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A Five-Coordinate Nickel(II) Fluoroalkyl Complex as a Precursor to a Spectroscopically Detectable Ni(III) Species

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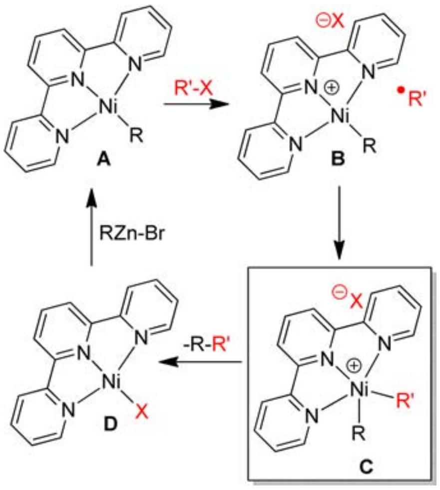
Supporting Information

ABSTRACT: Mechanistic proposals for nickel-catalyzed coupling reactions often invoke five-coordinate alkyl- or aryl-bound Ni(II) and/or high-valent nickel(III) species, but because of their reactive nature, they have been difficult to study and fingerprint. In this work, we invoked the stabilizing properties of fluoroalkyl ligands to access such nickel species bearing ligands that are commonplace in organic coupling reactions. We show that five-coordinate Ni(II) complexes containing nickel−carbon bonds can readily be prepared given the appropriate precursor, and we also present evidence for the formation of Ni(III) species upon chemical and electrochemical oxidation of the five-coordinate complexes.

In recent years, nickel has proven to be an effective metal for mediating the cross-coupling of alkyl substrates.[1,2] Researchers have shown that under the right conditions, *β*-hydride eliminations can be avoided through the use of proper ligand/metal combinations. One of the more active ligands for nickel in promoting the synthetic methodology of alkyl groups is the terpyridine (tpy) ligand.[1t,u,y,2f−h,3,4] In the case of alkyl−alkyl cross-coupling reactions under Negishi-like conditions, a mechanism of action for the terpyridylnickel catalyst has been proposed as outlined in Scheme 1.[2h]

The intermediates **A**, **B**, and **D** in Scheme 1 have been structurally characterized and in most cases analyzed spectroscopically and computationally.[2f−h,3] The most unique feature of the intermediates characterized to date is that **A** is properly described as a Ni(II) species bearing a reduced terpyridine ligand while **D** is a Ni(I) species in which the unpaired electron is localized on the metal center. Electron paramagnetic resonance (EPR) spectroscopy data were critical in assigning the electronic structures for the odd-electron complexes.[2h,3] The only species in this putative catalytic cycle that has yet to be fingerprinted is the high-valent Ni(III) species **C**. A Ni(III) intermediate has been invoked in the vast majority of proposed catalytic cycles involving nickel and alkyl radicals, yet to our knowledge no fundamental details of a Ni(III) species bearing nickel−carbon bonds and a catalytically relevant ligand for cross-couplings have ever been reported.

Scheme 1. Possible Catalytic Cycle for Alkyl−Alkyl Cross-Couplings Mediated by Terpyridylnickel Complexes



To study the chemistry of **C** in detail, its reactivity had to be tempered. Fluoroalkyl ligands are known to stabilize the higher oxidation states of metals,[5] and we previously reported on the basis of computational work that for bipyridine (bpy) complexes of nickel, the highest occupied molecular orbital of $[(bpy)Ni(CF_3)_2]$ was stabilized by over 1 eV relative to its nonfluorinated counterpart $[(bpy)Ni(CH_3)_2]$.[6] Therefore, we wondered whether replacing the alkyl groups in **C** (Scheme 1) with fluoroalkyl groups would generate a species with a lifetime long enough to allow its detection by a convenient method such as EPR spectroscopy.

