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Square-Planar (Pentafluorophenyl)nickel(II) Complexes by Derivatization of a C–F Activation Product

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The NHC-stabilized C–F activation product [Ni(*i*Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**1**) was isolated from the reaction of [Ni(cod)$_2$] with 1,3-diisopropylimidazol-2-ylidene (*i*Pr$_2$Im) and hexafluorobenzene. Square-planar (pentafluorophenyl)nickel complexes of the type [Ni(*i*Pr$_2$Im)$_2$(X)(C$_6$F$_5$)] were obtained by a systematic derivatization of **1**. The reaction of **1** with silylated compounds and organyllithium compounds led smoothly to replacement of the fluorido ligand in **1** by halogenido, trifluoromethanesulfonato, cyanido, organyl, selenolato, thiolato, and hydrido ligands. According to these procedures, the NHC-stabilized (pentafluorophenyl)nickel complexes [Ni(*i*Pr$_2$Im)$_2$(X)(C$_6$F$_5$)] (X = Cl **2**, I **3**, CF$_3$SO$_3$ **4**, CN **5**), [Ni(*i*Pr$_2$Im)$_2$(R)(C$_6$F$_5$)] (R = Me **6**, Ph **7**, C$_2$Ph **8**, η^1-Cp **9**), [Ni(*i*Pr$_2$Im)$_2$(SR)(C$_6$F$_5$)] (R = Ph **10**, *n*Pr **11**), [Ni(*i*Pr$_2$Im)$_2$(SeR)(C$_6$F$_5$)] (R = Ph **12**, *i*Pr **13**), and [Ni(*i*Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**14**) were prepared. The complexes **4**, **6**. **9**, **11**, **13** and **14** were structurally characterized.

Introduction

There has been a growing interest during the past decade in transition-metal-mediated C–F activation reactions and in the development of new catalytic processes for the functionalization of fluoroorganics.[1] One strategy for the synthesis or modification of fluoroorganic compounds involves the metal-mediated selective removal or the metal-mediated replacement of a fluorine atom from readily available precursors, which should, in principle, provide routes to new building blocks and high-value fluorinated compounds. Most of the investigations so far are concerned with hydrodefluorination reactions of highly fluorinated molecules.[1] Routes for the generation of fluoroorganics by transition-metal-mediated conversions of an aromatic C–F bond into C–C or C–heteroatom bonds are barely developed so far. Transition-metal-mediated cross-coupling reactions of monofluoroarenes, for example, to give non-fluorinated aromatic compounds are known for several years,[2] but there are, however, only few examples for cross-coupling reactions using poly- or perfluorinated arenes.[3] Activation of the carbon–fluorine bond of fluoroaromatics by coordinatively unsaturated transition-metal complex fragments is now a well-recognized route to metal fluoride complexes. The C–F activation products, i.e. aryl fluoride complexes [ML$_n$(F)(Ar$_F$)], which are formed by the insertion of [ML$_n$] into the C–F bond of the fluoroaromatic compound, are proposed to be key intermediates in these (catalytic) cycles. Therefore, investigations of the reactivity of these intermediates [ML$_n$(Ar$_F$)(F)] as well as of the reactivity of the resulting products should be vital for a better understanding and a further development of the functionalization of polyfluoroorganics.

We recently reported the facile and clean oxidative addition of hexafluorobenzene to an NHC-stabilized complex fragment {Ni(*i*Pr$_2$Im)$_2$} [*i*Pr$_2$Im = 1,3-bis(isopropyl)imidazol-2-ylidene], as provided by [Ni$_2$(*i*Pr$_2$Im)$_4$(cod)].[4] The reaction of C$_6$F$_6$ with [Ni$_2$(*i*Pr$_2$Im)$_4$(cod)] at room temperature leads to *trans*-[Ni(*i*Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**1**) in a preparatively reasonable timescale and thus provides a major improvement as compared to the activation of hexafluorobenzene (in terms of an oxidative addition) using other transition-metal complexes. Usually, this particular reaction needs C$_6$F$_6$ as a solvent and/or very long reaction times to proceed to completeness, as exemplified by the work of Hofmann, Pörschke, Perutz, and others.[1,5] Long reaction times usually hamper useful protocols to desired complexes, systematic investigations on the reactivity of these compounds and applications in stoichiometric synthesis as well as catalysis. Quite recently, we reported Suzuki-type cross-coupling reactions of perfluorinated aromatics with boronic acids using [Ni$_2$(*i*Pr$_2$Im)$_4$(cod)] as a catalyst,[6] and thus we are interested in the C–F activation step as well as the reactivity of complexes of the type [Ni(*i*Pr$_2$Im)$_2$(F)(Ar$_F$)].

Although several (pentafluorophenyl)nickel derivatives of the type *trans*-[NiL$_2$(X)(C$_6$F$_5$)][7,8] have been reported, a detailed investigation on the reactivity of the Ni–F bond in (pentafluorophenyl)nickel fluoride derivatives is presently unknown. Reactivity studies on the C–F activation product

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of pentafluoropyridine or tetrafluoropyrimidine at the $\{Ni(PEt_3)_2\}$ complex fragment, *trans*-$[Ni(PEt_3)_2(F)(2\text{-}C_5F_4N)]$ and *trans*-$[Ni(PEt_3)_2(F)(C_3F_3N_2)]$, respectively, by Braun and Perutz et al.[9] have shown that the fluorido ligand can be replaced by various nucleophiles including triflate, azide, cyanide, phenyl, phenoxide and methyl to produce new (2-tetrafluoropyridyl)nickel derivatives. The subsequent reductive elimination of such complexes leads to otherwise inaccessible 2-substituted tetrafluoropyridines by C–C coupling reactions, as was observed for the generation of $2\text{-}C_5NF_4Me$ and $2\text{-}C_5NF_4(CO)Me$ from *trans*-$[Ni(PEt_3)_2(Me)(2\text{-}C_5F_4N)]$. Reductive elimination of these compounds, however, succeeds only in a limited number of cases. Since *trans*-$[Ni(i\text{Pr}_2\text{Im})_2(F)(C_6F_5)]$ (**1**) can be easily prepared on a multigram scale in a one-pot procedure without the isolation of $[Ni_2(i\text{Pr}_2\text{Im})_4(\text{cod})]$, simply by the subsequent reaction of $[Ni(\text{cod})_2]$ with $i\text{Pr}_2\text{Im}$ and C_6F_6, we decided to closer investigate the reactivity of this particular compound as a model for other C–F activation products[10] in some detail, and we wish to report here first results on displacement reactions of the fluorido ligand using a variety of nucleophiles.

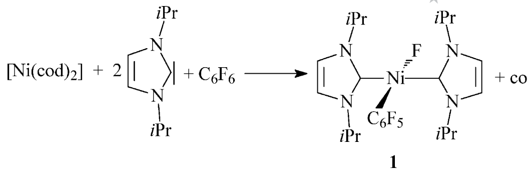
Results and Discussion

In the work reported here, we were interested to find routes to selectively replace the fluorido ligand in *trans*-$[Ni(i\text{Pr}_2\text{Im})_2(F)(C_6F_5)]$ (a) by other widely applied leaving groups in organometallic chemistry, such as chloride, iodide and triflate, (b) by typical carbon ligands that bind through sp^3-, sp^2-, and sp-carbon atoms to the transition-metal atom, and (c) by ligands that bind through heteroatoms such as sulfur or selenium to the metal atom. Furthermore, we were interested in further studies to replace the fluorido ligand by a hydrido ligand as an entry into systematic investigations of hydrodefluoration processes using $\{Ni(i\text{Pr}_2\text{Im})_2\}$. As a general route to these complexes, we envisaged the reaction of **1** with silylated compounds, which should be thermodynamically favored because of the very strong Si–F bond (approximately 560 kJ/mol) in the resulting byproduct fluorosilane formed during the reaction. In the case of the introduction of the carbon ligands, readily available organolithium compounds seemed to be the reagents of choice, since the formation of lithium fluoride should be an excellent thermodynamic driving force in these cases.

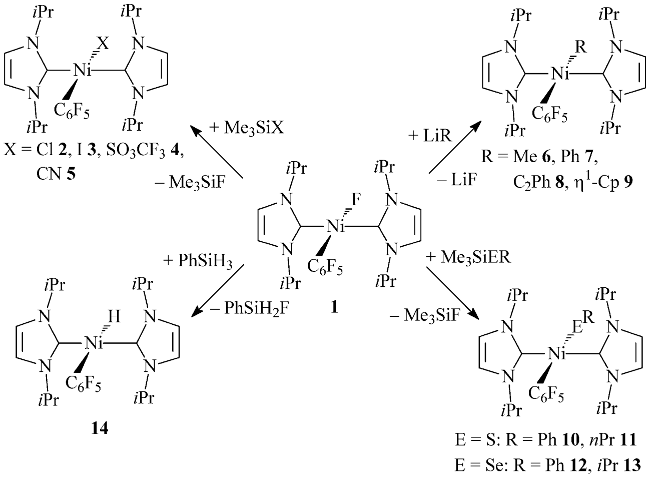
The complex *trans*-$[Ni(i\text{Pr}_2\text{Im})_2(F)(C_6F_5)]$ (**1**)[4a] used in this study was obtained in 56% yield by the consecutive reaction of $[Ni(\text{cod})_2]$ with $i\text{Pr}_2\text{Im}$ and C_6F_6 in thf (see Scheme 1).

