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Complete List of Authors:	Andrella, Nicholas; university of Ottawa, Chemistry and Center for Catalysis Research and Innovation Sicard, Alexandre; university of Ottawa, Chemistry and Center for Catalysis Research and Innovation Gorelsky, Serge; university of Ottawa, Chemistry and Center for Catalysis Research and Innovation Korobkov, Ilia; university of Ottawa, Chemistry and Center for Catalysis Research and Innovation Baker, R; University of Ottawa, Department of Chemistry

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EDGE ARTICLE

A T-shaped Ni[κ^2-(CF$_2$)$_4$-] NHC complex: Unusual C$_{sp3}$-F and M-C^F bond functionalization reactions†

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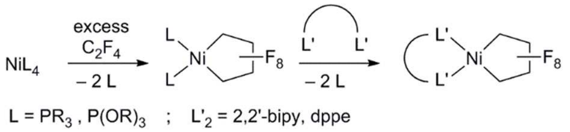
Nicholas O. Andrella,[a] Alexandre J. Sicard,[a] Serge I. Gorelsky,[a] Ilia Korobkov[a] and R. Tom Baker[a]*

Abstract: A T-shaped octafluoronickelacyclopentane–NHC complex is prepared and characterized. While the solid-state structure includes a weak isopropyl-CH$_3$ agostic interaction, the reactivity of this complex with Lewis- and Brønsted acids is clearly enhanced by its low coordination number. Reaction with Me$_3$SiOTf, for example, yielded a rare metal-heptafluorocyclobutyl complex whereas carboxylic acids gave substitution at the α-carbon and/or Ni-C^F bond protonolysis to afford thermally robust 4H-octafluorobutyl Ni complexes.

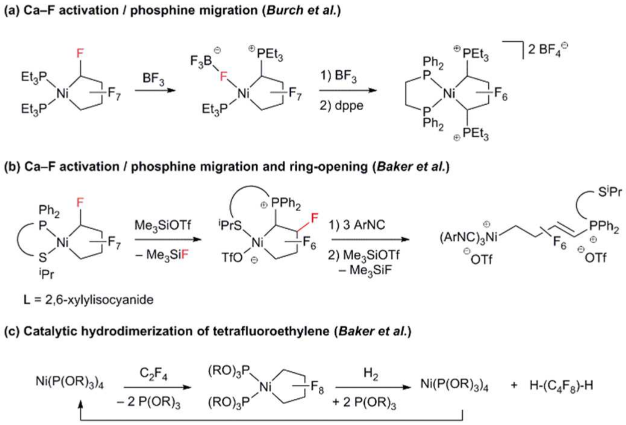
Introduction

Fluorocarbons and their derivatives are valuable as refrigerants, agrochemicals, unique solvents/surfactants and fluoropharmaceuticals, with annual sales of the latter alone in the billions of dollars.[1] As the demand for fluorinated chemicals has increased, so too have synthetic methods for introducing fluorine and fluorocarbon groups.[2-4] Despite recent advances, transition metal-mediated/-catalyzed routes are rare in comparison to the well-developed organometallic chemistry of hydrocarbons.[5] The challenge rests in the stability of metal-perfluoroalkyl (M-R^F) bonds, relative to metal-alkyl bonds.[6] M-C^F bonds are typically inert to processes such as insertion/alkyl migration reactions, vital to metal-mediated catalytic cycles.[7] Moreover, C-F bonds are stronger than C-H bonds,[1a,b] posing another obstacle to metal-based approaches.

We are investigating perfluoronickelacyclopentane complexes (PNCPs) as platforms for functionalized fluorocarbons with an initial focus on fundamental stoichiometric reactions. PNCPs have been synthesized previously by reaction of tetrafluoroethylene (TFE, CF$_2$=CF$_2$) with Ni^0 complexes. The displacement of P ligands by bidentate ligands has also been reported (Scheme 1).[8]



Scheme 1 Synthesis of perfluoronickelacyclopentanes



Scheme 2 Previously reported reactivity of perfluoronickelacyclopentanes.

