Coligand role in the NHC nickel catalyzed C–F bond activation: investigations on the insertion of bis(NHC) nickel into the C–F bond of hexafluorobenzene†

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The reaction of [Ni(Mes2Im)2] (1) (Mes2Im = 1,3-dimesityl-imidazolin-2-ylidene) with polyfluorinated arenes as well as mechanistic investigations concerning the insertion of 1 and [Ni(Pr2Im)2] (1′) (Pr2Im = 1,3-diisopropyl-imidazolin-2-ylidene) into the C–F bond of C6F6 is reported. The reaction of 1 with different fluoroaromatics leads to formation of the nickel fluoroaryl fluoride complexes trans-[Ni(Mes2Im)2(F)(ArF)] (ArF = 4-CF3-C6F4 2, C6F5 3, 2,3,5,6-C4F4N 4, 2,3,5,6-C6F4H 5, 2,3,5-C6F3H3 6, 3,5-C6F3H7 7) in fair to good yields with the exception of the formation of the pentafluorophenyl complex 3 (less than 2%). Radical species and other diamagnetic side products were detected for the reaction of 1 with C6F6, in line with a radical pathway for the C–F bond activation step using 1. The difluoride complex trans-[Ni(Mes2Im)2(C6F5)2] (9), the bis(aryl) complex trans-[Ni(Mes2Im)2(C6F3H)2] (15), the structurally characterized nickel(ii) complex trans-[Ni(Mes2Im)2(C6F3)] (11), and the metal radical trans-[Ni(Mes2Im)2(F)] (12) were identified. Complex 11, and related [Ni(Mes2Im)2(2,3,5,6-C6F4H3)] (13) and [Ni(Mes2Im)2(2,3,5-C6F3H)] (14), were synthesized independently by reaction of trans-[Ni(Mes2Im)2(F)(ArF)] with PhSiH3. Simple electron transfer from 1 to C6F6 was excluded, as the redox potentials of the reaction partners do not match and [Ni(Mes2Im)2]+, which was prepared independently, was not detected. DFT calculations were performed on the insertion of [Ni(Pr2Im)2] (1′′) and [Ni(Mes2Im)2] (1) into the C–F bond of C6F6. For 1′′, concerted and NHC-assisted pathways were identified as having the lowest kinetic barriers, whereas for 1, a radical mechanism with fluoride abstraction and an NHC-assisted pathway are both associated with almost the same kinetic barrier.

Introduction

Fluorinated organic compounds have exceptional properties that are being exploited in many applications including materials, pharmaceuticals and agrochemicals. The development of methods to introduce fluorinated aromatic building blocks selectively into organic molecules is thus of fundamental interest in many areas of chemical research. One strategy for such transformations is the selective activation and subsequent functionalization of C–F bonds of readily available fluoroorganic compounds such as fluoroaromatics. The challenge here is the selective cleavage of very stable C–F bonds. We have recently established a protocol for the transformation of commercially available fluoroaromatics via a selective C–F defluoroborylation process to obtain polyfluorinated aryboronic esters, which may be further used in late stage functionalization, for example in Suzuki–Miyaura cross-coupling reactions. Defluoroborylation of polyfluoroaromatics can be achieved by a thermal [Ni(Mes2Im)2]-catalyzed (Mes2Im = 1,3-dimesityl-imidazolin-2-ylidene) transformation of polyfluoroarenes into fluoroaryl boronic acid pinacol esters via C–F bond activation and transmetalation with bis(pinacolato) diboron (B2pin2) as the boron source (see Scheme 1). Various arenes with different degrees of fluorination were converted into their corresponding boronate esters in this way. One particularly interesting finding of our study was that activation of the C–F bond by the nickel(0) complex is fast at ambient temperature. This step yields the oxidative addition product.
trans-[Ni(Mes₂Im)₂(F)(ArF)] \( \text{(ArF} = \text{fluoroaryl)} \), which represents the
resting state in the catalytic cycle. The subsequent defluoro-
oborylation step with B₂pin₂ is the rate determining step
and requires elevated temperatures. A boryl complex
trans-[Ni(Mes₂Im)₂(Bpin)(ArF)] \( \text{, a likely intermediate, was never}
observed and stoichiometric reactions of trans-[Ni(Mes₂-
Im)₂(F)(ArF)] with B₂pin₂ led directly to the formation of ArF–Bpin.
This finding implied that reductive elimination is very fast and
that [Ni(Mes₂Im)₂(Bpin)(ArF)] \( \text{, once formed, will eliminate \text{ArF–Bpin}
immediately (Scheme 1).} \)

As an alternative to the thermally-induced C–F bond
activation and subsequent borylation of fluoroarenes, we have
developed a process that employs visible-light photocata-
lysis, which has emerged as a powerful tool in organic
synthesis.⁸ Our highly selective and general photocatalytic C–F
borylation protocol¹⁸ employs a rhodium biphenvyl complex⁷ as
triplet sensitizer combined with the nickel catalyst [Ni(Mes₂-
Im)₂] \( \text{(1 for the C–F bond activation step and the defluoroboryla-
tion process. This Rh/Ni tandem catalyst system operates
with visible light (400 nm) and achieves the highly selective}
boration of a wide range of polyfluorooarenes with B₂pin₂ at
room temperature in excellent yields. Both procedures, the
thermal and photochemical defluoroborylation, work well for
partially fluorinated aromatics but fail, or afford only low yields,
for perfluoroaromatics such as hexafluorobenzene or octa-
fluorotoluene.

Utilizing the dinuclear complex \[ \text{[Ni₃(Pr₃Im)₄]}\text{[μ-(η²-C₅H₄)}\text{]}\text{COD} \] \( \text{[Pr₃Im = 1,3-diisopropylimidazolin-2-yldiene) or the}
ethylene complex \[ \text{[Ni(Pr₃Im)₄]}\text{[η²-C₅H₄]}\text{]}\text{as sources of \[ \text{[Ni(Pr₃-
Im)₄]}\text{]}\text{(1PP)} \] \), we previously found that both readily undergo C–F
bond insertion with a wide variety of per- and poly-
fluoroaromatics on a time scale suitable for catalysis (exempli-
arily shown for C₆F₆ in Scheme 2).⁹ Mechanistic
investigations⁹ of the insertion process were performed using
the ethylene complex \[ \text{[Ni(Pr₃Im)₄]}\text{[η²-C₅H₄]}\text{]} as nickel precursor.
Ethylene exchange at the \[ \text{[Ni(Pr₃Im)₄]}\text{[η²-C₅H₄]}\text{]} complex with
hexafluorobenzene and octafluoronaphthalene occurs at low
temperatures (–80 °C and –30 °C, respectively; Scheme 2).
Subsequent insertion reactions occur at higher temperatures
(0 °C and 20 °C, respectively) to form the trans-[Ni(Pr₃Im)₂-
(F)(C₆F₅)] and trans-[Ni(Pr₃Im)₂(F)(C₁₀F₇)] fluorooaryl fluoride
complexes.⁹ We studied the C–F bond activation kinetics and,
based on the decay rates of the octafluoronaphthalene complex
\[ \text{[Ni(Pr₃Im)₂]}\text{[η²-C₁₀F₇]}\text{]} \] determined by variable-temperature
NMR spectroscopy, we derived an activation enthalpy of \( \Delta H^* = 27.7 ± 1.9 \text{ kcal mol}^{-1} \text{ (ΔS}^* \approx 8.8 ± 6.0 \text{ cal K}^{-1} \text{ mol}^{-1} \).

