



Short Communication

A perfluorometallacycloheptane complex of nickel bipyridine



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ABSTRACT

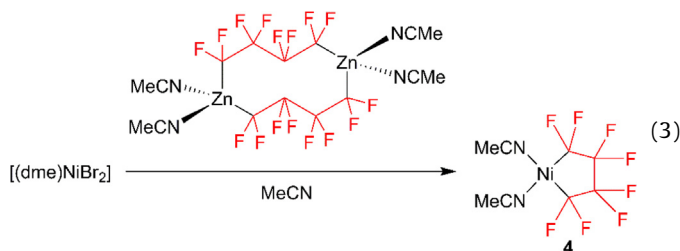
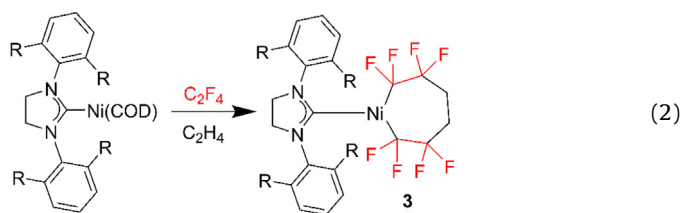
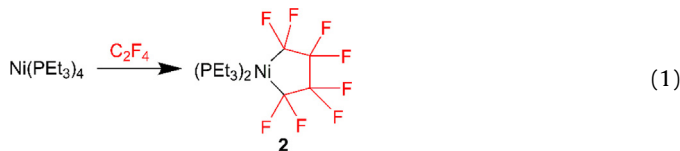
Reaction of [(bpy)NiEt₂] with 1,6-dibromododecafluorohexane in THF at room temperature led to [(bpy)Ni(η²-C₂F₄-C₆F₁₂)] (**1**) in 13% isolated yield. Compound **1** represents the first example of a perfluorinated metallacycloheptane and a rare example of an isolable metallacycloheptane in general. X-ray diffraction studies confirmed the structure of **1**. Key nickel bond distances, in Å, are: Ni-C6 1.903(9); Ni-C1 1.925(10); Ni-N1 2.004(7); Ni-N2 2.011(8).

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1. Introduction

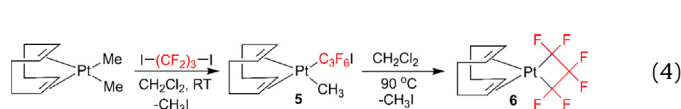
Transition metal fluoroalkyl complexes are often important intermediates in the preparation of high value fluoroalkylated chemicals [1–4]. Fluoroalkylated metallacycles are a special subset of transition metal fluoroalkyl complexes that can partake in a wide range of chemical reactions [5–12]. If one can prepare well-defined and isolable fluoroalkylated metallacycles, then one can study in detail how to further develop both catalytic and stoichiometric reactions of interest. Four different ways to prepare fluoroalkylated metallacycles are shown in Eqs. (1)–(4). One possible method, exemplified in Eq. (1), is an oxidative cyclization reaction of tetrafluoroethylene (TFE), which usually produces a perfluoroalkyl metallacyclopentane such as **2** [13]. This general method is compatible with a variety of different transition metals, as the resulting perfluoroalkyl metallacyclopentanes are typically thermally and chemically robust [14]. Oxidative coupling routes to such perfluorometallacyclopentanes have now been well documented, but the limited commercial availability of TFE may curb future method developments via such protocols. Ogoshi and co-workers recently demonstrated that if a mixture of TFE and ethylene are subjected to similar oxidative coupling conditions with low valent *N*-heterocyclic carbene complexes of nickel, partially fluorinated metallacycles like that shown in Eq. (2) can be produced. Complex **3** is fundamentally interesting, as it is a rare example of a metallacycloheptane that has been isolated and structurally characterized [15–20], and it is

the first one containing difluoromethylene groups in its metallacyclic ring.



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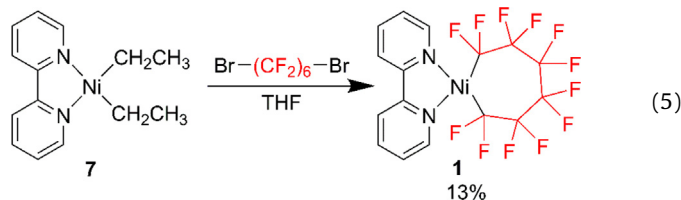
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Eqs. (3) and (4) describe two protocols that avoid the use of TFE to prepare fluoroalkylated metallacycles. It was shown that perfluoroalkylated dizinc reagents react with nickel precursors like [(dme)NiBr₂] in MeCN to afford metallacycles like **4** (Eq. (3)) [14,21]. The labile acetonitrile ligands in **4** allow for a variety of [nickel-C₄F₈] complexes to be prepared through ligand substitution reactions [7,14]. In a complementary approach, [(COD)PtMe₂] (COD=1,5-cyclooctadiene) was shown to react with 1,3-diiodohexafluoropropane to first yield the monosubstituted complex **5** (Eq. (4)), which then went on under more forcing conditions to form the perfluoroalkyl metallacyclobutane species **6**. We wondered if a similar reaction between a metal dialkyl complex with 1,6-diiodo- or 1,6-dibromododecafluorohexane could produce a *perfluorinated* metallacycloheptane, which so far has been inaccessible through the oxidative coupling of TFE. If so, this would expand the number of known and isolable perfluoroalkylated metallacycles at nickel. Currently, perfluorometallacyclobutane [9] and perfluorometallacyclopentane [13,14] structures are known with nickel, but to our knowledge there is no report of any longer-chained derivatives.