To date, reports concerning the reactivity of PNCPs are sparse: Burch and co-workers found that Lewis acidic BF$_3$ effects fluoride abstraction from Cα and phosphine migration to the activated carbon (Scheme 2a).[9] Extending this reaction to the unsymmetrical P^S chelate, we showed that treatment with excess isonitrile effected cleavage of the Ni-C^F bond (Scheme 2b).[10] With phosphite co-ligands, a remarkable hydrogenolysis reaction enables the selective catalytic hydrodimerization of TFE (Scheme 2c).[11] As far as we know, this reaction is the only example of a perfluorometallacyclopentane participating in a catalytic cycle.[12]

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[a] Department of Chemistry and Centre for Catalysis Research and Innovation(CCRI), University of Ottawa, 30 Marie Curie, Ottawa, ON K1N 6N5 Canada

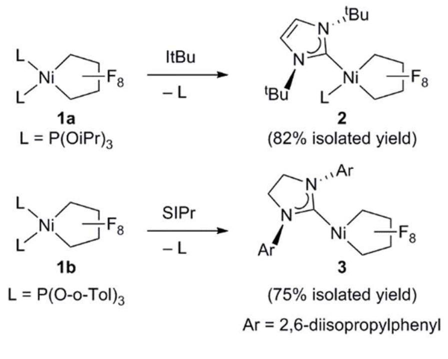
† Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra and X-ray crystallographic information. CCDC files 968465 (**2**), 968466 (**3**), 968467 (**4a**), 1028645 (**5c**) and 1412522 (**3**•H$_2$O); For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Our approach to metallacycle functionalization hinges on the reactivity of metal-activated Cα-F bonds[13] wherein we replace a C-F bond by C-Nu *vs* the current paradigm C-L (Nu = Nucleophile, L = Ligand). Using N-heterocyclic carbenes (NHCs),[14] we aimed to access low-coordinate PNCPs wherein the strong $M-C_{NHC}$ bond may also prevent ligand migration to Cα. There is considerable precedent for such an approach to low-coordinate metal complexes.[15] Hillhouse and coworkers prepared a two-coordinate nickel-imido complex bearing the exceptionally bulky IPr* ligand (analog of IPr with 2,6-bis(diphenyl-methyl)phenyl groups instead of 2,6-diisopropylphenyl).[16] Similarly, Miyazaki and coworkers synthesized a T-shaped three-coordinate nickel(I) chloride species $[Ni(IPr)_2Cl]$ by treatment of two-coordinate $[Ni(IPr)_2]$ with aryl chlorides.[17] Also, Hartwig *et al.* synthesized a low-valent, three-coordinate palladium(II) norbornyl species [Pd(SIPr)(NHAr)(Nor)], which underwent facile C-N bond reductive elimination when heated.[18]

In this report we show that low-coordinate NHC Ni perfluorometallacycles undergo facile C_{sp3}-F and $M-C^F$ bond cleavage as well as Cα-functionalization.[9] We also demonstrate the first migration of a fluoroalkyl to a reactive carbon center. This is significantly different from the reactivity previously observed for phosphine Ni perfluorometallacycle complexes.[9]

Results and discussion

Starting from bis(phosphite) PNCPs[10] (**1a**,**b**) we were able to cleanly synthesize coordinatively-saturated or -unsaturated nickel perfluorometallacycles. Thus, **1a** reacts smoothly with 1 equiv. of ItBu (ItBu = 1,3-di-tert-butylimidazol-2-ylidene) to afford the NHC/phosphite product **2** (Scheme 3, top; X-ray structural characterization presented in Supporting Information).[19] Significantly, the reaction between the larger SIPr ligand [SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] and a nickel metallacycle with sterically-demanding co-ligands (**1b**) results in displacement of both phosphite ligands, yielding the pseudo-three-coordinate/14e- Ni(II) metallacycle **3** (Scheme 3, bottom).



