Coordination and oxidative addition of octafluoronaphthalene at a nickel centre: isolation of an intermediate in C–F bond activation†

Letter

Thomas Braun, Leroy Cronin, Catherine L. Higgitt, John E. McGrady, Robin N. Perutz* and Meike Reinhold

Department of Chemistry, University of York, York, UK YO10 5DD. E-mail: rnp1@york.ac.uk

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Reaction of [Ni(COD)$_2$] with PEt$_3$ and octafluoronaphthalene yielded the complex [Ni(η^2-1,2-C$_{10}$F$_8$)(PEt$_3$)$_2$] 1, which was converted thermally into the C–F activation product *trans*-[NiF(2-C$_{10}$F$_7$)(PEt$_3$)$_2$] 2. The crystal structure of 1 shows asymmetric η^2 coordination with significant distortions of the naphthalene unit compared to the "free" ligand; DFT calculations reproduce the principal features of the geometry.

Several methods have been described for the activation of carbon–fluorine bonds of fluoroaromatic compounds by reaction at transition metal centres.[1–4] Although a wide variety of electron configurations and metals appear capable of C–F activation, nickel has assumed a prominent role.[3–5] We have studied the oxidative addition of fluorinated aromatics and heteroaromatics such as hexafluorobenzene, pentafluoropyridine and 2,4,6-trifluoropyrimidine at a nickel(0) centre yielding *trans*-[NiF(C$_6$F$_5$)(PEt$_3$)$_2$], *trans*-[NiF(2-C$_5$NF$_4$)(PEt$_3$)$_2$] and *trans*-[NiF(4-C$_4$N$_2$F$_2$H)(PEt$_3$)$_2$].[3,4] We have proposed that these reactions proceed by initial coordination of the aromatic compounds through a C=C bond or nitrogen followed by oxidative addition of the C–F bond, but no reaction intermediates have yet been detected.[3,4] Of particular note are the different rates of these reactions: the C–F activation of the heteroaromatics is very fast, while the reaction of hexafluorobenzene is extremely slow. Mechanistic information on C–F oxidative addition is very limited. Crespo *et al.* have obtained kinetic evidence for concerted *intramolecular* oxidative addition of fluoroaromatic substituents at platinum.[6] Bach *et al.* have synthesized [Ni(η^2-C$_6$F$_6$){^{t}Bu$_2$P(CH$_2$)$_2$P^{t}Bu$_2$}] and shown that on heating it forms [NiF(C$_6$F$_5$){^{t}Bu$_2$P(CH$_2$)$_2$P^{t}Bu$_2$}]. The product was identified by ^{19}F and ^{31}P NMR spectroscopy, but no kinetics was reported.[7] Here we show the coordination of octafluoronaphthalene to nickel in a η^2 mode and its thermal C–F bond activation at the nickel centre. The crystal structure of the complex [Ni(η^2-1,2-C$_{10}$F$_8$)(PEt$_3$)$_2$] **1** shows remarkable distortions when compared to structures of η^2-C$_6$F$_6$ complexes.

The stepwise treatment of [Ni(COD)$_2$] with PEt$_3$ and octafluoronaphthalene in hexane solution at room temperature results in the regioselective formation of [Ni(η^2-1,2-C$_{10}$F$_8$)(PEt$_3$)$_2$] **1**.‡ The ^{31}P NMR spectrum displays a triplet at δ 18.0 (average J_{PF} 18.5 Hz) for the equivalent phosphorus nuclei. The ^{19}F NMR spectrum shows four multiplets at room temperature at $\delta - 162.72$, -160.87, -160.49 and -145.93 consistent either with a structure with mirror symmetry (*e.g.* η^4-C$_{10}$F$_8$) or a fluxional structure (*e.g.* η^2-C$_{10}$F$_8$). On cooling to 190 K the resonances at $\delta - 162.72$ and -160.87 broaden, but those at $\delta - 160.49$ and -145.93 stay fairly sharp, indicating the occurrence of fluxional behaviour.

