

Magnitudes of Electron-Withdrawing Effects of the Trifluoromethyl Ligand in Organometallic Complexes of Copper and Nickel

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A variety of nickel and copper complexes bearing the trifluoromethyl ligand have been prepared in order to quantify by electrochemical methods the redox potentials relative to their chloro and methyl counterparts. The effects of coordination number and geometry, as well as the oxidation state of the metal, on the relative ease with which trifluoromethyl complexes can be oxidized have for the first time been identified. In the d¹⁰ system [(NHC)Cu(X)] (NHC = N-heterocyclic carbene, X = methyl or trifluoromethyl), a single substitution of methyl for trifluoromethyl raised the oxidation potential of the organometallic complex by approximately +0.6 V versus the ferrocene/ferrocenium (Fc/Fc⁺) couple, a testament to the extreme electron-withdrawing properties of the trifluoromethyl ligand. The ΔE_{ox} (methyl vs trifluoromethyl) for d⁸ nickel complexes were of similar magnitude; however the absolute oxidation potentials were dramatically dependent on the ligand (dippe = 1,2-bis(diisopropylphosphino)ethane vs BOXAM = bis(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)amine).

Introduction

The introduction of fluorine into an organic molecule can bring about many changes in physical properties such as increased chemical and metabolic stability, enhanced lipophilicity, conformational changes, and changes in polarity.^{1,2} Fluorination can also serve as a diagnostic tool, enabling such techniques as ¹⁹F NMR spectroscopy or positron emission tomography.¹ The trifluoromethyl group, the simplest perfluoroalkyl, is a chemical functionality with growing importance in the agricultural, pharmaceutical, and materials industries.^{3–6} This small, fluorinated analogue of a simple methyl group has also gained notoriety in the synthetic community because catalytic methods to incorporate the trifluoromethyl group into aryl bromides and chlorides have yet to be developed.^{7,8}

Copper and nickel are two promising candidate metals for catalyzing the introduction of a trifluoromethyl group into an organic halide. There is a rich history of *stoichiometric*

trifluoromethylations of aryl halides using copper,^{9–15} however the first example of a process catalytic in copper to couple the trifluoromethyl group with aryl iodides was only recently reported in 2009.¹⁶ The promise of nickel is related to its recent widespread success in the ability to catalytically cross-couple nonfluorinated alkyl substrates.^{17–23} Considering the fact that alkyl groups and perfluoroalkyl groups such

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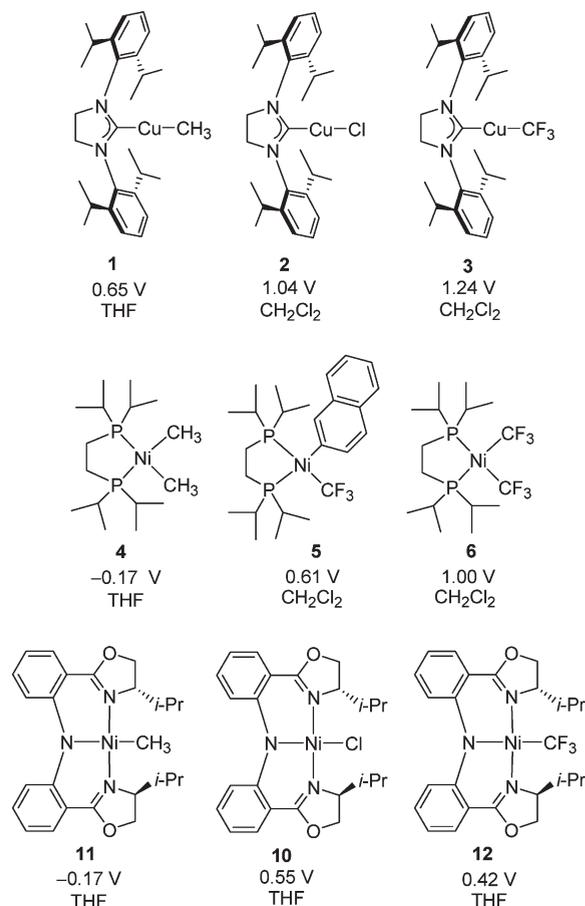
as trifluoromethyl are all sp^3 -hybridized, it is not unreasonable to predict that nickel may also be a suitable metal to catalyze the coupling of the trifluoromethyl group. Stoichiometric studies with well-defined [(dippe)Ni(Aryl)(CF₃)] (dippe = 1,2-bis(diisopropylphosphino)ethane) complexes suggest, however, that the reactivity of nickel-alkyl and nickel-perfluoroalkyl complexes are drastically different²⁴ and that more fundamental studies are needed to rationally control perfluoroalkyl manipulations at a metal center.