Scheme 3 Synthesis of NHC perfluoronickelacyclopentane complexes

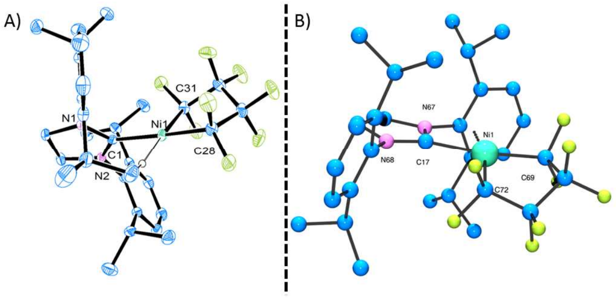


Figure 1 A) ORTEP representation of the molecular structure of **3**. Thermal-ellipsoid probabilities are set to 35% with hydrogen atoms omitted for clarity. The Ni-C(1) distance is 1.854(2) Å. B) Optimized structure of low energy Ni-aryl isomer **3'**; $Ni-C_{aryl}$ distances are = 2.818, 3.329, 3.379, 4.166, 4.204, 4.543 Å. The Ni-C(17) distance is 1.989 Å.

The molecular structure of complex **3**, as determined by single crystal X-ray diffraction, exhibits a T-shaped coordination about the Ni and features a weak agostic interaction with the isopropyl methyl group (Ni-C = 2.757(1) Å; compare $Ni-C^F$ bond distance trans to the NHC (1.934(1)Å) with that trans to the agostic interaction (1.875(1) Å) (Figure 1a). The ^{19}F NMR spectrum of **3** in C_6D_6 is consistent with ideal C_{2v} symmetry at room temperature, with only two distinct singlet resonances at -101.9 (Fβ) and -138.6 ppm (Fα). While these resonances both broaden significantly at 213K, it is apparent that the T-flip interconversion encounters only a small energy barrier.[20] To confirm this, we carried out DFT calculations (at the B3LYP/TZVP level with and without the empirical dispersion correction of Grimme).[21] Intriguingly, the calculations reveal two spin-singlet structures with a very small energy difference (ΔG_{298K} = 0.0-1.5 kcal/mol). The first computed structure coincides well with the observed solid-state structure of **3**; the 3-center bond order index between the Ni and the corresponding C-H bond of 0.05 is much less than 8/27 (~0.3), the maximum possible value for a 3-center 2-electron bond. As a result, the Mayer valence index for Ni in structure **3** is only 3.09. The second structure (**3'**) features a weak η^3 interaction between the aryl group of the NHC ligand at the 4th coordination site of the Ni atom (Figure 1b). Mayer bond orders for the corresponding three Ni-C interactions are in the 0.02-0.05 range, with a total bond order of 0.09. This suggests a semi-bidentate binding mode for the class of NHC ligands possessing pendant aryl groups. From calculations with the dispersion correction, structure **3'** has the same Gibbs free energy as **3**. Without the dispersion correction, structure **3'** is actually 1.5 kcal/mol lower in energy than **3**. The 3-coordinate structure with trigonal coordination around Ni and symmetric binding of the C_4F_8 ligand is a transition state with a low energy ($\Delta G^{\ddagger 298K}$ = 2.1 kcal/mol relative to **3**). Thus, it is clear that cleavage of the weak agostic and/or η^3-aryl bond is facile and allows for rapid reorientation of the ligands around the Ni center. Attempts to obtain evidence for structure **3'** by low temperature NMR were frustrated by dynamic processes associated with the T-flip and hindered rotations about the M-C and perhaps N-C bonds.

