

Efficient C–F and C–C Activation by a Novel N-Heterocyclic Carbene–Nickel(0) Complex

Thomas Schaub and Udo Radius*^[a]

Dedicated to Herbert W. Roesky on the occasion of his 70th birthday

Abstract: The NHC-stabilized complex $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{cod})]$ (**1**) was isolated in good yield from the reaction of $[\text{Ni}(\text{cod})_2]$ with 1,3-diisopropylimidazole-2-ylidene (*iPr*₂Im). Compound **1** is a source of the $[\text{Ni}(\text{iPr}_2\text{Im})_2]$ complex fragment in stoichiometric and catalytic transformations. The reactions of **1** with ethylene and CO under atmospheric pressure or with equimolar amounts of diphenylacetylene lead to the compounds $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$ (**2**), $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{Ph}_2)]$ (**3**), and $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{CO})_2]$ (**4**) in good yields. In all cases the $[\text{Ni}(\text{iPr}_2\text{Im})_2]$ complex

fragment is readily transferred without decomposition or fragmentation. In the infrared spectrum of carbonyl complex **4**, the CO stretching frequencies are observed at 1847 and 1921 cm^{-1} , and are significantly shifted to lower wavenumbers compared with other nickel(0) carbonyl complexes of the type $[\text{NiL}_2(\text{CO})_2]$. Complex **1** activates the C–F bond of hexafluorobenzene very efficiently to give $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{F}-$

$\text{C}_6\text{F}_5)]$ (**5**). Furthermore, $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{cod})]$ (**1**) is also an excellent catalyst for the catalytic insertion of diphenylacetylene into the 2,2' bond of biphenylene. The reaction of **1** with equimolar amounts of biphenylene at low temperature leads to $[\text{Ni}(\text{iPr}_2\text{Im})_2(2,2'\text{-biphenyl})]$ (**6**), which is formed by insertion into the strained 2,2' bond. The reaction of diphenylacetylene and biphenylene at 80 °C in the presence of 2 mol % of **1** as catalyst yields diphenylphenanthrene quantitatively and is complete within 30 minutes.

Keywords: C–C activation • carbene ligands • carbenes • nickel

Introduction

During the past decade there has been considerable interest in N-heterocyclic carbenes (NHC) as spectator ligands in organometallic chemistry, particularly as alternatives to phosphane ligands in the field of homogeneous catalysis.^[1] Although the first metal compounds synthesized from isolated N-heterocyclic carbenes were nickel complexes,^[2a,3a] NHC nickel(0) chemistry generally lacks compounds of the type $[(\text{NHC})_2\text{NiL}_n]$ similar to the ubiquitous nickel(0) bisphosphane complex fragments. Structurally characterized, well-defined NHC nickel(0) complexes are rare, known examples including a few NHC adducts of nickel carbonyls^[2] and two-coordinate nickel(0) biscarbene complexes.^[3] Starting with $[\text{Ni}(\text{cod})_2]$ (COD = 1,5-cyclooctadiene) and sterically de-

manding carbene ligands, the homoleptic complexes $[\text{Ni}(\text{Mes}_2\text{Im})_2]$ (Mes = 2,4,6-Me₃C₆H₂),^[3a] and $[\text{Ni}(\text{DIP}_2\text{Im})_2]$ (Dip = 2,6-*iPr*₂C₆H₄)^[3d] have been synthesized by the groups of Arduengo and Herrmann, respectively. Cloke et al. have reported the synthesis of $[\text{Ni}(t\text{Bu}_2\text{Im})_2]$ in 10% yield from the co-condensation reaction of nickel vapor and 1,3-di(*tert*-butyl)imidazole-2-ylidene,^[3c] and more recently the molecular structure of $[\text{Ni}(t\text{Bu}_2\text{Im})_2]$ as well as the attempted conventional synthesis by reaction of *t*Bu₂Im with $[\text{Ni}(\text{cod})_2]$.^[3g] For the *tert*-butyl-substituted NHC, this reaction proceeds with *tert*-butyl cleavage to give different mono(NHC)-stabilized complexes. Recent reports show that Mes₂Im- and Dip₂Im-stabilized nickel(0) complexes generated in situ are precatalysts for catalytic transformations such as C–C and C–N coupling reactions, dehalogenation, and transfer hydrogenation reactions,^[3d,4] although no intermediates have been characterized, isolated, or synthesized by means of stoichiometric organometallic transformations. In this contribution we report some of our results on the synthesis and reactivity of the dimeric complex $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{cod})]$ (**1**), which is stabilized by the sterically less-demanding isopropyl-substituted NHC ligand.

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Results and Discussion

We are interested in electron-rich yet sterically not too demanding NHC nickel(0) complexes. To avoid too much steric crowding and to keep the NHC as electron rich as possible we chose 1,3-diisopropylimidazole-2-ylidene (*iPr₂Im*). This isopropyl-substituted carbene was synthesized similarly to a procedure published by Erker et al.^[5] Some improvements in the preparative details provided the carbene in better yield and with a significantly higher purity. This NHC reacts readily in toluene with [Ni(cod)₂] to afford the dimeric complex [Ni₂(*iPr₂Im*)₄(cod)] (**1**) as a yellow, extremely air- and moisture-sensitive solid after workup, which decomposes at approximately 60 °C in solution and in the solid state. This type of dinuclear, COD-bridged compound is unprecedented in nickel NHC chemistry and is the first binuclear complex in which the two nickel centers are surrounded by one olefinic ligand and two terminal NHC ligands.