In the context of improving perfluoroalkyl cross-couplings, one must consider the fact that first-row transition metals often react with organic halides via radical-based mechanisms involving one-electron changes in metal oxidation states.^{18,25–31} It is therefore important to understand the degree to which the trifluoromethyl ligand may affect such one-electron redox shuttles so that strategies may be developed to better direct reactivity of potential perfluoroalkyl organometallic intermediates of a catalytic cycle, especially considering the fact that trifluoromethyl ligands often stabilize higher oxidation states of metals.^{32,33} Electrochemical studies of well-defined metal-perfluoroalkyl complexes may aid in this regard; however we were surprised to discover that there is not a single report on the electrochemical properties of nickel- or copper-trifluoromethyl complexes. To begin to fill this gap in knowledge, we report herein a comparison of the redox properties of nickel and copper organometallic and perfluoro-organometallic complexes.

Results and Discussion

The redox properties of NHC-copper complexes (NHC = N-heterocyclic carbenes) were first established, as [(NHC)-Cu(CF₃)] complexes have recently been reported to be active stoichiometric trifluoromethylation agents.^{9,10} The one-electron oxidations were all irreversible, which limits largely the meaning of the measured potentials. However, by applying reasonably similar conditions (concentration, solvent, temperature, electrode) to all complexes we are confident that at least a qualitative comparison is feasible. The results, shown in Chart 1, demonstrate that the potential required to oxidize these copper complexes follows the order [(SIPr)Cu(CH₃)] (**1**) < [(SIPr)CuCl] (**2**) < [(SIPr)Cu(CF₃)] (**3**) (SIPr = *N,N'*-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) with relative magnitudes of 0.65, 1.04, and 1.24 V, respectively.³⁴ Thus, it is extremely difficult to oxidize the [(SIPr)Cu(CF₃)]

Chart 1. First Oxidation Potential for Selected Metal Complexes^a



^a All values measured as the peak potential relative to Fc/Fc⁺.

complex **3**. In fact, there are few practical chemical oxidants capable of oxidizing **3** by an outer-sphere electron transfer mechanism.³⁵ It is important to clarify here that the intrinsic difficulty in oxidizing [(NHC)Cu(CF₃)] at the anode does not mean that these copper complexes are chemically unreactive; in fact solutions of [(NHC)Cu(CF₃)] complexes are extremely air-sensitive.⁹ The data may imply, however, that the mechanism for aryl halide activation by [(NHC)Cu(CF₃)] is likely similar to that recently suggested for [LCu(NR₂)] (L = chelating ligands such as 1,10-phenanthroline), involving either an inner-sphere electron transfer event or η^2 -arene intermediates.³⁶

The oxidation potentials of the two-coordinate copper complexes are perhaps the best measure of the inductive nature of the trifluoromethyl ligand since electron-withdrawing effects can be reasonably separated out from changes in orbital energies caused by molecular deformations that might be seen in higher-coordinate, more sterically encumbered species. Steric effects can be considerable for metal-trifluoromethyl complexes because the CF₃ ligand has a calculated cone angle of 133°,³⁷ much larger than a methyl (90°) and near the reported value of a *tert*-butyl ligand (126°).³⁸ Indeed,