The most significant spectroscopic features of **1** are three signals at δ = –116.0, –163.3, and –165.0 ppm for the perfluorinated phenyl ligand and a resonance at a high chemical shift of δ = –373.3 ppm for the fluorido ligand in the ^{19}F NMR spectrum of **1**.

All reactions of **1** with silylated reagents and organolithium compounds are summarized in Scheme 2. Generally, these replacement reactions proceeded smoothly and afforded reaction products in moderate to good isolated yields.



Scheme 1. Preparation of $[Ni(i\text{Pr}_2\text{Im})_2(F)(C_6F_5)]$ (**1**).



Scheme 2. Reactions of **1** with silylated reagents and organolithium compounds.

Compounds **2**–**14** were characterized by ^1H, ^{13}C and ^{19}F NMR and IR spectroscopy as well as mass spectrometry. Usually, the replacement of the fluorido ligand during product formation can be monitored by ^{19}F NMR spectroscopy, i.e. the disappearance of fluoride signal at δ = –373.3 ppm in the starting compound. The ^{19}F NMR spectra of **2**–**14** typically reveal the resonances of the pentafluorophenyl ligand in the region between δ = –115 and –165 ppm.

The replacement of the fluorido ligand in **1** by a new anionic ligand provides an entry to compounds of the general structure *trans*-$[Ni(i\text{Pr}_2\text{Im})_2(X)(C_6F_5)]$ (X = monoanionic ligand). To enhance the complexes at our disposal with heteroligands X, which are known good leaving groups in organometallic chemistry (such as chlorine, iodine or triflate), we investigated the reaction of **1** with trimethylsilylated reagents Me_3SiX (X = Cl, I, CF_3SO_3). Compound **1** reacts cleanly with these substances to afford the complexes $[Ni(i\text{Pr}_2\text{Im})_2(X)(C_6F_6)]$ (X = Cl **2**, I **3**, CF_3SO_3 **4**) in isolated yields of 93% (**2**), 84% (**3**), and 63% (**4**). However, if performed on an NMR scale, these reactions are almost quantitative. The ^1H NMR spectra of these compounds reveal signal patterns typically obtained for *trans*-configured complexes of pseudo-C_{2v} symmetry in solution, featuring two doublets for the isopropyl methyl protons, one septet for the isopropyl methine protons and a singlet for the olefinic protons of the NHC ligands.

In **1**, the ^1H NMR spectrum at room temperature in deuteriobenzene reveals a well-defined septet at δ = 6.46 ppm for the isopropyl methine hydrogen atoms, a singlet at δ = 6.31 ppm for the hydrogen atoms of the carbene backbone and two broad resonances at δ = 1.38 and 1.10 ppm for the isopropyl methyl hydrogen atoms. In contrast, all resonances of compounds **2**–**4** are well resolved. In the case of **1** a well-resolved doublet for the *i*Pr methyl hydrogen atoms at δ = 1.29 ppm with a coupling constant of 6.6 Hz was only observed at the high temperature limit of 363 K in [D$_8$]toluene. Upon cooling, this doublet at δ = 1.29 ppm broadens significantly at 323 K and 313 K, and finally splits into two resonances. At 273 K, two well-resolved doublets appear at δ = 1.06 and 1.36 ppm for the carbene methyl groups with coupling constants of 6.6 Hz. We attributed this dynamic behavior to a hindered rotation of the carbene ligand about the Ni–C$_{carbene}$ axis, i.e. the passing of the bulky *i*Pr groups through the coordination plane is restricted. If this process is slow on the NMR time scale, the methyl groups at each *i*Pr substituent of the carbene ligand become prochiral. For the significantly larger ligands X in *trans*-[Ni(*i*Pr$_2$Im)$_2$(X)(C$_6$F$_5$)] (**2**–**4**), rotation of the carbene ligand around the Ni–C$_{carbene}$ axis is more restricted as compared to the fluorido complex leading to the observed signal pattern featuring doublets for the *i*Pr methyl groups with coupling constants in the range between 6.5 and 6.7 Hz. In the ^{19}F NMR spectra of **1**–**4**, the resonances typically obtained for the pentafluorophenyl ligand are observed in the range between δ = 115 and 165 ppm. In addition, the CF$_3$ resonances are detected as a broadened singlet at δ = –78.29 ppm for complex **4**. In the IR spectrum of **4** the asymmetric sulfonyl stretching frequency is detected at 1326 cm^{-1}, and this observation is consistent with a metal-bonded triflate group with the assumed η^1-coordination mode.[11]

The triflate complex **4** was crystallized from the reaction mixture at room temperature. Complex **4** adopts a square-planar geometry in the solid state with angles between the adjacent ligands at the nickel atom varying from 88.8(3) to 91.0(3)° (Figure 1). The dihedral angle between the nickel coordination plane and the plane of the pentafluorophenyl ring is 89.73°. The Ni–C(carbene) distances of 1.929(7) and 1.903(8) Å are similar to those found in other *trans*-bis(carbene)nickel complexes reported so far.[4,6,12] The Ni–C(Ar$_F$) distance of 1.884(8) Å is significantly shorter than the Ni–C(carbene) distances, but differs only little from the values found for the perfluorotoluene derivative [Ni(*i*Pr$_2$Im)$_2$(F){4-(CF$_3$)C$_6$F$_4$}] [1.870(8) Å].[6] and the complex *trans*-[Ni(*i*Pr$_2$Im)$_2$(F){4-(SiMe$_3$)C$_6$F$_4$}] [1.873(6) Å].[10] The triflate anion is monodentately oxygen-bonded with an Ni–O bond length of 1.975(5) Å, which is similar to the Ni–O distance found in *trans*-[Ni(PEt$_3$)$_2$(OTf)(2-C$_5$F$_4$N)] [1.957(2) Å].[9a]

As observed similarly for the formation of **1**–**4**, reaction of **1** with trimethylsilyl cyanide afforded *trans*-[Ni(*i*Pr$_2$Im)$_2$(CN)(C$_6$F$_5$)] (**5**) in good yield after workup. Unfortunately, we could not detect the cyanide carbon resonance in the ^{13}C NMR spectrum, but elemental analysis, mass spectrometry, ^1H NMR spectroscopy and the lack of a fluoride resonance in the ^{19}F NMR spectrum support the idea of the replacement of the fluorido ligand. Most significantly, the cyanide stretch in the IR spectrum of **5** is observed in the characteristic region at 2112 cm^{-1}.

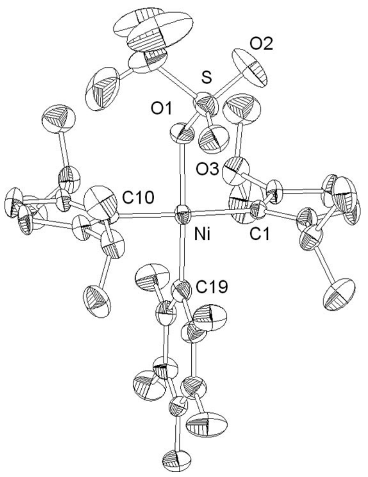


Figure 1. ORTEP diagram of the molecular structure of [Ni(*i*Pr$_2$Im)$_2$(CF$_3$SO$_3$)(C$_6$F$_5$)] (**4**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.929(7), Ni–C10 1.903(8), Ni–C19 1.884(8), Ni–O1 1.975(5), S–O1 1.468(6), S–O2 1.421(7), S–O3 1.430(6); C1–Ni–C10 175.9(3), C19–Ni–O1 174.0(3), C10–Ni–O1 89.2(3), C1–Ni–O1 88.8(3), C10–Ni–C19 91.0(3), C1–Ni–C19 90.7(3), O1–S–O2 113.6(5), O1–S–O3 113.6(4), O2–S–O3 117.3(5), Ni–O1–S 123.1(4).