The molecular structure of **1** is given in Figure 1 and shows a dinuclear nickel(0) complex with distorted square-planar geometry at the nickel atom. The Ni–C_{carbene} distances of 1.904(3) and 1.906(3) Å are slightly longer than those observed in the structurally characterized homoleptic compounds [Ni(Mes₂Im)₂] (1.827(6) and 1.830(6) Å)^[3a] and [Ni(*t*Bu₂Im)₂] (1.874(2) Å),^[3b] either due to the threefold coordination in **1** or due to reduced back-bonding to the carbene carbon atom. It is noteworthy that the nickel atom reveals an agostic interaction to the methine hydrogen atoms of the isopropyl group, resulting in Ni–HC(CH₃)₂ bond lengths in a range between 2.807 and 2.903 Å (*d*{Ni–C_{ipr}} 3.308–3.458 Å).

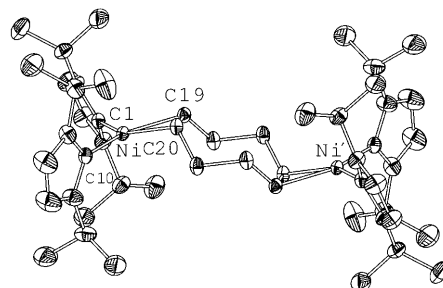
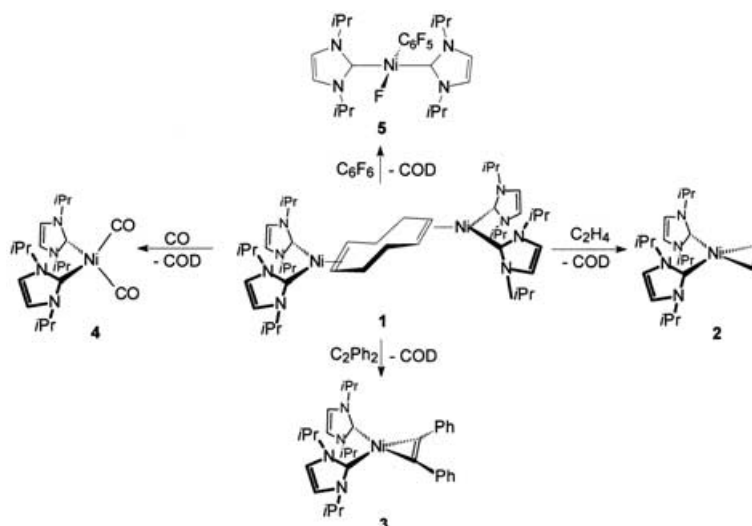


Figure 1. ORTEP diagram of the molecular structure of [Ni₂(*iPr₂Im*)₄(cod)] (**1**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.906(3), Ni–C10 1.904(3), Ni–C19 1.995(3), Ni–C20 1.989(3); C1–Ni–C10 118.11(14), C1–Ni–C20 142.55(14), C1–Ni–C19 100.97(13), C10–Ni–C19 140.89(14), C10–Ni–C20 99.01(14), C19–Ni–C20 41.94(13).

Compound **1** is a useful synthon for transfer reactions of the [Ni(*iPr₂Im*)₂] complex fragment in solution (see Scheme 1). It reacts smoothly at room temperature with ethylene and CO under atmospheric pressure or with stoichiometric amounts of diphenylacetylene to give the complexes [Ni(*iPr₂Im*)₂(η²-C₂H₄)] (**2**), [Ni(*iPr₂Im*)₂(η²-C₂Ph₂)] (**3**), and [Ni(*iPr₂Im*)₂(CO)₂] (**4**) in good yields. In all cases the [Ni(*iPr₂Im*)₂] complex fragment is readily transferred from **1** without decomposition or fragmentation. The ¹H and ¹³C NMR spectra of complexes **2** and **3** reveal significantly shifted resonances for the ethylene and acetylene hydrogen and carbon atoms. The coordination shifts in both cases are of a magnitude typically found for alkene or alkyne complexes with a high degree of π backbonding into the carbon–carbon multiple bond. The molecular structures of complexes **2** and **3** (Figures 2 and 3, respectively) show that the nickel atoms are threefold coordinated to two *iPr₂Im* ligands and the ethylene or alkyne ligand, respectively. The Ni–C_{carbene} distances of 1.905(2) and 1.915(2) Å in **2** and 1.904(3) and 1.914(2) Å in **3** are similar to those found in **1** (1.904(3) and 1.906(3) Å), whereas the C_{carbene}–Ni–C_{carbene} angles of 102.41(9)° (**2**) and 108.33(11)° (**3**) are significantly smaller (118.11(14)° in **1**).

The excellent charge transfer from the nickel atom to the ethylene and diphenylacetylene ligands was a first indication of the high metal basicity of the [Ni(*iPr₂Im*)₂] complex fragment. This was substantiated by an analysis of the CO stretching frequencies of the carbonyl complex [Ni(*iPr₂Im*)₂(CO)₂] (**4**) and comparison with other known complexes of the type [NiL₂(CO)₂]. First of all, compound **4** is suitable to achieve a deeper understanding of the fundamental steric and electronic factors of the ligand system. Where-