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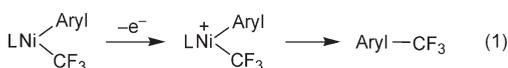
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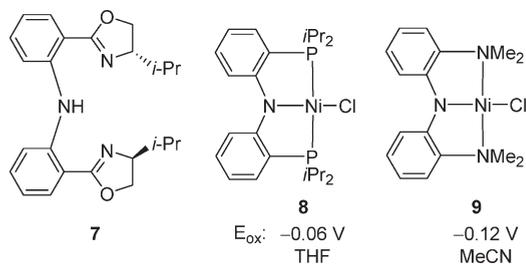
(34) Complexes **2** and **3** were insoluble in THF; therefore CH₂Cl₂ was used as solvent. Complex **1** decomposed in CH₂Cl₂, so a different solvent (THF) had to be used.

crystal structures of [(dippe)Ni(CH₃)₂] (**4**, dippe = 1,2-bis-(diisopropylphosphino)ethane) and [(dippe)Ni(CF₃)₂] (**7**) do show substantial differences in bond angles for only minor changes in chemical composition.²⁴ The copper complexes reported herein maintain a linear two-coordinate form, even for the chloride complex **2**.³⁹

The nickel complexes **4–6** (Chart 1) all display one irreversible oxidation (see Supporting Information) with the trend in redox potentials mirroring that seen with copper.⁴⁰ Thus, [(dippe)Ni(CH₃)₂] is much easier to oxidize than [(dippe)Ni(CF₃)₂] (−0.17 vs 1.00 V, respectively).⁴¹ The [(dippe)Ni(aryl)(CF₃)] derivative **5**, a reasonable model for an intermediate in an aryl–CF₃ cross-coupling reaction,²⁴ displays a large positive oxidation potential (0.61 V) in between the values for **4** and **6**. These values for the nickel derivatives offer insight into our previous efforts to oxidatively induce reductive eliminations of trifluoroarenes from Ni^{II} with chemical oxidants (eq 1).²⁴ The electrochemical data in Chart 1 suggest that this approach is feasible, although very powerful oxidants are required to oxidize Ni(Ar)CF₃ complexes such as **5**.³⁵



The electrochemical data in Chart 1 for compounds **1–6** provide a glimpse into the extreme electron-withdrawing properties of the trifluoromethyl ligand, which raises the oxidation potentials relative to the methyl complexes by at least 500 mV. This large ΔE_{ox} presents daunting challenges for doing any further oxidative chemistry at trifluoromethyl complexes of Cu^I or Ni^{II}. In order to circumvent the large barriers associated with oxidizing a late transition-metal complex bearing a trifluoromethyl ligand, we explored the use of tridentate nitrogen-donor ligands to bring the oxidation potential to a more reasonable window. A bis(4-isopropyl-4,5-dihydrooxazol-2-yl)phenylamine (BOXAM) ligand (**7**)⁴² was chosen as our model tridentate ligand, since oxidations of nickel complexes bearing similar amido-pincer ligands such as **8**⁴³ and **9**⁴⁴ have E_{ox} values much lower than those seen for **4–6**.



The preparation of a series of BOXAM nickel complexes proceeded as described in Scheme 1. Upon addition of free

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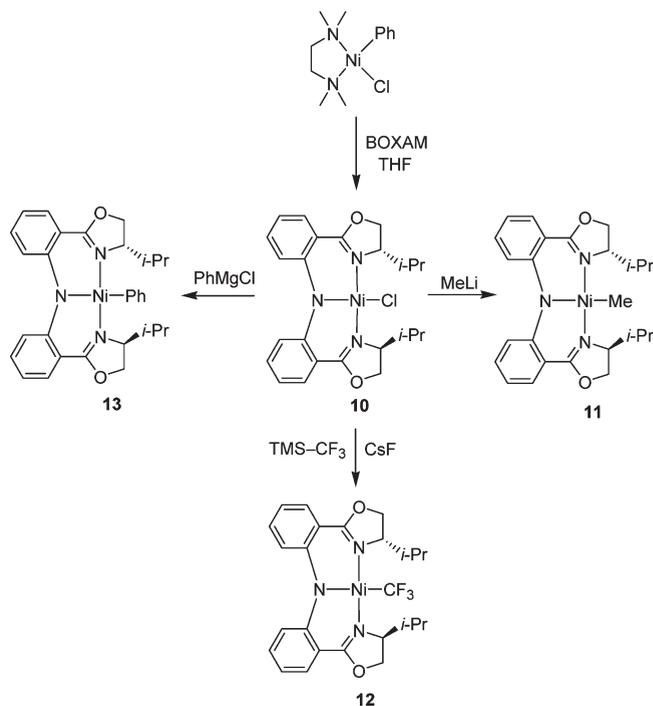
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Scheme 1. Preparation of New BOXAM Nickel Complexes