Although hexafluorobenzene itself reacts readily with nucleophiles,[13] the reaction of **1** with different organolithium compounds leads to the replacement of the fluorido ligand at the metal center. The reaction of **1** with methyllithium, phenyllithium, phenylacetylenyllithium and cyclopentadienyllithium in toluene afforded the complexes *trans*-[Ni(*i*Pr$_2$Im)$_2$(R)(C$_6$F$_5$)] (R = CH$_3$ **6**, C$_6$H$_5$ **7**, C≡CPh **8**, η^1-C$_5$H$_5$ **9**) (see Scheme 2). The ^1H NMR spectra of these substances reveal the signal pattern typically observed for a *trans* configuration of the carbene ligands in these compounds. The protons of the methyl ligand of **6** were detected as a singlet at δ = –0.47 ppm. In all structures we have reported so far of *trans*-configured complexes *trans*-[Ni(*i*Pr$_2$Im)$_2$(X)(Y)][4,6] we observed contacts between the nickel atom and the methine hydrogen atoms of the *i*Pr groups of the carbene ligands within van der Waals contact, which led to the idea that the chemical shift of these proton signals in the ^1H NMR spectrum is indicative of the electronic situation at the nickel atom. Whereas the resonances of these groups for the halido and triflato complexes **1**–**4** lie in a range between δ = 6.35 and 6.61 ppm, we observe the septets for these protons of the complexes with carbon-based ligands **6**–**9** in the range between δ = 5.99 and 6.21 ppm. There is, however, no direct relationship between the ligand-group electronegativity and the chemical shift of the resulting complexes. The resonances of the carbene carbon atoms in the ^{13}C NMR spectra seem to be a better probe for the electronic situation at the metal atom and the influence of the ligand in *cis* position. In the complexes **9**–**10** as well as in the hydrido complex *trans*-[Ni(iPr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**14**) (vide infra) these resonances are detectable in C$_6$D$_6$ in the range between δ = 180 and 191 ppm, the carbene carbon resonances for all the other complexes lie at $\delta >$ 180 ppm. For example, we detected these signals at δ = 175.4 ppm for **1**, at δ = 172.5 ppm for **2**, and at δ = 174.3 ppm for **3**, for the methyl complex **6** at δ = 191.0 ppm and for the hydrido complex at δ = 187.4 ppm. The fact that the more electron-donating ligands (such as CH_3^- or H^-) lead to a downfield shift of the carbene resonances is somewhat counterintuitive, but might be explained by increased electron repulsion between the lone-pair-containing ligands and the metal electrons.

Crystals of **6** suitable for X-ray diffraction were obtained from saturated pentane solutions at –40 °C. The molecular structure of **6** (see Figure 2) reveals a nickel atom in a slightly distorted square-planar geometry with the pentafluorophenyl group coordinated *trans* to the methyl ligand. The Ni–C(NHC) distances of 1.904(3) Å are, however, unaffected by the different ligand substitution pattern in the complexes *trans*-[Ni(iPr$_2$Im)$_2$(X)(C$_6$F$_5$)] as compared to the other structures reported here. The Ni–C(methyl) distance is 2.053(3) Å.

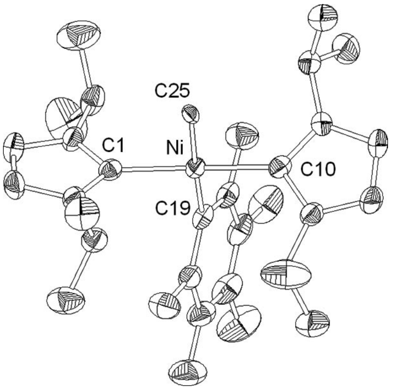


Figure 2. ORTEP diagram of the molecular structure of [Ni(iPr$_2$Im)$_2$(Me)(C$_6$F$_5$)] (**6**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity except the hydrido ligand. Selected bond lengths [Å] and angles [°]: Ni–C1 1.904(3), Ni–C10 1.904(3), Ni–C19 1.963(3), Ni–C25 2.053(3); C1–Ni–C10 173.57(13), C25–Ni–C19 177.57(14), C1–Ni–C25 87.73(13), C1–Ni–C19 94.29(14), C10–Ni–C19 90.49(14).

In the ^{1}H NMR spectra of **9** at room temperature, the cyclopentadienyl protons were detected as a singlet at δ = 5.98 ppm, whereas three signals are expected for a C$_5$H$_5$ ligand in the η^1-coordination mode. The observed singlet at room temperature is in accordance with a sigmatropic rearrangement of the η^1-bonded ligand, which is fast on the NMR time-scale. Attempts to observe the expected A$_2$B$_2$X pattern failed even at low temperatures. At 203 K in [D$_8$]-toluene, only one signal was observed for the cyclopentadienyl protons. A similar behavior was observed in the ^{13}C NMR spectra of **9**, where one signal was detected at δ = 114.0 ppm for the cyclopentadienyl carbon atoms.

In the room-temperature ^{1}H NMR spectra of the NHC-stabilized Ni^{II} complex [Ni(1,3-bis(4-bromo-2,6-dimethyl)-imidazol-2-ylidene)(η^5-C$_5$H$_5$)(η^1-C$_5$H$_5$)],[14] the resonances of the η^1-bonded Cp ligand has been found as a singlet at δ = 5.73 ppm, whereas the η^5-coordinated cyclopentadienyl ligand shows a singlet at δ = 4.22 ppm. The similarities of the ^{1}H NMR chemical shift (δ =5.98 ppm in **9** vs. 5.73 ppm) as well as electron-count reasons lead to the proposal that the cyclopentadienyl ligand is η^1-coordinated to the nickel atom. To unequivocally confirm this bonding situation, crystals of **9** were grown from saturated diethyl ether solution at –40 °C. The molecular structure of square-planar **9** (see Figure 3) clearly establishes this bonding mode. The best planes thorough the cyclopentadiene carbon atoms C25–C29 and through the atoms Ni1, C1, C10, and C19 intersect each other by 39.795° The alternating C–C bond lengths within the cyclopentadienyl ligand of 1.452(6) (C25–C26), 1.342(7) (C26–C27), 1.425(7) (C27–C28), 1.358(7) (C28–C29) and 1.467(6) Å (C29–C25) are in the expected range.

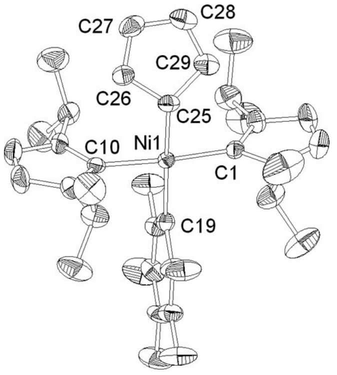


Figure 3. ORTEP diagram of the molecular structure of [Ni(iPr$_2$Im)$_2$(η^1-C$_5$H$_5$)(C$_6$F$_5$)] (**9**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1 1.904(4), Ni1–C10 1.904(4), Ni1–C19 1.945(5), Ni1–C25 2.079(5), C25–C26 1.452(6), C26–C27 1.342(7), C27–C28 1.425(7), C28–C29 1.358(7), C29–C25 1.467(6); C1–Ni1–C10 175.02(19), C19–Ni1–C25 90.21(18), C1–Ni1–C19 92.20(18), C1–Ni1–C25 89.41(18), C10–Ni1–C25 89.10(18), C10–Ni1–C19 90.21(18), Ni1–C25–C26 118.0(3), Ni1–C25–C29 117.3(3).

So far we succeeded in the replacement of the fluorido ligand in **1** by halides, triflates, and organic groups. For future systematic studies on catalytic functionalizations of polyfluorinated aromatics using NHC-stabilized nickel complexes, we were interested to introduce ligands attached through heteroatoms to the metal center. For these first investigations, we chose to explore the reactivity of silylated sulfur and selenium organyls.

Complex **1** cleanly reacts in thf at room temperature with silylated sulfanes RSSiMe$_3$ (R = Ph, nPr) and selenanes RSeSiMe$_3$ (R = Ph, iPr) with elimination of fluorotrimethylsilane to the corresponding thiolato and selenolato complexes *trans*-[Ni(iPr$_2$Im)$_2$(SR)(C$_6$F$_5$)] (R = Ph **10**, nPr **11**) and *trans*-[Ni(iPr$_2$Im)$_2$(SeR)(C$_6$F$_5$)] (R = Ph **12**, iPr **13**). For the NHC ligands, the signal patterns typically obtained for *trans*-configured complexes of C_{2v} symmetry in solution are observed in the ^{1}H NMR spectra featuring two sharp doublets for the methyl protons, one septet for the methine protons and a singlet for the olefinic protons of the NHC ligands. Additionally, the typical signal pattern for the organic substituents of the thiolato and selenolato ligands, respectively, can be observed.

Crystals of **11** and **13** were isolated from saturated hexane solution at –40 °C, and the single-crystal X-ray structures confirmed the formation of these complexes.

Both complexes **11** (Figure 4) and **13** (Figure 5) adopt a square-planar geometry. The Ni–C(carbene) and Ni–C(Ar_F) bond lengths are in the same range as observed for the other structurally characterized complexes reported here. The nickel–sulfur distance in **11** of 2.2055(6) Å is slightly shorter than the bond length of 2.232(2) Å observed in the related complex [Ni(P*n*Bu$_3$)$_2$(SC$_6$F$_5$)(C$_6$F$_5$)].[15] The Ni–Se distance of 2.3378(13) Å in **13** is also rather unusual. In the phosphane-stabilized nickel complex [Ni(PEt$_3$)$_2$(4-MeC$_6$H$_4$COSe)$_2$],[16] an Ni–Se distance of 2.3426(7) Å has been found.