Abstract in German: Der NHC stabilisierte Komplex [Ni₂(*iPr₂Im*)₄(cod)] (**1**) wurde aus der Reaktion von [Ni(cod)₂] mit 1,3-Diisopropylimidazole-2-ylidene (*iPr₂Im*) in guter Ausbeute isoliert. Verbindung **1** ist eine Quelle für das Komplexfragment [Ni(*iPr₂Im*)₂] sowohl in stöchiometrischen als auch in katalytischen Transformationen. So liefert die Reaktion von **1** mit Ethylen und CO bei Atmosphärendruck oder mit äquimolaren Mengen an Tolan die Verbindungen [Ni(*iPr₂Im*)₂(η²-C₂H₄)] (**2**), [Ni(*iPr₂Im*)₂(η²-C₂Ph₂)] (**3**) bzw. [Ni(*iPr₂Im*)₂(CO)₂] (**4**) in guten Ausbeuten. In allen Fällen wurde das Komplexfragment [Ni(*iPr₂Im*)₂] ohne Zersetzung oder Fragmentierung auf das organische Substrat übertragen. Im Infrarotspektrum des Carbonylkompleses **4** wurden die CO Streckschwingungen bei 1847 und 1921 cm⁻¹ detektiert, also bei signifikant niedrigeren Wellenzahlen als sie für andere Nickel(0) Carbonylkomplexe des Typs [NiL₂(CO)₂] beobachtet werden konnten. Verbindung **1** addiert sehr effizient eine der C–F-Bindungen von Hexafluorobenzol unter Ausbildung des Komplexes [Ni(*iPr₂Im*)₂(F)(C₆F₅)] (**5**). Darüber hinaus ist [Ni₂(*iPr₂Im*)₄(cod)] (**1**) ein ausgezeichneter Katalysator für die katalytische Insertion von Tolan in die 2,2'-Bindung des Biphenylens. Die Reaktion von **1** mit äquimolaren Mengen an Biphenylen führt schon bei tiefen Temperaturen zu [Ni(*iPr₂Im*)₂(2,2'-biphenyl)] (**6**), dem Insertionsprodukt in die gespannte 2,2'-Bindung des Biphenylens. Die Umsetzung von Tolan mit Biphenylen bei 80 °C unter Verwendung von 2 mol % **1** als Katalysator liefert innerhalb einer halben Stunde quantitativ Diphenylphenanthren.



Scheme 1. Reactivity of $[\text{Ni}_2(\text{iPr}_2\text{Im})_2(\text{cod})]$ (**1**).

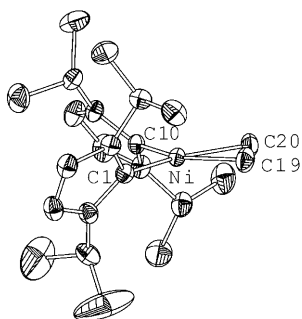


Figure 2. ORTEP diagram of the molecular structure of $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$ (**2**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Ni–C1 1.905(2), Ni–C10 1.915(2), Ni–C19 1.950(3), Ni–C20 1.946(2), C19–C20 1.420(4); C1–Ni–C10 102.41(9), C1–Ni–C20 151.25(11), C1–Ni–C19 108.53(11), C10–Ni–C19 149.04(11), C10–Ni–C20 106.28(11), C19–Ni–C20 42.76(12), C19–C20–Ni 68.77(14), C20–C19–Ni 68.48(14).

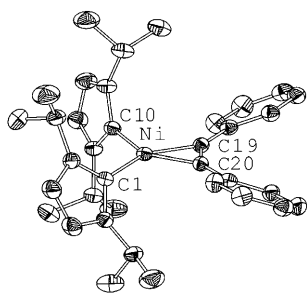


Figure 3. ORTEP diagram of the molecular structure of $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{Ph}_2)]$ (**3**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Ni–C1 1.914(2), Ni–C10 1.904(3), Ni–C19 1.870(3), Ni–C20 1.881(3), C19–C20 1.290(3); C19–Ni–C20 40.22(10), C1–Ni–C10 108.33(11), C1–Ni–C20 108.85(10), C10–Ni–C19 102.65(11), C19–C20–C27 142.5(3), C20–C19–C21 143.8(3).

as Hermann et al.^[2a] synthesized $[\text{Ni}(\text{Me}_2\text{Im})_2(\text{CO})_2]$ from the reaction of $[\text{Ni}(\text{CO})_4]$ and 1,3-dimethylimidazole-2-ylidene, Nolan and co-workers^[2d] synthesized the four-coordi-

nate complexes $[\text{Ni}(\text{X}_2\text{Im})(\text{CO})_3]$ (X = Mes, Dip, cyclohexyl) and three-coordinate compounds $[\text{Ni}(\text{X}_2\text{Im})(\text{CO})_2]$ with the sterically more demanding carbenes (X = *t*Bu) as ligands.

In the infrared spectrum of **4**, the carbonyl stretching frequencies are detected at 1847 and 1921 cm^{-1} and thus confirm the high metal basicity of the $[\text{Ni}(\text{iPr}_2\text{Im})_2]$ fragment. These frequencies are significantly shifted to lower wavenumbers compared to other nickel(0) carbonyl complexes of the type $[\text{NiL}_2(\text{CO})_2]$ (see Table 1), which is an experimental proof

of the excellent donor properties of the iPr_2Im ligand compared to other widely used ligands, including other NHC ligands with different substituents, such as Me_2Im .

Table 1. Frequencies of the CO stretches of symmetry A_1 and B_1 for selected nickel carbonyl complexes of the type $[\text{NiL}_2(\text{CO})_2]$.^[a]

Complex	A_1 [cm^{-1}]	B_2 [cm^{-1}]
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{CO})_2]$ (4)	1927	1847
$[\text{Ni}(\text{Me}_2\text{Im})_2(\text{CO})_2]$ ^[2a]	1946	1873
$[\text{Ni}(\text{bipy})(\text{CO})_2]$ ^[6a]	1950	1861
$[\text{Ni}(\text{bdepe})(\text{CO})_2]$ ^[6a]	1984	1920
$[\text{Ni}(\text{P}(\text{iPr})_3)_2(\text{CO})_2]$ ^[6b]	1984	1922
$[\text{Ni}(\text{Me}_4\text{Triaz})_2(\text{CO})_2]$ ^[6c]	1982	1906
$[\text{Ni}(\text{PMe}_3)_2(\text{CO})_2]$ ^[6b]	1990	1926
$[\text{Ni}(\text{bdppm})(\text{CO})_2]$ ^[6d]	1991	1925
$[\text{Ni}(\text{PPh}_3)_2(\text{CO})_2]$ ^[6b]	1994	1936
$[\text{Ni}(\text{Dip}_2\text{DAB})(\text{CO})_2]$ ^[6e]	2014	1954
$[\text{Ni}(\text{bdppp})(\text{CO})_2]$ ^[6f]	2020	1968

[a] Abbreviations used: bipy: 2,2'-bipyridyl; bdepe: 1,2-bis(diethylphosphanyl)ethane; Me_4Triaz : 1,2,3,4-tetramethyl-1,2,4-triazole-2-ium-5-ylidene; bdppm: bis(diethylphosphanyl)methane; Dip_2DAB : *N,N'*-bis(2,6-di(isopropylphenyl)glyoxylimine); bppp: 1,3-bis(diethylphosphanyl)propane.

