Mixed Azido-N-Heterocyclic Carbene Complexes of Nickel(II) as a Template for New Organometallics Bearing Carbodiimido, Tetrazolato, and Abnormal Tetrazolin-5-ylidene Ligands

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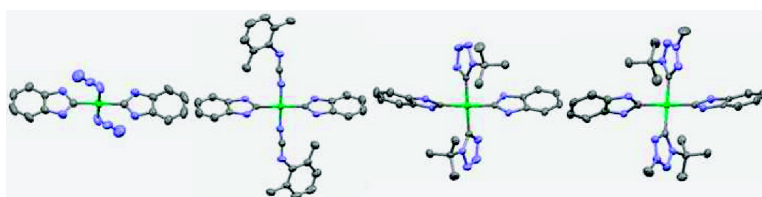
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Mixed Azido-N-Heterocyclic Carbene Complexes of Nickel(II) as a Template for New Organometallics Bearing Carbodiimido, Tetrazolato, and Abnormal Tetrazolin-5-ylidene Ligands

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Salt metathesis reaction of the dihalo-bis(carbene) complex *trans*-[NiBr$_2$(NHC)$_2$] (**1**, NHC = 1,3-diisopropylbenzimidazolin-2-ylidene) with NaN$_3$ in DMF at elevated temperature afforded the diazido-bis(carbene) complex *trans*-[Ni(N$_3$)$_2$(NHC)$_2$] (**2**) as a red crystalline solid in a yield of 78%. Complex **2** served as a metal-template for the 1,3-dipolar cycloaddition of 2,6-dimethylphenylisocyanide (CN-Xyl) to the azido ligands to yield the mixed tetrazolato-carbodiimido complex *trans*-[Ni(CN$_4$-Xyl)(NCN-Xyl)(NHC)$_2$] (**3**) at ambient temperature and the dicarbodiimido complex *trans*-[Ni(NCN-Xyl)$_2$(NHC)$_2$] (**4**) at 70 °C. Reaction of alkyl isocyanides with **2** at ambient temperature gave the ditetrazolato complexes *trans*-[Ni(CN$_4$-R)$_2$(NHC)$_2$] (**5**, R = *tert*-butyl; **6**, R = cyclohexyl) in good yields. The novel cationic "abnormal" tetrazolin-5-ylidene complex *trans*-[Ni(CN$_4$-^{t}Bu,Me)$_2$(NHC)$_2$](BF$_4$)$_2$ (**7**, ^{t}Bu = *tert*-butyl) was synthesized by direct methylation of **5** with [Me$_3$O]BF$_4$. All compounds have been fully characterized by multinuclear NMR spectroscopies and ESI mass spectrometry. The solid state molecular structures of complexes **2**, **4**, **5**, and **7**·2CH$_2$Cl$_2$ have also been confirmed by X-ray diffraction studies.

Introduction

1,3-Dipolar Huisgen addition involving azides is nowadays a common and very well-explored organic reaction to synthesize various heterocyclic compounds.[1] Of particular interest is the "click chemistry" of organic azides with alkynes, giving rise to triazole derivatives. Analogously, Beck and co-workers have reported in the early 1970s that metal azido complexes easily undergo dipolar cycloaddition reactions with various dipolarophiles.[2] Unsaturated organic compounds such as isocyanides, nitriles, and alkynes would undergo cycloaddition reaction with a coordinated azido ligand to form metal complexes containing C- or N-coordinated heterocycles.[3] In most cases, palladium(II) and platinum(II) azido complexes containing amine or phosphine ligands have been investigated.[4] N-Heterocyclic carbenes (NHCs) have proven to be suitable alternatives for phosphine ligands, and their metal complexes show enhanced stabilities to air and moisture, allowing for an easier handling. Thus it is

surprising that azido complexes supported by N-heterocyclic carbenes[5] and their properties as well as reactivities are literally unexplored.[6] In relation to our recent study on NHC complexes with carboxylato[7] and thiolato[8] as anionic nonhalo co-ligands, we became interested in mixed NHC-pseudohalo complexes. We have also reported a facile and low-cost methodology for the synthesis of Ni(II) complexes of benzimidazolin-2-ylidenes.[9] As an extension of our research in Ni-NHC complexes, we herein describe the synthesis of the first mixed diazido-bis(carbene) Ni(II) complex and the application of NHCs as ancillary ligands in metal-template-assisted synthesis of novel organometallic complexes, one of which bears an abnormal tetrazolin-5-ylidene ligand.

Results and Discussion

Synthesis and Characterization of a *trans*-Diazido-bis(carbene) Ni(II) Complex. Recently we have reported a facile approach for the preparation of *trans*-dihalo-bis(benz-imidazolin-2-ylidene) complexes of nickel(II).[9] The metathesis reaction of such species with 2 equiv of NaN$_3$ is expected to afford the desired diazido analogues. Indeed, anionic ligand exchange occurs readily when the complex *trans*-[NiBr$_2$(NHC)$_2$]

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(1) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633. (c) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403. (d) L'abbé, G. *Chem. Rev.* **1969**, *69*, 345. (e) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 627. (f) Padwa, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 123. (g) Himo, F.; Demko, Z. P.; Noodleman, L.; Sharpless, K. B. *J. Am. Chem. Soc.* **2003**, *125*, 9983. (h) Moses, J. E.; Moorhouse, A. D. *Chem. Soc. Rev.* **2007**, *36*, 1249.

(2) (a) Beck, W.; Schuierer, E.; Feldl, K. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 249. (b) Beck, W.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 169. (c) Beck, W.; Feldl, K.; Schuierer, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 439.

(3) (a) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (b) Chang, C.-W.; Lee, G.-H. *Organometallics* **2003**, *22*, 3107.

(4) (a) Kim, Y.-K.; Kim, D.-H.; Lee, J.-Y.; Lee, S.-W. *J. Organomet. Chem.* **1997**, *538*, 189. (b) Kim, Y.-J.; Kwak, Y.-S.; Lee, S.-W. *J. Organomet. Chem.* **2000**, *603*, 152. (c) Kim, Y.-J.; Kwak, Y.-S.; Joo, Y.-S.; Lee, S.-W. *Dalton Trans.* **2002**, 144. (d) Kim, Y.-K.; Joo, Y.-S.; Han, J.-T.; Han, W. S.; Lee, S.-W. *Dalton Trans.* **2002**, 3611. (e) Kim, Y.-K.; Han, J.-T.; Kang, S.; Han, W. S.; Lee, S.-W. *Dalton Trans.* **2003**, 3357. (f) Kim, Y.-J.; Lee, S.-H.; Lee, S.-H.; Jeon, S. I.; Lim, M. S.; Lee, S.-W. *Inorg. Chim. Acta* **1997**, *254*, 105.