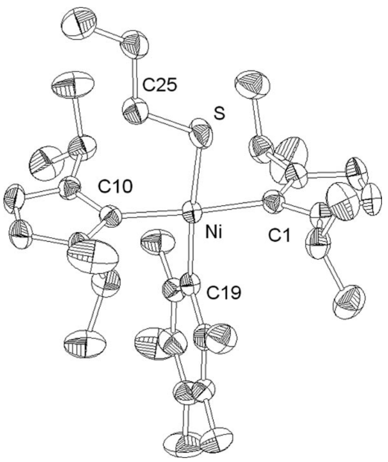


Figure 4. ORTEP diagram of the molecular structure of [Ni(*i*Pr$_2$Im)$_2$(S*n*Pr)(C$_6$F$_5$)] (**11**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.9214(19), Ni–C10 1.8911(18), Ni–C19 1.950(2), Ni–S 2.2055(6), S–C25 1.826(2); C1–Ni–C10 175.20(9), C19–Ni–S 174.91(6), C10–Ni–C19 90.60(8), C1–Ni–C19 91.17(8), C10–Ni–S 92.86(6), C1–Ni–S 85.66(6), Ni–S–C25 116.15(7).

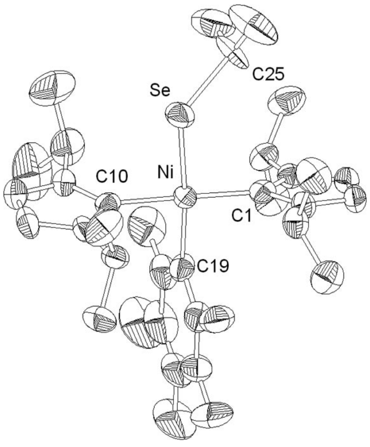


Figure 5. ORTEP diagram of the molecular structure of [Ni(*i*Pr$_2$Im)$_2$(Se*i*Pr)(C$_6$F$_5$)] (**13**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.909(8), Ni–C10 1.907(8), Ni–C19 1.941(7), Ni–Se 2.3378(13), Se–C25 2.037(7); C1–Ni–C10 178.0(3), Se–Ni–C19 174.0(3), C10–Ni–Se 84.92(18), C1–Ni–Se 94.94(18), Ni–Se–C25 117.4(3).

After Milstein and Aizenberg's[3a,3b] seminal work on the catalytic F/H exchange between hydrosilanes and hexa- or pentafluorobenzene under mild conditions using silylrhodium complexes, some of the research in fluorocarbon chemistry is aimed at the development of effective methods for hydrodehalogenation reactions of fluorocarbons. Typically, hydrodehalogenation reactions require strongly reducing conditions and formation of a halide salt as a necessary driving force. The current commercial method of chlorofluorocarbon disposal, for example, is a slow process, using sodium in liquid ammonia.[1a] An alternative route to dehalogenation and C–F activation reactions involves the use of organometallic complexes in homogeneous solution. Thus, organometallic systems may serve as catalytic models which can circumvent the conventional hydrodehalogenation reaction requirements. The reaction of **1** with phenylsilane afforded the very sensitive, pale yellow (hydrido)nickel complex [Ni(*i*Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**14**), which can only be handled under rigorously anhydrous and anaerobic conditions and only in hydrocarbons such as pentane, hexane, benzene or toluene. In halogenated solvents, it decomposes readily to the chlorido complex **2**, in thf or diethyl ether under decomposition and formation of a black oil. Most significantly, the resonance of the hydrido ligand can be observed as an irregular septet with a coupling constant of 5.4 Hz in the ^{1}H NMR spectrum of **14** (see Figure 6).

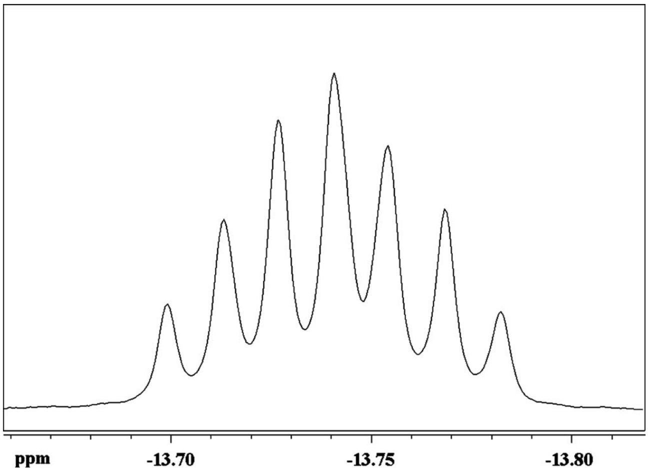


Figure 6. ^{1}H NMR resonance of the hydrido ligand of **14** in C$_6$D$_6$.

The occurrence of a septet can be explained by a coupling of the hydrido ligand with the fluorine atoms of the pentafluorophenyl ligand. Similar H–F couplings have been observed before in other hydrido(pentafluorophenyl) complexes such as [Pt(dmpe)(H)(C_6F_5)],[17] [Pt(dcpe)(H)-(C_6F_5)][17] and [Zr(Cp*)$_2$(H)(C_6F_5)].[18] In contrast to the other complexes reported here, the *i*Pr methyl protons are detected as one doublet. This can be attributed to unhindered rotation of the carbene ligands due to the very small hydrido ligand. In the IR spectrum of complex **14** the Ni–H stretch is observed as a broad, intensive intense band at 1808 cm^{-1}. Single crystals of **14** suitable for X-ray crystal structure analysis were obtained from saturated hexane solutions of the compound at –40 °C (see Figure 7).

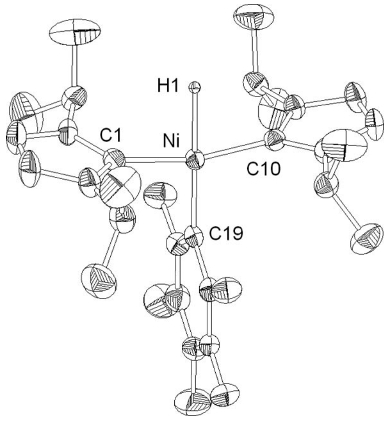


Figure 7. ORTEP diagram of the molecular structure of [Ni(*i*Pr$_2$Im)$_2$(H)(C_6F_5)] (**14**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity except the hydrido ligand. Selected bond lengths [Å] and angles [°]: Ni–H1 1.975(8), Ni–C1 1.886(3), Ni–C10 1.886(3), Ni–C19 1.968(3); C10–Ni–H1 85.89(1), C1–Ni–H1 81.000(9), C10–Ni–C1 166.31(11), C10–Ni–C19 96.63(11), C1–Ni–C19 96.85(11).

The nickel atom of **14** adopts a square-planar geometry, which is more distorted than observed in the other complexes [Ni(*i*Pr$_2$Im)$_2$(X)(C_6F_6)]. Both carbene ligands are bent away from the pentafluorophenyl ligand towards the hydrido ligand. The angle C(2)–Ni–C(10) of 166.31(11)° thus differs significantly from an ideal value of 180°. Although the hydrido ligand was localized during refinement, the observed position [distance Ni–H1 1.975(8)] gives of course not the correct Ni–H bond length due to the limitations of X-ray crystallography. Therefore, a geometry optimization on a full model of **14** was carried out by using density functional theory. Some values of selected bond lengths of the geometry-optimized molecule in comparison to the experimental data are summarized in Table 1.

Table 1. Comparison of selected bond lengths [Å] of **14** as obtained by X-ray crystallography and DFT calculations (BP86, TZVPP).

	Experimental	Calculated
Ni–C1	1.882(3)	1.8885
Ni–C10	1.886(3)	1.8894
Ni–C19	1.968(3)	1.9821
Ni–H1	1.975(8)	1.4919

Generally, the Ni–C distances obtained by X-ray diffraction are in good agreement with the bond lengths determined by our DFT calculations. The experimentally obtained Ni–H1 bond length of 1.975(8) Å is considerably longer than the calculated Ni–H1 distance of 1.4919 Å. This calculated value, however, is similar to other Ni–H distances observed for other (hydrido)nickel complexes before. The Ni–H bond length in {(dippm)NiCl}$_2$(μ-H),[19] for example, which was determined by neutron diffraction, was reported to be 1.588(13) Å. Therefore, we consider an Ni–H1 distance of approximately 1.5 Å as realistic in our case.

