NEW NICKEL COMPLEXES FOR TRIFLUOROMETHYLATION STUDIES

A THESIS SUBMITTED TO THE GRADUATE DIVISION
OF THE UNIVERSITY OF HAWAIʻI AT MĀNOA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

DECEMBER 2012

BY

Hiromi Ichioka

Thesis Committee:

David Vicic, Chairperson

Marcus A. Tius

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Acknowledgements

I would like to thank the members of my thesis committee for spending their time to modify my thesis. I would like to appreciate Professor Vicic for overall advice. I would like to thank help and support from many individuals in the Chemistry Department, from faculty and staff. I would like to thank University of Hawaii for financial support in the form of teaching assistant.

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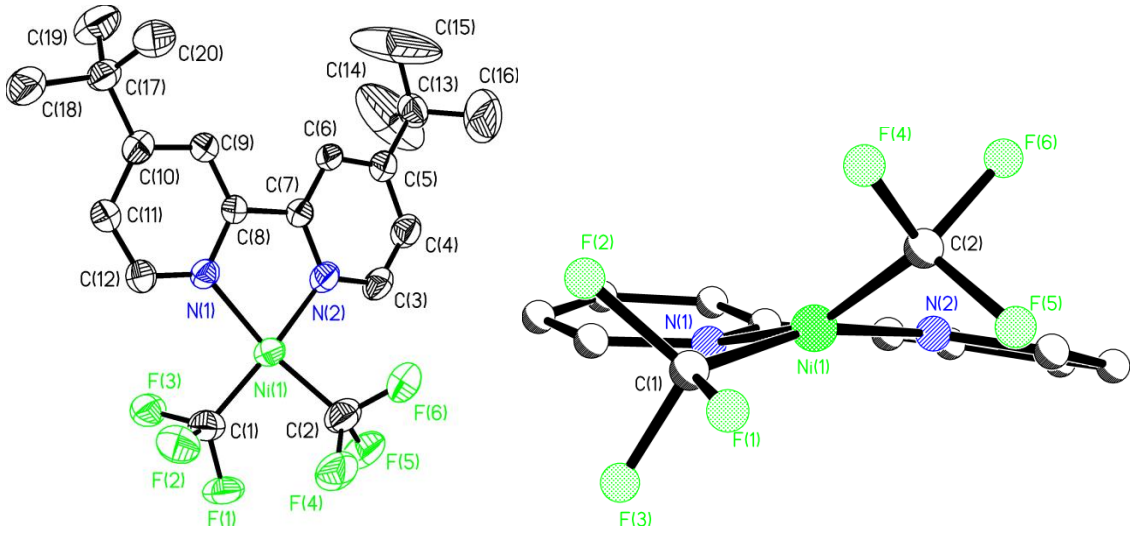
Abstract

We decided to prepare bis-perfluoroalkyl nickel complexes bearing a bipyridine ligand for investigation of the fundamental nickel perfluoroalkyl chemistry and reductive elimination of perfluoroethylene. Moreover, we envisioned a new precursor for investigation of Ar-CF_3 reductive elimination. We have successfully demonstrated the syntheses of [(dtbpy)Ni$(CF_3)_2$] and [(dtbpy)Ni$(CF_2CF_3)_2$] in moderate yields. The key intermediate nickel complex, [(tmeda)Ni(CF_3)Br] allowed for the preparation of new complexes in good yields.



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List of Abbreviations

Ac	acetyl
acac	acetylacetone
Alk	alkyl
Ar	aryl
Brettphos	2-(dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl
Bz	benzyl
bpy	2,2'-dipyridyl
^{o}C	degrees Celsius
^{13}C	carbon-13 isotope
cm^{-1}	wave number
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
d	doublet
d	day(s)
dba	dibenzylideneacetone
DCM	dichloromethane
dippe	1,2-bis(diisopropylphosphino)ethane
DMF	*N*,*N* –dimethyl formamide
DME	dimethoxymethane
DMI	1,3-dimethyl-2-imidazolidinone

dppbz	1,4-bis(diphenylphosphino)butane
dtbpy	4,4'-di-*tert*-butyl bipyridine
eq	equation
eq.	equivalent(s)
^{19}F	fluorine-19 isotope
g	gram(s)
^{1}H	proton isotope
Hz	hertz(s)
J	coupling constant (in Hz)
λ	lambda
m	mili-
M	molarity
Me	methyl
MHz	megahertz
min	minute(s)
NFTP	*N*-fluoro-2,4,6-trimethylpyridinium triflate
NHC	*N*-heterocyclic
NMR	nuclear magnetic resonance
O	Ortho
Ph	phenyl
Phen	phenanthroline
rt	room temperature
s	singlet