The HOMO of **3** (ε = -6.01 eV; Figure 2, left;) is localized on the Ni (87 %), primarily from a d_{z^2} orbital contribution (71 %). Lower-lying orbitals display interactions between metal d_{xz}, d_{yz} orbitals and the π-system of the aryl group.[22] The LUMO (ε = -

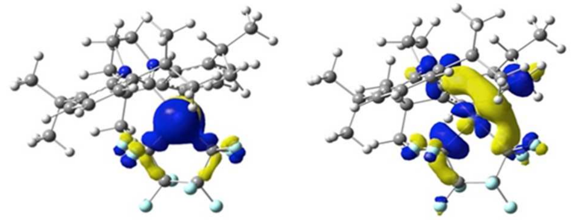


Figure 2 The HOMO (left) and LUMO (right) of **3**. Isosurface values of 0.04 au are used

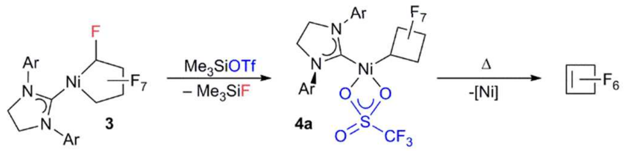
1.96 eV; Figure 3, right) is an anti-bonding combination of the metal d_{x2-y2} orbital (total Ni character of 45%) with the π-donor orbitals of the NHC and C_4F_8 ligands. Thus, reactivity of the M-C bond is likely under orbital control and arises from an interaction with the HOMO of **3**. In contrast, C-F bond activation is likely a combination of orbital and charge control with a slant towards the latter as the hardness of the Lewis acid increases.[23]

Initial studies on the C–F bond activation reactions of **3** are promising in the context of synthesizing functionalized fluoro-carbons by metal-mediated approaches. Firstly, when **3** is treated with the Lewis acid TMSOTf (TMS = Me_3Si, OTf = SO_3CF_3), α-fluoride-abstraction, accompanied by $Ni–C^F$ bond cleavage and $C^F–C^F$ bond formation, furnishes a rare perfluorocyclobutyl complex **4a** (Scheme 4, 75% isolated yield).[24] The driving force behind this transformation is likely related to the triflate leaving group ability and the formation of a strong C-C bond.[25] Importantly, the NHC remains bound to the nickel atom (i.e., does not migrate to Cα), potentially opening new pathways to functionalized fluorocarbon derivatives. Upon heating complex **4a** (80 °C in C_6D_6, 24 h), perfluorocyclobutene is produced, presumably via a β-fluoride elimination mechanism, although the metal-containing co-product(s) have not yet been identified.[26] Interestingly, a single OTf containing product can be discerned by ^{19}F NMR (-93.37 ppm) but a Ni-F signal could not be located. The ^{1}H NMR shows that the NHC remains intact. Upon addition of PPh_3 to the reaction mixture, PPh_3F_2 was identified as a major product, suggesting formation of a Ni-F thermolysis co-product.

The distorted square planar structure of complex **4a** (Figure 3) features a bidentate triflate ligand which can also likely access the κ^1-mode in solution as evidenced by the simple ^{19}F NMR spectrum[27] and observed tendency to eliminate. The perfluorocyclobutyl ring is nearly planar, the Ni-C bond is short [1.890(2) Å] due to the weak σ-trans influence ligand, and the Cα-F bond distance (1.384(3) Å) is considerably longer than the other C-F bonds (average of 1.33 Å).

The reactivity enhancement offered by low-coordinate **3** is evidenced by the sluggish reaction of 4-coordinate complex **2** with TMSOTf to give a mixture of unidentified products. Indeed, monitoring the reaction of **3** and TMSOTf at -25 °C allowed for the identification of a Ni-C_4F_7 intermediate **5a** apparently containing a Cα-OTf linkage (triflate CF_3 ^{19}F NMR resonance is coupled to Cα-F: $^5J_{FF}$ = 11 Hz). This is in contrast to previous suggestions of a metal fluorocarbene intermediate (Scheme 5).[9]

Having established that the NHC ligand remains bound to the metal upon fluoride-abstraction from **3**, we shifted our focus to C-F bond functionalization using Brønsted acids.



Scheme 4 Synthesis and decomposition of **4a**.

Scheme 5 Possible intermediates in the reaction of **3** with TMSOTf.