Conclusions

In continuation of earlier work on the C–F activation of fluoroaromatics using the {Ni(*i*Pr$_2$Im)$_2$} complex fragment as provided by [Ni$_2$(*i*Pr$_2$Im)$_4$(cod)][4a] and a first report on the usage of this complex in Suzuki cross-coupling reactions,[6] we have demonstrated in this contribution that the Ni–F bond in our NHC-stabilized complexes *trans*-[Ni(*i*Pr$_2$Im)$_2$(F)(Ar$_F$)] is silaphilic, making the fluorido complexes valuable synthetic precursors for new molecules with a variety of ligands. We also succeeded in the preparation of *trans*-[Ni(*i*Pr$_2$Im)$_2$(F)(R)] by salt metathesis using organyllithium compounds. In all cases, the pentafluorophenyl ligand remains attached to the nickel atom. Although hexafluorobenzene or similar perfluorinated aromatics easily undergo nucleophilic substitution (usually preferably in the *para* position of compounds R–C_6F_5), we have at the moment no indications of substitution on the metal-bonded perfluorinated ring in these reactions. In future work we shall further exploit this kind of reaction and try to systematically investigate the conditions of possible subsequent reductive elimination reactions in complexes of the type *trans*-[Ni(*i*Pr$_2$Im)$_2$(F)(R)].

Experimental Section

General Methods and Instrumentation: All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen using standard Schlenk techniques, as reported previously.[20] Elemental analyses were performed in the microanalytical laboratory of the authors' department. In some cases, it was not possible to obtain satisfactory results (despite NMR-spectroscopically pure samples; the corresponding NMR spectra are given in the Supporting Information) for the elemental analysis, due to the high fluorine content of these compounds. In these cases, high-resolution mass spectra with the correct isotopic pattern are provided. These EI mass spectra were recorded with a Varian MAT 3830 (70 eV). NMR spectra were recorded with a Bruker AV 400 or a Bruker AMX 300. ^{13}C NMR spectra were broad-band decoupled. NMR spectroscopic data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H and ^{13}C) and CFCl$_3$ (^{19}F). Coupling constants are quoted in Hertz (Hz). Because there was no access to ^{19}F-decoupled ^{13}C NMR spectroscopy, we usually did not detect the carbon signals of the pentafluorophenyl groups in the ^{13}C NMR spectra. In all cases, however, ^{19}F NMR spectroscopic data of these complexes are provided. IR spectra were recorded as KBr pellets with a Bruker IFS 28 and are reported in cm^{-1}. Me$_3$SiSePh,[21] 1,3-diisopropylimidazol-2-ylidene (*i*Pr$_2$Im),[4b] Me$_3$SiSe*i*Pr,[22] Me$_3$SiSPh[23] and Me$_3$SiS*n*Pr[23] were prepared according to literature procedures. Me$_3$SiCl, Me$_3$SiI, Me$_3$SiCN, Me$_3$SiOSO$_2$CF$_3$, PhSiH$_3$, PhLi, MeLi, *n*BuLi, phenylacetylene and C$_6$F$_6$ were purchased from ABCR and used without further purification.

Preparation of Complexes

***trans*-[Ni(*i*Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (1):** At –78 °C, a solution of *i*Pr$_2$Im (5.50 g, 36.2 mmol) in thf (40 mL) was added to a stirred solution of [Ni(cod)$_2$] (5.00 g, 18.2 mmol) in thf (180 mL). Then, hexafluorobenzene (2.10 mL, 18.2 mmol) was added at this temperature. The reaction mixture was warmed to room temperature overnight. Insoluble material was then filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The yellow residue was suspended in hexane (60 mL), all insoluble material was filtered off, washed with a small portion of hexane, and dried in vacuo to give a yellow powder (5.90 g, 56 %). C$_{24}$H$_{34}$F$_6$N$_4$NiO (**1**·H$_2$O) (567.2): calcd. C 50.82, H 6.04, N 9.88; found C 50.46, H 6.57, N 9.93. MS: *m*/*z* (%) = 549.2 (3) [M]$^+$, 362.3 (40) [Ni(*i*Pr$_2$Im)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 438 (m), 477 (m, $\nu_{Ni–F}$), 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 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 1.10 (br. s, 12 H, *i*Pr C*H*$_3$), 1.38 (br. s, 12 H, *i*Pr C*H*$_3$), 6.25 (s, 4 H, C*H*C*H*), 6.51 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*) ppm. ^{1}H NMR (300 MHz, –40 °C, [D$_8$]toluene): δ = 1.03 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, C*H*$_3$), 1.32 (d, $^3J_{HH}$ = 6.3 Hz, 12 H, C*H*$_3$), 6.25 (s, 4 H, C*H*C*H*), 6.40 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*) ppm. ^{1}H NMR (300 MHz, 90 °C, [D$_8$]toluene): δ = 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, C*H*$_3$), 6.37 (s, 4 H, C*H*C*H*), 6.46 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, C$_6$D$_6$): δ = 23.15 (br., *C*H$_3$), 25.18 (br., *C*H$_3$), 52.82 (*i*Pr *C*H), 116.88 (N*CC*N), 175.35 (d, $^2J_{FC}$ = 7.5 Hz, N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C$_6$D$_6$): δ = –116.0 (d, $^3J_{HH}$ = 28.6 Hz, 2 F, aryl-*F$_o$*), –163.3 (t, $^3J_{FF}$ = 20.3 Hz, 1 F, aryl-*F$_p$*), –165.0 (m, 2 F, aryl-*F$_m$*), –373.7 (s, 1 F, Ni-*F*) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(Cl)(C$_6$F$_5$)] (2):** Me$_3$SiCl (109 mg, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and the mixture stirred at room temp. overnight. All volatiles were removed in vacuo to afford a yellow powder (530 mg, 93 %). MS: *m*/*z* (%) = 564 (20) [M]$^+$, 362 (100) [Ni(*i*Pr$_2$Im)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 449 (w), 579 (w), 630 (vw), 673 (m), 709 (s), 734 (m), 745 (m), 776 (m), 802 (m), 851 (w), 880 (w), 952 (s), 1040 (s), 1050 (s), 1099 (m), 1128 (m), 1177 (w), 1219 (s), 1262 (m), 1304 (m), 1344 (w), 1372 (m), 1394 (m), 1414 (m), 1448 (s), 1497 (s), 1574 (w), 1594 (w), 1631 (w), 1679 (w), 1700 (w), 2876 (m), 2943 (m), 2977 (s), 3087 (m), 3096 (m), 3116 (m), 3128 (m), 3155 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, CDCl$_3$): δ = 1.40 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, C*H*$_3$), 1.60 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, C*H*$_3$), 6.35 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H, *i*Pr C*H*), 6.84 (s, 4 H, C*H*C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, CDCl$_3$): δ = 22.68 (*C*H$_3$), 24.27 (*C*H$_3$), 52.01 (*i*Pr *C*H), 116.70 (N*CC*N), 172.50 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, CDCl$_3$): δ = –116.89 (d, $^3J_{FF}$ = 25.2 Hz, 2 F, aryl-*F$_o$*), –162.94 (t, $^3J_{FF}$ = 19.8 Hz, 1 F, aryl-*F$_p$*), –165.05 (t, $^3J_{FF}$ = 21.6 Hz, 2 F, aryl-*F$_m$*) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(I)(C$_6$F$_5$)] (3):** Me$_3$SiI (200 mg, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and the mixture stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (20 mL); all insoluble material was filtered off, and the remaining yellow powder was dried in vacuo (551 mg, 84 %). MS: *m*/*z* (%) = 656 (1) [M]$^+$, 529 (1) [Ni(*i*Pr$_2$Im)$_2$ – C$_6$F$_5$]$^+$, 362 (100) [Ni(*i*Pr$_2$Im)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 445 (w), 488 (w), 578 (m), 630 (w), 643 (w), 675 (vs), 692 (vs), 771 (vs), 789 (w), 815 (w), 846 (w), 881 (m), 949 (vs), 1001 (s), 1027 (vs), 1054 (vs), 1078 (m), 1096 (m), 1130 (s), 1173 (s), 1211 (vs), 1274 (s), 1302 (vs), 1340 (s), 1371 (vs), 1392 (vs), 1407 (vs), 1445 (vs), 1468 (vs), 1499 (s), 1528 (s), 2674 (w), 2813 (w), 2870 (s), 2939 (vs), 2976 (vs), 2996 (s), 3133 (w), 3155 (w), 3183 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 1.50 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 6.19 (s, 4 H, C*H*C*H*), 6.50 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*Pr *C*H) ppm. ^{13}C NMR (100 MHz, 25 °C, C$_6$D$_6$): δ = 23.59 (*C*H$_3$), 24.04 (*C*H$_3$), 52.90 (*i*Pr *C*H), 118.15 (N*CC*N), 174.30 (N*C*N) ppm. ^{19}F NMR (364 MHz, 25 °C, C$_6$D$_6$): δ = –117.10 (d, $^3J_{FF}$ = 25.8 Hz, 2 F, aryl-*F$_o$*), –162.33 (t, $^3J_{FF}$ = 20.6 Hz, 1 F, aryl-*F$_p$*), –164.67 (m, 2 F, aryl-*F$_m$*) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(SO$_3$CF$_3$)(C$_6$F$_5$)] (4):** Me$_3$SiOSO$_2$CF$_3$ (222 mg, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in toluene (20 mL) and the mixture stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (15 mL). Insoluble material was filtered off, and the remainig solid was dried in vacuo to give an orange-yellow powder (430 mg, 63 %). Crystals suitable for X-ray diffraction were obtained by storing the reaction mixture at –40 °C. MS: *m*/*z* (%) = 678 (21) [M]$^+$, 511 (33) [Ni(*i*Pr$_2$Im)$_2$(SO$_3$CF$_3$)]$^+$, 362 (30) [Ni(*i*Pr$_2$Im)$_2$]$^+$, 319 (100) [Ni(*i*Pr$_2$Im)$_2$ – C$_3$H$_7$]$^+$. IR (KBr): $\tilde{\nu}$ = 452 (w), 516 (w), 577 (w), 633 (m), 706 (m), 741 (m), 780 (m), 852 (w), 885 (w), 954 (s, ν_{SO}), 1017 (s, ν_{SO}), 1132 (m), 1237 (vs), 1326 (vs), 1378 (m), 1433 (vs), 1498 (s), 1630 (w), 2878 (m), 2942 (m), 2989 (s), 3107 (w), 3138 (m), 3176 (m) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 1.45 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, C*H*$_3$), 1.64 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, C*H*$_3$), 6.61 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H, *i*Pr C*H*), 6.92 (s, 4 H, C*H*C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, CDCl$_3$): δ = 23.43 (*C*H$_3$), 23.90 (*C*H$_3$), 52.46 (*i*Pr *C*H), 117.61 (N*CC*N), 165.86 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, CDCl$_3$): δ = –78.29 (s, 3 F, C*F*$_3$), –117.36 (d, *J* = 2 F, $^3J_{FF}$ = 23.7 Hz, aryl-*F$_o$*), –161.68 (t, *J* = 1 F, $^3J_{FF}$ = 20.6 Hz, aryl-*F$_p$*), –164.58 (t, $^3J_{FF}$ = 21.3 Hz, 2 F, aryl-*F$_m$*) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(CN)(C$_6$F$_5$)] (5):** Me$_3$SiCN (99.0 mg, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and the mixture stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (20 mL). Insoluble material was filtered off, and the remaining solid was dried in vacuo to give a colorless powder (480 mg, 85 %). MS: *m*/*z* (%) = 555 (45) [M]$^+$, 362 (100) [Ni(*i*Pr$_2$Im)$_2$]$^+$, 152 (100) [*i*Pr$_2$Im]$^+$. IR (KBr): $\tilde{\nu}$ = 470 (m), 578 (w), 628 (vw), 671 (m), 707 (s), 738 (m), 770 (m), 803 (m), 845 (m), 881 (w), 949 (s), 1041 (s), 1132 (m), 1179 (w), 1216 (s), 1260 (m), 1307 (m), 1373 (m), 1396 (m), 1446 (vs), 1497 (s), 1582 (w), 1630 (w), 2112 (s, $\nu_{C\equiv N}$), 2878 (m), 2939 (m), 2979 (s), 3097 (m), 3128 (m), 3159 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, CDCl$_3$): δ = 1.39 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 5.78 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*Pr C*H*), 6.92 (s, 4 H, C*H*C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, CDCl$_3$): δ = 22.49 (*C*H$_3$), 23.69 (*C*H$_3$), 52.16 (*i*Pr *C*H), 117.17 (N*CC*N), 173.43 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, CDCl$_3$): δ = –117.09 (d, $^3J_{FF}$ = 26.1 Hz, 2 F, aryl-*F$_o$*), –162.55 (t, $^3J_{FF}$ = 19.8 Hz, 1 F, aryl-*F$_p$*), –164.32 (m, 2 F, aryl-*F$_m$*) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(Me)(C$_6$F$_5$)] (6):** Methyllithium (0.63 mL, 1.00 mmol of a 1.6 N solution in diehtyl ether) was added to a solution of compound **1** (550 mg, 1.00 mmol) in toluene (20 mL) and the mixture stirred at room temp. overnight. Insoluble material was filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The residue was suspended in pentane