TBAF	tetra-*n*-butylammonium fluoride
t-Bu	tertiary butyl
TCNE	tetracyanoethylene
TES	tetraethylsilane
Tf	triflyl
THF	tetrahydrofuran
TLC	thin layer chromatography
tmeda	tetramethylethylenediamine
TMS	tetramethylsilane
tol	tolyl
Ts	tosyl
UV	ultraviolet
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

New Nickel Complexes for Trifluoromethylation Studies

1.1. Introduction

1.1.1. Fluorinated Organic Compounds

The number of naturally occurring fluorinated organic compounds is very few whereas inorganic fluorides are plentiful on earth. Therefore all fluorinated compounds are exclusively synthesized by organic or organometallic methodology. Today, fluorinated organic compounds have an essential role in pharmaceutical, veterinary, agrochemical, and material sciences. For example, fluorine and trifluoromethyl compounds can be found in commercially available pharmaceuticals such as Prozac, Celebrex, and Arava as shown in Figure 1.1.[1-2] The introduction of a fluorine atom or trifluoromethyl group into an organic compound can alter the physical properties of organic molecules, and can also affect their conformational behavior, biological activity, and metabolic stability.[3-5] Fluorine is the most electronegative element, and its small size makes it an interesting surrogate for a hydrogen atom.[6] The trifluoromethyl or fluorine functional groups in biologically active compounds can modify the biological activities through improved lipophilicity and superior metabolic stability. Thus, the introduction of fluorine and trifluoromethyl groups in candidates for clinical drug development has become an important tool in drug development. Metal-mediated trifluoromethylations have been slowly developing, as discussed in section 1.4-6, whereas today the tremendous expansion of fluorinated compounds introduced by a wide scope of applications has been established by the field of organic chemistry.[8] Only a few trifluoromethyl nickel complexes have been examined in trifluoromethylations (section 1.6). So nickel is one of the promising candidates to achieve nickel-catalyzed trifluoromethylations (section 1.7)

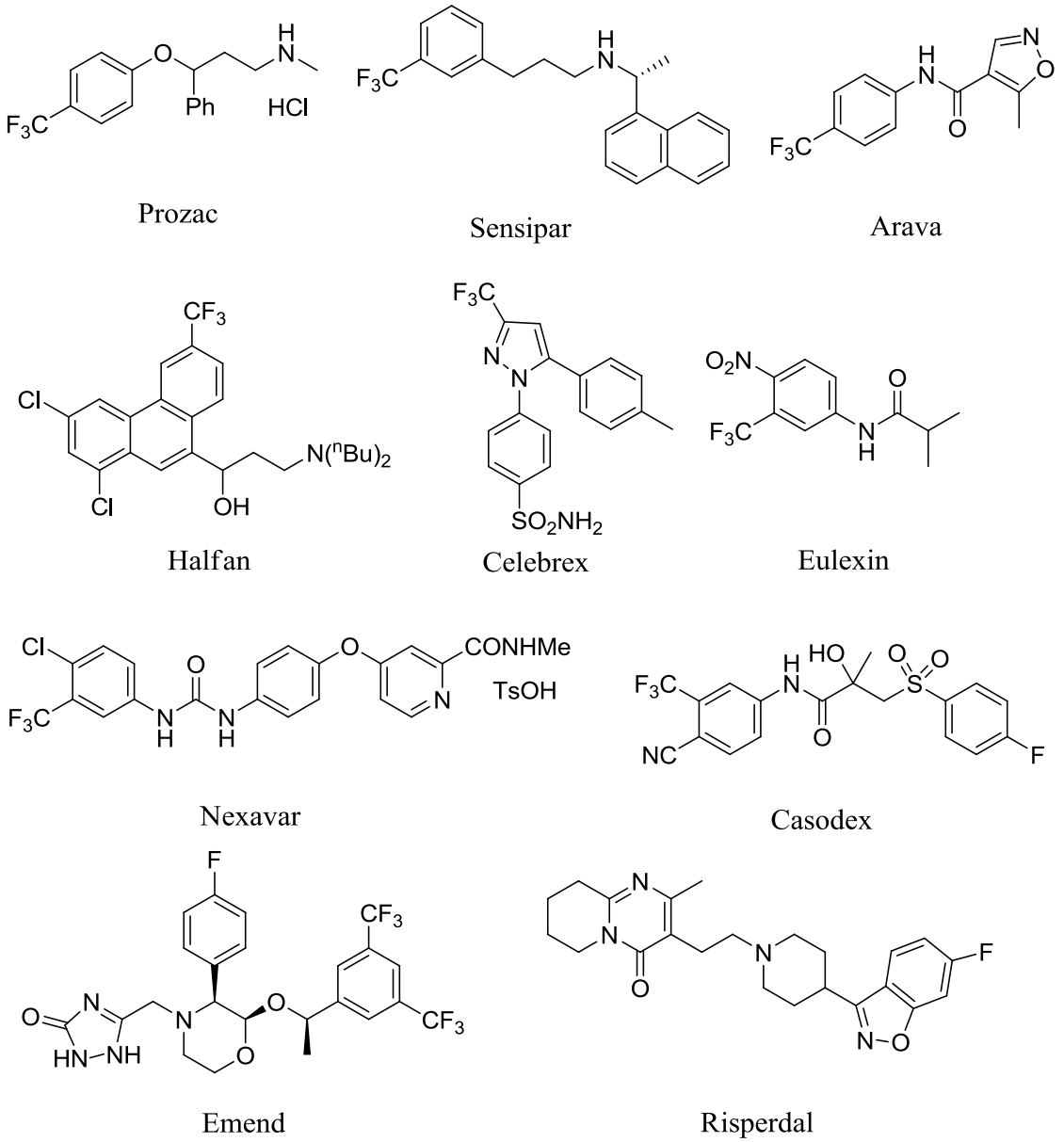
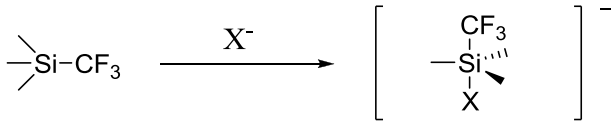


