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Consecutive C–F Bond Activation of Hexafluorobenzene and Decafluorobiphenyl

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The reaction of [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**) {*i*Pr_2Im = 1,3-bis(isopropyl)imidazolin-2-ylidene} with hexafluorobenzene and decafluorobiphenyl results at room temperature in the formation of the products of a C–F bond activation reaction, i.e. [Ni(*i*Pr_2Im)$_2$(F)(C_6F_5)] (**2**) and [Ni(*i*Pr_2Im)$_2$(F)($C_{12}F_9$)] (**4**). The reactions of **2** and **4** with **1** or the reactions of hexafluorobenzene and decafluorobiphenyl with 1 equiv. or excess of dinuclear **1** (stoichiometric ratio nickel/substrate $>$ 2:1) at higher temperatures afford the complexes of a consecutive C–F bond-activation reaction, [1,4-{Ni(*i*Pr_2Im)$_2$(F)}$_2$(C_6F_4)] (**3**) and [4,4′-{Ni(*i*Pr_2Im)$_2$(F)}$_2$($C_{12}F_8$)] (**5**). Complexes **3** and **5** cleanly react in THF at room temperature with chlorotrimethylsilane and (isopropyl)(trimethylsilyl)selenane under elimination of fluorotrimethylsilane to yield the corresponding chloro and selenolato complexes [1,4-{Ni(*i*Pr_2Im)$_2$(X)}$_2$(C_6F_4)] [X = Cl (**6**), *i*PrSe (**7**)] and [4,4′-{Ni(*i*Pr_2Im)$_2$(X)}$_2$($C_{12}F_8$)] [X = Cl (**8**), *i*PrSe (**9**)].

Introduction

Many modern pharmaceuticals and agrochemicals contain fluorinated substituents, which are commonly accessed by using selective fluorinating reagents.[1] The use of transition-metal complexes in the catalytic activation and functionalization of C–F bonds provides a unique way to derivatize fluoroorganic compounds and to access fluorinated building blocks.[2] We have shown that zero-valent nickel–NHC (N-heterocyclic carbene) complexes are attractive for these kinds of transformations for perfluorinated as well as partially fluorinated aromatic compounds. We have demonstrated that the compound [Ni_2(*i*Pr_2Im)$_4$(COD)] [**1**; *i*Pr_2Im = 1,3-bis(isopropyl)imidazolin-2-ylidene; Figure 1] acts as an excellent source for the very electron-rich[3] bis(carbene)nickel(0) complex fragment {Ni(*i*Pr_2Im)$_2$} in C–C, C–S[4], and C–F[5] bond-activation reactions.

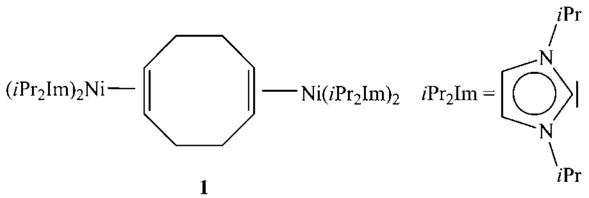

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Figure 1. [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**).