(20 mL), all insoluble material was filtered off, and the remaining solid was dried in vacuo to afford a yellow powder (250 mg, 45%). Crystals suitable for X-ray diffraction were obtained from saturated pentane solutions at –40 °C. $C_{25}H_{35}F_5N_4Ni$ (545.3): calcd. C 55.07, H 6.47, N 10.28; found C 54.81, H 6.09, N 9.87. MS: *m*/*z* (%) = 529 (14) [M – Me]$^+$, 363 (100) [Ni(*i*Pr_2Im)$_2$ + H]$^+$. IR (KBr): ṽ = 501 (w), 578 (w), 672 (w), 697 (s), 748 (w), 802 (w), 879 (w), 937 (s), 1034 (s), 1055 (m), 1080 (m), 1130 (m), 1150 (m), 1170 (w), 1213 (s), 1262 (w), 1299 (m), 1369 (m), 1389 (s), 1427 (s), 1466 (m), 148 (m), 1601 (w), 1627 (w), 2874 (m), 2934 (m), 2977 (s), 3156 (w), 3182 (w) cm$^{–1}$. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = –0.47 (s, 3 H, Ni-C*H*$_3$), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr C*H*$_3$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, *i*Pr C*H*$_3$), 6.21 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*), 6.24 (s, 4 H, C*H*C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 2.16 (Ni-*C*H$_3$), 23.65 (*i*Pr *C*H$_3$), 24.71 (*i*Pr *C*H$_3$), 52.27 (*i*Pr *C*H), 116.70 (N*CC*N), 191.03 (N*C*N) ppm. ^{19}F NMR (364 MHz, 25 °C, C_6D_6): δ = –114.64 (m, 2 F, aryl-*F*$_o$), –164.71 (m,3 F, aryl-*F*$_{m,p}$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(Ph)(C_6F_5)] (7):** Phenyllithium (0.50 mL, 1.00 mmol of a 2.0 N solution in di-*n*-butyl ether) was added to a solution of compound **1** (550 mg, 1.00 mmol) in toluene (20 mL) and the mixture stirred at room temp. overnight. Insoluble material was filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The residue was suspended in pentane (20 mL), insoluble material was filtered off, and the remaining solid was dried in vacuo to give a yellow powder (160 mg, 26%). $C_{30}H_{37}F_5N_4Ni$ (607.3): calcd. C 59.33, H 6.14, N 9.23; found C 58.98, H 5.85, N 9.06. MS: *m*/*z* (%) = 529 (10) [Ni(*i*Pr_2Im)$_2$(C_6F_5)]$^+$, 362 (100) [Ni(*i*Pr_2Im)$_2$]$^+$. IR (KBr): ṽ = 449 (w), 579 (w), 646 (w), 698 (s), 742 (s), 818 (w), 881 (w), 942 (s), 1030 (s), 1050 (m), 1085 (m), 1129 (m), 1173 (w), 1213 (s), 1299 (m), 1370 (m), 1427 (s), 1488 (s), 1560 (m), 1607 (w), 1644 (w), 2873 (m), 2936 (m), 2993 (s), 3046 (m), 3110 (m), 3139 (m), 3176 (w) cm$^{–1}$. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 0.91 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 1.03 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 5.99 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*Pr C*H*$_3$), 6.14 (s, 4 H, C*H*C*H*), 6.87 (m, 1 H, aryl-*H*$_p$), 6.96 (m, 2 H, aryl-*H*$_m$), 7.30 (m,2 H, aryl-*H*$_o$) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 23.58 (*C*H$_3$), 23.98 (*C*H$_3$), 52.52 (*i*Pr *C*H), 116.84 (N*CC*N), 122.02 (aryl *C*$_p$), 126.87 (aryl *C*$_m$), 140.07 (aryl *C*$_o$), 185.53 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C_6D_6): δ = –114.39 (m, 2 F, aryl-*F*$_o$), –163.87 (t, $^3J_{FF}$ = 20.7 Hz, 1 F, aryl-*F*$_p$), –164.27 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(C≡CPh)(C_6F_5)] (8):** *n*-Butyllithium (0.63 mL, 1.00 mmol of a 16% solution in hexane) was added to a solution of phenylacetylene (0.11 mL, 1.00 mmol) in toluene (20 mL) and the mixture stirred at room temp. for 1 h. A solution of compound **1** (550 mg, 1 mmol) in toluene (20 mL) was then added and the reaction mixture stirred overnight. Insoluble material was filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The residue was suspended in hexane (20 mL), insoluble material was filtered off, and the remaining solid was dried in vacuo to give a yellow powder (380 mg, 60%). $C_{32}H_{37}F_5N_4Ni$ (631.3): calcd. C 60.88, H 5.91, N 8.87; found C 61.06, H 5.63, N 8.31. MS: *m*/*z* (%) = 630 (8) [M]$^+$, 362 (20) [Ni(*i*Pr_2Im)$_2$]$^+$. IR (KBr): ṽ = 459 (w), 507 (vw), 527 (w), 579 (w), 631 (w), 642 (w), 676 (m), 697 (s), 732 (vw), 761 (s), 793 (w), 879 (w), 913 (w), 946 (s), 1003 (m), 1035 (s), 1049 (s), 1069 (m), 1131 (m), 1173 (w), 1214 (s), 1280 (w), 1304 (m), 1325 (w), 1370 (m), 1391 (m), 1427 (vs), 1467 (m), 1493 (s), 1547 (w), 1566 (w), 1595 (m), 2094 (vs, $\nu_{C\equiv C}$), 2870 (m), 2937 (m), 2974 (s), 3073 (w), 3112 (w), 3149 (m), 3179 (w) cm$^{–1}$. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, C*H*$_3$), 1.50 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 6.19 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*), 6.25 (s, 4 H, C*H*C*H*), 6.87 (m, 1 H, aryl-*H*$_p$), 6.99 (m, 2 H, arl-*H*$_m$), 7.26 (m, 2 H, aryl-*H*$_o$) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 23.12 (*C*H$_3$), 24.46 (*C*H$_3$), 52.89 (*i*Pr *C*H), 117.23 (N*CC*N), 125.15 (aryl *C*$_i$), 128.68 (aryl *C*$_m$), 130.84 (aryl *C*$_p$), 131.51 (aryl *C*$_o$), 180.31 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C_6D_6): δ = –116.22 (m, 2 F, aryl-*F*$_o$), –163.48 (t, $^3J_{FF}$ = 20.3 Hz, 1 F, aryl-*F*$_p$), –164.50 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(Cp)(C_6F_5)] (9):** LiCp (72.0 mg, 1 mmol) and compound **1** (550 mg, 1 mmol) were dissolved in thf (20 mL), and the reaction mixture was stirred overnight. Insoluble material was then filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The residue was suspended in hexane (20 mL), insoluble material was filtered off, and the remaining solid was dried in vacuo to give a yellow powder (150 mg, 25%). Crystals suitable for X-ray diffraction were obtained from saturated diethyl ether solutions of **9** at –40 °C. $C_{29}H_{37}F_5N_4Ni$ (595.3): calcd. C 58.51, H 6.26, N 9.41; found C 58.37, H 6.26, N 9.27. MS: *m*/*z* (%) = 442 (36) [Ni(*i*Pr_2Im)(C_6F_5)Cp]$^+$, 362 (24) [Ni(*i*Pr_2Im)$_2$]$^+$. IR (KBr): ṽ = 478 (w), 577 (w), 608 (w), 699 (s), 758 (m), 829 (w), 877 (m), 948 (s), 974 (m), 1053 (s), 1215 (s), 1271 (w), 1303 (m), 1495 (s), 1602 (w), 1630 (w), 2872 (m), 2981 (s), 3079 (m), 3124 (m), 3148 (m) cm$^{–1}$. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, C*H*$_3$), 1.34 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 5.98 (s, 5 H, Cp C*H*), 6.21 (m, 8 H, *i*Pr C*H*, C*H*C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 24.45 (*C*H$_3$), 24.71 (*C*H$_3$), 52.62 (*i*Pr *C*H), 114.04 (*C*$_5$H$_5$), 117.70 (N*CC*N), 180.15 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, [D$_8$]toluene): δ = –113.92 (d, $^3J_{FF}$ = 27.7 Hz, 2 F, aryl-*F*$_o$), –163.21 (t, $^3J_{FF}$ = 20.5 Hz, 1 F, aryl-*F*$_p$), –164.70 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(SPh)(C_6F_5)] (10):** Me_3SiSPh (0.18 mL, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (15 mL). Insoluble material was filtered off, and the remaining solid was dried in vacuo to give an orange-yellow powder (520 mg, 82%). MS: *m*/*z* (%) = 638 (10) [M]$^+$, 529 (10) [Ni(*i*Pr_2Im)$_2$(C_6F_5)]$^+$, 361 (100) [Ni(*i*Pr_2Im)$_2$ – H]$^+$. IR (KBr): ṽ = 485 (w), 577 (w), 699 (s), 742 (m), 765 (w), 802 (vw), 882 (vw), 947 (s), 1041 (m), 1084 (w), 1130 (w), 1175 (vw), 1212 (s), 1267 (vw), 1301 (w), 1372 (m), 1392 (m), 1428 (vs), 1467 (m), 1495 (s), 1576 (m), 1629 (w), 2873 (w), 2936 (m), 2976 (s), 3060 (w), 3135 (w), 3167 (w) cm$^{–1}$. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 6.24 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*Pr C*H*), 6.78 (m, 3 H, aryl-*H*), 6.82 (s, 4 H, C*H*C*H*), 6.85 (m, 2 H, aryl-*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 23.93 (*C*H$_3$), 24.36 (*C*H$_3$), 52.87 (*i*Pr *C*H), 117.91 (N*CC*N), 122.80 (aryl *C*$_p$), 127.77 (aryl *C*$_m$), 133.99 (aryl *C*$_o$), 149.36 (aryl *C*$_i$), 176.10 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C_6D_6): δ = –115.26 (d, $^3J_{FF}$ = 25.5 Hz, 2 F, aryl-*F*$_o$), –163.20 (t, $^3J_{FF}$ = 20.2 Hz, 1 F, aryl-*F*$_p$), –164.52 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(S*n*Pr)(C_6F_5)] (11):** Me_3SiS*n*Pr (0.18 mL, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (15 mL). Insoluble material was then filtered off, and the remaining solid was dried in vacuo to afford an orange-yellow powder (300 mg, 49%). Crystals suitable for X-ray diffraction were obtained from saturated hexane solutions of **5** at –40 °C. MS: *m*/*z* (%) = 362 (100) [Ni(*i*Pr_2Im)$_2$]$^+$. IR (KBr): ṽ = 451 (vw), 577 (vw), 627 (vw), 673 (w), 699 (s), 730 (vw), 761 (m), 802 (vw), 882 (w), 946 (s), 1051 (m), 1085 (w), 1132 (w), 1174 (w), 1211 (s), 1274 (w), 1301 (m), 1370 (m), 1390 (m), 1426 (s), 1495 (s), 1630 (w), 2872 (m), 2935 (m), 2978 (s), 3137 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.02 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, *n*Pr C*H*$_3$), 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr C*H*$_3$), 1.47 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, S-C*H*$_2$), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, *i*Pr C*H*$_3$), 1.72 (sext, $^3J_{HH}$ = 7.3 Hz, 2 H, S-CH$_2$C*H*$_2$), 6.25 (s, 4 H, C*H*C*H*), 6.48 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 15.35 (*n*Pr *C*H$_3$), 23.86 (*i*Pr *C*H$_3$), 24.47 (*i*Pr *C*H$_3$), 29.49 (S-CH$_2$*C*H$_2$), 33.17 (S-*C*H$_2$), 52.74 (*i*Pr *C*H), 117.53 (N*CC*N), 179.81 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, $CDCl_3$): δ = –115.64 (d, $^3J_{FF}$ = 26.3 Hz, 2 F, aryl-*F*$_o$), –163.88 (t, $^3J_{FF}$ = 20.1 Hz, 1 F, aryl-*F*$_p$), –165.30 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(SePh)(C$_6$F$_5$)] (12):** $Me_3SiSePh$ (0.24 mL, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (15 mL). Insoluble material was filtered off, and the remaining solid was dried in vacuo to give an orange-yellow powder (500 mg, 73%). MS: *m*/*z* (%) = 686 (10) [M]$^+$, 529 (14) [Ni(*i*Pr$_2$Im)$_2$(C$_6$F$_5$)]$^+$, 361 (100) [Ni(*i*Pr$_2$Im)$_2$ – H]$^+$. IR (KBr): ṽ = 470 (w), 577 (vw), 693 (s), 739 (m), 763 (m), 807 (vw), 847 (vw), 880 (vw), 947 (s), 1000 (w), 1022 (m), 1051 (s), 1130 (w), 1173 (vw), 1212 (s), 1270 (w), 1301 (w), 1373 (m), 1440 (vs), 1469 (m), 1494 (s), 1572 (m), 1629 (w), 2871 (w), 1937 (m), 1974 (s), 3047 (w), 3109 (w), 3138 (w), 3170 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*$_3$), 6.19 (s, 4 H, C*H*C*H*), 6.42 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*Pr C*H*), 6.85 (m, 3 H, aryl-*H*$_{o,p}$), 7.19 (m, 2 H, aryl-*H*$_m$) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 24.06 (*C*H$_3$), 24.25 (*C*H$_3$), 52.93 (*i*Pr *C*H), 118.18 (N*CC*N), 126.59 (aryl *C*$_p$), 130.14 (aryl *C*$_m$), 132.47 (aryl *C*$_o$), 136.14 (aryl *C*$_i$), 176.14 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C_6D_6): δ = –115.10 (d, $^3J_{FF}$ = 25.7 Hz, 2 F, aryl-*F*$_o$), –162.85 (t, $^3J_{FF}$ = 20.5 Hz, 1 F, aryl-*F*$_p$), –164.98 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(Se*i*Pr)(C$_6$F$_5$)] (13):** Me$_3$SiSe*i*Pr (0.20 mL, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in thf (20 mL) and stirred at room temp. overnight. All volatiles were removed in vacuo, and the residue was suspended in hexane (15 mL). Insoluble material was filtered off, and the remaining solid was dried in vacuo to yield an orange-yellow powder (580 mg, 89%). Crystals suitable for X-ray diffraction were obtained from saturated hexane solutions of **3** at –40 °C. $C_{27}H_{39}F_5N_4NiSe$ (652.2): calcd. C 49.72, H 6.03, N 8.59; found C 49.61, H 5.41, N 8.71. MS: *m*/*z* (%) = 652 (8) [M]$^+$, 529 (7) [Ni(*i*Pr$_2$Im)$_2$(C$_6$F$_5$) – HF]$^+$, 362 (100) [Ni(*i*Pr$_2$Im)$_2$]$^+$. IR (KBr): ṽ = 577 (w), 698 (s), 761 (m), 813 (w), 880 (w), 944 (s), 1049 (s), 1094 (m), 1130 (m), 1171 (w), 1210 (s), 1273 (m), 1301 (m), 1371 (m), 1423 (vs), 1494 (s), 1606 (w), 1631 (w), 2847 (m), 2874 (m), 2938 (s), 2975 (s), 3169 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 1.19 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, N-*i*Pr C*H*$_3$), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, N-*i*Pr C*H*$_3$), 1.54 (d, ^3J = 6.2 Hz, 6 H, Se-*i*Pr C*H*$_3$), 1.65 (sept, $^3J_{HH}$ = 6.2 Hz, 1 H, Se-C*H*), 6.23 (s, 4 H, C*H*C*H*), 6.42 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, N-C*H*) ppm. ^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ = 23.11 (Se-*i*Pr *C*H$_3$), 24.07 (N-*i*Pr *C*H$_3$), 24.49 (N-*i*Pr *C*H$_3$), 31.58 (Se-*C*H), 52.70 (N-*C*H), 117.78 (N*CC*N), 178.77 (N*C*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C_6D_6): δ = –115.23 (d, $^3J_{FF}$ = 24.8 Hz, 2 F, aryl-*F*$_o$), –162.23 (t, $^3J_{FF}$ = 20.6 Hz, 1 F, aryl-*F*$_p$), –165.03 (m, 2 F, aryl-*F*$_m$) ppm.