Figure 1.1. Fluorinated organic compounds

1.1.2. Trifluoromethyl Nucleophilic Attack

The extensive study of fluorine chemistry has focused on developing new protocols to introduce trifluoromethyl groups into specific sites on target molecules. One of the most widely employed trifluoromethylation reagents is $TMSCF_3$, or Ruppert's reagent as shown in Figure 1.2 which generates a trifluoromethyl anion equivalent by exposure to a fluoride anion.[8-9] Low temperature NMR studies (X = F) and X-ray diffraction (X = CF_3) support the formation of a five coordinated structure considered as a trifluoromethyl anion equivalent.



$X=F^-$, $AlkO^-$, CO_3^{2-}, AcO^-

Figure 1.2. Ruppert`s reagent activated by an anion

Ruppert's reagent has been widely used as nucleophiles and as transmetalating agents for metal complexes. For example, Prakash and co-workers reported the efficient trifluoromethylation reactions of ketones using Ruppert's reagent in the presence of fluoride anion to give the corresponding alcohol shown in Figure 1.3.[10]

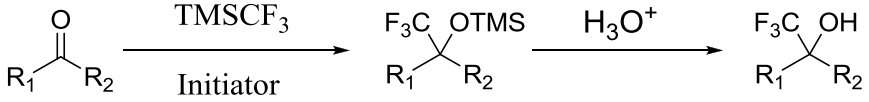
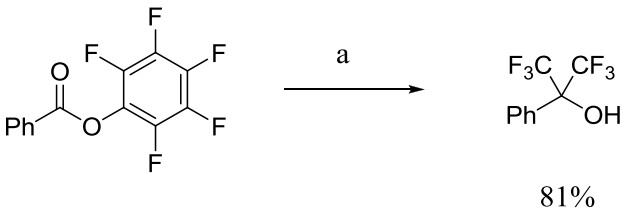


Figure 1.3. Nucleophilic attack of a trifluoromethyl group on a ketone carbonyl

This reaction proceeds by fluoride activation of Ruppert's reagent followed by transfer of the trifluoromethyl group to the ketone. Desilylation of the intermediate during quenching with water gives the trifluoromethylated alcohol. Other electrophiles such as imines and aldehydes

afford the corresponding trifluoromethyl compounds.[10] When esters were reacted with the combination of Ruppert's reagent and fluoride at -78 ^{o}C, trifluoromethylated ketones were obtained. However, when esters were reacted with excess or 2 equivalents of Ruppert's reagent and fluoride anion, *bis*-trifluoromethyl alcohols were isolated. For example, when pentafluorophenyl esters were reacted with 2 equivalents of Ruppert's reagent and TBAF, the corresponding *bis*-trifluoromethyl compounds were obtained as shown in Scheme 1.1.[11]

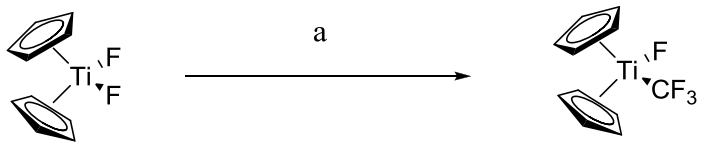


81%

Scheme. 1.1. Reagents and conditions: a) $TMSCF_3$ (2 eq.), TBAF, DME, -50 ^{o}C to rt, 12 h.