The reaction of [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**) with different fluorinated arenes occurs with a high chemo- and regioselectivity. In the case of polyfluorinated aromatic compounds of the type C_6F_5X (Ar_F–X) such as hexafluorobenzene (X = F), octafluorotoluene (X = CF_3), trimethyl(pentafluorophenyl)silane (X = $SiMe_3$), or decafluorobiphenyl (X = C_6F_5) the C–F bond activation regioselectively takes place at the C–F bond in the *para* position to the X group to afford the complexes *trans*-[Ni(*i*Pr_2Im)$_2$(F)(Ar_F)].[5c] The reactions of **1** with partially fluorinated aromatic substrates $C_6H_xF_y$ also lead to products of C–F bond activation. The detection of intermediates as well as kinetic studies gave some insight into the mechanistic details for the activation of an aromatic carbon–fluorine bond at the {Ni(*i*Pr_2Im)$_2$} complex fragment. The intermediates of the reactions of the ethylene complex [Ni(*i*Pr_2Im)$_2$(η^2-C_2H_4)] with hexafluorobenzene and octafluoronaphthalene, [Ni(*i*Pr_2Im)$_2$(η^2-C_6F_6)] and [Ni(*i*Pr_2Im)$_2$(η^2-$C_{10}F_8$)], have been detected in solution, and the activation enthalpy was determined for the C–F activation step of **1** with octafluoronaphthalene. Furthermore, we reported Suzuki-type cross-coupling reactions of perfluorinated aromatic compounds with boronic acids using [Ni_2(*i*Pr_2Im)$_4$(COD)] (**1**) as a catalyst.[5b] By using stoichiometric reactions, square-planar (pentafluorophenyl)nickel complexes of the type [Ni(*i*Pr_2Im)$_2$(X)(C_6F_5)] have been obtained from a systematic derivatization of [Ni(*i*Pr_2Im)$_2$(F)(C_6F_5)].[5d] The reactions of [Ni(*i*Pr_2Im)$_2$(F)(C_6F_5)] with silylated compounds and organolithium compounds led to substitution of the fluorido ligand with halogenido, trifluoromethanesulfonato, cyanido, organo, selenolato, thiolato, and hydrido ligands. Herein, we report first results on the rare example of a consecutive C–F bond activation of perfluorinated arenes[6] and some preliminary studies on the reactivity of the resulting compounds.

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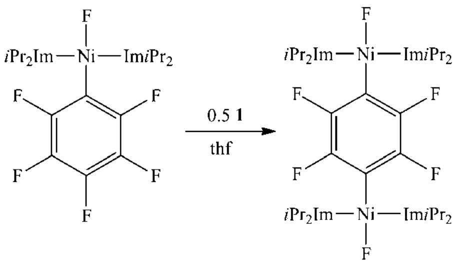
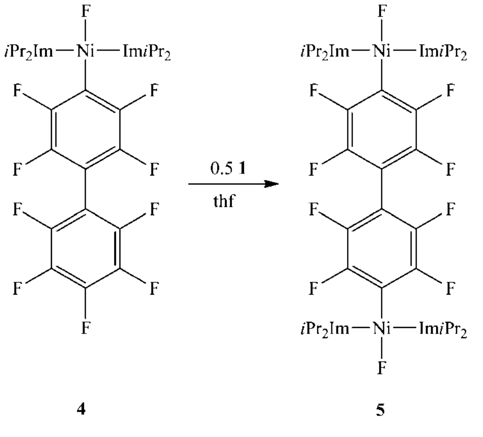
Results and Discussion

Since substrates of the type C_6F_5X (X = CF_3, $SiMe_3$, C_6F_5) are readily activated by using **1** in *para* position to the heteroatom X of the polyfluorinated arene ring, we were interested in learning whether two oxidative additions of carbon–fluorine bonds at one polyfluorinated substrate was feasible or not. To our knowledge, there is currently no example of two oxidative additions of C–F bonds of hexafluorobenzene by using transition-metal complexes known in the literature, but there is precedent that the reactions of hexafluorobenzene with strong nucleophiles may lead to complete defluorination of the fluorinated arene.[1] From previous investigations we know that such twofold C–F bond activation plays no role in the case of the reaction of stoichiometric amounts of **1** with hexafluorobenzene (reactions of 0.5 equiv. of the dinuclear nickel complex **1** with 1 equiv. of hexafluorobenzene) at low or ambient temperatures. To test the feasibility of a second C–F activation[6] in polyfluorinated arenes we decided to investigate the reaction of [Ni(iPr$_2$Im)$_2$(F)(C_6F_5)] (**2**) and [Ni(iPr$_2$Im)$_2$(F)($C_{12}F_9$)] (**4**) with [Ni$_2$(iPr$_2$Im)$_4$(COD)] (**1**). Both compounds react smoothly at temperatures of 60 °C or above to give [1,4-{Ni(iPr$_2$Im)$_2$(F)}$_2$(C_6F_4)] (**3**) and [4,4′-{Ni(iPr$_2$Im)$_2$(F)}$_2$($C_{12}F_8$)] (**5**) after a couple of hours [see Equations (1) and (2)]. Alternatively, these complexes can be obtained from the reaction of C_6F_6 and $C_{12}F_{10}$ with 1 equiv. of **1** at 60 °C after 16 h in almost quantitative yield.