***trans*-[Ni(*i*Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (14):** Phenylsilane (0.13 mL, 1.00 mmol) was added to a solution of compound **1** (550 mg, 1.00 mmol) in toluene (20 mL), and the reaction mixture was stirred at room temp. overnight. Insoluble material was then filtered off through a pad of Celite, and all volatiles of the filtrate were removed in vacuo. The product was extracted at room temp. with pentane (30 mL) and crystallized by storing the solution at –40 °C overnight (crystals obtained this way are usually suitable for X-ray diffraction). The crystalline fraction was filtered off and dried in vacuo to give the product in form of a pale yellow microcrystalline powder (160 mg, 30%). Compound **8** is extremely air- and moisture-sensitive (pyrophoric) and decomposes immediately in thf und diethyl ether as well as in halogenated solvents (such as $CHCl_3$ and CH_2Cl_2). MS: *m*/*z* (%) = 530 (58) [M]$^+$, 510 (93) [M – HF]$^+$, 361 (90) [Ni(*i*Pr$_2$Im)$_2$]$^+$, 153 (100) [*i*Pr$_2$Im, H]$^+$. IR (KBr): ṽ = 527 (w), 577 (w), 611 (vw), 628 (vw), 673 (m), 692 (s), 706 (m), 749 (m), 809 (vw), 881 (w), 939 (s), 999 (m), 1037 (s), 1056 (m), 1081 (w), 1134 (m), 1170 (vw), 1214 (s), 1280 (vw), 1302 (s), 1368 (s), 1431 (vs), 1488 (s), 1601 (w), 1627 (w), 1808 (br. s, $\nu_{Ni–H}$), 2875 (m), 2939 (m), 2979 (s), 3145 (w), 3181 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = –13.74 (sept, *J* = 5.4 Hz, 1 H, Ni-*H*), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, C*H*$_3$), 5.91 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*Pr C*H*), 6.32 (s, 4 H, C*H*C*H*) ppm. ^{13}C NMR (100 MHz,