The synthesis of such a species first required access to a precursor bearing two perfluoroalkyl groups bound to nickel. The most versatile one was prepared by reacting "$AgCF_3$"[7] in acetonitrile with a Ni(II) source to give $[(MeCN)_2Ni(CF_3)_2]$ (**1**) (eq 1). The reaction was not limited to trifluoromethyl groups, as $[(MeCN)_2Ni(C_2F_5)_2]$ (**2**) was also prepared using a similar procedure. Complex **1** indeed proved to be a valuable synthetic precursor. A glimpse of its reactivity is described in

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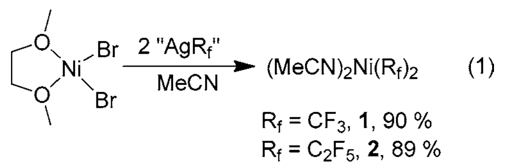
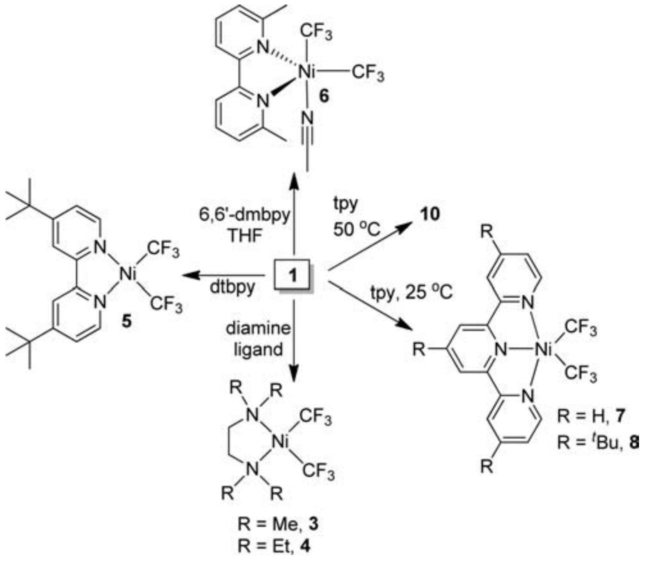


Scheme 2. It was found that the two acetonitrile ligands could be replaced with a variety of bidentate ligands under mild room-temperature conditions. For instance, the reactions of **1** with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA) led to complexes **3** and **4** yields of in 91 and 82%, respectively (Scheme 2). The reaction of **1** with 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) led to the known complex **5**[6] in 86% yield. The synthetic route shown in Scheme 2 to prepare **5** is vastly superior to the only other known route, which afforded the product in 11% yield.[6]

Scheme 2. Reactivity of the Precursor [(MeCN)$_2$Ni(CF$_3$)$_2$] (1) toward Ligand Substitution



In the reported crystal structure of **5**,[6] the nickel center adopts a geometry that is extremely distorted from square planarity as a result of the steric interactions of the trifluoromethyl groups with the 6- and 6′-hydrogens of the dtbpy ligand. The new precursor provided an opportunity to study just how great the distortions from square planarity can be. When **1** was treated with 6,6′-dimethylbipyridine (6,6′-dmbpy), a clean reaction ensued, and the remarkable complex **6** was isolated in 79% yield (Scheme 2). In the solid state, **6** displays very different Ni−N$_{bpy}$ bond distances of 2.419(10) and 2.001(10) Å, signifying that the pyridyl ring trans to the trifluoromethyl group is more strongly coordinated. The Ni−N$_{MeCN}$ bond distance is 1.940(11) Å. The ORTEP diagram of **6** is provided in Figure 1.

Finally, precursor **1** was found to react with terpyridine derivatives to afford the similarly five-coordinate species **7** and **8** in yields of 81 and 65%, respectively (Scheme 2). Moreover, the bis(perfluoroethyl) complex **2** was used to prepare the five-coordinate terpyridyl variant [(tpy′)Ni(C$_2$F$_5$)$_2$] (**9**) (tpy′ = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine) in 92% yield; the structure of **9** is shown in Figure 1. Access to **6**, **7**, **8**, and **9** is noteworthy. Four-coordinate Ni(II) alkyl complexes can readily be prepared (e.g., eq 2), but decomposition to a reduced species such as **12** typically occurs upon formation of higher-coordinate intermediates (e.g., eq 3). It is anticipated that with precursor **1**, routes to a variety of new five-coordinate Ni(II) perfluoroalkyl complexes will be readily available and will facilitate fundamental studies on this difficult-to-access geometry of organonickel species. The spin states of the five-coordinate complexes were evaluated computationally. For **6**, the $S = 0$ state was found to be lower in energy than the $S = 1$ state by 16 kcal/mol, while for **7**, the $S = 1$ state was more stable by only 0.18 kcal/mol. Experimentally, **6** was found to be diamagnetic in solution, while the μ_{eff} values determined for **8** and **9** were $2.38\mu_B$ and $2.59\mu_B$, respectively.