The X-ray analysis of **4** (Figure 4) reveals a distorted tetrahedral structure in which the C10–Ni–C10' angle between the carbonyl carbon atoms (108.47(12) $^\circ$) is very close to the tetrahedral angle, whereas the C1–Ni–C1' angle between the carbene carbon atoms of the sterically much more demanding NHC ligands is significantly smaller (95.85(9) $^\circ$). Both iPr_2Im ligands are roughly oriented along the C10–Ni–C10' plane, which intersects the planes through the atoms N1, C1, and N2, with an angle of 6.96 $^\circ$. The Ni–C10 distance to the carbon atom of the carbonyl ligand of 1.758(2) \AA is similar to those found for other nickel carbonyl complexes such as $[\text{Ni}(\text{Me}_2\text{Im})_2(\text{CO})_2]$ ^[2a] (1.758(5) \AA) and $[\text{Ni}(\text{PPh}_3)_2(\text{CO})_2]$ ^[7] (1.763(3) \AA). The Ni–C1 bond length to the carbene carbon atom of 2.002(2) \AA is approximately 0.25 \AA longer than the Ni–C_{CO} distance due to much stronger back-bonding between the nickel atom and the carbonyl ligand. This Ni–C1

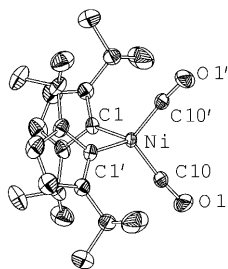


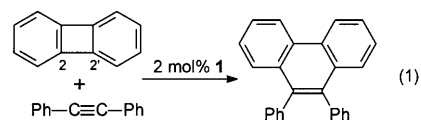
Figure 4. ORTEP diagram of the molecular structure of $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{CO})_2]$ (**4**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 2.002(2), Ni–C10 1.758(2), C10–O1 115.5(2); C1–Ni–C1' 95.85(9), C10–Ni–C10' 108.47(12).

distance is even longer than Ni–C single bonds found in different organyl complexes such as $[\text{Ni}(\eta^4\text{-cod})(\text{C}_6\text{F}_5)_2]$ (1.921(2) Å),^[8a] $[\text{Ni}(\text{acac})(\text{PPh}_3)(\text{Et})]$ (1.970(1) Å),^[8b] $[\text{Ni}(\text{acac})(\text{PPh}_3)(\text{PhC}=\text{CPh})(\text{CH}_3)]$ (1.897 Å),^[8c] and $[\text{Ni}(\text{dippe})(\text{Ph})(\text{CN})]$ (1.935(2) Å for Ni–Ph),^[8d] which indicates that nickel–carbene π back-bonding is rather unimportant in **4**. The Ni–C_{carbene} distances in **1–3** are approximately 10 pm, and those of $[\text{Ni}(\text{Mes}_2\text{Im})_2]$ and $[\text{Ni}(t\text{Bu}_2\text{Im})_2]$ more than 10 pm,^[3a,g] shorter than the corresponding distances in **4**. This effect might arise from the different coordination numbers, but it presumably also reflects the different electronic situations at the metal atoms in these compounds. The Ni–C_{carbene} distances are short for the electron-rich complex $[\text{Ni}(\text{X}_2\text{Im})_2]$ and approximately 20 pm longer for the carbonyl complex **4**, in which electron density at the metal atom is lower due to back-bonding to the carbonyl ligand. This observation supports recent reports that NHC ligands may very well be capable of efficient π back-bonding to stabilize electron-rich complexes.^[9] Thus, the NHC ligand system reveals a remarkable electronic flexibility and is suitable, due to its σ donating and π accepting properties, for the stabilization of metal atoms in both low and high oxidation states.

The activation of aromatic carbon–fluorine bonds has nowadays been observed with a wide variety of transition metals with different electron configurations.^[10] In particular, it has been proven that nickel complex fragments such as $[\text{Ni}(\text{PEt}_3)_2]$ ^[11] and $[\text{Ni}(\text{dtbpe})]$ (dtbpe = $t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}t\text{Bu}_2$)^[12] are effective in C–F activation reactions and exhibit selectivity for C–F over C–H bonds. In this field, the activation of hexafluorobenzene is an especially demanding problem, since the activation of C_6F_6 usually requires long reaction times under thermal conditions. The oxidative-addition chemistry of $[\text{Ni}(\text{PEt}_3)_2(\text{cod})]$ was first examined by Fahey and Mahan,^[11a] who provided evidence for the oxidative addition of hexafluorobenzene in the reaction with $[\text{Ni}(\text{cod})_2]$ in the presence of PEt_3 . A more thorough study by Perutz et al. demonstrated that the reaction of $[\text{Ni}(\text{PEt}_3)_4]$ and 1.2 equivalents of C_6F_6 requires four weeks to be driven to completeness.^[11b] Pörschke and co-workers have described a detailed study of the reactivity of the 14-electron fragment $[\text{Ni}(\text{dtbpe})]$ with a variety of arenes.^[12] This fragment reacts in the presence of an excess of C_6F_6 to give the η^2 -coordinate