A suitable single crystal of complex **1** was obtained from hexane at 253 K and its structure determined by X-ray crystallography (Fig. 1).[8],§ The structure shows an η^2-C$_{10}$F$_8$ ligand coordinated to a nickel centre with approximately trigonal planar geometry. The Ni–C(1)–C(2) plane forms an angle of 108° with the naphthalene ligand, and an angle of 13.0° with the Ni–P(1)–P(2) plane. The bond C(1)–C(2) is significantly lengthened to 1.438(6) Å on coordination, but the C(1)–C(10) separation is also extremely long [1.472(6) Å], while the C(3)–C(4) bond length is shortened to 1.341(6) Å. No reliable structural data for free C$_{10}$F$_8$ are available for comparison, but the bond lengths of the uncoordinated ring in **1** may be used as a reference; they range from 1.356(8) to 1.412(7) Å (the C–C bond length of free C$_6$F$_6$ is 1.394(7) Å).[9] A similar disruption of the aromaticity in the bound naphthalene ring is found in [Ru(η^5-C$_5$Me$_5$)(η^2-C$_{10}$H$_8$)(NO)].[10]

The benzenoid ring that is bound to nickel in **1** is very distorted: C(1) lies 0.197(6) Å above the plane defined by C(3) to C(10). The buckling effect is also apparent in the torsion angles (Table 1). As found for the fluorine atoms attached to the η^2-bound carbons in [Ni(η^2-C$_6$F$_6$){^{t}Bu$_2$P(CH$_2$)$_2$P^{t}Bu$_2$}][7] and other η^2-C$_6$F$_6$ complexes,[11] the atoms F(1) and F(2) in **1** lie out of the octafluoronaphthalene plane with F(2) further out than F(1) (Fig. 1). In line with this observation, the Ni–C(2) bond [1.899(4) Å] is shorter than the Ni–C(1) bond [1.959(4) Å]. For comparison, the Ni–C bond length in a related σ bond in *trans*-[NiF(C$_6$F$_5$)(PEt$_3$)$_2$] is 1.878(7) Å.[3] The C(1)–F(1) and C(2)–F(2) bonds of **1** are extended to

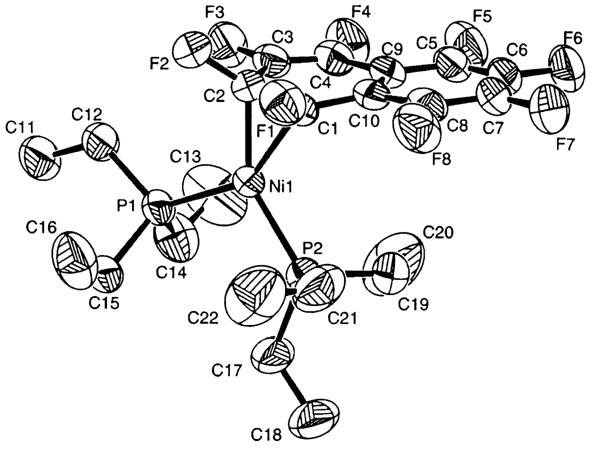

Fig. 1 An ORTEP[8] diagram of **1**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.959(4), Ni–C(2) 1.899(4), C(1)–F(1) 1.390(5), C(2)–F(2) 1.397(5), C(3)–F(3) 1.350(6), C(4)–F(4) 1.353(6), C(1)–C(2) 1.438(6), C(2)–C(3) 1.429(6), C(3)–C(4) 1.341(6), C(4)–C(9) 1.435(7), C(9)–C(10) 1.412(7), C(1)–C(10) 1.472(6); C(1)–Ni–C(2) 43.7(2), Ni–C(1)–F(1) 111.2(3), Ni–C(2)–F(2) 119.6(3), Ni–C(2)–C(3) 112.9(3), Ni–C(1)–C(10) 123.4(3), C(1)–Ni–P(1) 146.19(14), C(2)–Ni–P(2) 146.82(14).

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† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/nj/b0/b006368l/

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Table 1 Experimental and calculated structural data for **1** (bond lengths/Å and torsional angles/°)

	X-ray	L = PEt_3 [a]	L = PEt_3 [b]
Ni–C(1)	1.959(4)	2.017	1.985
Ni–C(2)	1.899(4)	1.959	1.985
C(1)–C(2)	1.438(6)	1.448	1.449
C(9)–C(10)	1.412(7)	1.437	1.438
C(1)–F(1)	1.390(5)	1.388	1.391
C(2)–F(2)	1.397(5)	1.393	1.389
C(3)–F(3)	1.350(6)	1.358	1.357
C(2)–C(3)–C(4)–C(10)	7.1	6	7
C(1)–C(9)–C(8)–C(7)	−175.3	−177	−178
C(1)–C(9)–C(10)–C(4)	−6.1	−5	−5
Δr[Ni–C(1) − Ni–C(2)]	0.060(6)	0.058	0