We report herein on the reactivity of 1 with polyfluorinated
arenes. We compare the results with those of earlier studies on
C–F bond activation processes using nickel complexes with
sterically less demanding NHCs, employing iPr instead of Mes
substituents, i.e., using \[ \text{[Ni(iPr₂Im)₄]}\text{]}\text{(1PP)} \) as the nickel source.
We demonstrate that the complex of the small NHC ligand
\text{Pr₃Im favors a concerted oxidative addition proceeding
through an \[ \eta²(C,C) \text{ intermediate in reactions with fluoroarenes
to yield trans-[Ni}^{\text{II}}\text{(NHC)}₂(F)(ArF)] \] complexes, whereas the
complex of the larger Mes₂Im ligand leads to fluorne atom
abstraction to yield \[ \text{[Ni}(\text{NHC})₂(F)] \) and a phenyl radical. For
both mechanisms, competitive NHC-assisted pathways are
found which account for the formation of diamagnetic products
by a C–F bond activation step across the Ni–C₆H₄C₆ bond. These
NHC-assisted pathways play an important role for complexes of
both sterically demanding and less bulky NHC ligands, and
should thus be of general importance and widely applicable for
the reactivity of NHC-stabilized transition metal complexes.

Results and discussion

C–F bond activation of fluoroaromatics

To gain insight into the C–F bond activation process using
[Ni(Mes₂Im)₂] \( \text{(1)} \) we first investigated stoichiometric reactions
of perfluorotoluene, perfluorobenzene, perfluoropyridine and
the partially fluorinated arenes pentafluorobenzene, 1,2,3,5,
4-tetrafluorobenzene and 1,3,5-trifluorobenzene with 1 (see
Scheme 3). We monitored the reactions by \( ^1 \text{H} \) and \( ^19 \text{F} \) NMR
spectroscopy and observed a significant effect of the degree of
fluorination on both reaction rate and yield. Reactions of 1 with
hexafluorobenzene and octafluoronaphthalene proceed within
seconds at room temperature, whereas the reactions with tetra-
and pentafluorobenzene take minutes to complete. With 1,3,5-
trifluorobenzene, full conversion of 1 takes weeks at room
temperature (see ESI, Fig. S1†), but can be accelerated at 80 °C
in thf to reach completion after 5 days.

These reactions can be performed in thf, toluene or hexane
at room temperature and lead, in each case, to the insertion
of the nickel complex into the C–F bond of the fluoroarene to form
the nickel fluoroaryl fluoride complexes \( \text{trans-[Ni(Mes₂Im)₂(F)}\text{(ArF)]} \)
\( \text{[ArF} = \text{4-CF₃-C₆F₅, C₆F₅, 3, 2,3,5,6-C₆F₅N, 4, 2,3,5,6-
C₆F₅H, 2, 2,3,5,6-C₆F₃H₆, 3, 5-C₆F₃H₇]} \) in fair to good isolated
yields. Notably, however, the reaction with C₆F₅ yields less than
20% of the pentafluorophenyl complex 3. Higher temperature,
different solvents (thf, toluene, hexane) or added [NMe₅]F does
not seem to affect the yield of the insertion product 3. Complexes 2–7 were characterized by elemental analysis, \(^{1}H\), \(^{19}F\) and \(^{13}C\) NMR spectroscopy (see ESI†). In the \(^{19}F\)\(^{1}H\) NMR spectra of these complexes, the resonances of the nickel-bound fluoride ligand were observed in the typical range between \(-361.9\) and \(-333.1\) ppm. Within the series presented (see ESI, Table S1†), the NMR shift of this resonance depends on the degree of fluorination of the fluoroaryl ligands, *i.e.*, an increase of the degree of fluorination of the aryl ligand leads to an upfield shift of the Ni–F resonance.

Crystals of 3, 4, and 5 suitable for X-ray diffraction were obtained from saturated solutions of these compounds either in pentane or hexane at \(-30\) °C (Fig. 1, Table 1; see also ESI Fig. S34–S36 and Table S2†). The crystal structure of 6 was published previously.44 All complexes of the type \([\text{Ni}((\text{Mes2Im})_2(F)(Ar^F))] (Ar^F = \text{C}_6\text{F}_3) 3, 2,3,5,6-\text{C}_5\text{F}_4\text{N} 4, 2,3,5,6-\text{C}_6\text{F}_5\text{H}_2 5, 2,3,5-\text{C}_6\text{F}_3\text{H}_2\) 6) adopt a square planar structure with a trans arrangement of the NHC ligands. An increasing degree of fluorination of the fluoroaryl ligand leads to a slight shortening of the Ni–F bond lengths (Ni–F: 6: 1.874(2) Å, 5: 1.856(2) Å, 4: 1.859(2) Å, 3: 1.844(2) Å), while the distances of the nickel center to the fluoroaryl ligand become gradually longer (Ni–C3: 6: 1.854(5) Å, 5: 1.896(3) Å, 4: 1.883(3) Å, 3: 1.944(5) Å). We assume that both the upfield shift of the Ni–F \(^{19}F\) NMR resonance and the shortening of the Ni–F bond lengths with increasing degree of aryl fluorination are indications of stronger Ni–F bonding.

Scheme 3 The reactions of \([\text{Ni}(\text{Mes2Im})_2]\) (1) with (a) octafluorotoluene, (b) hexafluorobenzene, (c) perfluoropyridine, (d) pentafluorobenzene, (e) 1,2,3,5-tetrafluorobenzene and (f) 1,3,5-trifluorobenzene to give the complexes trans-\([\text{Ni}(\text{Mes2Im})_2(F)(4-\text{CF}_3-\text{C}_6\text{F}_4)]\) (2), trans-\([\text{Ni}(\text{Mes2Im})_2(F)(\text{C}_6\text{F}_5)]\) (3), trans-\([\text{Ni}(\text{Mes2Im})_2(F)(2,3,5,6-\text{C}_6\text{F}_4\text{N})]\) (4), trans-\([\text{Ni}(\text{Mes2Im})_2(F)(2,3,5,6-\text{C}_6\text{F}_4\text{H})]\) (5), trans-\([\text{Ni}(\text{Mes2Im})_2(F)(2,3,5-\text{C}_6\text{F}_3\text{H}_2)]\) (6) and trans-\([\text{Ni}(\text{Mes2Im})_2(F)(3,5-\text{C}_6\text{F}_5\text{H}_2)]\) (7), respectively. Isolated yields are given.

As the low yield of trans-\([\text{Ni}(\text{Mes2Im})_2(F)(\text{C}_6\text{F}_3)]\) (3) is in sharp contrast with the results we obtained previously for the reaction of \([\text{Ni}_2(\text{iPr}_2\text{Im})_4(\mu-\eta^2:\eta^2-\text{COD})])\) or \([\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2-\text{C}_2\text{H}_4)]\) with \(\text{C}_6\text{F}_6\), we decided to take a closer look at the corresponding reaction using \([\text{Ni}(\text{Mes2Im})_2]\) (1). Performing the stoichiometric reaction of 1 with \(\text{C}_6\text{F}_6\) in an NMR tube in \(\text{C}_6\text{D}_6\) led to an immediate color change from dark-violet, the color of concentrated complex 1, to orange after addition of \(\text{C}_6\text{F}_6\) at room temperature. A quantitative conversion of 1 was achieved after 5 min as monitored by \(^{1}H\) NMR spectroscopy (see ESI, Fig. S2†). However, the spectroscopic yield determined by \(^{19}F\)\(^{1}H\) NMR spectroscopy after 5 min at room temperature, *vs*. a Ph–F containing capillary as internal standard, revealed the formation of 3 in approximately 17% yield and, in addition, the formation of small amounts of fluoride-containing side products (see ESI, Fig. S3†). Even after 72 h at room temperature, no increase in the spectroscopic yield of 3 was observed. In further control experiments, neither the use of an excess of 1 (2.85 equiv.) nor \(\text{C}_6\text{F}_6\) (2.5 equiv.) increased the yield of 3 substantially. These experiments demonstrate that the low isolated yield of 3 is not a problem of the isolation process for this complex, but rather an intrinsic problem associated with its formation and the C–F bond activation step. Low temperature NMR experiments (\(-50\) °C to +20 °C) revealed that a nickel fluoride resonance at \(-358\) ppm appeared for this reaction in the \(^{19}F\)\(^{1}H\) NMR spectrum already at \(-50\) °C (see ESI, Fig. S4†), but also that, at these temperatures, all resonances are significantly broadened in the \(^{1}H\) NMR spectrum of the reaction mixture (see ESI, Fig. S5†). Although we previously observed some line...
broadening for the N-alkyl groups of the related complex trans-
[Ni(Pr$_2$Im)$_2$(F)(C$_6$F$_5$)],$\text{9}$ which arose due to hindered rotation of
the NHC ligand about the Ni–C axis, all resonances observed for
the reaction of 1 with C$_6$F$_6$ are involved in the broadening. This
led to the assumption that radical species are involved in the
process. Subsequent EPR experiments were performed at
−203 °C for the reaction of 1 with C$_6$F$_6$ which confirmed the
presence of metal-centered radicals in the mixture.