BOXAM ligand to [(TMEDA)Ni(Ph)Cl],⁴⁵ loss of benzene occurred with formation of the convenient precursor [(BOXAM)NiCl] (**10**) in 96% yield. Complex **10** can then be transmetalated with methyllithium to afford [(BOXAM)Ni(CH₃)] (**11**), a combination of TMS–CF₃ and CsF to afford [(BOXAM)Ni(CF₃)] (**12**), and PhMgCl to afford [(BOXAM)Ni(Ph)] (**13**) (Scheme 1). Compounds **11–13** have all been structurally characterized, and ORTEP plots of their molecular structure are shown in Figures 1–3. Each of the three organometallic compounds has a structure that is C₂ symmetric, with the nickel centers all adopting square-planar arrangements. While the nickel–carbon bond lengths for [(BOXAM)Ni(CH₃)] and [(BOXAM)Ni(CF₃)] are comparable (2.077(4) and 2.040(4) Å, respectively), the [(BOXAM)Ni(Ph)] was relatively shorter at 1.910(2) Å.

The redox behavior of the BOXAM nickel complexes **10–12** strongly depends on the co-ligand Cl, CF₃, or CH₃, and they display the same trends in oxidation potentials observed for the phosphine complexes **4–6** in the sense that the [(BOXAM)Ni(CF₃)] complex was much more difficult to oxidize than the [(BOXAM)Ni(CH₃)] complex (−0.17 vs +0.42 V). The cyclic voltammograms of **10–12** are shown in Figure 4 for comparison. First of all we can note that while the one-electron oxidation of the CH₃ complex **11** is completely irreversible (also at lower temperature and higher scan rates), the CF₃ and Cl derivatives exhibit a certain degree of reversibility. When measuring **11**, the first irreversible oxidation wave is followed by a reversible wave at higher potential. This wave was also obtained when a solution of the methyl complex was treated with oxygen prior to measurement. Following the idea that the CH₃ co-ligand might cleave after one-electron oxidation, we prepared the complex [(BOXAM)Ni(THF)]⁺ (**14**) by abstraction of Cl[−] from the precursor complex [(BOXAM)NiCl] (**10**) using

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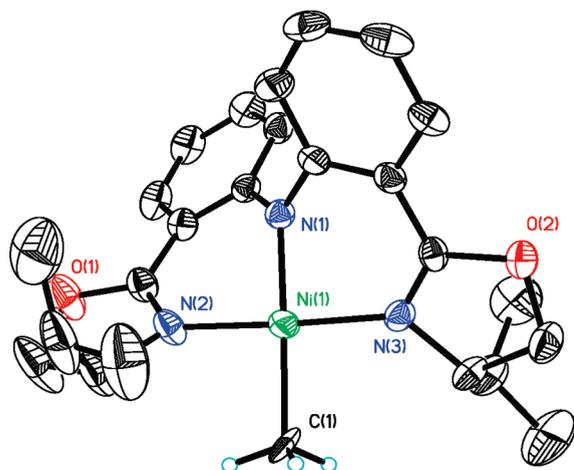


Figure 1. ORTEP diagram of **11**. All hydrogen atoms except those on methyl have been omitted for clarity. Selected bond lengths (Å): Ni(1)–N(2) 1.894(3), Ni(1)–N(3) 1.898(3), Ni(1)–N(1) 1.933(3), Ni(1)–C(1) 2.077(4). Selected bond angles (deg): N(2)–Ni(1)–N(3) 175.63(15), N(2)–Ni(1)–N(1) 88.19(14), N(3)–Ni(1)–N(1) 89.47(13), N(2)–Ni(1)–C(1) 90.07(15), N(3)–Ni(1)–C(1) 92.32(14), N(1)–Ni(1)–C(1) 178.06(14).