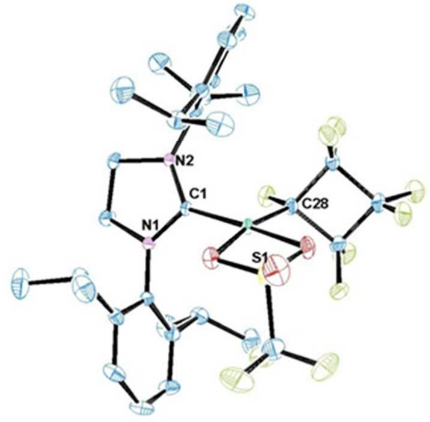


Figure 3 ORTEP representation of the molecular structure of **4a** with thermal ellipsoid probabilities set to 30 % and hydrogen atoms omitted for clarity. The Ni-C(1) distance is 1.854(2) Å.

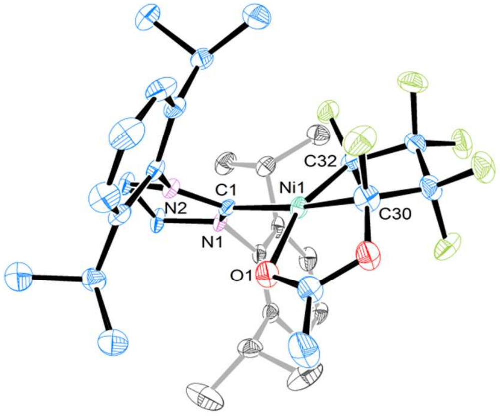


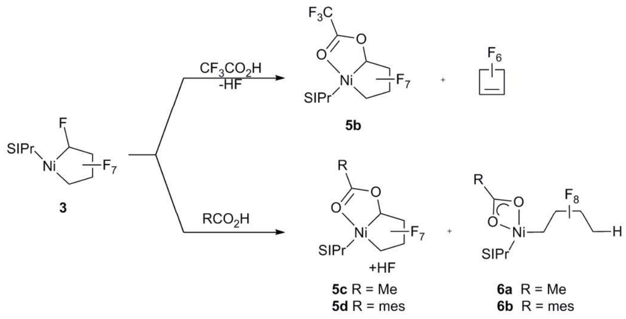
Figure 4 ORTEP representation of the molecular structure of **5c** with thermal ellipsoid probabilities set to 30 % and hydrogen atoms omitted for clarity. The Ni-C(1) distance is 1.928(2) Å.

Treatment of **3** with trifluoroacetic acid [TFA; pKa = 3.4 (DMSO)][28a] gives HF and the more stable (vs. **5a**) trifluoroacetate-substituted metallacycle **5b** that could be characterized spectroscopically at room temperature. Nonetheless, accompanying formation of perfluoro-cyclobutene, presumably formed via an analogous structure to **4a**, led us to move to weaker Brønsted acids. Remarkably, reaction of **3** with acetic acid [pKa = 12 (DMSO)][28b] (Scheme 5, bottom) yielded the stable ester metallacycle **5c** (30 % isolated yield) as well as the Ni-C^F bond cleavage product **6a** in a 1:1 ratio. At a similar acidity [pKa = 11 (DMSO)][28c] but increased steric bulk, 2,4,6-trimethyl-benzoic acid gave a 10:1 mixture favouring the ring cleavage product, **6b**.

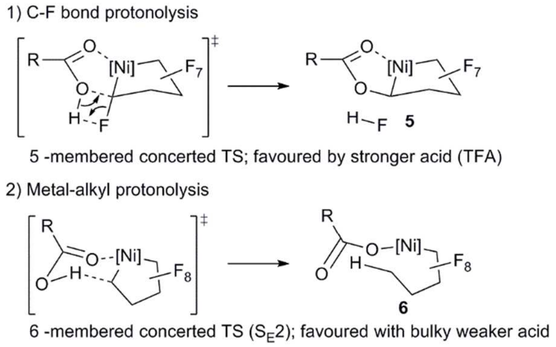
The molecular structure of **5c** features similar Ni-C bond distances (1.895(7) vs. 1.896(6) Å) and a distorted square planar coordination (Figure 4). The functionalized heptafluoro-metallacyclopentane ring is puckered with the smallest C-C bond distance being C(32)α-C(39)β [1.49(1) Å]. The carbonyl oxygen completes the nickel coordination sphere (Ni-O1 = 1.969(4) Å).