For EPR spectroscopic investigations, 1 and C$_6$F$_6$ were
combined in an EPR tube with thf at −78 °C and the sample was
frozen immediately in liquid nitrogen. The EPR tube containing
the frozen reaction mixture was transferred to the cooled EPR
cavity at −203 °C and a spectrum was recorded.$\text{10}$ The resulting
EPR spectrum displays a superposition of resonances of three
different products, of which I and II represent the two dominant
species (Fig. 2, I: 40%, II: 50%, III: 10%).

Cyclic voltammetry results exclude a simple electron transfer
from 1 to C$_6$F$_6$ as the origin of radical generation in the reaction
mixture (see ESI, Fig. S6†), as 1 shows a reversible oxidation/
reduction associated with a redox potential of −2.03 V for the
redox-couple Ni$^0$/Ni$^I$, and an irreversible oxidation at 0.14 V for
the redox-couple Ni$^I$/Ni$^{II}$. Although the reduction of C$_6$F$_6$ at
−2.87 V is irreversible, we exclude simple one electron transfer
because of the large separation of 0.84 V.

For further scrutiny, complex 1 was oxidized by adding fer-
ocenium tetrafluoroborate in thf at room temperature to
a suspension of 1 in thf. A few min after addition of the fer-
ocenium salt the metal-centered radical [Ni(Mes$_2$Im)$_2$][BF$_4$]$\text{8}$
precipitated as an o-
ff-white solid (83% isolated yield, Scheme 4),
which is only sparingly soluble in common organic solvents.

The Ni$^I$ complex 8 was characterized by $^{11}$B($^1$H) and $^{19}$F($^1$H)
NMR spectroscopy in acetonitrile (decomposition occurs after

![Fig. 2](image)

**Scheme 4** Synthesis of [Ni(Mes$_2$Im)$_2$][BF$_4$]$\text{8}$.

<table>
<thead>
<tr>
<th>Crystallographic data for compounds 1, 3, 4, 5, 6, 8, 9, 11, 13, 14, [Ni($^6$-Mes)$_2$][Br]$\text{11}$ and [Ni($^3$Pr$_3$)$_2$(C$_6$F$_5$)]$\text{22}$</th>
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<td>[Ni($^3$Pr$_3$)$_2$(C$_6$F$_5$)]$\text{22}$</td>
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Fig. 2 EPR spectrum (−203 °C) of the reaction mixture of 1 with C$_6$F$_6$
after 5 s at −78 °C in thf.

**Table 1** Crystallographic data for compounds 1, 3, 4, 5, 6, 8, 9, 11, 13, 14, [Ni($^6$-Mes)$_2$][Br]$\text{11}$ and [Ni($^3$Pr$_3$)$_2$(C$_6$F$_5$)]$\text{22}$.
some time) and IR spectroscopy, elemental analysis and high-resolution mass spectroscopy. The $^{11}$B$^1$H and $^{19}$F$^1$H NMR spectra revealed an intact counter anion [BF$_4$]$^-$ (see ESI, Fig. S64†). Crystals of 8 suitable for X-ray diffraction (Fig. 3, Table 1; see also ESI, Table S2 and Fig. S37†) were obtained by slow evaporation of a saturated solution of 8 in a 1:1 toluene/ethanol mixture under an argon atmosphere at room temperature. The X-ray crystal structure reveals a nearly linear alignment of the NHC ligands with slightly elongated Ni–C distances compared to those of the starting material 1.

The results of the EPR spectroscopic investigations$^{10}$ performed on solid-state samples of [Ni(Mes$_2$Im)$_2$][BF$_4$] (8) are shown in Fig. 4. The general insolubility of 8 precluded determination of its magnetic moment by the Evans method. The spectrum reveals two sets of signals, i.e., 8a ($g_{xx} = 2.02, g_{yy} = 2.47, g_{zz} = 2.62; 70\%$) and 8b ($g_{xx} = 1.98, g_{yy} = 2.06, g_{zz} = 2.13; 30\%$), both in line with nickel-centered radicals. Note that in previous studies of two other homoleptic two-coordinate cationic d$^9$-nickel(i) complexes, [Ni(6-Mes)$_2$][Br] (6-Mes = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) and [Ni(P$^t$Bu$_3$)$_2$][Al(O(CF$_3$)$_2$)$_3$], no EPR signals were observed.$^{11}$ To obtain further insight, we performed density functional theory (DFT) calculations on the molecular geometries, electronic structures and EPR parameters ($g$ tensors) of a variety of potential candidates for 8 (PBE0-D/pcSseg-2, see the ESI for details†).$^{12}$

The DFT-optimized, $D_2$-symmetric geometry of the [Ni(Mes$_2$Im)$_2$]$^+$ radical cation of 8 agrees very well with the X-ray structure (Fig. 5; e.g., $d_{Ni-C} = 1.89 \text{ Å, exp: 1.894(3) Å}$). In the $^2A$ electronic ground state, the spin density is localized at the metal center, with the unpaired electron residing in an s/d$_z^2$-type orbital (Fig. 5a). The calculated $g$ values for the radical cation [Ni(Mes$_2$Im)$_2$]$^+$ ($g_{xx} = 2.01, g_{yy} = 2.65, g_{zz} = 2.98$), computed under gas-phase conditions, strongly differ from the experimental data with a maximum deviation of 0.36 (8a) and 0.85 (8b; see Table 2 and ESI, Table S3†). However, computations in the presence of the counter ion result in further structural motifs with impact on

![Fig. 3](image)

**Fig. 3** Molecular structure of [Ni(Mes$_2$Im)$_2$][BF$_4$] (8) in the solid state (ellipsoids drawn at the 50% probability level). Hydrogens atoms are omitted for clarity.

![Fig. 4](image)

**Fig. 4** EPR spectrum of 8 in the solid state at $-203^\circ \text{C}$ with NBu$_4$Br.

![Fig. 5](image)

**Fig. 5** (a) Spin density plot for [Ni(Mes$_2$Im)$_2$]$^+$; (b) molecular structure of 8DFT$_1$ showing Ni–F$_{BF_4}^-$ contacts (isolvalue $\pm 0.0075 \text{ Å}^{-3}$, lengths of Ni–F contacts in Å; hydrogen atoms not shown).
the computed $g$ tensors (see ESI, Fig. S7†). A Ni–F contact with the counter ion in $8_{\text{DFT}}$ (Table 2, entry 4, Fig. 5b) results in $g$ tensor components closely corresponding to those of $8a$ (maximum deviation: 0.03), while no species matching the EPR parameters of $8b$ were identified in our computational exploration. However, none of the EPR signatures detected for the electrochemically-formed complex $8$ appeared during the reaction of $1$ with C$_6$F$_6$ (Fig. 2) and, in light of our CV results, it is unlikely that the $[\text{Ni(Mes}_2\text{Im)}_2]^+$ cation is involved here.