(5) (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (b) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006. (c) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F. A., Ed.; Springer: Berlin, 2007.

(6) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2005**, 37.

(7) (a) Han, Y.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2007**, *692*, 3606. (b) Huynh, H. V.; Neo, T. C.; Tan, G. K. *Organometallics* **2006**, *25*, 1298. (c) Huynh, H. V.; LeVan, D.; Hahn, F. E.; Hor, T. S. A. *J. Organomet. Chem.* **2004**, *689*, 1766.

(8) Huynh, H. V.; Jothibasu, R.; Koh, L. L. *Organometallics* **2007**, *26*, 6852.

(9) (a) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, F. E. *Organometallics* **2006**, *25*, 245. (b) Huynh, H. V.; Wong, L. R.; Ng, P. S. *Organometallics* **2008**, *27*, 2231.
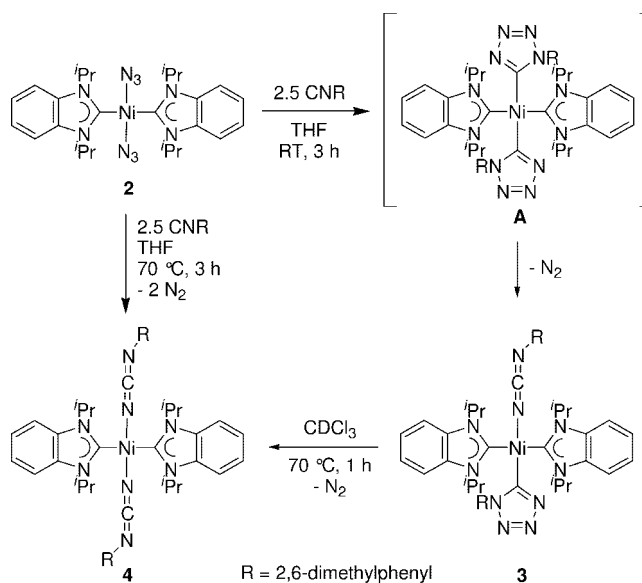
Scheme 1. Synthesis of Complex 2
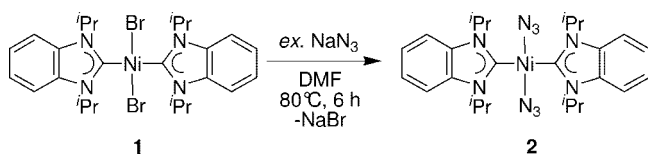
(**1**, NHC = 1,3-diisopropylbenzimidazolin-2-ylidene) was treated with excess NaN$_3$ in DMF at elevated temperature, affording the diazido-bis(carbene) complex *trans*-[Ni(N$_3$)$_2$(NHC)$_2$] (**2**) as a red crystalline solid in a yield of 78% (Scheme 1). Complex **2** shows improved solubility compared to its precursor **1** and can be easily dissolved in halogenated solvents and polar organic solvents such as DMSO and DMF. In H$_2$O and nonpolar solvents such as diethyl ether, hexane, and toluene it proves insoluble. The presence of the azido ligands is indicated by an IR band at 2032 cm^{-1}. The ^{1}H chemical shifts for the carbene ligand remain largely unaffected by the halo-azido exchange, and as expected, a multiplet at 7.14 ppm and a doublet at 2.08 ppm are observed for the CH and CH$_3$ protons of the isopropyl substituents, respectively. The improved solubility of **2** allows for the determination of the carbene carbon resonance, which is found at 179.7 ppm. Finally, the positive mode ESI spectrum of **2** is dominated by an isotopic pattern at *m/z* = 504 for the [M − N$_3$]$^+$ fragment.

To characterize complex **2** unambiguously, X-ray quality crystals were obtained by slow evaporation of a concentrated CH$_2$Cl$_2$ solution of complex **2**. Its molecular structure depicted in Figure 1 confirms the trans arrangement of the carbene ligands in an essentially square-planar Ni(II) center. The carbene ring planes are oriented almost perpendicularly to the NiC$_2$N$_2$ coordination plane with a dihedral angle of 87.40°. The Ni−C$_{carbene}$ bond distances of 1.923(3) Å are slightly longer than the corresponding bonds in its precursor,[9b] and the two azido ligands are oriented anti to each other with respect to the N−Ni−N vector.

Reaction with Isocyanides. In order to investigate the reactivity of complex **2** toward organic isocyanides, it was treated with the aromatic 2,6-dimethylphenyl isocyanide (CN-Xyl). It was anticipated that the isocyanide would attack the coordinated azido ligands, giving rise to a template-directed dipolar cycloaddition reaction. Surprisingly, this reaction afforded the complex *trans*-[Ni(CN$_4$-Xyl)(NCN-Xyl)(NHC)$_2$] (**3**) as a pale yellow powder in 90% yield, which bears a tetrazolato and a carbodiimido as new anionic co-ligands (Scheme 2). Most likely, complex **3** has formed as a result of dinitrogen elimination from the initial cycloaddition product **A**, which could not be isolated. With the exception of

Figure 1. Molecular structure of complex **2** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1−C1 1.912(3), Ni1−N3 1.937(3); C1−Ni1−C1A 180.0, N3−Ni1−N3A 180.0, C1A−Ni1−N3A 90.95(13), C1−Ni1−N3A 89.05(13).

Scheme 2. Synthesis of Complexes 3 and 4

R = 2,6-dimethylphenyl

nonpolar solvents such as hexane, diethyl ether, and toluene, complex **3** proves soluble in most common organic solvents. IR spectroscopy reveals a weak band at 2143 cm^{-1} for the carbodiimido group, whereas the azido band is absent. The ^{1}H NMR spectrum shows two singlets at 1.64 and 1.63 ppm for methyl protons of the two inequivalent xylyl-containing anionic ligands. The presence of four doublets for the isopropyl-CH$_3$ groups ranging from 1.76 to 2.00 ppm further points to an unsymmetrical environment around the carbene ligands. Consequently, multiple signals are also observed for all methyl groups from 22.9 to 21.7 ppm in the ^{13}C NMR spectrum. The carbene carbon found at 184.9 ppm is downfield from that found in precursor **2**, which indicates a more electron-rich metal center. A signal at 158.8 ppm is assigned to the tetrazolato-C-donor, whereas a weaker ^{13}C resonance is observed at 122.4 ppm characteristic for the NCN moiety of the carbodiimido ligand. Further support for the formation of **3** was provided by its positive mode ESI spectrum, which is dominated by a peak at *m/z* = 781 for the [M + H]$^+$ ion.