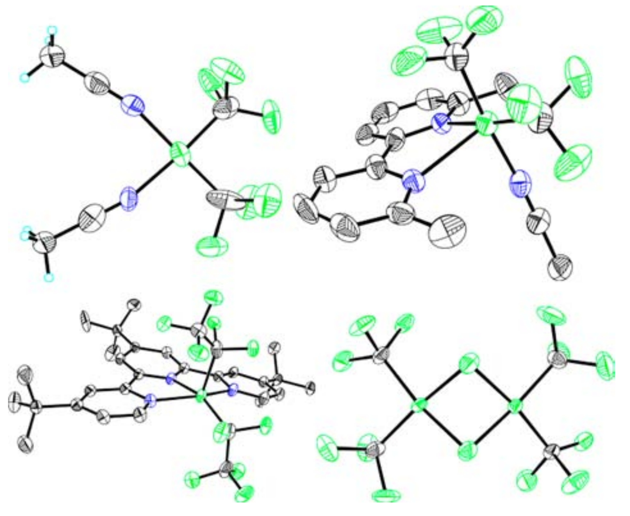
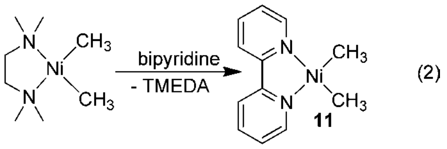
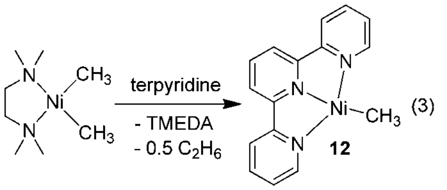


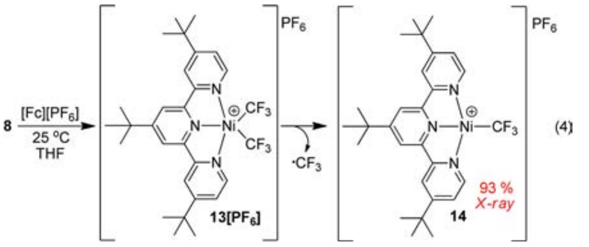
Figure 1. ORTEP diagrams of (top left) **1**, (top right) **6**, (bottom left) **9**, and (bottom right) the dianion in **10**. Bond lengths and angles are provided in the SI. The dicationic counterion in **10** has been omitted for clarity.





The ease of ligand substitution at **1** at *room temperature* was critical in the preparation of the thermally sensitive five-coordinate terpyridyl complexes. When the reaction to prepare **7** was run at 50 °C, we observed decomposition to give the complex metal salt [(tpy′)$_2$Ni][(CF$_3$)$_2$Ni(μ-F)]$_2$ (**10**); the structure of the dianion in **10** is shown in Figure 1. The bridging fluorides in **10** [which exhibit an average Ni−F bond distance of 1.9045(8) Å] were found to constrain the Ni−Ni bond distance to 2.7285(11) Å.