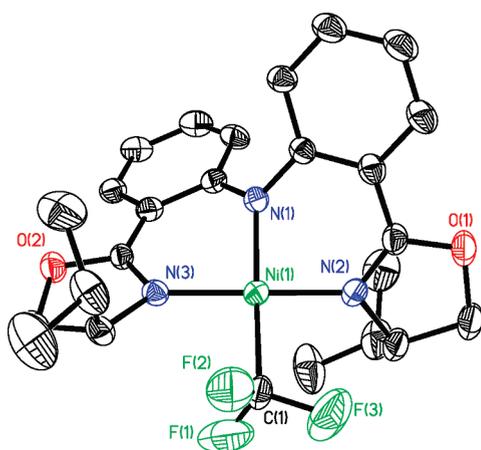


Figure 2. ORTEP diagram of **12**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–N(2) 1.909(3), Ni(1)–N(1) 1.921(3), Ni(1)–N(3) 1.923(3), Ni(1)–C(1) 2.040(4). Selected bond angles (deg): N(2)–Ni(1)–N(1) 87.03(12), N(2)–Ni(1)–N(3) 171.46(13), N(1)–Ni(1)–N(3) 89.85(12), N(2)–Ni(1)–C(1) 92.37(14), N(1)–Ni(1)–C(1) 172.99(15), N(3)–Ni(1)–C(1) 91.68(14).

thallium acetate (see Experimental Section) and measured its cyclic voltammogram and UV–vis absorption spectrum (for details see Supporting Information). Thus, we provide evidence that the [(BOXAM)Ni(CH₃)] complex undergoes rapid splitting of the methyl co-ligand upon oxidation (at the anode or by oxygen) and forms **14**, supporting our assumption that one-electron oxidation induces labilization of the Ni–CH₃ bond (eq 1). This reactivity is in line with what is observed for the methyl coenzyme M reductase (MCR), where CH₃–Ni^{III}F₄₃₀M is considered to be the

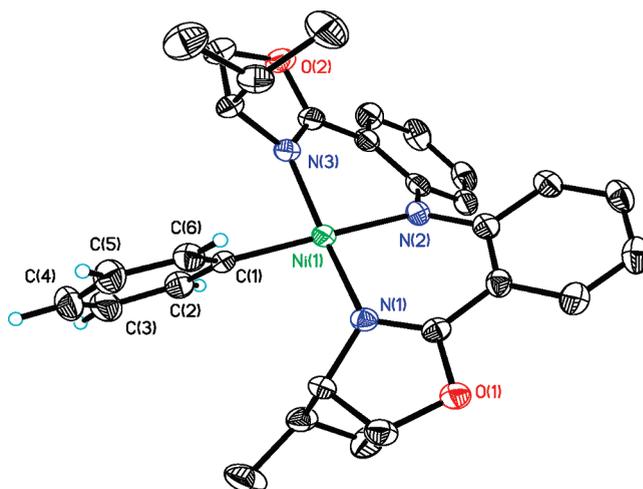


Figure 3. ORTEP diagram of **13**. All hydrogen atoms except those on phenyl have been omitted for clarity. Selected bond lengths (Å): Ni(1)–N(3) 1.891(2), Ni(1)–N(1) 1.8961(19), Ni(1)–C(1) 1.910(2), Ni(1)–N(2) 1.9385(19). Selected bond angles (deg): N(3)–Ni(1)–N(1), 172.46(9), N(3)–Ni(1)–C(1) 88.60(9), N(1)–Ni(1)–C(1) 91.62(9), N(3)–Ni(1)–N(2) 89.80(8), N(1)–Ni(1)–N(2) 90.97(8), C(1)–Ni(1)–N(2) 172.15(10).