2 **3** (1)

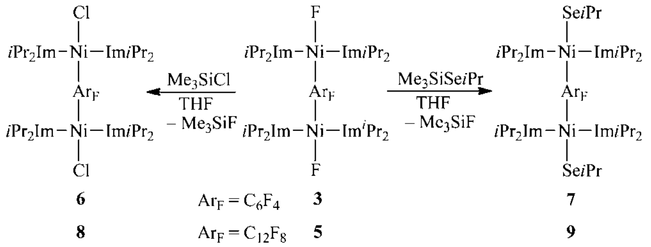


4 **5** (2)

In contrast to the formation of **2** and **4** higher temperatures are required for the generation of **3** and **5**. The usage of starting compound **1** in excess also affords the complexes **3** and **5**, since the remaining C–F bonds are not reactive with respect to further bond cleavage facilitated by the bis(carbene)nickel complex fragment. The formation of **3** and **5** is clearly indicated by the ^{19}F NMR spectra of these compounds. In the ^{19}F NMR spectrum of [1,4-{Ni(iPr$_2$Im)$_2$(F)}$_2$(C_6F_4)] (**3**) two characteristic signals have been obtained at δ = –121.82 ppm for the fluoroarene bridge and at δ = –353.48 ppm for the fluorido ligand. In the case of [4,4′-{Ni(iPr$_2$Im)$_2$(F)}$_2$($C_{12}F_8$)] (**5**) two multiplets at δ = –118.42 and –145.80 ppm for the octafluorobiphenyl bridge and one resonance at δ = –372.09 ppm for the fluorido ligand have been observed in an integration ratio of 2:2:1. Similarly to the behavior observed for the complex [Ni(iPr$_2$Im)(F)(C_6F_5)] (**2**),[5c] the resonances of the iPr methyl protons in the ^1H NMR spectrum of [1,4-{Ni(iPr$_2$Im)$_2$(F)}$_2$(C_6F_4)] (**3**) at δ = 1.20 and 1.50 ppm and [4,4′-{Ni(iPr$_2$Im)$_2$(F)}$_2$($C_{12}F_8$)] (**5**) at δ = 1.27 and 1.52 ppm have been observed as broadened singlets at room temperature due to a hindered rotation of the iPr groups at the N–C bond and of the NHC ligand at the Ni–C bond. We have shown in some detail earlier, that the ^1H NMR spectrum of **2** at room temperature in deuteriobenzene reveals a well-refined septuplet 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.[5c] A well-resolved doublet for the iPr methyl hydrogen atoms at δ = 1.29 ppm with a coupling constant of 6.6 Hz was observed for this compound at the high-temperature limit of 363 K in [D$_8$]toluene. In the case of [1,4-{Ni(iPr$_2$Im)$_2$(F)}$_2$(C_6F_4)] (**3**) we detected at the high-temperature limit these methyl resonances as resolved doublets at δ = 1.18 and 1.55 ppm, as expected for a blocked rotation of the NHC ligand and free rotation of the iPr substituents.