Complex **3** is not stable in solution and slowly converts to the dicarbodiimido complex *trans*-[Ni(NCN-Xyl)$_2$(NHC)$_2$] (**4**) through release of an additional equivalent of dinitrogen. The conversion of **3** to **4** is also accompanied by a color change of the initially yellow solution to deep red. This transformation is complete after ∼4 days, and ESI mass spectrometry corroborates the formation of **4** by a new base peak at *m/z* = 639, corresponding to the [M − NCN − Xyl + CH$_3$OH]$^+$ fragment, whereas the initial base peak at 781 for **3** was absent. The reaction can be accelerated by heating, and ^{1}H NMR monitoring in CDCl$_3$ shows complete conversion after 1 h at 70 °C (Scheme 2).

Complex **4** can also be directly obtained by heating a mixture of complex **2** and 2,6-dimethylphenyl isocyanide in THF at 70 °C for 3 h. Under these optimized conditions, **4** can be isolated exclusively in more than 95% yield (Scheme 2). Its solubility is comparable to that of **3**, but in contrast to the latter complex **4** is stable in both solution and solid state. The clean formation of **4** is supported by ESI mass spectrometry, which reveals a base peak *m/z* = 753 for the molecular ion [M + H]$^+$. Furthermore, its IR spectrum shows a strong band at 2155 cm^{-1} due to the presence of carbodiimido ligands. Its ^{1}H NMR spectrum is also much simpler, exhibiting only one set of signals for each carbene and carbodiimido ligands. Thus one heptet and a doublet are observed at 7.08 and 1.98 ppm, respectively, for the aliphatic methine and methyl groups of the two NHCs,
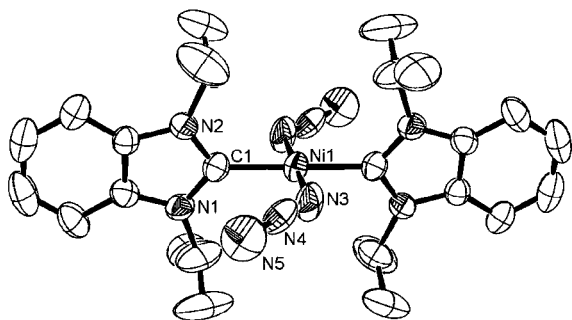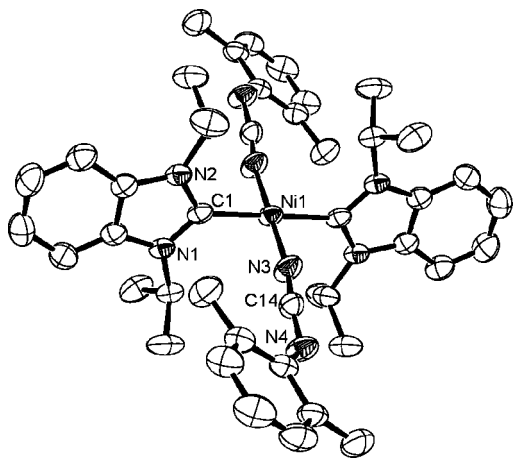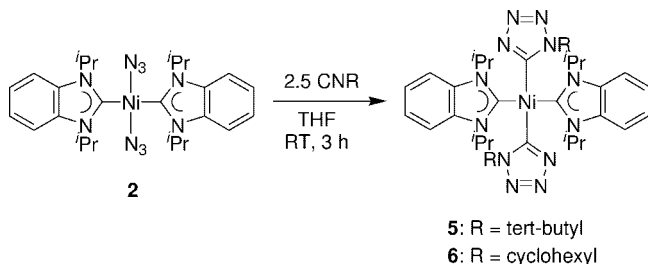
Figure 2. Molecular structure of complex **4** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1−C1 1.923(2), Ni1−N3 1.852(17), N3−C14 1.154(3), C14−N4 1.266(3); C1−Ni1−C1A 180.0, N3−Ni1−N3A 180.0, C1−Ni1−N3 90.20(8), C1−Ni1−N3A 89.80(8).

Scheme 3. Synthesis of Complexes 5 and 6

5: R = tert-butyl
6: R = cyclohexyl

whereas one singlet at 1.83 ppm was found for the methyl protons of the carbodiimido ligand. More importantly, the tetrazolato-carbodiimido ligand transformation leads to a more Lewis acidic metal center, which is manifested in a high-field shift of the carbene carbon to 179.0 ppm.

X-ray diffraction on a single crystal of complex **4** obtained from slow evaporation of a concentrated CH_2Cl_2 solution finally confirmed its identity as a mixed dicarbodiimido-bis(carbene) complex. The molecular structure of the square-planar Ni(II) complex is depicted in Figure 2. The increased steric bulk around the metal center compared to **2** leads to a slight elongation of the Ni−$C_{carbene}$ bond lengths. The Ni−N bond distances amounting to 1.8522 Å are in line with reported values.[4d] Notably, the N3−C14 bond distance of 1.154 Å in the carbodiimido ligand reflects some C≡N triple bond character (e.g., 1.16 Å), whereas the C14−N4 bond distance of 1.266 Å is as expected closer to a double bond.

In an attempt to isolate primary cycloaddition products of type **A**, the reaction of complex **2** with aliphatic isocyanides was also studied. The addition of *tert*-butyl isocyanide (CN-^{t}Bu) to a red suspension of complex **2** in THF at ambient temperature (Scheme 3) and subsequent stirring for 3 h led to a clear yellow solution. This straightforward reaction afforded the new mixed tetrazolato-NHC complex *trans*-[Ni(CN$_4$-^{t}Bu)$_2$-(NHC)$_2$] (**5**) as a white powder in almost quantitative yield. Complex **5** is air- and moisture stable and soluble in most common organic solvents with the exception of hexane and toluene.