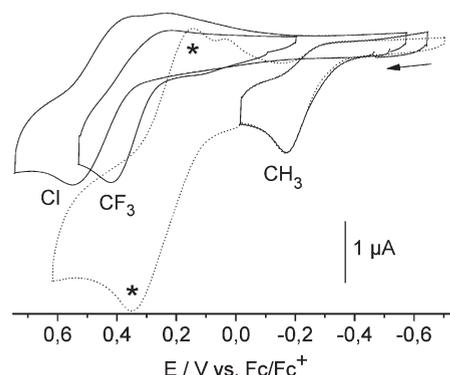


Figure 4. Cyclic voltammograms of (BOXAM)Ni complexes **10–12** (each about 10 mM) in THF/[ⁿBu₄N][PF₆] (100 mM), at 100 mV/s scan rate and 298 K. Potentials referenced vs Fc/Fc⁺. The reversible wave marked * is assigned to the solvent complex [(BOXAM)Ni(THF)]⁺²⁺ (see text).

active methylating species.⁴⁶ Interestingly, the trifluoromethyl derivative **12** also appears to lose CF₃ from the complex when treated with O₂ (bubbling at atmospheric pressure). However the rate of conversion to **14** is far slower from **12**, and total conversion is only achieved within 24 h, while the complete disappearance of **11** occurs within one minute. Therefore we assume that within the time scale of the CV experiment the CF₃ co-ligand remains on the nickel atom. Furthermore, the similarity of the oxidation potentials for the two nickel complexes **10** and **12**, in contrast to the marked difference for **5** and **6**, suggests that the redox chemistry is occurring on the common BOXAM ligand, while the redox chemistry of the methyl derivative **11** resembles far more that of the phosphine complex **4** and might be more centered on the nickel atom. Investigations providing more evidence for such assignments using EPR spectroscopy and UV–vis spectroelectrochemistry are under way.

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Experimental Section

General Considerations. All manipulations were performed using standard Schlenk and high-vacuum techniques⁴⁷ or in a nitrogen-filled drybox, unless otherwise noted. Solvents were distilled from Na/benzophenone or CaH₂. All reagents were used as received from commercial vendors unless otherwise noted. Celite was dried at 200 °C under vacuum for two days prior to use. ¹H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent peaks. ¹⁹F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz and were referenced to CFC1₃ set to zero. A Rigaku SCXMini diffractometer was used for X-ray structure determinations. Cyclic voltammetry was carried out at 100 mV/s scan rate in 0.1 M [ⁿBu₄N][PF₆] solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and an Autolab PG STAT 30 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal standard. UV-vis absorption spectra were recorded in 1 cm quartz cells using a Varian Cary50 Scan photospectrometer. Complexes **1**,⁴⁸ **2**,³⁹ and **4–6**²⁴ were prepared according to literature procedures.

Preparation of [(SIPr)Cu(CF₃)₃] (3). [(SIPr)CuCl] (979 mg, 2 mmol) and ^tBuOK (224 mg, 2 mmol) were dissolved in 7 mL of DMF and stirred 2 h at room temperature. The solution was then filtered through a pad of Celite and washed two times with 1 mL of DMF. CF₃Si(CH₃)₃ (588 μL, 4 mmol) was then added to the filtrate, and the resulting solution was stirred 16 h at room temperature. The product precipitated as a white solid and was filtered, washed with 1 mL of DMF then 3 mL of pentane, and dried under vacuum. Yield: 94%. ¹H NMR (CD₂Cl₂): δ 1.33 (d, *J* = 6.7 Hz, 12H), 1.35 (d, *J* = 6.7 Hz, 12H), 3.08 (hept., *J* = 6.7 Hz, 4H), 4.03 (s, 4H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.45 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 204.5, 147.4, 134.7, 130.3, 125.0, 124.9, 29.4, 25.6, 24.1. (Note: the resonance for the carbon atom of the trifluoromethyl group was not observed.) ¹⁹F{¹H} NMR (CD₂Cl₂): δ -32.2 (s, 3F, CF₃).