The ^{19}F NMR spectra of **5a-d** are very similar and support our original proposal for the low temperature intermediate **5a** in the reaction of **3** with TMSOTf. The Cα-F 19F chemical shifts of the functionalized carbon, (-117.2 and -119.2 ppm) can be compared with those of the phosphonium analogs (-115.6 and -117.8 ppm) shown in Scheme 2.

As expected, the ring-opened products **6a,b** display nearly identical ^{19}F NMR chemical shift patterns with the Cγ- and Cδ–F resonances distinguished by F-H coupling of 6 and 52 Hz, respectively. These unique complexes have been identified as their potassium cation adducts using ESI-MS (747.2 g/mol and 851.4 g/mol respectively) and are surprisingly inert to thermolysis at 80 °C in C6D6 for 20 h.



Scheme 6 Reaction of **3** with trifluoroacetic, acetic and 2,4,6-trimethylbenzoic acids



Scheme 7 Proposed reaction pathways for C-F activation *vs.* Ni-R^F protonolysis.

Considering the importance of esters as synthons in organic transformations[29] this C–O bond-forming reaction **3→5** is very appealing from the standpoint of synthesizing functionalized fluorocarbons. As such, understanding competing pathways for M-C vs. C-F bond cleavage would be valuable.[30] Viable reaction pathways can be considered as proceeding via either 5- or 6-membered transition states (Scheme 6). The selective HF elimination observed for TFA, is eroded as Ni-C bond protonolysis (orbital control) competes using acids of intermediate acidity (e.g. pKa ~11).[31] With the bulkier trimethylbenzoic acid, kinetic acidity factors in the tighter 5-membered ring transition state could severely limit HF elimination.[32]

Conclusions

In summary, we have prepared the first NHC-perfluorometallacyclopentane complexes and exploited the bulky SIPr ligand to stabilize a pseudo-three-coordinate nickelacycle, **3**. Importantly, **3** undergoes Cα-F abstraction reactions without migration of the NHC ligand. Instead, we see an unprecedented migration of the fluoroalkyl to the reactive carbon center, giving rise to the novel perfluorocyclobutyl complex via Ni-C^F bond cleavage. More importantly, the low-coordinate nature of **3** allows for ring functionalization. Strong acids favour selective Cα functionalization, but the resulting products are unstable with respect to competing metallacycle ring contraction and elimination of perfluorocyclobutene. With less acidic reagents stable ring-functionalized products are formed but a competing Ni-C^F bond cleavage pathway comes into play and dominates for bulkier carboxylic acids. These are the first examples of selective functionalization of a PNCP and synthesis of thermally stable Ni–C$_4$F$_8$H complexes. These results are encouraging in the context of developing metallacycle-based routes to functionalized fluorocarbons.

Ongoing work is focused on (a) expanding the scope of ring functionalization substrates suitable for reactions with **3** and (b) reductive (see Scheme 2, above) and oxidative approaches for removing the functionalized fluorocarbon fragments from the metal. Preliminary results of the hydrogenolysis of compound **3** indicate enhanced reactivity towards H$_2$ (i.e., at 7 psig and 25 °C) vs. reported 4-coordinate phosphite variants.[11a] However, loss of selectivity[33] is observed with the synthesis of two distinct products. Full details of these results will be published in due time.

Acknowledgements

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Economic Development and Innovation for essential infrastructure. N.O.A. gratefully acknowledges support from the province of Ontario, NSERC and the University of Ottawa (OGS and CGS-M/D).

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