Upon formation of the sterically demanding *N-tert*-butyltetrazolato ligands, the N-substituents of the carbene ligands become inequivalent, as evidenced by two multiplets at 7.10
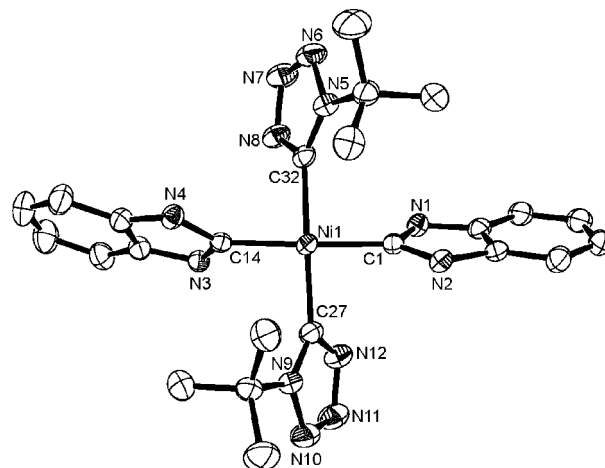

Figure 3. Molecular structure of complex **5** showing 50% probability ellipsoids. Hydrogen atoms and isopropyl substituents have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1−C1 1.922(2), Ni1−C14 1.929(3), Ni1−C27 1.942(3), Ni1−C32 1.947(3), C32−N5 1.360(3), N5−N6 1.367(3), N6−N7 1.279(3), N7−N8 1.368(3), N8−C32 1.355(3), C27−N9 1.367(3), N9−N10 1.370(3), N10−N11 1.293(4), N11−N12 1.359(3), N12−C27 1.348(3); C1−Ni1−C14 165.94(10), C27−Ni1−C32 174.22(11), C1−Ni1−C27 87.42(11), C1−Ni1−C32 91.07(11), C14−Ni1−C27 93.92(11), C14−Ni1−C32 86.21(11), N1−C1−N2 106.5(2), N3−C14−N4 105.9(2), N5−C32−N8 105.1(2), N9−C27−N12 105.0(2).

and 5.42 ppm for the methine protons of the isopropyl groups. Accordingly, four sets of doublets are observed for the isopropyl-CH$_3$ groups, whereas the *tert*-butyl substituents of the new anionic ligands only give rise to one singlet at 1.62 ppm, pointing to a trans arrangement of the ligands. The restricted rotation around the Ni−$C_{carbene}$ bond as a consequence of the sterically demanding *tert*-butyl groups can also be observed in the ^{13}C NMR spectrum of **5**. Four signals for the CH$_3$ and two resonances for the CH groups of the isopropyl substituents are found. Notably, a significant downfield shift of the carbenoid signal to 188.4 ppm indicates the formation of a stronger donating co-ligand compared to that in its precursor **2**. Finally, the coordinated tetrazolato-carbon resonates at 162.2 ppm, which is in the same range reported for phosphine analogues.[4c] The formation of complex **5** has also been corroborated by its positive mode ESI mass spectrum, which shows a base peak at $m/z = 713$ assignable to the [M + H]$^+$ ion.

Single crystals of **5** were obtained by slow evaporation of a concentrated CH_2Cl_2 solution and subjected to X-ray diffraction analysis. The molecular structure depicted in Figure 3 confirms the trans arrangement of the ligands around a distorted square-planar Ni(II) center. As commonly observed, the two carbene ring planes are oriented almost perpendicularly to the NiC$_4$ coordination plane with dihedral angles of 67.06° and 66.65°, respectively. To avoid steric congestion, both tetrazolato ring planes are similarly twisted out of the coordination plane with angles of 61.01° and 57.37°. The Ni−$C_{carbene}$ distances amounting to 1.922 and 1.929 Å, respectively, have become slightly elongated compared to those in **2**, which is in line with a less Lewis acidic nickel center due to the coordination of two strongly donating tetrazolato ligands. The Ni−$C_{tetrazolato}$ bond distances of the latter are found in the typical range of 1.942 and 1.947 Å.[4c,f] Surprisingly, the bulky *tert*-butyl groups of the tetrazolato ligands are oriented syn to each other, pointing to the same side of the NiC$_4$ coordination plane. This unusual arrangement forces the transoid carbene ligands out of linearity,

resulting in a substantial decrease of the C1−Ni−C14 angle to 165.94° (180° in a perfect square plane).

In order to test the general feasibility of this template-assisted 1,3-dipolar cycloaddition, complex **2** was also treated with cyclohexyl isocyanide in THF at ambient temperature. In analogy with the formation of compound **5**, this reaction gave complex *trans*-[Ni(CN₄-Cy)₂(NHC)₂] (**6**, Cy = cyclohexyl) as an off-white powder in 82% yield (Scheme 3) soluble in chlorinated and more polar organic solvents. Due to the known fluxionality of the cyclohexyl moiety, only a broad singlet was observed at 5.99 ppm for the isopropyl CH protons in the ¹H NMR spectrum. The resonances for the isopropyl CH₃ protons overlap with those of the cyclohexyl ring, resulting in a very broad signal centered at 1.51 ppm. More importantly, the chemical shift for the carbene carbon arises in an even more deshielded region at 192.4 ppm, indicating a very electron-rich metal center. The signal for the tetrazolato carbon at 165.7 ppm, on the other hand, is closer to its analogue **5**. Positive mode ESI mass spectrometry also supports the formation of complex **6** with an isotopic envelope at *m/z* = 765 for the [M + H]⁺ ion.

Template-Directed Synthesis of a Tetrazolin-5-ylidene Carbene Complex. Common methods for the preparation of carbene complexes include direct coordination of free carbenes, in situ deprotonation of azolium salts by basic metal precursors, or their oxidative addition to low-valent metal complexes. Raubenheimer et al. have described an elegant, but less common method to synthesize carbene complexes by N-protonation or N-alkylation of C-azolato complexes.[10] By doing so, the anionic azolato ligand is converted into a neutral carbene ligand. This procedure has the distinct advantage that it enables the direct comparison of azolato complexes with the subsequently formed carbene complexes. To this point, Fehlhammer et al. have proposed the formation of a tetrazole-derived carbene complex by acidification of a homoleptic tetrakis-tetrazolato Au(III) species with diluted HCl.[11] However, complete evidence for the formation of this complex could not be obtained. On the other hand, some tetrazolin-5-ylidene complexes have been obtained by in situ deprotonation of tetrazolium salts[12,13] and through oxidative addition of a 5-chlorotetrazolium salt to Pd(0).[13] We anticipated that N-alkylation of tetrazolato complex **5** should afford the respective tetrazolin-5-ylidene compound in a straightforward way. Thus, complex **5** was treated with excess ethyl iodide in acetonitrile for 12 h under reflux conditions. To our disappointment, no reaction was observed and only starting material was recovered. However, methylation of **5** took place when the stronger electrophile trimethyloxonium tetrafluoroborate was used under inert atmosphere (Scheme 4). Upon alkylation, the cationic reaction products precipitated from CHCl₃ and could be isolated as a white solid after filtration. Although excess oxonium salt was used, the formation of the monomethylated complex as byproduct was observed.