Dinuclear metal complexes with tetrafluorophenyl and octafluorobiphenyl bridging ligands are known but have been synthesized so far from the reaction of the dilithiated fluoroarene with suitable metal complexes under formation of lithium halide and the metal-containing dinuclear species. By using this strategy, the synthesis of compounds such as [1,4-{Fe(Cp)(CO)$_2$}$_2$(C_6F_4)][7a] and [4,4′-{Ni(PMePh$_2$)(Br)}$_2$($C_{12}F_8$)][7b] has been accomplished. These complexes have been discussed as building blocks in materials chemistry, for example for applications as one-dimensional conductors or for applications in the field of nonlinear optics. Fluoride substitution reactions of **3** or **5** with suitable bifunctional reagents would lead, for example, to linear coordination polymers. We have shown previously in some detail that the NHC-stabilized C–F bond-activation product [Ni(iPr$_2$Im)$_2$(F)(C_6F_5)] (**2**) reacts to square-planar (pentafluorophenyl)nickel complexes of the type [Ni(iPr$_2$Im)$_2$(X)(C_6F_5)] upon treatment of **2** with silylated compounds and organolithium compounds.[5d] To prove that these substitution reactions are also valid for the dinuclear complexes **3** and **5** we tested the substitution of the fluorido ligands of **1** with chlorido and selenolato ligands using chlorotrimethylsilane and silylated isopropylselenane.

Complexes **3** and **5** cleanly react in THF at room temperature with chlorotrimethylsilane and (isopropyl)(trimethylsilyl)selenane under elimination of fluorotrimethylsilane to the corresponding chlorido and selenolato complexes [1,4-{Ni(*i*Pr$_2$Im)$_2$(X)}$_2$(C$_6$F$_4$)] [X = Cl (**6**), *i*PrSe (**7**)] and [4,4′-{Ni(*i*Pr$_2$Im)$_2$(X)}$_2$(C$_{12}$F$_8$)] [X = Cl (**8**), *i*PrSe (**9**)], see Scheme 1. The chlorido complexes **6** and **8** are already formed when the fluorido compounds **3** and **5** are stirred at room temperature in solvents such as chloroform and dichloromethane. For the NHC ligands in **6**–**9**, the signal pattern typically obtained for *trans*-configured complexes in solution was observed. The ^{1}H NMR spectra feature two sharp doublets for the methyl protons, one septuplet for the methine protons, and a singlet for the olefinic protons of the NHC ligands. Additionally, the signal pattern for the isopropyl substituents of the selenolato ligand has been obtained in the case of **7** and **9**. In the ^{19}F NMR spectra of **6**–**9** the resonances for the polyfluorinated bridge were observed, in the case of **6** and **7** as a singlet at δ = –121.91 (**6**) and –119.58 (**7**) ppm, in the case of **8** and **9** as two multiplets at δ = –117.86 and –143.39 ppm (**8**) and at δ = –116.60 and –143.47 ppm (**9**).



Scheme 1. Syntheses of complexes **6**–**9**.

Crystals of **6** suitable for X-ray crystallography were obtained from a 1:1 mixture of dichloromethane/hexane at room temperature. Compound **6** crystallizes in the monoclinic space group *P*2$_1$/*n* with half of the molecule and two solvent molecules in the asymmetric unit. The center of inversion is located at the center of the tetrafluorophenyl ring. The nickel atom is square-planar coordinated by two NHC ligands in *trans* position, the chlorido ligand and the carbon atom of the fluoroaryl bridge. The nickel–carbon and nickel–chlorine distances are unexceptional and in a range found for other nickel–NHC complexes.[4,5] The tetrafluorophenyl bridge is almost perpendicularly orientated to the nickel coordination plane [best plane through Ni, C(1), C(19), C(10), Cl(1)]; the plane through the six-membered ring intersects the square plane with an angle of 71.81°. The carbene ligands are slightly bent away from the arene bridge with angles C(1)–Ni–C(19) of 92.20(15)° and C(10)–Ni–C(19) of 91.29(14)°. The NHC ligands are also not exactly perpendicularly oriented with respect to the square plane through Ni, C(1), C(19), C(10), and Cl(1). The planes through the NHC rings intersect this plane with angles of 78.37(13)° [ring at C(1)] and 78.85(13)° [ring at C(10)] (Figure 2).