1.1.3. Introduction of the Trifluoromethyl Group by Transmetalation

A variety of complexes bearing trifluoromethyl group have been synthesized and investigated for their unique properties. Ruppert's reagent was extensively used to transmetalate halogenated metal complexes. For example, Kiplinger reported that Cp_2TiF_2 treated with Ruppert's reagent and CsF gave the desired trifluoromethyl titanium complex, $[Cp_2Ti(CF_3)F]$ as shown in Scheme 1.2.[12]



60 %

Scheme. 1.2. a) $TMSCF_3$ (10 eq.), CsF, THF, rt, 15 h.

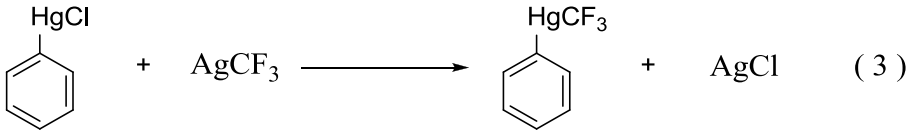
The combination of Ruppert's reagent and fluoride has often been employed to transmetalate various complexes such as copper, palladium, and nickel (section 1.1.4-1.1.6). However, $AgCF_3$ also functions as a transmetalating agent.[13] Initially, $AgCF_3$ was prepared from the treatment of $Cd(CF_3)_2{\cdot}2CH_3CN$ with $AgNO_3$ (eq 1).

$$Cd(CF_3)_2 \cdot 2CH_3CN + 2AgNO_3 \xrightarrow[DMF]{} 2AgCF_3 \cdot DMF + Cd(NO_3)_2 + 2CH_3CN \qquad (1)$$

However, the presence of Cd^{2+} catalyzes the decomposition of $AgCF_3$ into Ag metal. Because of this trend and cadmium toxicity, only a few reactions of $AgCF_3$ were reported. Wieland reported the synthesis of $AgCF_3$ from the reaction of Ruppert's reagent with AgF in quantitative yield in solvents such as acetonitrile, pyridine, *N*- methylimidazole, and DMF (eq 2).

$$TMSCF_3 + AgF \longrightarrow AgCF_3 + TMSF \qquad (2)$$

Previously reported $AgCF_3$ was decomposed to give elemental silver, Ag (I) and $[Ag(CF_3)_4]^-$ (III) with metal ions like Cd^{2+}. The big advantage of the reported synthesis of $AgCF_3$ was the absence of metal ions. It was reported that $AgCF_3$ synthesized by the reaction of Ruppert's reagent and AgF did not decomposed for 14 days, because no metal was not employed. $AgCF_3$ could not be isolated from the reaction mixture, but could be employed *in situ* to perform furthermore reactions. $AgCF_3$ was shown to be a good transmetalation agent in (eq 3) and (eq 4). For example, the reaction of PhHgCl with $AgCF_3$ freshly prepared from Ruppert's reagent and AgF (eq 2) gave $PhHgCF_3$. When TMSCl and Me_3SnCl were treated with $AgCF_3$, they also afforded the desired transmetalated products.

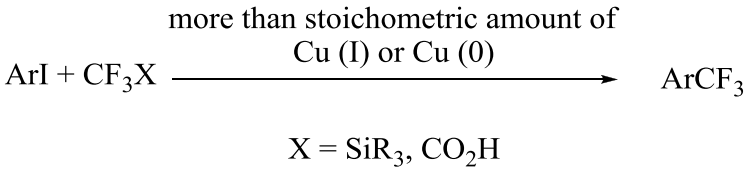


(3)

$$Me_3MCl + AgCF_3 \xrightarrow[M = Si, Sn]{} Me_3MCF_3 + AgCl \qquad (4)$$

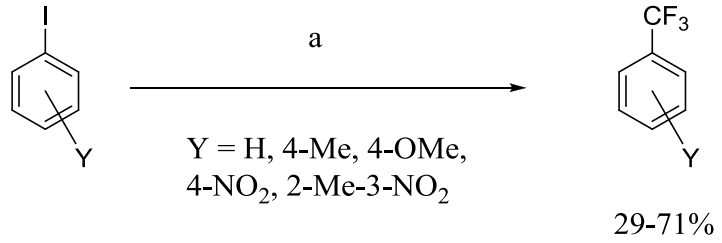
1.1.4. Aryl Trifluoromethylations by Copper