However, the desired dicationic mixed tetracarbene complex [Ni(CN₄-ᵗBu,Me)₂(NHC)₂](BF₄)₂ (**7**) shows a better solubility in CH₂Cl₂, and washing with that solvent afforded pure **7** in

Scheme 4. Synthesis of Complex 7

R = tert-butyl
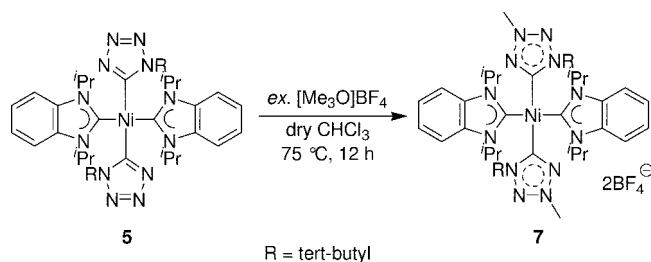
63% yield. It is soluble in DMSO, DMF, CH₃CN, CH₂Cl₂, CH₃OH, and acetone. ESI mass spectrometry confirmed its formation by a base peak at *m/z* = 371 for the [M − 2BF₄]²⁺ complex cation. In the ¹H NMR spectrum, a singlet for the newly introduced methyl group is observed at 4.33 ppm. The resonance for the same group appears at 42.5 ppm in the ¹³C NMR spectrum. Notably, the formation of the tetrazolin-5-ylidene ligands leads to a substantial high-field shift of the benzimidazolin-2-ylidene carbene carbon to 176.8 ppm. This observation is in line with an increased Lewis acidity of the metal center in dicationic **7**. The carbenoid resonance for the newly formed tetrazolin-5-ylidene is observed ∼10 ppm downfield from **5** (162.2 ppm) at 172.0 ppm, which is similar to previously reported values for Pd analogues.[13] Furthermore, two signals at −76.63 and −76.68 ppm are observed in the ¹⁹F NMR spectrum of complex **7** for the BF₄⁻ counteranions.

An X-ray diffraction analysis on single crystals obtained as solvate **7**·2CH₂Cl₂ by slow evaporation of a concentrated CH₂Cl₂ solution unambiguously corroborates the identity of **7** as the first mixed tetracarbene Ni(II) complex (Figure 4). Notably, the overall distorted square-planar geometry including the syn orientation of the bulky *tert*-butyl groups is retained upon alkylation of the two tetrazolato ligands in **5**. The methylation occurred at the least hindered 3-position of the tetrazole rings (i.e., N7, N11), giving rise to the formation of two new 1-*tert*-butyl-3-methyltetrazolin-5-ylidene ligands. All
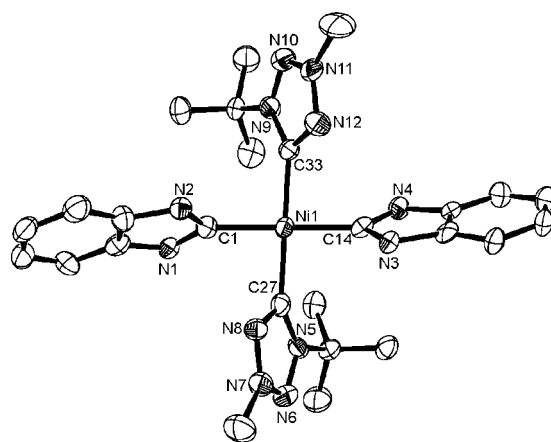

Figure 4. Molecular structure of complex **7**·2CH₂Cl₂ showing 50% probability ellipsoids. Hydrogen atoms, isopropyl substituents, solvent molecules, and BF₄⁻ counteranions have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1−C1 1.946(9), Ni1−C14 1.936(8), Ni1−C27 1.911(9), Ni1−C33 1.923(8), C27−N5 1.396(11), N5−N6 1.335(9), N6−N7 1.301(10), N7−N8 1.330(10), N8−C27 1.329(11), C33−N9 1.395(10), N9−N10 1.322(10), N10−N11 1.294(10), N11−N12 1.323(10), N12−C33 1.354(10); C1−Ni1−C14 165.9(3), C27−Ni1−C33 172.9(4), C1−Ni1−C27 86.7(4), C1−Ni1−C33 92.9(4), C14−Ni1−C27 92.5(4), C14−Ni1−C33 86.2(3), N1−C1−N2 107.1(7), N3−C14−N4 106.5(7), N5−C27−N8 103.6(7), N9−C33−N12 103.4(7).

(10) (a) Raubenheimer, H. G.; Cronje, S. *J. Organomet. Chem.* **2001**, *617*, 170. (b) Schuster, O.; Raubenheimer, H. G. *Inorg. Chem.* **2006**, *45*, 7997. (c) Raubenheimer, H. G.; Scott, F.; Roos, M.; Otte, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1722. (d) Raubenheimer, H. G.; Cronje, S. *Dalton Trans.* **2008**, 1265.

(11) Wehlan, M.; Thiel, R.; Fuchs, J.; Beck, W.; Fehlhammer, W. P. *J. Organomet. Chem.* **2000**, *613*, 159.