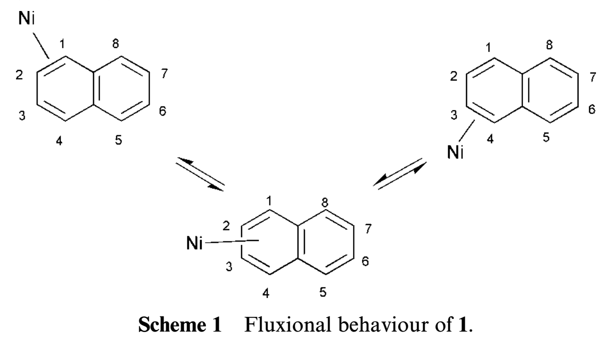
[a] Optimisation starting from X-ray coordinates. [b] Optimisation with Ni–C bond lengths constrained equal at 1.985 Å.

1.390(5) and 1.397(5) Å compared to C(3)–F(3) to C(8)–F(8) which range from 1.341(6) to 1.356(6) Å.

The pattern of crystallographic bond lengths in **1** is suggestive of an incipient transition state for concerted C–F activation at C(2).[12] We examined the origin of the unusual geometry of [Ni(η^2-1,2-$C_{10}F_8$)(PEt_3)$_2$] using density functional theory.¶ Optimised structural parameters are summarised in Table 1, together with the corresponding crystallographically determined values. The calculations correctly reproduce the principal features of the molecular structure, most noticeably the difference between Ni–C(1) and Ni–C(2) (calc.: 0.058, X-ray 0.060(6) Å). (Calculations on the PH_3 analogue of **1** gave similar results.) However, an examination of the potential energy surface in the region of the minimum reveals that small (0.05 Å) variations in the two Ni–C bond lengths have an almost negligible influence on the calculated total energy. In fact, when Ni–C(1) and Ni–C(2) are constrained to be equal, the resulting optimised structure lies less than 3 kJ mol^{-1} above the global minimum. Thus DFT calculations suggest that the Ni(η^2-1,2-$C_{10}F_8$) interaction exhibits a soft potential for distortion of the coordination geometry. Since the distortion energies are so small we cannot describe the structure of **1** as an incipient transition state with confidence.

The solution NMR spectra are consistent with the crystallographic data if the Ni(η^2-$C_{10}F_8$) unit undergoes a suprafacial [1,3] shift from the 1,2-η^2-coordinated form to the 3,4-η^2-isomer (Scheme 1). A similar low energy process, involving an exchange of coordinated and non-coordinated C=C bonds, has been observed for [Ni(η^2-$C_{10}H_8$){$^iPr_2P(CH_2)_2P^iPr_2$}] and [Ni(η^2-$C_{10}H_8$){$^iPr_2P(CH_2)_3P^iPr_2$}] as well as for the hexafluorobenzene complex [Ni(η^2-C_6F_6){$^tBu_2P(CH_2)_2P^tBu_2$}].[7,17] An η^4-coordinated arene species is proposed as an intermediate for these dynamic processes. However, *ring-whizzing via* an η^3-bound transition state as predicted in extended Hückel calculations for [Ni{η^2-$C_6(CF_3)_6$}(CO)$_2$] is also conceivable.[18]

On isolating **1**, redissolving in toluene and heating to 348 K for 24 h, the C–F activation product *trans*-[NiF(2-$C_{10}F_7$)(PEt_3)$_2$] **2** is obtained.‖ The ^{19}F NMR spectrum of **2** shows a triplet of virtual triplets at δ − 387.25 (J_{PF} 47, $|J_{FF} + J_{FF'}|$ 12 Hz) characteristic of the metal fluoride and seven further signals indicating the presence of a heptafluoronaphthyl group. The assignment of **2** as *trans*-[NiF(2-$C_{10}F_7$)(PEt_3)$_2$] is based on the values of J_{FF} measured through selective ^{19}F–^{19}F NMR decoupling experiments and the presence of *two* low field ^{19}F resonances (Fig. 2).** The ^{31}P NMR spectrum displays a doublet resonance at δ 13.3 (J_{PF} 47.6 Hz) for the two equivalent phosphorus nuclei coupled to the metal-bound fluoride.