We then focused on identifying the byproducts of the reaction of $1$ with C$_6$F$_6$. Stoichiometric reaction of $1$ with C$_6$F$_6$ in thf overnight at room temperature led to a very small amount of a dark-green precipitate which was removed by filtration. After removal of all volatiles from the filtrate, the residue was washed with a large amount of hexane to extract the C–F bond activation product. The yellow residue, which remained after washing, was identified as the difluoride complex trans-$[\text{Ni(Mes}_2\text{Im)}_2(\text{F})_2]$ ($9$) by elemental analysis, X-ray diffraction and $^1$H, $^{19}$F($^1$H) and $^{13}$C($^1$H) NMR spectroscopy (see ESI†). Most significantly, the fluoride resonance, detected as a singlet at $-560$ ppm in the $^{19}$F($^1$H) NMR spectrum, is shifted ca. 200 ppm to higher field compared to those of the mono-fluoride complexes $2$–$7$ ($-333$ ppm to $-362$ ppm, *vide supra*). A similar high-field shifted fluoride resonance was also observed for the phosphine-stabilized platinum complex $[\text{Pt(PPPh}_3)_2(F)(\text{C}_6\text{H}_5)]$ ($-455.9$ ppm) compared to

![Fig. 6](image)

**Fig. 6** Molecular structure of trans-$[\text{Ni(Mes}_2\text{Im)}_2(\text{F})_2]$ ($9$) in the solid state (ellipsoids drawn at the 50% probability level). Hydrogens atoms are omitted for clarity.

![Fig. 7](image)

**Fig. 7** Molecular structure of trans-$[\text{Ni(Mes}_2\text{Im)}_2(\text{C}_6\text{F}_5)]$ ($11$) (top) in the solid state (ellipsoids drawn at the 50% probability level) and EPR spectrum at $-203$ °C of the isolated compound $11$ (bottom). Hydrogen atoms are omitted for clarity.

Table 2  Experimental and DFT calculated $g$ tensors for species 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Exp. (solid state)</th>
<th>DFT</th>
<th>DFT-optimized structure with Ni–FBF$_4$ contacts.</th>
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<td>$8b$</td>
<td>1.98</td>
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<tr>
<td>$[\text{Ni(Mes}_2\text{Im)}_2]^+$</td>
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<tr>
<td>$8_{\text{DFT}}$</td>
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<td>2.59</td>
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An independent sample of complex $9$ was synthesized in $38\%$ yield by fluorination of $[\text{Ni(Mes}_2\text{Im)}_2(I)_2]$ ($10$) using an excess (2.5 equiv.) of silver(I) fluoride in CH$_2$Cl$_2$ at $0$ °C (Scheme 5). Complex $10$ was synthesized by reaction of $1$ with I$_2$, isolated in $80\%$ yield and characterized by elemental analysis, and $^1$H and $^{13}$C($^1$H) NMR spectroscopy (see ESI†). Interestingly, the resonance of the carbene carbon atoms is almost unaffected by substitution of the fluoride by the more electropositive

![Scheme 5](image)

**Scheme 5** Synthesis of $[\text{Ni(Mes}_2\text{Im)}_2(I)_2]$ ($10$) and $[\text{Ni(Mes}_2\text{Im)}_2(F)_2]$ ($9$).
iodide ligand, and was detected at 176.5 ppm (cf. [Ni(Mes2Im)2(F)2] (9): 174.6 ppm).

Thus, [Ni(Mes2Im)2(F)2] (9) was clearly identified as one of the side products of the reaction of 1 with C6F6. This complex is formed in low yield (17%) but in an amount similar to that of the insertion product trans-[Ni(Mes2Im)2(F)(C6F5)] (3). The amounts of complexes 9 and 3 total ca. 40% when the reaction of 1 with C6F6 is performed at room temperature, and thus the majority of the products formed in this reaction is still unaccounted for.

Storing the concentrated hexane mother liquor of the extract from the isolation of 9 (vide supra) for 3 days at −30 °C led to crystallization of the remaining C–F bond insertion product trans-[Ni(Mes2Im)2(F)(C6F5)] (3) and a novel nickel(II) complex trans-[Ni4−(Mes2Im)2(F)(C6F5)] (11) as yellow (3) and orange (11) crystals, respectively, which were manually separated in a glovebox (see ESI, Fig. S8†). The paramagnetic compound 11 was characterized by elemental analysis, EPR spectroscopy and X-ray diffraction. Determination of the room-temperature magnetic moment of 11 in solution (Evans method) gave a μeff value of 1.80 μB, which is consistent with the presence of one unpaired electron. The molecular structure (Fig. 7, top, Table 1; see also ESI, Table S2 and Fig. S39†) and the EPR spectrum (Fig. 7, bottom) of 11 confirm that this complex is a three-coordinate nickel(II) radical. Simulation of the EPR spectrum of 11 gave a g tensor of gxx = 2.04, gyy = 2.16 and gzz = 2.31, which was also observed in the EPR spectrum of the crude reaction mixture of 1 and C6F6 (Fig. 2). With the experimentally obtained g tensors and the molecular structure of the radical species 11 in hand, we carried out computational studies of the electronic properties of complex 11 and a likely radical counterpart from the reaction of 1 and C6F6, [Ni4−(Mes2Im)2(F)] (12) (Fig. 8). Both complexes 11 and 12 would be the result of a one-electron oxidative addition reaction of two equiv. of 1 with one equiv. C6F6 (Scheme 6).

Molecular geometries, electronic structures and EPR parameters (g tensors) were thus calculated for the metal radicals trans-[Ni4−(Mes2Im)2(C6F5)] (11) and trans-[Ni4−(Mes2Im)2(F)] (12) (Fig. 8) in order to connect the experimentally observed EPR spectra from the reaction mixture of 1 and C6F6 (Fig. 2), the EPR spectra of the isolated compound 11, and the corresponding isotropic g tensor components with the assigned structure of 11 (Fig. 7).

According to DFT calculations, complexes 11 and 12 are C2-symmetric doublet ground state species. The spin density is located at the metal center and the unpaired electron resides in an s/dz2-type orbital, yielding 2A electronic ground states (Fig. 8). Calculated and experimental g tensor components are in good agreement for species 11, with a maximum difference of 0.03 in gzz. With the largest deviation being 0.08 for 12, the agreement is still reasonable (Table 3).

To provide further evidence for the existence of trans-[Ni4−(Mes2Im)2(C6F5)] (11) and trans-[Ni4−(Mes2Im)2(F)] (12), we attempted to synthesize these complexes independently. The

![Fig. 8 Spin density plots for trans-[Ni4−(Mes2Im)2(C6F5)] (11) (top) and trans-[Ni4−(Mes2Im)2(F)] (12) (bottom) (isovalue 0.0075 a0−3; hydrogen atoms are omitted for clarity).](image)

**Table 3** Comparison of experimental and calculated g tensors for species 11 and 12

<table>
<thead>
<tr>
<th>Compound</th>
<th>DFT/Expa</th>
<th>g tensor componentsb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gxx</td>
<td>gyy</td>
</tr>
<tr>
<td>11</td>
<td>Exp. (isol.)</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>Exp. (react. mix.)</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td>2.06</td>
</tr>
<tr>
<td>12</td>
<td>Exp. (react. mix.)</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td>2.01</td>
</tr>
</tbody>
</table>

a The experimental g-tensor components are reorganized in ascending order from gxx to gzz. b EPR parameter have been calculated using DFT. The calculated values are rounded to match the number of digits of the experimental values. c Exp. (isol.); see Fig. 7 (bottom). d Exp. (react. mix.); see Fig. 2 I and II (I corresponds to compound 12; II corresponds to compound 11).
reaction of [Ni(Mes2Im)2][BF4] (8) with CsF led to a mixture of two complexes, which we were not able to separate. One of them was identified via 19F{1H} NMR spectroscopy as trans-[Ni(Mes2Im)2(F)2] (9) (19F{1H} NMR resonance at –560 ppm), and the resulting mixture reveals an EPR resonance with g tensors (gxx = 2.05, gyy = 2.42, gzz = 2.61) which are close to the g-tensors calculated for trans-[Ni(Mes2Im)2(F)] (12). We are thus confident that the second metal radical obtained in the reaction mixture is the monofluoride complex trans-[NiI(Mes2Im)2(F)] (12).