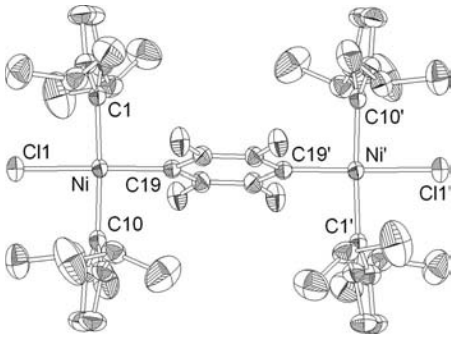


Figure 2. ORTEP diagram of the molecular structure of [1,4-{Ni(*i*Pr$_2$Im)$_2$Cl}$_2$(C$_6$F$_4$)] (**6**) in the solid state (ellipsoids are set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–Cl(1) 223.3(1), Ni–C(1) 191.5(4), Ni–C(10) 190.4(4), Ni–C(19) 191.9(3); C(1)–Ni–Cl(1) 88.61(11), C(10)–Ni–Cl(1) 87.90(11), C(19)–Ni–Cl(1) 179.08(12), C(1)–Ni–C(10) 176.43(15), C(1)–Ni–C(19) 92.20(15), C(10)–Ni–C(19) 91.29(14).

Conclusions

We have shown that consecutive C–F bond activation of hexafluorobenzene and decafluorobiphenyl is feasible at elevated temperatures by using [Ni$_2$(*i*Pr$_2$Im)$_4$(COD)] (**1**). The oxidative addition reactions regioselectively take place in *para* positions with respect to heterosubstitution to afford [1,4-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_6$F$_4$)] (**3**) and [4,4′-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_{12}$F$_8$)] (**5**). Complexes **3** and **5** cleanly react in THF at room temperature with chlorotrimethylsilane and (isopropyl)(trimethylsilyl)selenane under elimination of fluorotrimethylsilane to the corresponding chlorido and selenolato complexes [1,4-{Ni(*i*Pr$_2$Im)$_2$(X)}$_2$(C$_6$F$_4$)] [X = Cl (**6**), *i*PrSe (**7**)] and [4,4′-{Ni(*i*Pr$_2$Im)$_2$(X)}$_2$(C$_{12}$F$_8$)] [X = Cl (**8**), *i*PrSe (**9**)]. The complexes **3** and **5** should be ideally suited for the synthesis of metallapolymers containing perfluoroarene bridges.

Experimental Section

General: All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen or argon by using standard Schlenk techniques, as reported previously.[8] 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 are 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. Because there was no access to ^{19}F-decoupled ^{13}C NMR spectroscopy, we usually do not detect the carbon signals of the pentafluorophenyl groups in the ^{13}C NMR spectrum. In all cases, however, ^{19}F NMR data of these complexes are provided. Infrared spectra were recorded as KBr pellets with a Bruker IFS 28 and are reported in cm$^{–1}$. Complex **1** was prepared as published previously.[4a]

Synthesis of [1,4-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_6$F$_4$)] (3): Hexafluorobenzene (0.18 mL, 1.50 mmol) was added to a solution of [Ni$_2$(*i*Pr$_2$Im)$_4$(COD)] (1.26 g, 1.51 mmol) in THF (50 mL), and the mixture was stirred at 60 °C for 16 h. All volatiles were removed in vacuo, and the remaining solid was suspended in pentane (40 mL). The product was filtered off and dried in vacuo to give a pale yellow powder (1.17 g, 91%). $C_{42}H_{64}F_6N_8Ni_2$ (912.4): calcd. C 55.29, H 7.07, N 12.28; found C 55.71, H 6.53, N 12.01. EI/MS: *m/z* (%) = 510 (100) $[Ni(iPr_2Im)_2C_6F_4]^+$, 362 (87) $[Ni(iPr_2Im)_2]^+$. IR (KBr): $\tilde{\nu}$ = 407 (w), 488 (m), 578 (w), 675 (w), 691 (m), 704 (m), 728 (m), 893 (s), 949 (w), 1001 (w), 1028 (w), 1132 (m), 1153 (m), 1210 (s), 1227 (s), 1263 (w), 1303 (m), 1384 (s), 1393 (s), 1413 (m), 1429 (m), 1470 (m), 1496 (w), 1562 (w), 2874 (m), 2975 (s), 3051 (w) cm^{-1}. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 1.20 (br. s, 12 H, C*H*$_3$), 1.50 (br. s, 12 H, C*H*$_3$), 6.33 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, *i*PrC*H*), 6.82 (s, 4 H, NC*H*C*H*N) ppm. ^{19}F NMR (376.4 MHz, [D$_8$]THF, 25 °C): δ = –122.07 (s, 4 F, aryl-*F*), –369.62 (s, 2 F, Ni-*F*) ppm.