Scheme 1 Fluxional behaviour of **1**.

The rates of loss of **1** and formation of **2** were monitored by ^{19}F NMR spectroscopy at 348 K with an integration standard contained in a capillary. They are both first order and the same within the experimental error (*ca.* 10^{-5} s^{-1}). There is appreciable variation (10–15%) in the rates from one run to the next due to decomposition reactions. However, the kinetic results are compatible with an intramolecular reaction of **1** forming the nickel(II) C–F activation product **2** (Scheme 2).

When the solution of initial reagents is heated directly without isolating complex **1**, product **2** is formed together with other fluorine containing compounds. The principal C–F activation products are **2** and another compound **3** containing a (Et_3P)$_2$Ni–F unit [δ(^{19}F) −385.94 (t, average J_{PF} 49.6 Hz)]. The structure of **3** is not yet proven but the spectra are consistent with *trans*-[NiF(1-$C_{10}F_7$)(PEt_3)$_2$], isomeric to **2**. However, we have not observed conversion of **2** into **3** or *vice versa.* There is also a loss of selectivity for **2** when a solution of pure compound **1** is heated in the presence of free PEt_3 (10 equivalents); the products include **3**. These observations provide evidence for a second mechanism of C–F activation.[2,6,20,21]

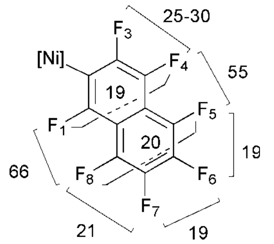
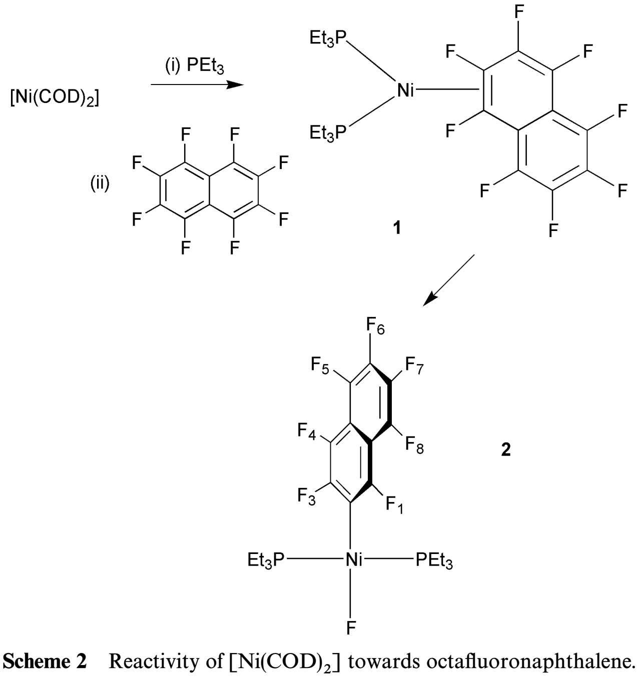


Fig. 2 Coupling constants J_{FF} Hz in **2**.



Scheme 2 Reactivity of [Ni(COD)$_2$] towards octafluoronaphthalene.

The results described lead to the conclusion that one mechanism of C–F activation of octafluoronaphthalene by [Ni(COD)(PEt$_3$)$_2$] proceeds *via* coordination at the nickel centre and subsequent intramolecular oxidative addition. Another mechanism may operate when the initial reagents are heated directly. The rate determining step is intramolecular insertion of nickel in the C–F bond in the 2 position. The unusual structure of [Ni(η^2-1,2-C$_{10}$F$_8$)(PEt$_3$)$_2$] **1** has been simulated by theory, but the energetic stabilisation induced by distortion is very slight. Intermediates similar to **1** with the fluorinated molecules coordinated to the metal centre *via* a C=C bond or a nitrogen atom are probable in the C–F activation of hexafluorobenzene, pentafluoropyridine and 2,4,6-trifluoropyrimidine at Ni(PEt$_3$)$_2$.[3–5,7,22]

Experimental

A suspension of [Ni(COD)$_2$] (82.2 mg, 0.30 mmol) in hexane (5 mL) was treated with PEt$_3$ (111 μL, 0.75 mmol). The solution was stirred for 5 min at room temperature until it changed from red-purple to yellow. After adding octafluoronaphthalene (128 mg, 0.47 mmol) the solution was stirred for 2 h and the volatiles were removed under vacuum. The orange residue was dissolved in hexane (10 mL). Orange crystals were obtained at -20 °C overnight. The NMR spectra of **1** always revealed the presence of free octafluoronaphthalene (ratio **1**: C$_{10}$F$_8$ $> 4:1$) preventing us from determining yields and analytical data. Heating a sample of **1** in toluene at 348 K for 24 h led to complex **2**. After removing the solvent under vacuum, the orange solid was recrystallised from hexane.