The complex trans-[Ni(Mes2Im)2(C6F5)] (11) as well as related trans-[Ni(Mes2Im)2(2,3,5,6-C6F4H)] (13) and trans-[Ni(Mes2Im)2(2,3,5-C6F3H2)] (14) can be synthesized from the reaction of [Ni(Mes2Im)2(F)(C6F5)] (ArF = C6F5, 2,3,5,6-C6F4H5, 2,3,5-C6F3H6) with PhSiH3 (Scheme 7, see also ESI Fig. S9 and S10).14

The metal radicals were characterized by elemental analysis, IR and EPR spectroscopy as well as single-crystal X-ray diffraction. All compounds are stable in the solid state as well as in solution for several days. If the reactions are performed in an NMR tube and followed by 1H and 19F{1H} NMR spectroscopy (see ESI; Fig. S9 and S10), the resonances for the Mes2Im, pentfluorophenyl and fluoride ligands vanish, indicating the formation of a paramagnetic species. For complexes of the type trans-[Ni(NHC)2(H)ArF], we expect hydride resonances in the region of ca. –13 ppm in the 1H NMR spectrum,α,β and a strong absorption in the IR spectrum in the region between 1600 and 2200 cm⁻¹ (we expect the Ni–H stretch to be at ca. 1850 cm⁻¹ based on DFT calculations). However, such signals were absent for 11, 13 and 14. Thus, although complexes of the type trans-[Ni(Mes2Im)2(ArF)] cannot easily be distinguished from the corresponding hydride complexes trans-[Ni(Mes2Im)2(H)ArF] by X-ray diffraction (see below), we are confident that 11, 13 and 14 are the metal radicals. Crystals of trans-[Ni(Mes2Im)2(C6F5)] (11), trans-[Ni(Mes2Im)2(2,3,5,6-C6F4H)] (13) and trans-[Ni(Mes2Im)2(2,3,5-C6F3H2)] (14) suitable for X-ray diffraction (Fig. 9, Table 1; see also ESI Table S2 and Fig. S39–S41f) were obtained by storing saturated solutions of these compounds either in pentane or hexane at –30 °C. Complexes 11–13 adopt a distorted T-shaped structure, in which the NHC ligands occupy mutually trans positions. Due to the absence of the fluoride ligand, 11, 13 and 14 exhibit shortened Ni–C distances to the fluoroaryl ligand and reduced C1–Ni–C2 angles compared to nickel(n) complexes 3, 4 and 5, which is also a further indication of the absence of a metal hydride. The data is in line with the data observed for [NiI(P3Pr3)(C6F5)] reported by Johnson and co-workers previously (Table 1, see also ESI Table S2†).14 EPR spectra of compounds 11, 13 and 14 were recorded in frozen thf solutions and reveal similar g tensors for the complexes, which are in good agreement with the calculated parameters (see ESI, Fig. S11–S13 and Table S4†).

Thus, the reaction of 1 with C6F6 affords the insertion product trans-[Ni(Mes2Im)2(F)2(C6F5)] (3) in approximately 20% isolated yield, the difluoride complex trans-[Ni(Mes2Im)2(F)2] (9) in approximately 17% isolated yield, the three-coordinate nickel(i) metal radicals trans-[Ni(Mes2Im)2(C6F5)] (11) (isolated yield: 10%), trans-[Ni(Mes2Im)2(F)] (12) (not isolated), and a small amount of a decomposition product, i.e., a dark green precipitate which was not characterized. trans-[Ni(Mes2Im)2(C6F5)] (12) was not isolated; it was only observed in the EPR spectra after 5 s at –78 °C, and the signals vanish after about 10 s during the course of the reaction. Further investigation of the hexane mother liquor of the reaction of 1 and C6F6 revealed that the bis(aryl) nickel(n) complex [Ni(Mes2Im)2(C6F5)] (15) remains in solution and was identified in the reaction mixture by 19F{1H} NMR spectroscopy. The radical species 11 and 12 were identified by EPR spectroscopy in a frozen thf solution at –78 °C (Fig. 2). The diamagnetic products trans-[Ni(Mes2-Im)2(F)2(C6F5)] (3), trans-[Ni(Mes2Im)2(F)] (9), and trans-[Ni(Mes2Im)2(C6F5)] (15) were identified by NMR spectroscopy (see Fig. S14 of the ESI†).

To expand our study to less fluorinated systems, we reacted 1 with pentfluorobenzene. After 48 h at room temperature, the 19F{1H} and 19F NMR spectra recorded in C6D6 reveal the formation of the C–F bond activation product trans-[Ni(Mes2-Im)2(2,3,5,6-C6F4H)] (5), the nickel difluoride complex [Ni(Mes2-Im)2(F)2] (9), and the corresponding bis(aryl) nickel(n) complex

![Scheme 7 Synthesis of the metal radicals [Ni(Mes2Im)2][BF4] (8) with CsF led to a mixture of two complexes, which we were not able to separate. One of them was identified via 19F{1H} NMR spectroscopy as trans-[Ni(Mes2Im)2(F)2] (9) (19F{1H} NMR resonance at –560 ppm), and the resulting mixture reveals an EPR resonance with g tensors (gxx = 2.05, gyy = 2.42, gzz = 2.61) which are close to the g-tensors calculated for trans-[Ni(Mes2Im)2(F)] (12).](Image 14x290 to 26x354)

![Fig. 9 Molecular structures of trans-[Ni(Mes2Im)2(C6F5)] (11) (top left), trans-[Ni(Mes2Im)2(2,3,5,6-C6F4H)] (13) (top right) and trans-[Ni(Mes2Im)2(2,3,5-C6F3H2)] (14) (bottom) in the solid state (ellipsoids drawn at the 50% probability level). Hydrogens atoms (with exception of the protons at fluoroarene rings) are omitted for clarity. Because of disorder of the fluoroaryl ligand of 14, the ligand is represented by a ball and stick model in two different colors for clarity.](Image 311x540 to 546x729)
[Ni(Mes₂Im)₂(C₆F₅H)₂] (see ESI, Fig. S15†). Furthermore, an EPR spectrum of the frozen reaction mixture of 1 with pentafluorobenzene in THF recorded after 5 s at −78 °C (see ESI, Fig. S16†) revealed resonances for three different products, one of which is in accordance with trans-[Ni(I⁻Mes₂Im)₂(F)F] (I2) and another has the same g tensor as observed for isolated [Ni(I⁻Mes₂Im)₂(C₆F₅H)] (I3). Thus, the reaction of 1 with C₆F₅H also follows a radical reaction mechanism akin to the reaction of 1 with C₆F₆ below.

**Mechanistic investigations**

Experimental investigations and DFT studies reported previously for the reaction of [Ni(Pr₂Im)₂(μ-η²:η²-C₃H₆)] and [Ni(Pr₂Im)₂(η²-C₃H₆)], used as source of [Ni(Pr₂Im)₂] (1br), with C₆F₆ suggested a concerted mechanism for the insertion of 1br into the C–F bond, and no indications for radical reactivity were obtained. As presented above, however, paramagnetic complexes clearly emerge in the reaction of 1 and C₆F₆. To obtain further insight, we performed a quantum-chemical investigation (COSMO(THF)-PBE0-D/def2-TZVP, for details see ESI†) on the reaction pathways of CₒF₆ with [Ni(Mes₂Im)₂] (I) and with the sterically less encumbered [Ni(Pr₂Im)₂] (1br).

C–F bond activation in the latter reaction commences with the formation of a rather stable 16-electron η² adduct between 1br and C₆F₆ (11, Scheme 8; see ESI, Fig. S17†). The DFT-optimized geometry of 11 is in good agreement with the structure of the closely related complex [Ni(Pr₂Im)₂(η²-C₆F₆)]°. Three distinct reaction pathways are then possible. First, direct oxidative addition of the C–F bond to the nickel atom proceeds through TS1 to yield the trans product 3br with an effective activation barrier of ΔG° = 23 kcal mol⁻¹ relative to 11 (see ESI, Fig. S18†). Alternative formation of the corresponding cis-

\[ \text{[Ni(Pr₂Im)₂(F)(C₆F₅)] (I2)} \]

and subsequent isomerization is kinetically disfavored (ΔG°eff = 27 kcal mol⁻¹, see ESI Fig. S19 and S20†), as is dissociation of an NHC ligand (ΔG°eff = 28 kcal mol⁻¹, see Fig. S32†).