The introduction of trifluoromethyl group is of importance in medicinal chemistry because fluorination of organic compounds changes its biological activity, metabolic stability, and lipophilicity. The cross-coupling reaction is one of the most useful protocols to introduce a trifluoromethyl group. Copper has been widely utilized for aryl trifluoromethylations as shown in Scheme 1.3.[14]



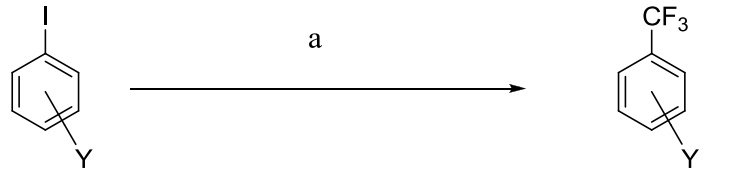
Scheme 1.3. Aryl trifluoromethylations by copper

Despite many attempts to develop copper catalyzed coupling reactions, an excess of copper is usually required to accomplish aryl trifluoromethylations. In addition, good yields are often limited to aryl iodides. However, Chen and Wu were the first to report in 1989 that the reaction of aryl iodides with $FSO_2CF_2CO_2Me$ in the presence of catalytic amount of CuI afforded the desired trifluoromethylated compounds in 29-71% yield as shown in Scheme 1.4.[15]



Scheme 1.4. a) $FSO_2CF_2CO_2Me$ (1.5 eq.), CuBr (0.012 eq.), DMF, 60-80 ^oC, 2-6 h.

Amii and his co-workers also reported copper catalyzed trifluoromethylations with aryl iodide, and Ruppert's reagent in moderate yield in 2009 (Scheme 1.5).[16]



> 9 examples

44-90%

Scheme 1.5. a) $TESCF_3$ (2 eq.), Phen (0.1 eq.), CuI (0.1 eq.), KF, (2 eq.) NMP/DMF, 60 ^oC, 24 h

Amii proposed a strategy of catalytic cycle of aromatic trifluoromethylations (Figure 1.4) Diimine ligands such as bpy and Phen can stabilize copper complexes by chelation, increase the electron density of copper, and improve the nucleophilicity of trifluoromethyl group. Thus, the use of diamine ligands was essential to regenerate dianime copper complexes. Recently, Hartwig isolated [(Phen)$CuCF_3$] suggested by Amii which reacted with iodoarenes to give trifluoromethylarenes in nearly quantitative yield in 2011.[17]

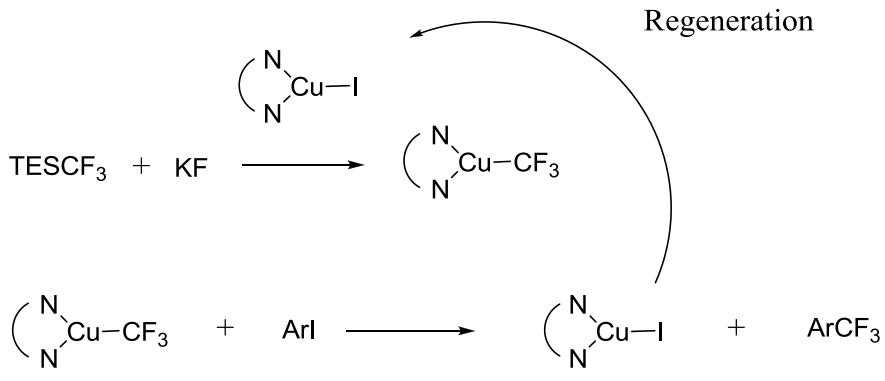
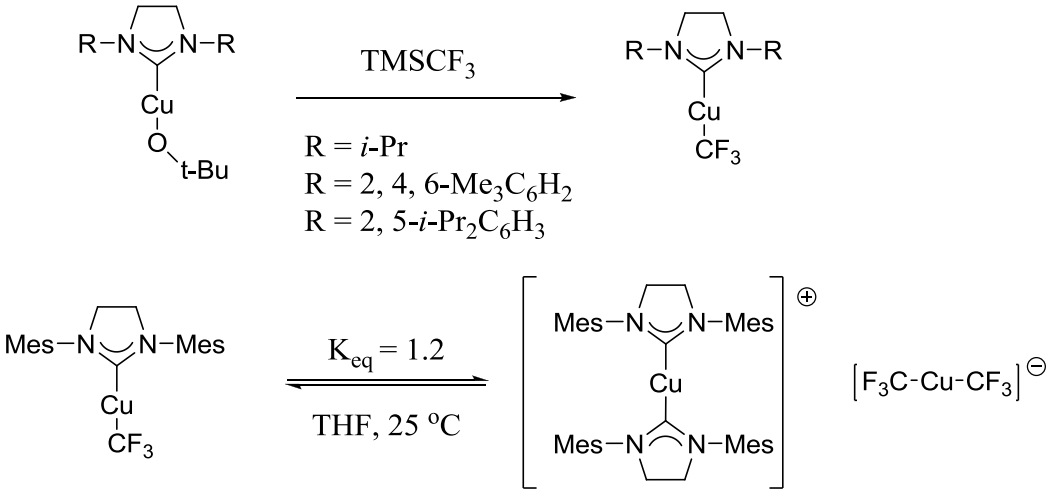