With the bis(trifluoromethyl)nickel terpyridyl complexes **7** and **8** in hand, we set out to explore oxidative chemistry in order to generate a fluorinated analogue of **C** in Scheme 1. Complex **8** cleanly reacted with [ferrocenium][PF$_6$] to produce initially what we speculate to be the targeted Ni(III) species **13** (eq 4). However, even upon rapid workup of the reaction mixture, **14** was obtained. Complex **14** is believed to arise from reductive homolysis of a trifluoromethyl radical from **13**. Analysis of the fluorine-containing products of eq 4 by NMR spectroscopy showed that C_2F_6 and CF_3H were produced in 11 and 47% yield. Complex **8** reacted with the oxidant AgOTf to yield C_2F_6 and CF_3H in 17 and 37% yield, respectively. Unrestricted density functional theory calculations on **13** indeed showed more asymmetry in the Ni−C bond lengths of the two trifluoromethyl ligands (Ni−C bond lengths of 1.9625 vs 1.9008 Å for the pseudoaxial vs equatorial CF_3 groups, respectively) [see the Supporting Information (SI)]. Interestingly, the reaction in eq 4 identifies an alternative to the pathway outlined in Scheme 1 for radical generation from nickel complexes bearing tridentate diimine ligands. Whether or not this pathway is viable in a catalytic cross-coupling cycle or is unique to fluoroalkyl ligands remains to be determined and is currently under further investigation.



(4)

Cyclic voltammetry (CV) and square-wave voltammetry (SQW) of **8** in tetrahydrofuran/tetrabutylammonium hexafluorophosphate (THF/nBu$_4$N[PF$_6$]) gave a very low potential of 0.3 V vs ferrocene/ferrocenium (Fc/Fc$^+$) for the irreversible and presumably nickel-centered one-electron oxidation, along with potentials of −1.72 and −1.99 V vs Fc/Fc$^+$ for the reversible reductions (tpy′-centered). Further reductions at −2.25 and −2.7 V vs Fc/Fc$^+$ were irreversible (see the SI). EPR spectra were recorded to characterize the one-electron-oxidized and -reduced forms of **8** spectroscopically. The electrolyses were performed in THF/nBu$_4$N[PF$_6$], and the spectra were recorded at 298 and 110 K (glassy frozen solution). Figure 2 shows the EPR spectra for oxidized **8** at both temperatures. At 298 K, an isotropic spectrum at g = 2.118 with no hyperfine splitting was observed. The axial spectrum recorded at 110 K was simulated with $g_\perp$ = 2.154 and $g_\parallel$ = 2.013, corresponding to an average value (g_{av}) of 2.107, which is almost identical to the signal at 298 K. Interestingly, when a solid sample of **8** was left to stand under an oxygen atmosphere, we found a very similar EPR signal (see the SI). Taken together, these data suggest that the EPR signal represents the complex radical **8**$^{\bullet+}$. The relatively high values of both g_{av} and the g anisotropy ($\Delta g = g_\perp - g_\parallel = 0.141$) and the axial character of the signal ($g_\perp > g_\parallel > 2$) point to a marked contribution of Ni d orbitals to the unpaired electron,[8] consistent with calculated data (Figure 3). The spectral features of the oxidized species are also similar to those of a related tridentate pyridylbis(imine)nickel(III) dithiolate complex reported by Mascharak.[9]

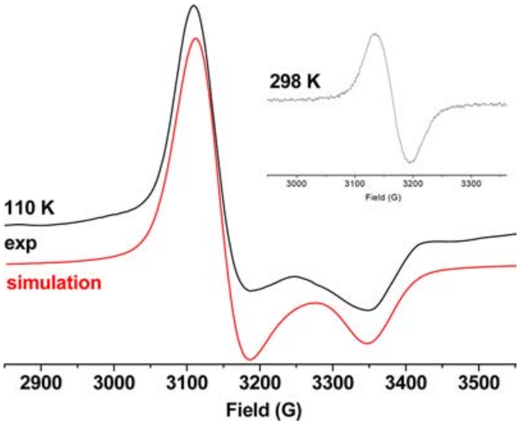


Figure 2. X-band EPR spectra obtained during anodic electrolysis of **8** in THF/nBu$_4$N[PF$_6$] at 110 K (glassy frozen solution) and (inset) 298 K. The red line represents the simulated 110 K spectrum obtained using the parameters $g_\perp$ = 2.154 and $g_\parallel$ = 2.013 with line widths of 45 and 60 G.