Second, NHC ligand cooperativity (see ESI; Fig. S21 and S23†) opens a kinetically competitive pathway to the trans-product 3pr, that is, addition of the C–F bond across the Ni–NHC bond through TS2 to yield intermediate 13, in which coordination of the fluorinated NHC–F ligand to the nickel atom involves a bridging C–N bonding interaction. In TS2, the Caryl–F bond of 1.93 Å is strongly elongated compared to C₆F₆ (Caryl–F bond: 1.32 Å) and TS1 (Caryl–F bond: 1.77 Å), while NHC–F bond formation is hardly visible (C/F distance: 2.40 Å). From 13, fluoride migration onto the nickel ion (TS3, with a low barrier of ΔG° = 15 kcal mol⁻¹) leads to 3pr with an overall barrier of ΔG°eff = 24 kcal mol⁻¹. Third, homolytic C–F bond cleavage involves an effective barrier of ΔG°eff = 31 kcal mol⁻¹ (TS4) and, hence, radical abstraction is kinetically disfavored here (see ESI, Fig. S22†).

C–F bond activation with the sterically more congested Mes-NHC complex 1 shows marked differences. Formation of the η²-MesF₆ adduct 15 (see ESI, Fig. S24†) is now endergonic by 12 kcal mol⁻¹, and consecutive oxidative C–F bond addition via TS5 (ΔG°eff = 21 kcal mol⁻¹, see ESI; Fig. S25†) leads to the cis-product 16. We attribute the endergonicity of the η²-MesF₆ adduct formation (15, ΔΔG = 28 kcal mol⁻¹ compared to the exergonic formation of 11) mainly to the increased steric demand of the mesityl groups. A trajectory to the trans-product is precluded by the steric demand of the mesityl substituents. NHC dissociation to yield [Ni(Mes₂Im)(η³-C₆F₆)] and subsequent insertion into the C–F bond is associated with a large barrier (ΔG°eff = 34 kcal mol⁻¹, see ESI; Fig. S32 and S33†) and is

![Scheme 8](image)

Scheme 8  Calculated pathways for the C–F bond activation of C₆F₆ with 1br (ΔG°eff in kcal mol⁻¹).
irrelevant here. Note that an alternative adduct formation stabilized by π-stacking interactions between $\text{C}_6\text{F}_6$ and one of the NHC mesityl substituents, such as $\text{I}7$ (see ESI; Fig. S26†), is also endergonic and less favorable than $\text{I}5$. Furthermore, a “concerted” NHC-assisted process as in the $\text{iPr}$ system does not exist. We found a multi-step sequence for the mesityl system instead (Scheme 9 and ESI; Fig. S27†), commencing with heterolytic C–F bond cleavage in $\text{I}5$, which exhibits a partially reduced $\text{C}_6\text{F}_6$ fragment ($\text{q}_{\text{NPA}}(\text{C}_6\text{F}_6) = -0.69$). The fluoride anion expelled from the nickel coordination sphere is loosely held within the cleft formed by the mesityl substituents in $\text{I}8$. A similar stabilizing association of a fluoride anion by the methyl

Scheme 9 Calculated pathways for the heterolytic C–F bond cleavage of $\text{C}_6\text{F}_6$ by $\text{I}$ and further reaction steps ($\Delta G^{298}$ in kcal mol$^{-1}$).

Scheme 10 Calculated pathways for the homolytic C–F bond cleavage of $\text{C}_6\text{F}_6$ by $\text{I}$ and further radical reaction steps ($\Delta G^{298}$ in kcal mol$^{-1}$; energies of $\text{TS10}$ and $\text{9}$ are given relative to $\text{12} + \text{C}_6\text{F}_6$).
groups of mesityl substituents has been reported by Macgregor et al. for the C-F bond activation step in hydrodefluorination reactions.\textsuperscript{19} Formation of the trans-product 3 from here involves binding to the carbene carbon atom and subsequent F-shift onto the Ni center. The overall path involves a low effective barrier of 16 kcal mol\(^{-1}\) (TS6).

Fluorine radical abstraction to yield C\(_6\)F\(_5\) and radical complex 12 via TS9 is slightly endergonic and exhibits a barrier of 16 kcal mol\(^{-1}\) (Scheme 10 and ESI, Fig. S26 and S28\textsuperscript{15}). Recombination of C\(_6\)F\(_5\) and 12 to 3 then provides a large thermodynamic driving force. Alternative addition of C\(_6\)F\(_5\) to the initial complex 1 to yield radical species 11 is also a highly exergonic process (–69.5 kcal mol\(^{-1}\)), as well as addition of a second equivalent of C\(_6\)F\(_5\) to yield 15 (–108.0 kcal mol\(^{-1}\)).

Endergonic formation of difluorocyclohexadiene 9 from 12 and another equiv. of C\(_6\)F\(_5\) can be compensated by consumption of C\(_6\)F\(_5\); however, a second fluorine abstraction step is prevented by the high kinetic barrier of 37 kcal mol\(^{-1}\) via TS10 (see ESI; Fig. S29\textsuperscript{15}). The mechanism for the formation of 9 remains obscure to us thus far. We compute the ligand exchange reaction 3 + 3 + 9 + 15 to be exceedingly endergonic (25.7 kcal mol\(^{-1}\)), and also the disproportionation reactions of radicals 11 and 12 yielding 1 + 15 (31.0 kcal mol\(^{-1}\)) or 1 + 9, (14.9 kcal mol\(^{-1}\)), are unlikely to contribute to the formation of 9 (see ESI, Fig. S30\textsuperscript{15}). A dinuclear complex \([\text{Ni}((\text{Mes})_2\text{Im})_2]_{2}[(\text{F}^–(\text{Mes})^–(\text{C}_6\text{F}_5))]\), which would be an intermediate for an one-electron oxidative addition, is too high in energy to be considered (35 kcal mol\(^{-1}\), see ESI; Fig. S31\textsuperscript{15}). Hence both, the radical pathway and the NHC-assisted multistep pathway represent kinetically competitive C-F bond activation steps in the reaction with [Ni((Mes)_2Im)]\(_2\) (1).

Discussion

It is now well established that nickel(0) complexes with phosphine, carbene, and even some nitrogen ligands undergo C-F oxidative addition with perfluoroarenes to yield complexes \(\text{trans-}[\text{Ni}(\text{L})_2(\text{F})(\text{C}_6\text{F}_5)]\).\textsuperscript{1,9,20} Although the lack of clean kinetics for many of the C-F oxidative additions indicate complex mechanistic scenarios, there were strong indications that the conversion of C\(_6\)F\(_5\) to the aryl fluoride complex follows the same type of mechanism as observed for typical C-H activation reactions of benzene. It has been demonstrated, for nickel NHC and phosphine complexes, that the first stage of C-F oxidative addition is the \(\eta^1\)-coordination of the fluoroarene.\textsuperscript{15-19,21,22} The introduction of fluorine substituents on the arene results in a lower lying LUMO, which renders the fluorinated arene a better electron acceptor compared to H-arenes and makes the reaction of electron-poor C\(_6\)F\(_5\) with an electron-rich, suitable nickel precursor more exothermic. The fluoroarene of [Ni(L)_2(\(\eta^1\)-C\(_6\)F\(_5\))] is ene-diene distorted, and the arene fluoride substituents are bent out of the plane, as observed for 11 and 15. Subsequent C-F oxidative addition is strongly exothermic for \(\text{trans-}[\text{Ni}(\text{Pr}_2\text{Im})_2(\text{F})(\text{C}_6\text{F}_5)](\Delta G^\text{TS}=–57\) kcal mol\(^{-1}\)) and \(\text{trans-}[\text{Ni}((\text{Mes})_2\text{Im})_2(\text{F})(\text{C}_6\text{F}_5)](\Delta G^\text{TS}=–52\) kcal mol\(^{-1}\)). Computational studies reported previously\textsuperscript{9,21} of the reaction pathways have supported the idea of concerted mechanisms involving a \(\sigma\)-complex as a three-center transition state between the C\(_6\)F\(_5\) carbon and fluorine atoms and the transition metal atom. The transition state structures typically show limited elongation of the C-F bond and interaction of the electron-rich transition metal ion with the C-F \(\sigma^*\) orbital leads to C-F bond breaking and formation of the M-C and M-F bond. We have demonstrated now for [Ni\(_3\)(Pr\(_2\)Im)\(_4\)(\(\mu\)-(\(\eta^3\)-\(\eta^1\)-\(\eta^1\)-C\(_6\)F\(_5\)))\(\text{COD}\)] and the related [Ni\(_4\)(Pr\(_2\)Im)\(_3\)]\(_2\) (1\textsuperscript{pip}) synthon complexes that C-F bond activation of C\(_6\)F\(_5\) occurs via both a concerted and an NHC-assisted pathway, as both are associated with very similar kinetic barriers of \(\Delta G^\text{eff}=23\) kcal mol\(^{-1}\) for the concerted and of \(\Delta G^\text{eff}=24\) kcal mol\(^{-1}\) for the NHC-assisted pathway. This situation will probably change if other substrates with other leaving groups, such as partially fluorinated arenes, fluoropryridines or other aryl halides, are involved in the reaction with the nickel complex; however, our calculations demonstrate that both reaction paths are feasible, at least for fluoroarenes.