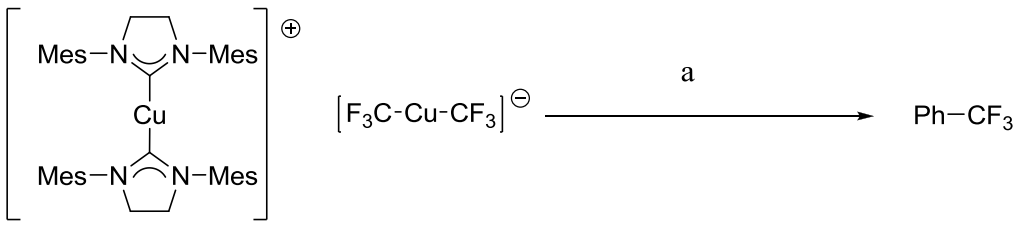
Figure 1.4. Proposed catalytic cycle for aryl trifluoromethylations

Copper has shown to be the most promising metal in terms of trifluoromethylations, but no well-defined $CuCF_3$ species have been isolated and investigated. Almost all copper trifluoromethylation reactions involved the generation of $CuCF_3$ species *in situ* without isolation. In 1986, Wiemers and Burton reported the first ^{19}F NMR studies of $CuCF_3$ species.[18] The metathesis reaction of CF_3CdX prepared from Cd treated with CF_2X_2 at room temperature in DMF occurred with CuX at -50 ^oC. When the metathesis reaction was followed by ^{19}F NMR, the resonances of $[CuCF_3]$ were consistent with -28.8 ppm at -50 ^oC. However, structural information on CF_3Cu species was still lacking. Vicic and co-workers were the first to demonstrate fully characterized Cu(I)-CF_3 complexes, which were stabilized by a known NHC carbene ligand shown in Scheme 1.6.[19] Treatment of LCu-OtBu with Ruppert's reagent yielded the desired Cu(I)-CF_3 complexes. Although [(SiIPr)Cu(CF_3)] and [(SIPr)Cu(CF_3)] did not redistribute their ligands in solution, [(SIMes)Cu(CF_3)] was interestingly in equilibrium with $[(SIMes)_2Cu]^+[Cu(CF_3)_2]^-$ in THF by the analysis of ^{19}F NMR and X-ray structure diffraction.



Scheme 1.6. Well-defined trifluoromethyl copper complexes

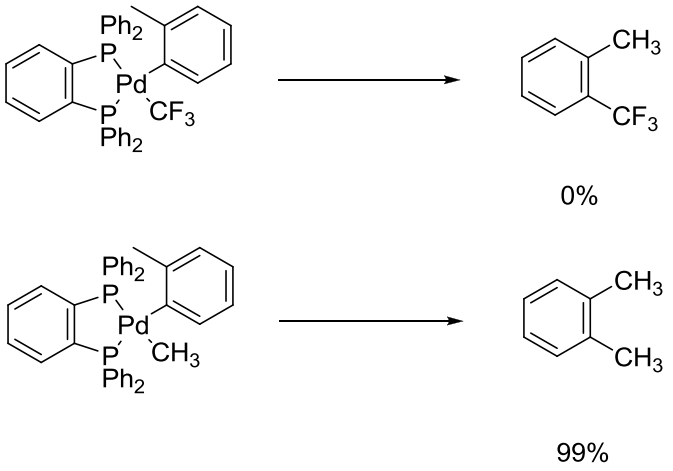
Isolated well-defined trifluoromethyl copper complexes are extremely air-sensitive, but thermally stable. Amazingly, these well-defined complexes react with aryl iodide in DMF to give the corresponding trifluoromethyl compounds in moderate to high yield although more than 5 equivalents of aryl iodide are required to get the best yield (Scheme 1.7). For example, isolated [(SIMes)Cu(CF_3)] was reacted with an excess of PhI to give the desired trifluoromethyl benzene in 86% yield.