(12) (a) Frey, G. D.; Öfele, K.; Krist, H. G.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chim. Acta* **2006**, *359*, 2622. (b) Hermann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

(13) Araki, S.; Wanibe, Y.; Uno, F.; Morikawa, A.; Yamamoto, K.; Chiba, K.; Butsugan, Y. *Chem. Ber.* **1993**, *126*, 1149.
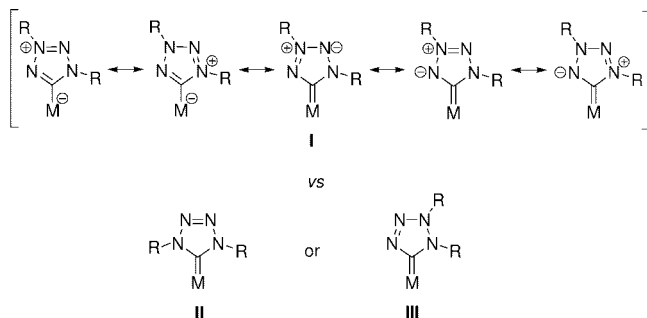
I

vs

II   or   III

Figure 5. Comparison of mesomeric Lewis structures of an "*abnormal*" 1,3-dialkyltetrazolin-5-ylidene (**I**) and "*normal*" 1,4- or 1,2- dialkyltetrazolin-5-ylidene (**II** and **III**).

carbene ring planes are almost perpendicular to the NiC$_4$ coordination plane with angles ranging from 56° to 67°. The C−N and N−N interatomic distances in the tetrazolin-5-ylidene rings are in the range found for 1,4-dialkyl analogues[12] and typical for aromatic bonds, reflecting some degree of delocalization. The Ni−C$_{tetrazolin}$ bond distances of 1.911 and 1.923 Å have become significantly shorter upon carbene formation, whereas the Ni−C$_{carbene}$ bonds with the ancillary benzimidazolin-2-ylidene ligands of 1.946 and 1.936 Å show a continuous elongation with transformations from **2** to **5** and finally to **7**. This bond elongation is in line with the increasing steric bulk of the co-ligands going from azido to tetrazolato and subsequently to tetrazolin-5-ylidene.

Interestingly, the 1,3-disubstitution pattern of the new tetrazole-based ligands in **7** results in so-called "*abnormal carbenes*", which cannot be represented by any neutral Lewis structure. As depicted in Figure 5 all mesomeric forms require additional charges (Figure 5, **I**). An isomeric 1,4- or 1,2-disubstituted tetrazolin-5-ylidene, on the other hand, is a normal NHC, which can be represented by a neutral Lewis formula (Figure 5, **II** and **III**). In contrast to all examples described in the literature so far,[14] the "*abnormal*" coordination mode of carbenes does not require the presence of two or more isomeric C-donor sites. In tetrazolin-5-ylidenes selective N-alkylation can simply influence "*abnormal*" versus "*normal*" coordination modes of NHCs.

Conclusion

In summary, we presented a straightforward and high-yielding synthesis for the NHC-supported Ni-azido complex **2**, which served as an excellent precursor for the template-directed 1,3-dipolar cycloaddition of isocyanides to azido ligands. Depending on the nature of the isocyanide and the reaction conditions, complexes with a ditetrazolato (**5** and **6**), a dicarbodiimido (**4**), or a mixed tetrazolato−carbodiimido (**3**) ligand sphere can be isolated in high yields. Moreover, a template-directed synthesis of an "*abnormal*" tetrazolin-5-ylidene complex (**7**) is also demonstrated by direct alkylation of **5** with [Me$_3$O]BF$_4$. To the best of our knowledge, **7** is the first example of a mixed benzimidazolin-2-ylidene/tetrazolin-5-ylidene complex.

Experimental Section

General Considerations. If not noted otherwise, all manipulations were carried out without taking precautions to exclude air

(14) (a) Han, Y.; Huynh, H. V. *Chem. Commun.* **2007**, 1089. (b) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 6581. (c) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596. (d) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534. (e) Albrecht, M. *Chem. Commun.* **2008**, 3601.

and moisture. All solvents and chemicals were used as received without further purification if not mentioned. CHCl$_3$ was dried over CaH$_2$ and distilled prior to use. Complex **1** was synthesized according to a literature procedure.[9b] ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker ACF 300 and Bruker AMX 500 spectrometer, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C) or externally to CF$_3$CO$_2$H (^{19}F). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Infrared spectra were recorded with a Varian 3100 FT-IR spectrometer using KBr pellets. Elemental analyses were done on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

***trans*-Diazidobis(1,3-diisopropylbenzimidazolin-2-ylidene)-nickel(II) (2).** Complex **1** (312 mg, 0.5 mmol) and NaN$_3$ (130 mg, 2 mmol) were suspended in DMF (10 mL) and stirred for 6 h at 80 °C. The suspension turned deep red with the precipitation of NaBr. The solvent was removed under vacuum, and the residue was dissolved in CH$_2$Cl$_2$ and filtered through a plug of Celite. The solvent of the filtrate was removed under reduced pressure to afford complex **2** (213 mg, 0.39 mmol, 78%) as a red powder. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.58 (m, br, 4 H, Ar−H), 7.21 (m, br, 4 H, Ar−H), 7.14 (m, 4 H, ^3J(H,H) = 6.95 Hz, NCH(CH$_3$)$_2$), 2.08 (d, 24 H, ^3J(H,H) = 6.95 Hz, NCH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 179.7 (s, NCN), 134.3, 122.9, 113.0 (s, Ar−C), 54.6 (s, NCH(CH$_3$)$_2$), 22.6 (s, NCH(CH$_3$)$_2$). Anal. Calcd for C$_{26}$H$_{36}$N$_{10}$Ni: C, 57.06; H, 6.53; N, 25.59. Found: C, 57.35; H, 6.60; N, 25.53. MS (ESI): m/z = 504 [M − N$_3$]$^+$. FT-IR (KBr pellet): $\tilde{\nu}$(N$_3$) 2032 cm^{-1} (m).