The direction of the concerted oxidative addition in TS1 to give the trans product is rather unusual.\textsuperscript{24} For the oxidative addition of A-B to d\(_{10}\)-ML\(_2\), the important orbital interactions of the transition state are those between the filled \(\sigma^*(A-B)\) orbital and the empty \(d_s\)-type orbital of the metal, leading to electron donation from A-B to the metal center, and a second interaction between the filled \(d_s\)-orbital of the metal and the \(\sigma^+(A-B)\), leading to electron transfer from the metal to the ligand. Strong back-donation will lead to fission of the A-B bond. This back-donation is strongest if A-B lies with the bent-d\(_{10}\)-ML\(_2\) plane and the \(\sigma^+(A-B)\) orbital can interact with the \(d_{s,y}\) orbital (actually a d--p hybrid orbital), which is pointing at the two ligands L.\textsuperscript{24}

However, it was also shown previously that concerted oxidative addition reactions may take place through a nonplanar transition state structure even for non-polar substrates with dihedral angle between ML\(_2\) and M(A-B) planes larger than 70°.\textsuperscript{25} It was demonstrated that this nonplanar transition state is connected to the planar product on the singlet surface and suggested that steric rather than electronic factors are responsible for the nonplanar transition state structure. Martin et al.\textsuperscript{26} for example, calculated at the B3LYP/LanL2DZ-level of theory a nonplanar transition state for the oxidative addition of C\(_6\)H\(_5\)-l to [Pd(dmpe)]\(_2\) (dmpe = bis(dimethylphosphino)ethane), in which the P-Pd-P and C-Pd-I planes are almost perpendicular to one another. Another example was provided by Jones et al.\textsuperscript{22} for the oxidative addition of the C-CN \(\sigma\)-bond of organonitriles to the low-valent nickel complex [Ni(dmpe)]. The C-C-N plane of the transition state (calculated at the B3LYP/6-31G(d,p)-level of theory), which leads to C-CN bond cleavage, is rotated by 38° relative to the P-Ni-P plane.

The \(\eta^1(C,C)\)-bonded complex [Ni\(_3\)(Pr\(_2\)Im)\(_4\)(\(\eta^1\)-C\(_6\)F\(_5\))] (11) is also the crucial reaction intermediate for the NHC-assisted pathway. The key step here is the addition of the C-F bond across the Ni-C\(_{\text{NHC}}\) bond and, thus, the unoccupied NHC \(p_\pi\) orbital plays a central role for this pathway as intramolecular fluoride acceptor. Fluoride transfer from the arene to the NHC leads to a \(\eta^1\)-fluoro-imidazoyl intermediate (13; Scheme 8) which rearranges with a second fluoride transfer step from the NHC to the nickel atom to give trans-[Ni\(_4\)(Pr\(_2\)Im)\(_3\)](1\textsuperscript{pip}).
A phosphine-assisted process has been proposed before for the C–F bond activation of pentafluoropyridine with [Ni(PR₃)₂], based on the experimental observation of an unusual selectivity for the insertion into the 2-position of C₅F₅ and on DFT calculations. However, another study performed on the reaction of pentafluoropyridine with [Ni(PEt₃)₂] suggested that pathways other than a concerted oxidative addition or a phosphine-assisted pathway account for the unusual selectivity. The detailed experimental analysis of the reactivity of a [Ni(PEt₃)₂] precursor with perfluoropyridine demonstrated the formation of a mononuclear adduct [Ni(PEt₃)₂][η²-C₅F₅N], of dinuclear adducts [Ni(PEt₃)₂][μ-(η²:η²)-C₅F₅N], some of which exhibit C–F bond activation, and a nickel(II) radical species [Ni(PEt₃)₂(2-C₅F₅N)]. Other heteroatom-assisted C–F bond activation processes have also been proposed for other metals mainly including boryl or silyl moieties.

Despite precedent in the oxidative addition of other aryl carbon–halide bonds to nickel, there is only little experimental evidence for the involvement of radicals in C–F bond activation processes. It is known that some polyfluoro pyridines react with [Ni(PR₃)₂] to yield EPR-active complexes as likely intermediates, and some studies on C–F bond activation have shown unusual products with highly-fluorinated arenes that may be indicative of radical pathways. However, the clear identification of radical intermediates has not been possible so far and alternate mechanisms cannot be ruled out. Although DFT calculations were performed to examine the traditional concerted oxidative addition and phosphine-assisted pathways for C–F bond activation, radical pathways involving Ni(i) intermediates were rarely considered computationally.

Thus, the reaction of 1 with different fluoroarenes leads to nickel insertion into the C–F bond to give the nickel fluoroaryl fluoride complexes trans-[Ni(Mes₂Im)₂(F)(ArF)]}, but EPR spectroscopy also provided evidence that at least three paramagnetic species are intermediates or products of the reaction of C₅F₅ with 1. We provide evidence that simple electron transfer from [Ni(Mes₂Im)]⁺ (1) to C₅F₅, often considered as the first step in radical oxidative additions at nickel, is unlikely to occur. The redox potentials are not in line with intramolecular electron transfer to yield [Ni(Mes₂Im)]⁺ and C₅F₅. The EPR resonance of [Ni(Mes₂Im)]⁺, which has been established for the authentic complex [Ni(Mes₂Im)][BF₄] in [8], was not detected in the reaction mixture. Furthermore, many diamagnetic and radical products of the reaction of [Ni(Mes₂Im)]⁺ (1) to C₅F₅ were identified, namely the insertion product trans-[Ni(Mes₂Im)₂(η²-F)(C₅F₅)] (3), the difluoro complex trans-[Ni(Mes₂Im)₂(F)₂] (9), the bis(aryl) complex trans-[Ni⁰(Mes₂Im)₂(C₅F₅)] (15), the nickel(II) complex trans-[Ni²(Mes₂Im)₂(C₅F₅)] (11), and the metal-centered radical trans-[Ni²(Mes₂Im)₂(F)] (12). DFT calculations performed on the reaction of [Ni(Mes₂Im)]⁺ (1) with C₅F₅ explain the occurrence of the radical species observed. Both an NHC-assisted and a radical process are kinetically equally favored routes for this reaction. Fluorine radical abstraction from C₅F₅ by 1 is associated with a barrier of only 16 kcal mol⁻¹ and subsequent radical recombination steps provide the thermodynamic driving force required.