Scheme 1.7. a) PhI (10 eq.), benzene/DMI (5:1), 50 ^{o}C, 28 h

1.1.5. Studies for Trifluoromethyl Palladium Complexes

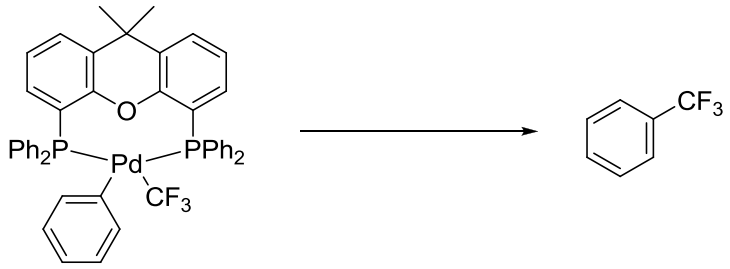
While several examples of copper-catalyzed trifluoromethylations were reported, palladium-catalyzed cross coupling reaction appeared to be challenging. For study of Ar-CF_3 reductive elimination, a number of[$LPd(Ar)CF_3$]complexes have been reported.[20] For example, Culkin and Hartwig succeeded to isolate [(dppbz)Pd(*o*-tol)CF_3] and comparable [(dppbz)Pd(*o*-tol)CH_3] complex.[21] [(dppbz)Pd(*o*-tol)CH_3] underwent reductive elimination to give *o*-xylene at 40 ^oC, whereas no reductive elimination was interestingly found in [(dppbz)Pd(*o*-tol)CF_3] complex for days at 130 ^oC (Scheme 1.8).



Scheme 1.8. a) PPh_3, toluene, 90-130 ^oC, days, b) DPPBz, toluene, 40 ^oC, 4 h

It was concluded that reductive elimination of [$LPd(Ar)CF_3$] was more difficult than that of related [$LnPd(Ar)CH_3$] because the Pd-CF_3 bond was stronger and a higher activation barrier was required for reductive elimination. However, [(Xantphos)Pd(Ph)CF_3] synthesized from the reaction of Ruppert's reagent and [(Xantphos)Pd(F)CF_3] surprisingly underwent reductive elimination and produced desired Ph-CF_3 in 2006 as shown in Scheme 1.9.[22] This was the first

example of Ar-CF_3 reductive elimination of palladium. Unfortunately, the attempt of Pd-catalyzed aromatic trifluoromethylation employed with Xantphos as a ligand failed.



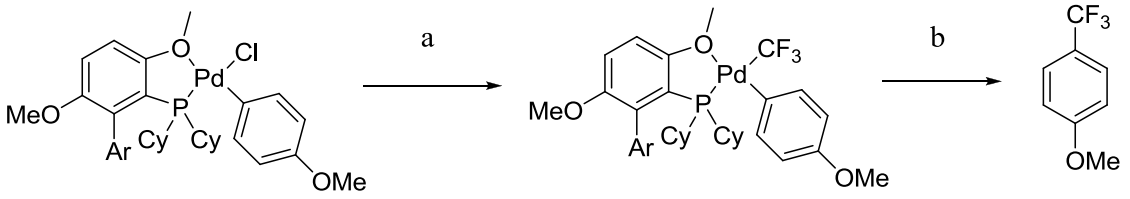
100%

Scheme 1.9. a) Xantphos, benzene, 50-80 ^oC, 3 h.

From this breakthrough of Ar-CF_3 reductive elimination in 2006, several reactions which underwent facile reductive elimination were reported. Sanford and co-workers reported Ar-CF_3 reductive elimination of Pd(IV) complex.[23] The treatment of [(dtbpy)Pd(Ar)CF_3] and NFTP gave [(dtbpy)Pd(CF_3)(F)(OTf)(Ar)]. [(dtbpy)Pd(Ar)CF_3] complex showed inactive toward reductive elimination, but [(dtbpy)Pd(CF_3)(F)(OTf)(Ar)] at 80 ^oC for three hours in $PhNO_3$ underwent reductive elimination to yield aryl trifluoromethyl compounds.