complex $[\text{Ni}(\text{dtbpe})(\eta^2\text{-C}_6\text{F}_6)]$, which undergoes thermal oxidative addition at 293 K to form $[\text{Ni}(\text{dtbpe})(\text{F})(\text{C}_6\text{F}_5)]$. Unfortunately, no kinetic data were provided in the paper, just a statement that the rearrangement requires days to be complete. Hofmann et al. have reported the direct oxidative addition of hexafluorobenzene after eight days reaction with $[\text{Pt}(\text{dtbpm})]$ using the substrate as a solvent.^[13] This inertness of C_6F_6 to undergo C–F addition to transition metal complex fragments, as well as two recent reports on catalytic C–F activation mediated by either $[\text{Ni}(\text{cod})_2]$ associated to aryl-substituted NHCs^[3d] or $[\text{Ni}(\text{acac})_2]$ and a mixture of aryl-substituted imidazolium salts in the presence of NaH,^[4e] led us to investigate the reactivity of **1** with respect to C–F activation of hexafluorobenzene in some detail. Surprisingly, the reaction of **1** with equimolar amounts of C_6F_6 in benzene or toluene proceeds rapidly but smoothly. The reaction is complete within one hour and gives a yellow reaction product, $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{F})(\text{C}_6\text{F}_5)]$ (**5**), which is readily soluble in nonpolar organic solvents. Three sets of signals at $\delta = -116.0$, -163.3 , and -165.0 ppm are observed for the per-fluorinated phenyl ligand in the ^{19}F NMR spectrum of **5** and, most significantly, a highly shifted resonance at $\delta = -373.7$ ppm for the fluoride ligand. Complex **5** presumably adopts a *trans* configuration, which is in accordance with the observation of equivalent NHC ligands in the ^1H and ^{13}C NMR spectra. This complex, however, could not be isolated in the form of crystals suitable for X-ray analysis. However, complex **1** activates aryl C–F bonds very efficiently and this is, to the best of our knowledge, the only example known for an oxidative addition of hexafluorobenzene with formation of a pentafluorophenyl fluoride complex on a reasonable timescale. We are currently further exploring the reactivity of **5** and the reaction behavior of **1** towards other fluorinated organic molecules.

In addition to the C–F activation of hexafluorobenzene we were interested in the performance of **1** in C–C activation reactions,^[14] in particular in the catalytic insertion of diphenylacetylene into the strained C–C bond of biphenylene to yield diphenylphenanthrene (see Equation (1)). For bis-(phosphane)nickel(0) complexes, this reaction has been investigated in the last few years mainly by Jones and co-workers.^[15–17]



The reaction of **1** with an equimolar amount of biphenylene at low temperature leads to the insertion product into the 2,2' bond, $[\text{Ni}(\text{iPr}_2\text{Im})_2(2,2'\text{-biphenyl})]$ (**6**; see Figure 5). Furthermore, both complexes **1** and **3** catalyze the insertion of diphenylacetylene into the 2,2' bond of biphenylene very efficiently. The reaction proceeds at room temperature, albeit very slowly, and is finished after a period of approximately three days with 2 mol% of **1** as catalyst. At 80 °C,

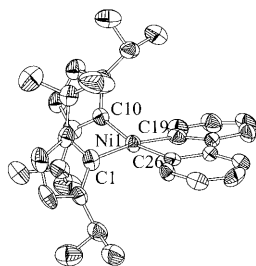


Figure 5. ORTEP diagram of the molecular structure of $[\text{Ni}(\text{iPr}_2\text{Im})_2(2,2'\text{-biphenyl})]$ (**6**) in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1 1.946(11), Ni1–C10 1.927(10), Ni1–C19 1.942(11), Ni1–C26 1.949(10); C1–Ni1–C10 95.3(4), C1–Ni1–C26 92.7(4), C10–Ni1–C19 90.4(4), C19–Ni1–C26 83.3(5).

however, the catalytic insertion is completed within 30 minutes.

Neither **1** nor **3** catalyzes the cyclooligomerization of diphenylacetylene. The reaction of this alkyne with 0.1 equivalents of **1** for three days in C_6D_6 at 80°C leads to complex **3** and unreacted alkyne; no oligomerization product such as hexaphenylbenzene was observed. Another major side-reaction, the dimerization of biphenylene, is very slow compared to the catalytic insertion. Thus, the reaction of biphenylene with 7 mol % of **1** in C_6D_6 at 80°C gave, after a period of three days, the dimerization product, tetraphenylene, in 58% yield.

Complexes **1** and **3** compete nicely with other known catalysts for the insertion of internal alkynes into the 2,2' bond of biphenylene and are superior to other well-defined catalytic systems reported to date. The corresponding bis(phosphanyl)-substituted complexes $[\text{Ni}(\text{dippe})(\eta^2\text{-C}_2\text{Ph}_2)]$ (dippe = $i\text{Pr}_2\text{PC}_2\text{H}_4\text{P}i\text{Pr}_2$) and $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{Ph}_2)]$ produce only small amounts of 9,10-diphenylphenanthrene (2.5% conversion after 40 h at 110°C using 12.5% of the dippe complex).^[17a] In these systems, however, the rate increases dramatically to a turnover frequency of 3 h^{-1} (10% catalyst, 70°C) if molecular oxygen (6 mol %) is present in the reaction mixture. Neither the role of the oxygen addition nor the catalytically active species and the nature of the precatalyst have ever been clarified, but it has been proposed that the oxygen removes the phosphane ligands to generate a reactive nickel species. We hope to shed further light on the mechanism of the reaction using **1** as a catalyst in the future.