Preparation of [(BOXAM)NiCl] (10). A solution of **8** (1.089 g, 2.78 mmol, 1 equiv) in THF (10 mL) was added under a nitrogen atmosphere to a suspension of [(tmeda)Ni(Ph)Cl] (800 mg, 2.78 mmol) in THF (40 mL) at room temperature and stirred overnight, during which time the orange solution turned dark green. The reaction mixture was filtered, concentrated in volume, and layered with pentane. Cooling to -30 °C afforded dark green crystals of **10** (1.29 g, 2.67 mmol, 96%). ¹H NMR (300 MHz, THF-*d*₈): δ 0.94 (d, *J* = 6.6 Hz, 6H) 0.95 (d, *J* = 6.6 Hz, 6H), 2.63–2.68 (m, 2H), 4.21–4.34 (m, 6H), 6.69 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (75 MHz, THF-*d*₈): δ 15.8, 18.5, 32.4, 67.6, 69.8, 117.5, 118.5, 125.1, 129.6, 132.9, 154.1, 161.1. HRMS (FAB+): calcd (*m/z*) for C₂₄H₂₈ClN₃NiO₂ 483.1224; obsd 483.1166.

Preparation of [(BOXAM)Ni(CH₃)₃] (11). A solution of **10** (388 mg, 0.8 mmol) in THF (30 mL) was cooled to -30 °C, and a solution of MeLi in hexane (1.6 M, 0.6 mL 0.96 mmol, 1.2 equiv) was added dropwise. The reaction mixture immediately turned red, and it was stirred 12 h at rt. 1,4-Dioxane (86 μL, 1 mmol) was added, the mixture was stirred for another hour, and then the volatiles were evaporated using a high-vacuum line. The residue was resolved in pentane, the solution was cooled 1 h at -30 °C and passed through a syringe filter (0.45 μm, cellulose acetate), and the filter was rinsed with pentane. The blood red solution was concentrated to half of its volume, cooled 1 h at

-30 °C, and passed again through a syringe filter (0.20 μm). Slow evaporation of pentane at atmospheric pressure yielded dark red crystals of **11** (229 mg, 0.493 mmol, 62%). ¹H NMR (300 MHz, THF-*d*₈): δ -0.99 (s, 3H), 0.84 (d, *J* = 6.9 Hz, 6H) 0.88 (d, *J* = 6.9 Hz, 6H), 2.35–2.42 (m, 2H), 3.89–3.93 (m, 2H), 4.21–4.23 (m, 4H), 6.48–6–53 (m, 2H), 6.95–6.98 (m, 4H), 7.48 (dd, *J* = 7.8 Hz, 1.8 Hz, 2H). ¹³C NMR (75 MHz, THF-*d*₈): δ -14.9, 15.5, 18.6, 33.1, 68.3, 116.2, 116.4, 122.8, 130.0, 132.5, 155.6, 161.3. HRMS (FAB+): calcd (*m/z*) for C₂₅H₃₁N₃NiO₂ 463.1770; obsd 463.1889.

Preparation of [(BOXAM)Ni(CF₃)₃] (12). TMSCF₃ (237 μL, 1.5 mmol, 6 equiv) was added dropwise to a solution of **10** (121 mg, 0.25 mmol) and CsF (272 mg, 1.5 mmol, 6 equiv) in dry DMF (10 mL) and stirred at rt under nitrogen. After 15 h the volatiles were evaporated using a high-vacuum line. The residue was resolved in pentane, and the solution was passed through a syringe filter (0.45 μm, cellulose acetate). The blood red solution was concentrated and crystallized from pentane to yield dark red crystals of **12** (106 mg, 0.205 mmol, 82%). ¹H NMR (300 MHz, THF-*d*₈): δ 0.88 (d, *J* = 6.9 Hz, 6H) 0.94 (d, *J* = 6.9 Hz, 6H), 2.21–2.29 (m, 2H), 3.93–3.95 (m, 2H), 4.32–4.36 (m, 4H), 6.66 (t, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 7.08 (td, *J* = 8.4 Hz, 1.5 Hz, 2H), 7.57 (td, *J* = 7.8 Hz, 1.5 Hz, 2H). ¹³C NMR (75 MHz, THF-*d*₈): δ 16.2, 17.9, 33.5, 70.5, 70.5 (q, ⁴*J*(C,F) = 3.2 Hz), 116.9, 117.7, 123.0, 126.7 (q, ¹*J*(C,F) = 371.2 Hz), 130.2, 133.5, 153.7, 163.0. ¹⁹F NMR (188 MHz, THF-*d*₈): δ -29.9 (s). HRMS (FAB+) calcd (*m/z*) for C₂₅H₂₈F₃N₃NiO₂ 517.1487; obsd 517.2883.