***trans*-(N′-2,6-Dimethylphenylcarbodiimido)(1-(2,6-dimethylphenyl)tetrazol-5-ato)bis(1,3-diisopropylbenzimidazolin-2-ylidene)nickel(II) (3).** 2,6-Dimethylphenyl isocyanide (93 mg, 0.7 mmol) was added to a THF (5 mL) suspension of complex **2** (192 mg, 0.35 mmol), and the mixture was stirred at ambient temperature. After 3 h the yellow mixture was filtered through Celite. The solvent of the filtrate was removed under reduced pressure, and the residue was washed with hexane to remove excess isocyanide. Drying under vacuum afforded the product as an off-white solid (246 mg, 0.315 mmol, 90%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55 (s, br, 4 H, Ar−H), 7.22 (s, br, 4 H, Ar−H), 7.08 (d, 3 H, Ar−H), 6.81 (m, 4 H, ^3J(H,H) = 6.95 Hz, NCH(CH$_3$)$_2$), 6.67 (d, 1 H, Ar−H), 6.62 (d, 1 H, Ar−H), 6.50 (m, 1 H, Ar−H), 2.00, 1.89, 1.82, 1.76 (d, 24 H, ^3J(H,H) = 6.9 Hz, NCH(CH$_3$)$_2$), 1.64, 1.63 (s, 12 H, Ar(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): 184.9 (s, NCN), 158.8 (s, CN$_4$), 145.1, 137.5, 137.0, 134.3, 131.4, 130.0, 129.2, 128.0, 122.8, 119.8, 113.3 (s, Ar−C), 122.4 (N═C═N), 54.6 (s, NCH(CH$_3$)$_2$), 22.9, 22.3, 22.1, 22.0, 21.9, 21.7 (s, NCH(CH$_3$)$_2$), 19.3, 17.9 (s, Ar(CH$_3$)$_2$). Anal. Calcd for C$_{44}$H$_{54}$N$_{10}$Ni: C, 67.61; H, 6.96; N, 17.92. Found: C, 67.32; H, 6.92; N, 17.65. MS (ESI): m/z = 781 [M + H]$^+$. FT-IR (KBr pellet): $\tilde{\nu}$(N═C═N) 2143 cm^{-1} (w).

***trans*-Di(N′-2,6-dimethylphenylcarbodiimido)bis(1,3-diisopropylbenzimidazolin-2-ylidene)nickel(II) (4).** 2,6-Dimethylphenyl isocyanide (132 mg, 1 mmol) was added to a THF (5 mL) suspension of complex **2** (219 mg, 0.4 mmol). The reaction mixture was heated to 70 °C for 3 h. After cooling to ambient temperature, the deep red solution was filtered through Celite. The solvent of the filtrate was removed under reduced pressure, and the residue was washed with hexane to remove excess isocyanide and dried under vacuum to afford a red solid (286 mg, 0.38 mmol, 95%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (dd, 4 H, Ar−H), 7.25 (dd, 4 H, Ar−H), 7.08 (m, 4 H, ^3J(H,H) = 6.25 Hz, NCH(CH$_3$)$_2$), 6.65 (d, 4 H, Ar−H), 6.50 (t, 2 H, Ar−H), 1.98 (d, 24 H, ^3J(H,H) = 6.25 Hz, NCH(CH$_3$)$_2$), 1.83 (s, 12 H, Ar(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 179.0 (s, NCN), 145.1, 134.2, 131.2, 128.2, 123.0, 120.0, 113.0 (s, Ar−C), 122.6 (s, N═C═N), 54.5 (s, NCH(CH$_3$)$_2$), 22.3 (s, NCH(CH$_3$)$_2$), 19.4 (s, Ar(CH$_3$)$_2$). Anal. Calcd for

Table 1. Selected X-ray Crystallographic Data for Complexes 2, 4, 5, and 7·2CH$_2$Cl$_2$

	2	4	5	7·2CH$_2$Cl$_2$
formula	C$_{26}$H$_{36}$N$_{10}$Ni	C$_{44}$H$_{54}$N$_8$Ni	C$_{36}$H$_{54}$N$_{12}$Ni	C$_{40}$H$_{64}$B$_2$Cl$_4$F$_8$N$_{12}$Ni
fw	547.36	753.66	713.62	1087.16
color, habit	red, block	red, block	colorless, block	pale yellow, needle
cryst size [mm]	0.30 × 0.20 × 0.20	0.44 × 0.40 × 0.20	0.20 × 0.10 × 0.10	0.46 × 0.02 × 0.02
temp [K]	223(2)	293(2)	223(2)	223(2)
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)2(1)2(1)	*P*2(1)/*c*
a [Å]	9.2752(7)	9.8734(14)	10.0088(6)	10.6035(15)
b [Å]	8.9186(6)	23.771(3)	18.0397(12)	28.218(4)
c [Å]	17.3011(13)	8.6533(13)	20.7107(13)	17.741(3)
α [deg]	90	90	90	90
β [deg]	93.650(2)	92.325(3)	90	101.612(4)
γ [deg]	90	90	90	90
V [Å^3]	1428.27(18)	2029.3(5)	3739.4(4)	5199.8(13)
Z	2	2	4	4
D$_c$ [g cm^{-3}]	1.273	1.233	1.268	1.389
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	0.712	0.519	0.562	0.649
θ range [deg]	2.36−27.49	1.71−27.50	1.50−27.50	1.38−25.00
no. of unique data	9847	14 182	26 235	29 886
max., min. transmn	0.8706, 0.8147	0.9033, 0.8038	0.9460, 0.8959	0.9871, 0.7544
final *R* indices [*I* > 2σ(*I*)]	$R_1 = 0.0642$, $wR_2 = 0.1589$	$R_1 = 0.0501$, $wR_2 = 0.1258$	$R_1 = 0.0445$, $wR_2 = 0.0926$	$R_1 = 0.1269$, $wR_2 = 0.2464$
R indices (all data)	$R_1 = 0.0716$, $wR_2 = 0.1639$	$R_1 = 0.0627$, $wR_2 = 0.1318$	$R_1 = 0.0595$, $wR_2 = 0.0986$	$R_1 = 0.2094$, $wR_2 = 0.2846$
goodness-of-fit on *F*^{2}	1.136	1.090	0.989	1.105
peak/hole [e Å^{-3}]	0.457/−0.333	0.662/−0.283	0.639/−0.227	0.750/−0.641

C$_{44}$H$_{54}$N$_8$Ni·H$_2$O: C, 68.48; H, 7.31; N, 14.52. Found: C, 68.48; H, 6.99; N, 14.44. MS (ESI): *m/z* = 753 [M + H]$^+$. FT-IR (KBr pellet): $\tilde{v}$(N=C=N) 2155 cm^{-1} (s).