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

	4·C_7H_8	**6**	**9**	**11**	**13**	**14**·1/2C_6H_{14}
Empirical formula	$C_{32}H_{40}N_4F_8O_3SNi$	$C_{25}H_{35}N_4F_5Ni$	$C_{58}H_{74}F_{10}N_8Ni_2$	$C_{27}H_{39}N_4F_5NiS$	$C_{27}H_{39}F_5N_4NiSe$	$C_{27}H_{40}F_5N_4Ni$
Formula mass	863.59	545.28	1191.68	605.39	652.29	617.43
Crystal system	monoclinic	orthorhombic	tetragonal	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$Pbca$	$I4_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a [Å]	20.1924(10)	14.6632(7)	23.6241(11)	16.1523(11)	11.856(2)	11.7589(12)
b [Å]	10.8164(8)	16.6273(6)	23.6241(11)	11.4930(13)	15.365(3)	12.1512(12)
c [Å]	17.4220(11)	22.1995(12)	21.1778(10)	17.6677(14)	17.347(4)	12.4228(13)
α [°]	90	90	90	90	90	95.106(12)
β [°]	108.311(6)	90	90	113.05(9)	96.24(3)	104.653(12)
γ [°]	90	90	90	90	90	116.210(10)
V [Å^3]	3612.5(4)	5412.5(4)	11819.3(10)	3019.0(5)	3141.2(11)	1499.0(3)
Z	4	8	8	4	4	2
μ [mm^{-1}]	1.418	0.771	0.712	1.332	1.827	1.272
Total/independent reflections	12330/5096	25102/4411	36278/11441	26084/5723	17764/4500	14086/5451
Observed reflections[a]	2753	2969	8033	4580	2554	3978
Parameters	425	317	703	343	343	338
Final R,[b] wR_2[c,d]	0.0761, 0.1645	0.0449, 0.0942	0.0484, 0.0808	0.0342, 0.0816	0.0616, 0.1325	0.0433, 0.0954

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

25 °C, C_6D_6): δ = 23.49 (CH_3), 52.55 (*i*Pr *C*H), 116.32 (N*CC*N), 187.41 (N*C*N) ppm. ^{19}F NMR (364 MHz, 25 °C, C_6D_6): δ = –114.15 (m, 2 F, aryl-F_m), –164.46 (m, 3 F, aryl-F_{o+p}) ppm.

Computational Details: All calculations were carried out with the DFT implementation of the TURBOMOLE program package.[24] For the DFT calculations we used the BP86 functional,[25] TZVPP basis sets and the RI-J approximation. Analytical second derivatives were calculated with the program AOFORCE[26] using the RI-J approximation.

Crystal Structure Determination of [Ni(*i*Pr$_2$Im)(Se*i*Pr)(C_6F_5)] (2), [Ni(*i*Pr$_2$Im)(S*n*Pr)(C_6F_5)] (5), [Ni(*i*Pr$_2$Im)(H)(C_6F_5)] (6), [Ni(*i*Pr$_2$Im)(CF_3SO_3)(C_6F_5)] (10), [Ni(*i*Pr$_2$Im)(Me)(C_6F_5)] (13) and [Ni(*i*Pr$_2$Im)(η^1-C_5H_5)(C_6F_5)] (14): 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-IPDS 1 image-plate diffractometer (Mo-K_α radiation) equipped with an FT AirJet low-temperature device. Data were collected at 200 K; equivalent reflections were merged, and the images were processed with the STOE-IPDS software package. Corrections for Lorentz polarization effects and adsorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all non-hydrogen atoms, and hydrogen atoms were included in all calculated positions. Extinction corrections were applied as required. Crystallographic calculation were performed using SHELXS-97 and SHELL-97.[27] CCDC-679571 (**2**), -679572 (**5**), -679573 (**6**), -679574 (**10**), -679575 (**13**), and -679576 (**14**) 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.

Supporting Information (see footnote on the first page of this article): NMR spectra of complexes **2–14**.

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