2. Results and discussion

Because the [(bpy)Ni(C₄F₈)] structure is known to be thermally stable [13], we explored the possibility of preparing a perfluorometallacycloheptane of nickel bipyridine. We found that reacting [(bpy)NiEt₂] (**7**) with 1,6-dibromododecafluorohexane in THF solution led mainly to the formation of insoluble nickel bromide salts, but also afforded the desired **1** in 13% isolated yield (Eq. (5)). Complex **1** was soluble in diethyl ether, which facilitated its isolation and purification from the nickel halide co-products. Higher yields of **1** were unable to be obtained, but enough material can be isolated to confirm its structure and gather details about how perfluorination affects bond lengths and angles in the metallacyclic ring. Crystals of **1** could be grown from THF/pentane at –30 °C, and an ORTEP diagram of **1** is shown in Fig. 1.



The crystal structure of **1** reveals a general square planar environment around the nickel(II) center, similar to what is known for the metallacyclopentane derivatives **8** and **9** (Table 1). The nickel-C6 and the nickel-C1 bond lengths for **1** of 1.903(9) and 1.925(10) Å, respectively, are somewhat longer than those observed in **8** and **9**, which suggests weaker bonds and likely instability of the perfluoroalkyl metallacyclic unit of **1** relative to **8** and **9**. More examples of both fluorinated and non-fluorinated metallacycloheptanes are needed, however, for conclusive correlations between bond lengths and bond strengths. Interesting, the nickel-C6 and the nickel-C1 bond lengths for **1** are also much longer than those reported for the partially fluorinated **3** (Table 1). The three-coordinate complex **3** also displays a much more open C1-Ni-C6 bond angle of 101.0(3)° relative to the 91.8(4)° observed for the same angle in complex **1**. Bond length and angle

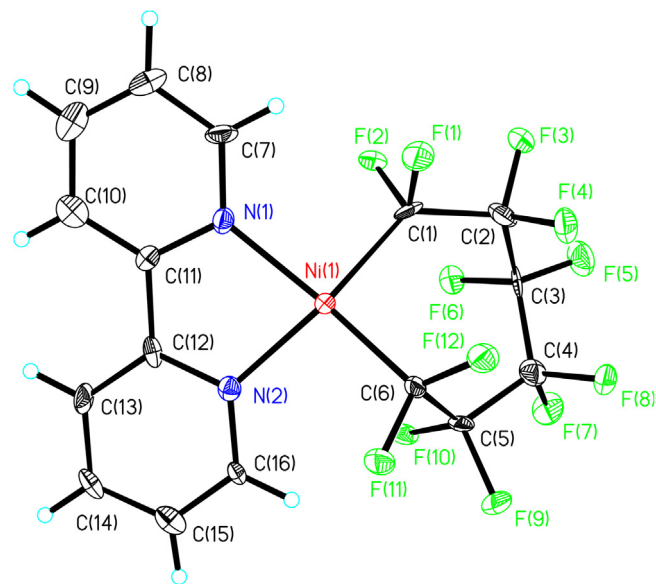


Fig. 1. ORTEP diagram of **1**. Ellipsoids shown at the 40% level. Selected bond lengths (Å): Ni1-C6 1.903(9); Ni1-C1 1.925(10); Ni1-N1 2.004(7); Ni-N2 2.011(8). Selected bond angles (°): C6-Ni1-C1 91.8(4); C6-Ni1-N1 164.6(4); C1-Ni1-N1 92.8(4); C6-Ni1-N2 97.5(4); C1-Ni1-N2 164.8(3); N1-Ni1-N2 81.3(3).

comparisons between **1** and **3** and the related compounds **8** and **9** are shown for completeness in Table 1.

Finally, it is well-known that the dihedral angles in molecules containing repeating CF₂ groups versus those with CH₂ groups vary significantly [2]. The magnitudes of the dihedral angles C1-C2-C3-C4 and C6-C5-C4-C3 in **1** are 81.2° and 64.5°, respectively. The same dihedral angles in **10** (one molecule of the asymmetric unit) are 64.7° and 41.2° [23]. For reference, the interior C-C-C-C dihedral angles of *n*-hexane versus *n*-perfluorohexane also vary significantly, with a calculated difference of 17.6° [2]. We were curious to see how the perfluorinated metallacyclic unit of **1** overlaps with a nonfluorinated metallacycloheptane that has been structurally characterized, such as **10**. Fig. 2 displays the overlap of **1** with **10**, by which one of the metal-carbon bonds were forced to be co-linear. Indeed, the differences in dihedral angles lead to a marked difference in overall ring geometry, as shown in Fig. 2, consistent with the inherent differences between alkyl and fluoroalkyl geometries.

Table 1

Selected bond distances (Å) and angles (°), where the primes are assigned to the element of the longest bond to nickel, if unsymmetrical. The crystal structure of **3** contains one disordered molecule and one ordered molecule in the asymmetric unit. Only the bond distances of the ordered molecule are listed.

	Complex 1	Complex 3	Complex 8 [22]	Complex 9 [10]
Ni-C	1.903(9)	1.832(7)	1.853(18)	1.883(3)
Ni-C'	1.925(10)	1.842(7)	1.903(15)	1.883(3)
Ni-N	2.004(7)	–	1.889(12)	1.932(3)
Ni-N'	2.011(8)	–	1.971(10)	1.932(3)
C-Ni-C'	91.8(4)	101.0(3)	89.9(7)	87.1(2)
N-Ni-N'	81.3(3)	–	84.0(5)	90.91(17)
C'-Ni-N	92.8(4)	–	90.5(6)	91.02(13)
C-Ni-N	164.6(4)	–	178.5(6)	177.97(14)
C'-Ni-N'	164.8(3)	–	174.4(6)	177.97(14)
C-Ni-N'	97.5(4)	–	95.6(6)	91.02(13)

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