Matsubara et al. and Louie et al. reported the clean isolation of T-shaped three-coordinate radical species [Ni⁺(NHC)₂(μ-X)] (X = Cl, Br, I; NHC = Mes₂Im, Dipp₂Im) from the reaction of [Ni(NHC)] with aryl halides. We have demonstrated earlier that [Ni⁺(PrIm)₃(μ-(η²:η²)-C₅F₅N)], a source of [Ni⁺(PrIm)₃] (11), reacts cleanly with aryl chlorides to yield the nickel(n) complexes trans-[Ni(NHC)₂Cl(Ar)]. Our calculations show now that a trajectory to the trans-product by a concerted oxidative addition is precluded for [Ni(Mes₂Im)]⁺ (1) (and most probably also for [Ni(Dipp₂Im)]⁺) by the steric demand of the mesityl substituents. As a consequence, other pathways such as electron transfer and radical abstraction must occur which are responsible for a limited or altered reactivity of complex [Ni(Mes₂Im)]⁺ (1) and analogues containing even more bulky N-aryl substituents compared to complexes of sterically less demanding NHCs. However, fluoride abstraction occurs for the reaction of 1 and C₅F₅ even at −78 °C to yield trans-[Ni¹(Mes₂-Im)₂(C₅F₅)] (11) and trans-[Ni¹(Mes₂Im)₂(F)] (12). The latter is, in contrast to the complexes of the heavier homologues, very reactive and has defied thus far isolation. In turn, the complexes trans-[Ni¹(Mes₂Im)₂(C₅F₅)] (11), [Ni¹(Mes₂Im)₂(2,3,5,6-C₆F₄H)] (12) and [Ni¹(Mes₂Im)₂(2,3,5-C₆F₃H₂)] (13) seem to be much more stable than [Ni¹(NHC)(C₆H₄)] and have been synthesized and characterized. The increased stability of [Ni¹(Mes₂-Im)₂(2,3,5,6-C₆F₃H₂)] (12) can be explained by the increased Ni-C₆ bond strength of the fluoroaryl ligand with respect to C₆H₄.

Nelson and Maseras reported computational investigations of the reaction of [Ni(NHC)₂] complexes with aryl halides Ph-X (X = Cl, Br, I) and demonstrated that steric effects determine the mechanism. Small NHC ligands (NHC = Mes₂Im) favor concerted oxidative addition via a η²(C,C) π-coordinated intermediate leading to trans-[Ni¹(NHC)₂(X)] whereas larger NHC ligands (e.g. NHC = Mes₂Im) lead to halide abstraction to form [Ni¹(X)] and a phenyl radical. We confirm here, by means of experiment and theory, that [Ni(NHC)₂] complexes of sterically less demanding NHCs favor the reaction with fluoroarenes via a concerted oxidative addition proceeding through an η²(C,C) intermediate, and that for the bulkier NHC Mes₂Im, C–F bond activation is achieved more easily by fluorine atom abstraction. However, for both mechanisms, we found an NHC-assisted pathway which is competitive, that accounts for the formation of diamagnetic products by a C–F bond activation step across the Ni-C_NHC bond. NHC-assisted pathways play an important role for complexes of both sterically demanding and less bulky NHC ligand. We believe that this dual reaction pathway concept, including NHC-assisted reaction pathways, should be of general importance and widely applicable for the reactivity of NHC transition metal complexes.

**Conclusions**

We present herein a detailed account of the C–F bond activation of polyfluoroaromatics, especially of C₅F₅ using the nickel(0) complex [Ni(Mes₂Im)]⁺. The reaction of 1 with different fluoroarenes leads to insertion of nickel into the C–F bond of the...
fluoroarene to give the nickel(un) complexes trans-[Ni(Mes2Im)2(F)(Ar=)] ([Ar=] = 4-CF3C6F4H2, 2, C6F3 3, 2,3,5,6-C6F4N 4, 4, 2,3,5,6-C6F4H 5, 2,3,5-C6F3H2 6, 3,5-C6F3H2 7) in good to fair yields with the exception of the formation of the pentafluorophenyl complex trans-[Ni(Mes2Im)2(F)(C6F3)] (3) (less than 20%). Whereas the C–F bond activation process of C6F4 using [Ni(Pr2Im)3] (1ppm) follows a concerted or NHC-assisted mechanism to give the insertion product via η2-coordinated intermediates, metal radical species were detected for the reaction of 1 with C6F4. EPR spectroscopy provided evidence that at least three paramagnetic products are intermediates or products of this reaction. The experiments reveal that simple electron transfer from [Ni(Mes2Im)] (1) to C6F4 is unlikely to occur as (i) the redox potentials do not match for an electron transfer between [Ni(Mes2Im)] (1) and C6F4 to give [Ni(Mes2Im)]+ and C6F4−, and (ii) the EPR resonance for [Ni(Mes2Im)]+ as established for the stable, isolated complex [Ni(lpr)2][BF4] (8), was not detected in the reaction mixture. Several other byproducts were identified aside from the insertion product 3, namely the difluoride complex trans-[Ni(Mes2Im)(F2)(C6F5)] (9), the bis(aryl) complex trans-[Ni([ipr]2)(C6F4)(C6F3)] (10), the structurally-characterized nickel(i) complex trans-[Ni(Mes3)(F)(C6F3)] (11) and the metal radical trans-[Ni([ipr]2)(F)(C6F4)] (12). Complex 11 and related complexes [Ni([ipr]2)(2,3,5,6-C6F4H)] (13) and [Ni([Mes2Im](2,3,5-C6F3H2)] (14) were synthesized and characterized independently from the reaction of trans-[Ni([Mes2Im](F)(Ar=))] with PhSiH3.

DFT calculations were performed on the insertion of [Ni(Pr2Im)3] (1ppm) and [Ni(Mes2Im)] (1) into the C–F bond of C6F4, which explain the formation of radical species for the reaction with [Ni(Mes2Im)] (1). For [Ni(Pr2Im)3] (1ppm), the crucial reaction intermediate is an η2(C,C)-bonded complex [Ni(Pr2Im)3(η2-C6F4)] from two favorable pathways with almost identical barriers, i.e., a concerted oxidative addition pathway and a NHC-assisted pathway, lead to the formation of trans-[Ni(Pr2Im)3(F)(C6F3)] For [Ni(Mes2Im)] (1), an NHC-assisted and a radical pathway were identified with similar kinetic barriers. Fluorine atom abstraction from C6F4 at [Ni(Mes2Im)] (1) occurs via end-on attack of C6F4, while the key intermediate for the NHC-assisted pathway is the η2(C,C) intermediate [Ni(Mes2Im)2(η2-C6F4)]. The NHC-assisted pathway can be interpreted as heterolytic C–F bond cleavage to yield ionic intermediates trans-[Ni(Mes2Im)(C6F4)]+ F− in which the fluoride anion is stabilized within the sphere of the trans-[Ni(Mes2Im)(C6F3)]+ cation. Several fluoride transfer steps, i.e., migration to the NHC, NHC rotation, and fluoride transfer to the metal cation lead to the formation of trans-[Ni(Mes2Im)(F)(C6F3)] (3).

Conflicts of interest
The authors declare no conflict of interest.

Acknowledgements
U. R., H. B. and T. B. M. thank the Julius-Maximilians-Universität Würzburg and U. R. the Deutsche Forschungsgemeinschaft (Ra720/12) for support. Quantum-chemical calculations were performed at the Center for Scientific Computing (CSC) Frankfurt on the Goethe-HLR computer cluster.

References

12 Molecular structures of the radical species discussed in this section were obtained at the RI-PBE-D/def2-SVP/W60 level of DFT. The PBE0-D functional and the pcSseg-2 basis set, which is specifically optimized for the calculation of magnetic properties, were employed to obtain EPR parameters (PBE0-D/pcSseg-2).


17 Optimized molecular structures and thermal/vibrational contributions to Gibbs free energies were obtained at the PBE0-D/def2-SVP level of DFT. The def2-TZVP basis set and the COSMO solvation model were employed to obtain improved relative energies (COSMO(THF)-PBE0-D/def2-TZVP).