To summarize, we have shown that the NHC ligand 1,3-diisopropylimidazole-2-ylidene ($i\text{Pr}_2\text{Im}$) provides a unique balance of donor properties and steric congestion that renders the carbene an ideal ligand for investigations directed at the isolation and characterization of nickel(0) bis(carbene) complexes. The reaction with $[\text{Ni}(\text{cod})_2]$ leads to an unprecedented dinuclear nickel(0) complex $[\text{Ni}_2(i\text{Pr}_2\text{Im})_4(\text{cod})]$ (**1**). Compound **1** is a source of the $[\text{Ni}(i\text{Pr}_2\text{Im})_2]$ fragment in stoichiometric and catalytic transformations. This was demonstrated for the reaction of **1** with CO, ethylene, and alkynes, and also for the activation of the C–F bond of

hexafluorobenzene and the C–C bond of biphenylene. Complex **1** activates the C–F bond of hexafluorobenzene most efficiently, and is, to the best of our knowledge, the best thermal C–F activator (in terms of an oxidative addition to a metal atom) for C_6F_6 reported so far. Furthermore, **1** also catalyzes the insertion of diphenylacetylene into the 2,2' bond of biphenylene very efficiently.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen using standard Schlenk techniques, as reported previously.^[18] 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 AV 400 at 298 K. ^{13}C NMR spectra are broad-band proton decoupled. NMR spectroscopic data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Coupling constants are quoted in Hertz. Residual solvent peaks used as internal standards: C_6D_6 : $\delta = 7.15$ ppm (^1H) or natural-abundance carbon signal at $\delta = 128.0$ ppm. Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 and are reported in cm^{-1} .

1,3-Diisopropylimidazolium chloride: A modified literature procedure was used for the synthesis of the imidazolium salt.^[5] Isopropyl amine (61.8 mL, 0.72 mol) was added dropwise to a suspension of formaldehyde (21.6 g, 0.71 mol) in toluene (120 mL). The temperature of the reaction mixture was kept below 40°C during the addition. Afterwards, the reaction mixture was stirred for ten minutes and then cooled to 0°C . Another equivalent of isopropylamine (61.8 mL, 0.72 mol) and 6 N HCl (120 mL, 0.72 mol) were then added slowly. The temperature of the solution was raised to 25°C and glyoxal (82.8 mL, 0.72 mol; 40% in H_2O) was added dropwise. The mixture was stirred overnight to give a dark solution. All volatile material was then removed in vacuo. The brown residue was vigorously dried in vacuo at 150°C for 6 h to yield a brown solid (113 g, 83%). ^1H NMR (400 MHz, D_2O , 25°C): $\delta = 1.43$ (d, 12 H, CH_3), 4.52 (m, 2 H, $i\text{Pr-CH}$), 7.47 (s, 2 H, NCHCHN), 8.76 ppm (s, 1 H, NCHN); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, D_2O , 25°C): $\delta = 22.07$ (CH_3), 53.04 ($i\text{Pr-CH}$), 120.47 (NCCN), 132.47 ppm (NCN).

1,3-Diisopropylimidazol-2-ylidene: THF (600 mL) was added at room temperature to a mixture of 1,3-diisopropylimidazole (113.0 g, 0.60 mol), sodium hydride (15.7 g, 0.65 mol), and potassium *tert*-butoxide (3.30 g, 29.4 mmol). The mixture was stirred overnight to give a dark suspension. All volatile material was then removed in vacuo and the resulting brown oil was distilled at 150°C into a trap cooled with liquid nitrogen to afford 1,3-diisopropylimidazol-2-ylidene (73 g, 80%) as a colorless liquid (melting point approximately 20°C). The carbene is thermally labile and forms a dark oil at room temperature, but it can be stored for a longer period of time at -40°C without decomposition. ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 1.27$ (d, 12 H, CH_3), 4.40 (m, 2 H, $i\text{Pr-CH}$), 6.63 ppm (s, 2 H, NCHCHN); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25°C): $\delta = 24.27$ ($i\text{Pr-CH}_3$), 52.12 ($i\text{Pr-CH}$), 115.74 (NCCN), 211.86 ppm (NCN); IR (KBr): $\tilde{\nu} = 407$ (m), 496 (w), 555 (m), 640 (w), 669 (m), 682 (m), 710 (s), 879 (m), 928 (w), 981 (m), 1089 (m), 1131 (s), 1215 (vs), 1242 (s), 1267 (s), 1328 (m), 1388 (vs), 1459 (s), 1669 (m), 2642 (w), 2874 (s), 2963 (vs), 3055 (m), 3103 cm^{-1} (m).

Compound 1: A solution of $[\text{Ni}(\text{cod})_2]$ (4.50 g, 16.4 mmol) in toluene (50 mL) was added at -78°C to a solution of 1,3-diisopropylimidazol-2-ylidene (5.00 mL, 32.8 mmol) in toluene (50 mL). The reaction mixture was allowed to warm to room temperature overnight. Insoluble material was then filtered off and all volatiles of the filtrate were removed in vacuo. The yellow residue was suspended in hexane (50 mL), filtered, washed with a small portion of hexane, and dried in vacuo to yield a yellow powder (3.70 g, 54%). Crystals suitable for X-ray diffraction were obtained from saturated THF solutions of **1** at 0°C . ^1H NMR (400 MHz, $\text{C}_4\text{D}_8\text{O}$, 25°C): $\delta = 1.27$ (m, 48 H, $i\text{Pr-CH}_3$), 1.46–2.09 (m, 12 H, COD),

5.29 (sept, 8H, $^3J_{\text{HH}} = 6.9$ Hz, *iPr-CH*), 6.75 ppm (s, 8H, *NCHCHN*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 23.81$ (*iPr-CH}_3*), 23.98 (*iPr-CH}_3*), 31.96 (COD- CH_2), 33.52 (COD- CH_2), 38.57 (COD- CH), 50.58 (*iPr-CH*), 50.69 (*iPr-CH*), 54.57 (COD- CH), 113.93 (NCCN), 114.29 (NCCN), 204.19 (NCN), 205.28 ppm (NCN); IR (KBr): $\tilde{\nu} = 3216$ (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 (m), 793 (m), 673 (s), 549 cm^{-1} (m); elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{76}\text{N}_8\text{Ni}_2$ (834.5): C 63.33, H 9.18, N 13.34; found: C 63.56, H 9.09, N 12.99; MS: m/z (%): 362.2 (24) [$(\text{iPr}_2\text{Im})_2\text{Ni}$] $^+$, 320.1 (8) [$(\text{iPr}_2\text{Im})_2\text{Ni-Pr}$] $^+$.

