/15 246
no. of obsd reflns^a	3151	3165	2296	2066	9620
no. of params	223	298	271	235	973
final R^b, $wR_2{}^c$	0.0304, 0.0659	0.0396, 0.0728	0.0449, 0.0873	0.046,0 0.0963	0.1003, 0.2691

^{a} Reflections with $I > 2\ \sigma(I)$. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$. ^{d} For data with $I > 2\ \sigma(I)$.

130.97 (aryl-C_i), 130.37 (aryl-C_o), 129.68 (aryl-$C_{1,8}$), 126.95 (aryl-C_m), 125.95 (aryl-$C_{2,7}$), 125.77 (aryl-$C_{3,6}$), 125.70 (aryl-C_p), 121.96 (aryl-$C_{4,5}$).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Me$_2$)] (18). 2-Butyne (54 mg, 1.00 mmol) was added to a solution of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (360 mg, 0.47 mmol) in 20 mL of toluene, and the reaction mixture was stirred overnight. All volatiles were removed in vacuo, and the remaining solid was dissolved in 20 mL of hexane and crystallized at −30 °C to afford 190 mg (53%) of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Me$_2$)] in the form of brown needles. EI/MS *m/z* (%): 362 (100) [Ni(^{i}Pr$_2$Im)$_2$]$^+$. IR ([cm^{-1}]): 336 (w), 381 (w), 474 (m), 575 (m), 628 (m), 676 (s), 689 (m), 708 (m), 796 (m), 876 (w), 1009 (s), 1127 (m), 1216 (vs), 1269 (s), 1286 (m), 1367 (m), 1397 (s), 1414 (s), 1465 (m), 1530 (w), 1566 (w), 1657 (w), 1778 (m), 2824 (m), 2874 (m), 2929 (m), 2968 (s), 3084 (w), 3114 (w), 3153 (w). ^{1}H NMR (C_6D_6): δ 1.11 (d, 24 H, ^{i}Pr-CH$_3$), 2.67 (s, 6 H, alkyne-C*H*$_3$), 5.61 (sept, 4 H, NC*H*C*H*N). ^{13}C NMR (C_6D_6): δ 23.99 (^{i}Pr-*C*H$_3$), 25.14 (alkyne-*C*H$_3$), 50.67 (*C*H), 114.63 (N*CC*N), 121.93 (*C*≡*C*), 203.93 (N*C*N).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Et$_2$)] (19). 3-Hexyne (0.11 mL, 1.00 mmol) was added at −78 °C to a solution of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (363 mg, 0.42 mmol) in 20 mL of toluene. The reaction mixture was stirred overnight and allowed to reach room temperature during this time. The resulting red-brown solution was filtered over a pad of Celite, and all volatile material was removed from the mother liquor. The remaining residue was suspended in 10 mL of hexane, and the product was filtered off and dried in vacuo to give 280 mg (74%) of a brown powder. IR (KBr [cm^{-1}]): 574 (w), 675 (s), 700 (m), 799 (m), 887 (m), 986 (m), 1009 (m), 1056 (m), 1131 (m), 1212 (vs), 1268 (s), 1283 (s), 1297 (m), 1369 (s), 1400 (s), 1412 (s), 1490 (m), 1506 (w), 1559 (w), 1607 (w), 1653 (w), 1783 (m, $\nu_{C\equiv C}$), 2819 (m), 2868 (s), 2916 (s), 2965 (vs). ^{1}H NMR (C_6D_6): δ 1.12 (d, 24 H, ^{i}Pr-C*H*$_3$), 1.38 (t, 6 H, C*H*$_3$), 3.06 (m, 4 H, C*H*$_2$), 5.58 (sept, 5 H, ^{i}Pr-C*H*), 6.51 (s, 4 H, NC*H*C*H*N). ^{13}C NMR (C_6D_6): δ 16.63 (*C*H$_3$), 22.38 (*C*H$_2$), 23.27 (^{i}Pr-CH$_3$), 50.49 (^{i}Pr-*C*H), 114.38 (N*CC*N), 127.78 (*C*≡*C*), 204.02 (N*C*N).

Computational Details. All calculations were carried out with the DFT implementation of the TURBOMOLE program package.[26] For the DFT calculations we used the BP86 functional,[27] SV(P) basis sets, and the RI-J approximation. The equilibrium structures of the complexes were optimized at the RIDFT level using a SV-(P) basis. Analytic second derivatives were calculated with the program AOFORCE using the RI-J approximation.[28]

Crystal Structure Determination of [Ni(Me$_2$Im)$_3$] (1), [Ni(Me^{i}Pr$_2$Im)$_2$(η^2-C$_2$Ph$_2$)] (11), [Ni(Me$_2$Im)(2,2′-biphenyl)] (13) in (13)·CH$_2$Cl$_2$, 9,10-Di(phenyl)phenanthrene (17), and [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$Me$_2$)] (18). CCDC-607595 to CCDC-607599 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

Crystal data collection and processing parameters are given in Table 2. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a STOE CDD diffractometer (Mo Kα radiation; **13**) equipped with an Oxford Cryosystems low-temperature device or a Stoe-IPDS I image plate diffractometer (Mo Kα radiation; **1**, **11**, **17**, **18**) equipped with a FTS AirJet low-temperature device. Data were collected at 150 K (**13**) or 200 K (**1**, **11**, **17**, **18**); equivalent reflections were merged and the images were processed with the STOE IPDS or CCD software package. Corrections for Lorentz−polarization effects and absorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.[29]

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Supporting Information Available: X-ray crystal data in CIF format and experimental details on the preparation of imidazolium salts and carbenes and the NMR spectra of complexes **6**, **7**, **14**, **18**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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