Synthesis of [4,4′-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_{12}$F$_8$)] (5): A mixture of decafluorobiphenyl (501 mg, 1.50 mmol) and [Ni$_2$(*i*Pr$_2$Im)$_4$(COD)] (1.26 g, 1.50 mmol) was dissolved in THF (50 mL), and the mixture was stirred at 60 °C for 16 h. All volatiles were removed in vacuo. The remaining residue was suspended in pentane (40 mL), the product was filtered off and dried in vacuo to give a yellow powder (1.30 g, 83%). $C_{48}H_{64}F_{10}N_8Ni_2$ (1060.5): calcd. C 54.37, H 6.08, N 12.57; found C 54.71, H 6.03, N 13.01. MS: *m/z* (%) = 676 (35) $[Ni(iPr_2Im)_2C_{12}F_9]^+$, 362 (100) $[Ni(iPr_2Im)_2]^+$. IR (KBr): $\tilde{\nu}$ = 380 (w), 481 (w), 506 (m), 577 (w), 673 (s), 709 (w), 775 (w), 838 (w), 881 (w), 925 (s), 955 (m), 998 (w), 1028 (w), 1081 (w), 1113 (w), 1133 (m), 1189 (m), 1212 (s), 1276 (w), 1304 (m), 1370 (m), 1393 (m), 1429 (v), 1469 (m), 1499 (w), 1526 (w), 1562 (w), 1628 (w), 2875 (w), 2940 (m), 2978 (s), 3057 (w) cm^{-1}. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 1.27 (br. s, 12 H, C*H*$_3$), 1.52 (br. s, 12 H, C*H*$_3$), 6.33 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, *i*PrC*H*), 7.03 (s, 4 H, NC*H*C*H*N) ppm. ^{19}F NMR (376.4 MHz, [D$_8$]THF, 25 °C): δ = –118.422 (m, 4 F, Aryl-*F*$_o$), –145.80 (m, 4 F, Aryl-*F*$_m$), –372.09 (s, 2 F, Ni-*F*) ppm.

Synthesis of [1,4-{Ni(*i*Pr$_2$Im)$_2$(Cl)}$_2$(C$_6$F$_4$)] (6): Me$_3$SiCl (51.0 µg, 0.40 mmol) was added to a suspension of [1,4-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_6$F$_4$)] (183 mg, 0.20 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo, and the residue was suspended in hexane (10 mL). The insoluble product was filtered off and dried in vacuo to give a yellow powder (110 mg, 60%). $C_{42}H_{64}Cl_2F_4N_8Ni_2$ (945.3): calcd. C 53.36, H 6.82, N 11.85; found C 52.99, H 6.98, N 11.62. IR (KBr): $\tilde{\nu}$ = 729 (m), 896 (s), 1028 (vw), 1132 (w), 1212 (vs), 1264 (vw), 1307 (w), 1369 (s), 1393 (s), 1413 (m), 1427 (s), 1437 (w), 1448 (w), 1458 (w), 1465 (w), 1472 (w), 1476 (w), 2873 (vw), 2934 (w), 2976 (m), 3082 (vw), 3121 (vw) cm^{-1}. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 1.17 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*$_3$), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*$_3$), 6.35 (sept, $^3J_{HH}$ = 6.7 Hz, 8 H, *i*Pr-C*H*), 6.83 (s, 8 H, NC*H*C*H*N) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF, 25 °C): δ = 21.6 (*C*H$_3$), 22.5 (*C*H$_3$), 51.3 (*C*H), 115.7 (N*CC*N), 176.7 (N*C*N) ppm. ^{19}F-NMR (376 MHz, [D$_8$]THF, 25 °C): δ = –121.91 (s, 4 F, aryl-*F*) ppm.