Compound 2: Ethylene was passed through a solution of complex **1** (363 mg, 0.42 mmol) in toluene (30 mL) at room temperature. All volatile material was removed in vacuo, and the residue was suspended in 20 mL of hexane, filtered, and dried in vacuo to afford **2** as a yellow powder (280 mg, 72%). Crystals suitable for X-ray diffraction were obtained from saturated hexane solutions of **2** at 0 °C ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 1.13$ (d, 24H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 1.95 (s, 4H, CH_2), 5.41 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, *iPr-CH*), 6.48 ppm (s, 4H, *NCHCHN*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 22.24$ (*iPr-CH}_3*), 24.85 (C_{ethene}), 49.71 (*iPr-CH*), 113.46 (NCCN), 203.00 ppm (NCN); IR (KBr): $\tilde{\nu} = 381$ (m), 478 (m), 572 (w), 675 (m), 709 (m), 801 (s), 921 (m), 958 (m), 1018 (vs), 1093 (s), 1139 (m), 1221 (s), 1263 (s), 1288 (m), 1368 (m), 1397 (m), 1415 (m), 1465 (m), 1669 (m), 2870 (m), 2944 (s), 3119 (w), 3158 cm^{-1} (w); MS: m/z (%): 362.3 (28) [$(\text{iPr}_2\text{Im})_2\text{Ni}$] $^+$.

Compound 3: Complex **1** (417 mg, 0.50 mmol) and diphenylacetylene (89.0 mg, 0.50 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 to afford **3** as a dark-red powder (310 mg, 57%). Crystals suitable for X-ray diffraction were obtained from saturated solutions of **3** in diethyl ether at -40 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 1.03$ (d, 24H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 5.53 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, *iPr-CH*), 6.55 (s, 4H, *NCHCHN*), 7.02 (m, 2H, aryl- H_p), 7.19 (m, 4H, aryl- H_m), 7.61 ppm (d, 4H, $^3J_{\text{HH}} = 7.0$ Hz, aryl- H_o); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 23.92$ (CH_3), 51.78 (*iPr-CH*), 115.78 (NCCN), 124.60 (aryl- C_p), 129.50 (aryl- C_m), 132.60 (aryl- C_o), 139.26 ($\text{C}\equiv\text{C}$), 139.69 (aryl- C_i), 201.49 ppm (NCN); IR (KBr): $\tilde{\nu} = 556$ (m), 668 (m), 697 (m), 763 (e), 911 (w), 1006 (w), 1013 (w), 1128 (8w), 1214 (vs), 1258 (m), 1274 (m), 1395 (m), 1413 (m), 1472 (m), 1490 (m), 1576 (m), 1741 (m, $\nu_{\text{C}\equiv\text{C}}$), 2866 (m), 2932 (m), 2966 (m), 3049 cm^{-1} (w); elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{42}\text{N}_4\text{Ni}$ (541.4): C 70.99, H 7.82, N 10.35; found: C 70.97, H 7.70, N 9.56; MS: m/z (%): 540 (1) [$M-\text{H}$] $^+$, 362.1 (15) [$(\text{iPr}_2\text{Im})_2\text{Ni-H}$] $^+$.

Compound 4: Carbon monoxide was passed through a solution of complex **1** (363 mg, 0.42 mmol) in toluene (30 mL) at room temperature. All volatile material was removed in vacuo to afford **4** as a yellow powder (310 mg, 88%). Crystals suitable for X-ray diffraction were obtained from saturated solutions of **4** in diethyl ether at -40 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 1.05$ (d, $^2J_{\text{HH}} = 6.8$ Hz, 24H, CH_3), 5.39 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, *iPr-CH*), 6.49 ppm (s, 4H, *NCHCHN*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 23.63$ (*iPr-CH}_3*), 51.68 (*iPr-CH*), 116.19 (NCCN), 198.01 (CO), 205.80 ppm (NCN); IR (KBr): $\tilde{\nu} = 473$ (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, br, ν_{CO}), 1927 (vs, br, ν_{CO}), 2872 (m), 2931 (m), 2979 (s), 3107 (w), 3142 (w), 3173 cm^{-1} (w); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{32}\text{N}_4\text{NiO}_2$ (419.2): calcd for C 57.31, H 7.69, N 13.37; found: C 56.94, H 7.65, N 12.95.

Compound 5: Complex **1** (363 mg, 0.42 mmol) was dissolved in toluene (20 mL) and hexafluorobenzene (0.12 mL, 1.00 mmol) was added. The resulting yellow solution was stirred overnight. The reaction mixture was then filtered through a pad of Celite and all volatile material was removed from the filtrate in vacuo. The remaining yellow solid was suspended in 20 mL of hexane, filtered, and dried in vacuo to afford **5** as a yellow powder (360 mg, 65%). ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 1.08$ (brs, 12H, CH_3), 1.40 (brs, 12H, CH_3), 6.25 (s, 4H, *NCHCHN*), 6.51 ppm (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, *iPr-CH}_3*); ^{19}F NMR (376.4 MHz, C_6D_6 , 25 °C, CFCl_3): $\delta = -116.0$ (d, 2F, $^3J_{\text{FF}} = 28.7$ Hz, aryl- F_o), -163.3 (t, 1F, $^3J_{\text{FF}} = 20.3$ Hz, aryl- F_p), -165.0 (m, 2F, aryl- F_m), -373.7 ppm (s, 1F, Ni- F); IR (KBr): $\tilde{\nu} = 438$ (m), 477 (m), 578 (w), 673 (m), 708 (w), 732 (m), 777 (m), 951 (s), 1013 (s), 1130 (m), 1215 (s), 1226 (s), 1263 (m), 1370 (m), 1394 (m), 1441 (s), 1495 (s), 2876 (w), 2936 (m), 2980 (s), 3050 (s), 3118 cm^{-1} (w); MS: m/z (%): 549.2 (3) [M] $^+$, 362.3 (40) [$(\text{iPr}_2\text{Im})_2\text{Ni}$] $^+$.