***trans*-Di(1-isobutyltetrazol-5-ato)bis(1,3-diisopropylbenz-imidazolin-2-ylidene)nickel(II) (5).** To a THF (5 mL) suspension of complex **2** (219 mg, 0.4 mmol) was added *tert*-butyl isocyanide (0.113 mL, 1 mmol). The reaction mixture was stirred at ambient temperature for 3 h. The resulting yellow solution was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. The residue was washed with hexane to remove excess *tert*-butyl isocyanide. Upon drying, complex **3** (274 mg, 0.384 mmol, 96%) was obtained as a white powder. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52 (d, 2 H, Ar−H), 7.37 (d, 2 H, Ar−H), 7.17 (br, 6 H, 4 H for Ar−H and 2 H for NC*H*(CH$_3$)$_2$), 5.42 (m, 2 H, ^3J(H,H) = 6.09 Hz, NC*H*(CH$_3$)$_2$), 2.13, 1.81, 0.77, 0.40 (d, 24 H, ^3J(H,H) = 6.09 Hz, NCH(C*H$_3$*)$_2$), 1.62 (s, 18 H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): 188.4 (s, NCN), 162.2 (s, CN$_4$), 134.8, 133.9, 122.6, 122.4, 114.0, 112.9 (s, Ar−C), 58.2 (s, *C*(CH$_3$)$_3$), 54.2, 53.3 (s, N*C*H(CH$_3$)$_2$), 31.6 (s, C(*C*H$_3$)$_3$), 21.8, 21.4, 20.9, 20.5 (s, NCH(*C*H$_3$)$_2$). Anal. Calcd for C$_{36}$H$_{54}$N$_{12}$Ni: C, 60.59; H, 7.63; N, 23.55. Found: C, 60.91; H, 7.63; N, 19.57. MS (ESI): *m/z* = 713 [M + H]$^+$, *m/z* = 735 [M + Na]$^+$.

***trans*-Di(1-cyclohexyltetrazol-5-ato)bis(1,3-diisopropylbenz-imidazolin-2-ylidene)nickel(II) (6).** Complex **2** (109 mg, 0.2 mmol) was reacted with cyclohexyl isocyanide (0.063 mL, 0.5 mmol) under the same reaction conditions described for the synthesis of complex **5** to afford complex **6** as an off-white powder (126 mg, 0.164 mmol, 82%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46 (s, br, 4 H, Ar−H), 7.16 (s, br, 4 H, Ar−H), 5.99 (s, br, 4 H, NC*H*(CH$_3$)$_2$), 4.25 (s, br, 2 H, −CH of cyclohexyl the ring), 2.20−0.70 (m, br, 44 H, 24 H for NCH(C*H$_3$*)$_2$ and 20 H for CH$_2$ of the cyclohexyl ring). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 192.4 (s, NCN), 165.7 (s, CN$_4$), 134.3, 122.7, 112.9 (s, Ar−C), 57.5 (s, −CH of cyclohexyl the ring), 54.6 (s, N*C*H(CH$_3$)$_2$), 33.9, 25.6, 25.4 (s, CH$_2$ of cyclohexyl the ring), 21.4 (s, NCH(*C*H$_3$)$_2$). Anal. Calcd for C$_{40}$H$_{58}$N$_{12}$Ni: C, 62.75; H, 7.64; N, 21.95. Found: C, 63.07; H, 7.53; N, 21.30. MS (ESI): *m/z* = 765 [M + H]$^+$, *m/z* = 778 [M + Na]$^+$.

***trans*-Bis(1,3-diisopropylbenzimidazolin-2-ylidene)bis(1-tertiarybutyl-3-methyltetrazolin-5-ylidene)nickel(II) Tetrafluoroborate (7).** Complex **5** (143 mg, 0.2 mmol) was dissolved in dry CHCl$_3$ (6 mL) and added to a suspension of [Me$_3$O]BF$_4$ (118 mg, 0.8 mmol) in dry CHCl$_3$ (4 mL). The resulting yellow suspension was stirred at 75 °C for 12 h and filtered. The residue was washed with CHCl$_3$ and diethyl ether. Subsequently, it was dissolved in CH$_2$Cl$_2$ (30 mL) and the solvent of the filtrate was removed under vacuum to afford complex **7** (116 mg, 0.126 mmol, 63%) as a white powder. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.67 (m, 2 H, Ar−H), 7.62 (m, 2 H, Ar−H), 7.34 (m, 4 H, Ar−H), 6.64, (m, 2 H, ^3J(H,H) = 6.9 Hz, NC*H*(CH$_3$)$_2$), 5.40 (m, 2 H, ^3J(H,H) = 6.9 Hz, NC*H*(CH$_3$)$_2$), 4.33 (s, 6 H, NCH$_3$), 2.09, 1.97, 0.91, 0.65 (s, br, 24 H, NCH(C*H$_3$*)$_2$), 1.70 (s, 18 H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): δ 176.8 (s, NCN), 172.0 (s, CN$_4$), 134.0, 133.4, 124.3, 124.2, 114.1, 113.8 (s, Ar−C), 65.8 (s, *C*(CH$_3$)$_3$), 54.7 (s, N*C*H(CH$_3$)$_2$), 42.5 (s, NCH$_3$), 30.1 C(*C*H$_3$)$_3$), 21.2 (s, NCH(*C*H$_3$)$_2$). ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −76.63, −76.68 (s, BF$_4$). Anal. Calcd for C$_{38}$H$_{60}$B$_2$F$_8$N$_{12}$Ni: C, 49.76; H, 6.59; N, 18.32. Found: C, 49.77; H, 6.75; N, 18.29. MS (ESI): *m/z* = 371 [M − 2BF$_4$]$^{2+}$.

X-ray Diffraction Studies. X-ray data for **2**, **4**, **5**, and **7**·2CH$_2$Cl$_2$ were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 223(2) K (for **2**, **5**, and **7**·2CH$_2$Cl$_2$) or at 293(2) K (for **4**) with the SMART suite of programs.[15] Data were processed and corrected for Lorentz and polarization effects with SAINT,[16] and for absorption effect with SADABS.[17] Structural solution and refinement were carried out with the SHELXTL suite of programs.[18] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the

(15) *SMART* version 5.628; Bruker AXS Inc.: Madison, WI, 2001.
(16) *SAINT+* version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.
(17) Sheldrick, G. W. *SADABS*, version 2.10; University of Göttingen, 2001.
(18) *SHELXTL*, Version 6.14; Bruker AXS Inc.: Madison, WI, 2000.

final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table 1.

Supporting Information Available: Crystallographic data for **2**, **4**, **5**, and **7** · 2CH$_2$Cl$_2$ as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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