Synthesis of [1,4-{Ni(*i*Pr$_2$Im)$_2$(*i*PrSe)}$_2$(C$_6$F$_4$)] (7): Me$_3$SiSe*i*Pr (0.20 mL, 1.00 mmol) was added to a solution of [1,4-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_6$F$_4$)] (429 mg, 0.50 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo, and the residue was suspended in hexane (20 mL). The insoluble product was filtered off and dried in vacuo to give an olive-colored powder (376 mg, 67%). $C_{48}H_{78}F_4N_8Ni_2Se_2$ (1118.5): calcd. C 51.54, H 7.13, N 10.18; found C 51.17, H 7.13, N 10.18. IR (KBr): $\tilde{\nu}$ = 451 (m), 579 (m), 629 (m), 700 (vs), 719 (s), 834 (m), 886 (vs), 931 (m), 1024 (s), 1128 (vs), 1216 (vs), 1266 (s), 1298 (vs), 1389 (vs), 1469 (s), 2972 (vs), 3136 (w), 3183 (w) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 1.12 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*3{L^1}), 1.52 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*3{L^1}), 1.61 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, C*H*3{L^2}), 1.74 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H, *i*Pr-CH{L^2}), 6.24 (s, 8 H, NC*H*C*H*N), 6.51 (sept, $^3J_{HH}$ = 6.7 Hz, 8 H, *i*Pr-C*H*{L^1}) ppm. ^{13}C NMR (100 MHz, 25 °C, C$_6$D$_6$): δ = 23 (*C*H$_3${L^2}), 24.5 (*C*H$_3${L^1}), 25.5 (*C*H$_3${L^1}), 32.2 (*C*H{L^2}), 52.4 (*C*H{L^1}), 117.7 (N*CC*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C$_6$D$_6$): δ = –119.58 (s, 4 F, aryl-*F*) ppm.

Synthesis of [4,4′-{Ni(*i*Pr$_2$Im)$_2$(Cl)}$_2$(C$_{12}$F$_8$)] (8): Me$_3$SiCl (45.0 µg, 0.36 mmol) was added to a suspension of [4,4′-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_{12}$F$_8$)] (160 mg, 0.15 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo, and the residue was suspended in hexane (5 mL). The insoluble product was filtered off and dried in vacuo to give a yellow powder (120 mg, 73%). $C_{48}H_{64}Cl_2F_8N_8Ni_2$ (1093.4): calcd. C 52.73, H 5.90, N 10.25; found C 52.97, H 5.86, N 10.47. IR (KBr): $\tilde{\nu}$ = 708 (s), 733 (vw), 925 (s), 958 (w), 1028 (vw), 1131 (w), 1188 (w), 1213 (vs), 1305 (w), 1370 (m), 1393 (m), 1411 (s), 1423 (s), 1427 (vs), 1431 (s), 1457 (w), 1465 (w), 1472 (w), 1476 (w), 1627 (vw), 2873 (vw), 2935 (vw), 2976 (w), 3091 (vw), 3125 (vw) cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 1.15 (d, $^3J_{HH}$ = 6.5 Hz, 24 H, C*H*$_3$), 1.47 (d, $^3J_{HH}$ = 6.5 Hz, 24 H, C*H*$_3$), 6.13 (s, 8 H, NC*H*C*H*N), 6.56 (sept, $^3J_{HH}$ = 6.5 Hz, 8 H, *i*Pr-C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ = 22.5 (*C*H$_3$), 24.3 (*C*H$_3$), 52.2 (*C*H), 116.6 (N*CC*N), 174.0 (N*C*N) ppm. ^{19}F NMR (376 MHz, C$_6$D$_6$, 25 °C): δ = –117.86 (m, 4 F, aryl-*F*$_o$), –143.39 (m, 4 F, aryl-*F*$_m$) ppm.