Compound 6: Complex **1** (363 mg, 0.42 mmol) and biphenylene (152 mg, 1.00 mmol) were dissolved in toluene (30 mL) and stirred overnight. Undissolved components were removed by filtration through a pad of Celite and all volatiles were removed from the filtrate in vacuo. The remaining orange solid was treated with small portions of hexane and dried in vacuo to afford **6** as an orange powder (345 mg, 66%). Crystals suitable for X-ray diffraction were obtained from saturated solutions of **6** in diethyl ether at -40 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 0.70$ (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 1.14 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 5.43 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, *iPr-CH*), 6.37 (d, 2H, aryl- H_m), 6.39 (s, 4H, *NCHCHN*), 6.97 (m, 2H, aryl- H_p), 7.18 (m, 2H, aryl- H_m), 7.70 ppm (m, 2H, aryl- H_o); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 23.26$ (*iPr-CH}_3*), 23.86 (*iPr-CH}_3*), 52.07 (*iPr-CH*), 116.76 (NCCN), 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 ppm (NCN); IR (KBr): $\tilde{\nu} = 575$ (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 cm^{-1} (m); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{40}\text{N}_4\text{Ni}$ (515.4): calcd for C 69.92, H 7.82, N 10.87; found: C 69.34, H 7.95, N 11.21.

9,10-Diphenylphenanthrene: Biphenylene (30.4 mg, 0.20 mmol), diphenylacetylene (36.0 mg, 0.20 mmol), and complex **1** (10 mg, 0.012 mmol) were mixed in an NMR tube and dissolved in C_6D_6 (1.00 mL). The reaction mixture was heated to 80 °C for 30 min. According to ^1H NMR spectroscopy, the yield was greater than 95%. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 6.94$ (m, 2H, aryl- CH_2), 6.98–7.13 (m, 10H, aryl- $\text{CH}_{\text{phenyl}}$), 7.41 (m, 2H, aryl- CH_3), 7.55 (m, 2H, aryl- CH_1), 8.74 ppm (m, 2H, aryl- CH_4); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 139.17$ (aryl- C_7), 136.70 (aryl- C_6), 131.55 (aryl- C_i), 130.97 (aryl- C_3), 130.37 (aryl- C_o), 129.68 (aryl- C_1), 126.95 (aryl- C_m), 125.95 (aryl- C_2), 125.77 (aryl- C_3), 125.70 (aryl- C_p), 121.96 ppm (aryl- C_4).

Table 2. X-ray data collection and processing parameters.

	1-C ₄ H ₈ O	2	3	4	6
formula	C ₂₆ H ₄₆ N ₄ NiO	C ₂₀ H ₃₆ N ₄ Ni	C ₃₂ H ₄₂ N ₄ Ni	C ₁₀ H ₁₆ N ₂ ONi	C ₁₂₀ H ₁₆₈ N ₁₆ Ni ₄
F_w	489.38	391.24	541.42	209.61	2069.56
crystal system	monoclinic	tetragonal	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P4_2/n$	$P2_1/n$	$Pbcn$	$P2_12_12_1$
a [Å]	16.061(2)	21.7887(14)	17.478(4)	9.5275(8)	20.1563(14)
b [Å]	9.4571(7)	–	10.101(2)	14.7564(14)	23.544(2)
c [Å]	18.5381(18)	9.5251(5)	17.817(4)	16.6747(12)	27.913(3)
β [°]	94.962(15)	–	108.79(3)	–	–
V [Å ³]	2805.2(5)	4522.0(5)	2977.9(10)	2342.7(3)	13246(2)
Z	4	8	4	8	4
μ [mm ⁻¹]	0.380	0.867	0.677	0.562	0.404
total/indep. reflns.	16183/5652	28737/4409	18790/7055	21008/2929	58561/19036
obsd reflns. ^[a]	4147	3227	4608	2038	10087
parameters	297	226	334	123	1255
final R , ^[b] wR_2 ^[c,d]	0.0560, 0.1334	0.0378, 0.0815	0.0588, 0.1664	0.0350, 0.0811	0.0779, 0.1668

[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 $I > 2\sigma(I)$.

Tetraphenylene: Biphenylene (50.0 mg, 0.33 mmol) and complex **1** (20.0 mg, 0.024 mmol) were mixed in an NMR tube and dissolved in C₆D₆ (1.00 mL). The reaction mixture was heated to 80 °C for three days. According to ¹H NMR spectroscopy, the yield of tetraphenylene in this reaction was 58%. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.13 (m, 8H, aryl-CH_o), 7.25 ppm (m, 8H, aryl-CH_m); ¹³C[¹H] NMR (100 MHz, C₆D₆, 25 °C): δ = 116.26 (aryl-C_i), 127.14 (aryl-C_o), 128.06 ppm (aryl-C_m).

Crystal structure determinations of [Ni₂(iPr₂Im)₄(cod)] (1**), [Ni(iPr₂Im)₂(η²-C₂H₄)] (**2**), [Ni(iPr₂Im)₂(η²-C₂Ph₂)] (**3**), [Ni(iPr₂Im)₂(CO)₂] (**4**), and [Ni(iPr₂Im)₂(2,2'-biphenyl)] (**6**):** Crystal data collection and processing parameters are given in Table 2. The crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS diffractometer (Ag_{Kα} radiation for compounds **1**, **4**, and **6**; Mo_{Kα} radiation for compounds **2** and **3**), equipped with an FTS AirJet low-temperature device. Data were collected at 203 K. The images were processed with the Stoe software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed, where necessary, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms; hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.^[19]

CCDC-262330–262334 (**1–4** and **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

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