Preparation of [(BOXAM)Ni(Ph)] (13). A solution of **10** (100 mg, 0.206 mmol) in THF (10 mL) was cooled to -30 °C, and a solution of PhMgCl in hexane (2 M, 0.125 mL 0.25 mmol, 1.2 equiv) was added dropwise. The reaction mixture immediately turned red, and it was stirred 12 h at rt. 1,4-Dioxane (43 μL, 0.5 mmol) was added, the mixture was stirred for another hour, and then the volatiles were evaporated using a high-vacuum line. The residue was resolved in pentane (30 mL), the solution was passed through a syringe filter (0.45 μm, cellulose acetate), and the filter was rinsed with pentane. The blood red solution was concentrated to half of its volume, cooled 1 h at -30 °C, and passed again through a syringe filter (0.20 μm). Slow evaporation of pentane at atmospheric pressure yielded dark red crystals of **13** (87 mg, 0.165 mmol, 80%). ¹H NMR (300 MHz, THF-*d*₈): δ 0.40 (d, *J* = 6.9 Hz, 6H) 0.55 (d, *J* = 6.9 Hz, 6H), 2.23–2.28 (m, 2H), 2.66–2.70 (m, 2H), 3.89–4.02 (m, 4H), 6.46–6.50 (m, 2H), 6.58–6.62 (m, 1H), 6.70 (m, 2H), 6.91–6.95 (m, 4H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (75 MHz, THF-*d*₈): δ 14.8, 18.6, 32.4, 70.5, 115.5, 117.0, 122.8, 123.21, 126.0, 130.1, 132.7, 138.4, 155.5, 159.4, 162.0. HRMS (FAB+): calcd (*m/z*) for C₃₀H₃₃N₃NiO₂ 525.1926; obsd 525.2120.

Preparation of [(BOXAM)Ni(THF)](OAc) (14). To a solution of **10** (100 mg, 0.206 mmol) in THF (10 mL) was added thallium acetate (65 mg, 0.247 mmol, 1.2 equiv). The reaction mixture immediately turned blue-green, and it was stirred 1 h at rt. The white precipitate of thallium chloride was removed by filtration. Evaporation of THF at low pressure yielded blue-green microcrystalline materials of **14** (87 mg, 0.165 mmol, 80%). ¹H NMR (300 MHz, CD₂Cl₂-*d*₂): δ 0.88 (m, 12H), 1.27 (s, 3H), 1.82 (t, *J* = 6.6 Hz, 4H), 2.68 (m, 2H), 3.42 (m, 2H), 3.68 (t, *J* = 6.8 Hz, 4H), 4.24 (m, 2H), 4.38 (t, *J* = 9.3 Hz, 2H), 6.71 (t, *J* = 7.1 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (75 MHz, CD₂Cl₂-*d*₂): δ 15.2, 18.9, 22.3, 26.1, 31.9, 67.0, 68.3, 69.5, 116.4, 118.3, 125.3, 129.3, 132.4, 153.8, 162.1, 176.2. Anal. Calcd (found) for C₃₀H₃₉N₃NiO₅ (579.22): C, 62.09 (61.89, 0.32%); H, 6.77 (6.74, 0.42%); N, 7.24 (7.20, 0.51%).

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Supporting Information Available: NMR spectra of all new compounds, cyclic voltammograms of **1–7** and **10–13**, crystallographic data for **11–13**, and UV–vis absorption spectra of complexes **10**, **11**, **12**, and **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.