Acknowledgements

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Notes and references

‡ NMR spectroscopic data for **1** ([^{2}H$_8$]toluene, 300 K, referenced to [^{2}H$_7$]toluene at δ 2.10): ^{1}H (500 MHz) δ 0.8 (m, br, 3H), 1.2 (m, br, 2H); ^{31}P (202.4 MHz, referenced to external H$_3$PO$_4$ at δ 0) δ 18.0 (t, average J_{PF} 18.5 Hz); ^{19}F (470.4 MHz referenced to external CFCl$_3$ at δ 0) δ -162.72 (m, 2 F), -160.87 (m, 2 F), -160.49 (m, 2 F), -145.93 (m, 2 F).

§ Crystal data _for **1**: C$_{22}$H$_{30}$F$_8$NiP$_2$, $M = 567.11$, triclinic, space group, $P1$, $a = 11.344(10)$, $b = 12.614(6)$, $c = 9.846(13)$ Å, $\alpha = 112.43(10)$, $\beta = 96.62(10)$, $\gamma = 98.50(9)°$, $U = 1265(3)$ Å^3, $T = 293$ K, $Z = 2$, μ(MoKα) = 0.960 mm^{-1}, 4701 data, 4457 unique data, $R_{\text{int}} = 0.0158$. Structure solution by direct methods (SHELXS), refined against F^2 using 4455 data (SHELXL 93). Final $R1$, $wR2$ values on all data 0.0857, 0.1334; [$I_o > 2\sigma(I_o)$] data 0.0442, 0.1114.
CCDC reference number 440/216. See http://www.rsc.org/suppdata/nj/b0/b006368l/ for crystallographic files in .cif format.

¶ All calculations were performed using the Amsterdam Density Functional package (ADF 1999.02).[13] In all cases, the local density approximation[14] was used in conjunction with the gradient corrections of Becke[15] and Perdew.[16] Triple-ζ and double-ζ + polarisation basis sets were used to describe nickel and main group atoms, respectively.

‖ NMR spectroscopic data for **2** (300 K): ^{1}H (500 MHz, C$_6$D$_6$ referenced to C$_6$D$_5$H at δ 7.15) δ 1.03 (m, 3H), 1.16 (m, 2H); ^{31}P (202.4 MHz, C$_6$D$_6$) δ 13.3 (d, J_{PF} 47.6 Hz); ^{19}F (376.3 MHz, [^{2}H$_8$]toluene) $\delta - 387.25$ (tvt, J_{PF} 47, $|J_{FF} + J_{FF'}|$ 12, 1 F, NiF), -160.61 (dd, $J_{F_5F_6}$ 19, $J_{F_6F_7}$ 19, 1F, F$_6$), -159.07 (dd, $J_{F_7F_8}$ 21, $J_{F_6F_7}$ 19, 1F, F$_7$), -153.56 (ddd, $J_{F_4F_5}$ 55, $J_{F_3F_4}$ 25–30, $J_{F_1F_4}$ 19, 1F, F$_4$), -148.19 (ddd, $J_{F_4F_5}$ 55, $J_{F_5F_6}$ 19, $J_{F_5F_8}$ 20, 1F, F$_5$), -147.52 (ddd, $J_{F_1F_8}$ 66, $J_{F_7F_8}$ 21, $J_{F_5F_8}$ 20, 1F, F$_8$), -109.08 (d, br, $J_{F_3F_4}$ 25–30 Hz, 1F, F$_3$), -95.15 (dm, $J_{F_1F_8}$ 66, $J_{F_1F_4}$ 19 Hz, 1F, F$_1$).**

** The assignment of the ^{19}F NMR spectrum was assisted by the coupling constants J_{FF} in free octafluoronaphthalene, 1,5-C$_{10}$H$_6$F$_2$, 1,8-C$_{10}$H$_8$F$_2$ and rhenium fluoroaryl complexes.[2e,19]

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