Synthesis of [4,4′-{Ni(*i*Pr$_2$Im)$_2$(*i*PrSe)}$_2$(C$_{12}$F$_8$)] (9): Me$_3$SiSe*i*Pr (0.12 mL, 0.62 mmol) was added to a solution of [4,4′-{Ni(*i*Pr$_2$Im)$_2$(F)}$_2$(C$_{12}$F$_8$)] (315 mg, 0.30 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo, and the residue was suspended in hexane (20 mL). The insoluble product was filtered off and dried in vacuo to give a brown powder (355 mg, 67%). $C_{54}H_{78}F_8N_8Ni_2Se_2$ (1266.6): calcd. C 51.21, H 6.21, N 8.85; found C 50.91, H 6.03, N 8.71. IR (KBr): $\tilde{\nu}$ = 706 (m), 804 (w), 954 (m), 1024 (w), 1098 (w), 1182 (w), 1213 (s), 1262 (w), 1299 (w), 1370 (w), 1392 (m), 1426 (s), 1629 (w), 1959 (vw), 2974 (m) cm^{-1}. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*3{L^1}), 1.47 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, C*H*3{L^1}), 1.55 (d, $^3J_{HH}$ = 6.2 Hz, 12 H, C*H*3{L^2}), 1.65 (sept, $^3J_{HH}$ = 6.2 Hz, 2 H, *i*Pr-C*H*{L^2}), 6.02 (s, 8 H, NC*H*C*H*N), 6.45 (sept, $^3J_{HH}$ = 6.7 Hz, 8 H, *i*Pr-C*H*{L^1}) ppm. ^{13}C NMR (100 MHz, 25 °C, C$_6$D$_6$): δ = 23.1 (*C*H$_3${L^2}), 24.0 (*C*H$_3${L^1}), 31.6 (*i*Pr-*C*H{L^2}), 52.7 (*i*Pr-*C*H{L^1}), 117.7 (N*CC*N) ppm. ^{19}F NMR (376 MHz, 25 °C, C$_6$D$_6$): δ = –116.60 (m, 4 F, aryl-*F*$_o$), –143.47 (m, 4 F, aryl-*F*$_m$) ppm.

Crystal Structure Determination of 0.5[1,4-{Ni(*i*Pr$_2$Im)$_2$Cl}$_2$-(C$_6$F$_4$)]·2CH$_2$Cl$_2$: Crystal data: $C_{23}H_{36}Cl_5F_2N_4Ni$, M_r = 642.52 g mol^{-1}, yellow prism, size 0.40 × 0.30 × 0.15 mm, monoclinic, space group $P2_1/n$, a = 9.920(2) Å, b = 16.715(3) Å, c = 18.561(4) Å, β = 90.39(3)°, V = 3077.5(11) Å^3, T = 203 K, Z = 4, $\rho_{calcd.}$ = 1.387 g cm^{-3}, μ(Mo-K_α) = 1.095 cm^{-1}, F(000) = 1332, 21330 reflections in h (–11/11), k (–18/20), l (–22/22), measured in the range 2.19° < θ < 25.85°, completeness 94.8%, 5641 independent reflections, R_{int} = 0.0851, 4019 reflections with $F_o > 2\sigma(F_o)$, 316 parameters, 0 restraints, R_{1obs} = 0.0564, wR_{2obs} = 0.1395, R_{1all} = 0.0832, wR_{2all} = 0.1543, GooF = 1.034, largest difference peak/hole 1.279/–1.113 e Å^{-3}. The crystal was immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a STOE-IPDS I 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 calculations were performed by using SHELXS-97 and SHELL-97.[9] CCDC-818891 contains 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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