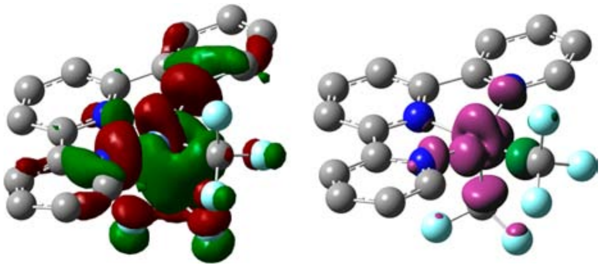
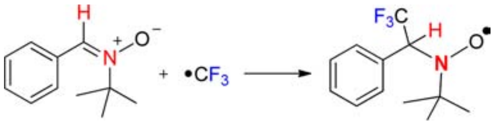


Figure 3. Calculated singly occupied molecular orbital (left, isovalue = 0.03) and spin density (right, isovalue = 0.004) for the [(tpy)Ni(CF$_3$)$_2$] cation in the gas phase. The Mulliken spin density at Ni was calculated to be 0.85.

We also studied the oxidation of **8** in THF/nBu$_4$N[PF$_6$] by EPR spectroelectrochemistry in the presence of the spin trap *N-tert*-butyl-α-phenylnitrone (PBN) (Scheme 3). When the complex was anodically electrolyzed in the presence of PBN, we detected a spectrum that could be clearly traced to the CF_3−PBN spin trap (Figure 4). The data reported in the literature[10] for the CF_3−PBN trap show splitting patterns similar to our observed values [a_N = 14.1 G, a_H = 1.17 G, and $a_F(CF_3)$ = 1.77 G].

Scheme 3. Reaction of the Spin Trap PBN with a Trifluoromethyl Radical[a]



[a]Nuclei in red and blue represent possible coupling partners for the unpaired electron.

Finally, we studied complex **8** under reductive electrolysis but could not get a reasonable signal. Upon addition of cobaltocene to a THF solution of **8**, an isotropic unresolved spectrum (no hyperfine splitting) was observed at g = 2.155 at 298 K, whereas at 110 K, a rhombic pattern (glassy frozen solution) was obtained, which was simulated using the parameters g_1 = 2.242, g_2 = 2.162, g_3 = 2.035 (g_{av} = 2.146; Δg = 0.207) and a partly resolved a_3(N) of 18.5 G for the three nitrogen atoms of tpy′ (the spectra are shown in the SI). The g and Δg values are quite high, indicating strong contributions of the Ni $d_{x^2-y^2}$ orbital to the unpaired electron in **8**$^{\bullet-}$, similar to what has been observed[3] for [(tpy)NiBr]$^\bullet$ and markedly

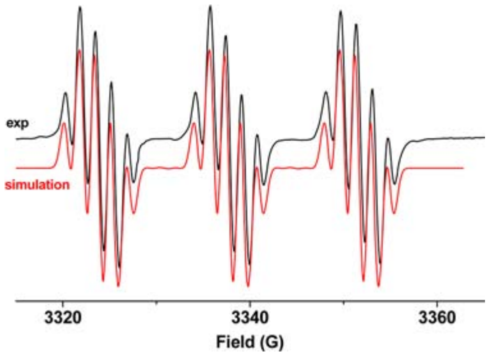


Figure 4. X-band EPR spectrum obtained during anodic electrolysis of **8** in THF/nBu$_4$N[PF$_6$] at 298 K in the presence of PBN. The black line represents the experimental spectrum, and the red line represents the expected CF$_3$−PBN spin trap, simulated with the parameters a_N = 14.1 G, a_H = 1.17 G, and $a_F(CF_3)$ = 1.77 G.

different from those for the essentially tpy-centered radical complexes $[(tpy)Ni(R)]^{\bullet}$ (R = Me,[2h] Ar[11]). On the basis of this data, we propose that the signal arises from the product of decomposition of $[(tpy')Ni(CF_3)_2]^-$, which was predicted by calculations to bear a largely terpyridine-centered radical.

In conclusion, we have reported the synthesis of a unique precursor that enabled the synthesis of rare five-coordinate Ni(II) species bearing Ni−C bonds similar to those that could be present in Ni-catalyzed cross-coupling reactions. The complexes were stable enough to isolate, which permitted fingerprinting of the elusive organonickel(III) species proposed in terpyridylnickel reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, X-ray data, optimized calculated Cartesian coordinates for all new compounds, CV and SQW plots, and EPR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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