Very recently, Buchwald and co-workers reported [(Brettphos)Pd(Ar)CF_3] complex prepared from [(Brettphos)Pd(Ar)Cl] treated with $TESCF_3$ and KF in 37% yield as shown Scheme 1.10.[24]

Notably, reductive elimination was occurred in dioxane at 80 ^oC and Ar-CF_3 was generated under conditions relevant to catalytic proposal (Figure 1.5)



Ar = 2,4,6- *i*-$Pr_3C_6H_2$ 37%

Scheme. 1.10. a) $TESCF_3$, (5 eq.), CsF (2 eq.), THF, rt, 24 h, b) dioxane, 80 ^oC

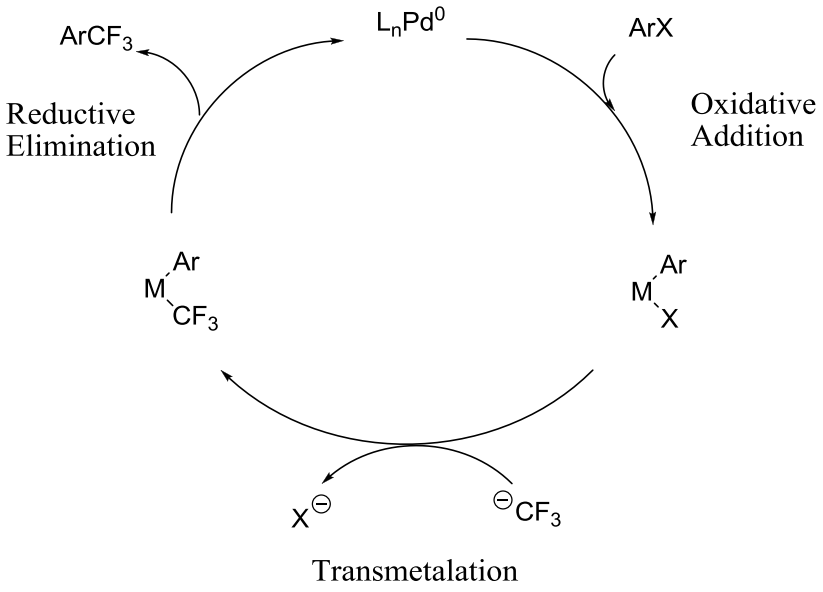
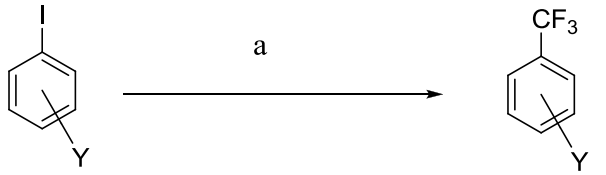


Figure 1.5. Generalized catalytic cycle for aryl trifluoromethylations

After screening the optimized condition included use of $TESCF_3$ (2 eq.) and KF (2 eq.) in the presence of 6-8 mol% [{Pd(allyl)Cl}$_2$] or [Pd(dba)$_2$] and 9-12mol% ligand in dioxane at 130 ^oC. These conditions yielded the desired trifluoromethylated compounds in 70-94% yield as shown in Scheme 1.11. This was the first example of palladium catalyzed aryl trifluoromethylations reported by Buchwald in 2010.



> 20 exmples

70-94%

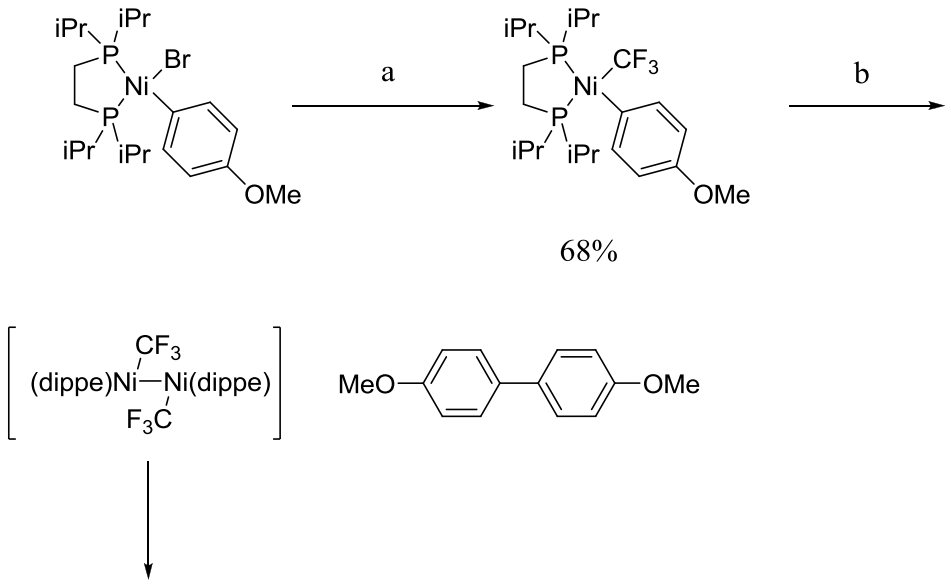
Scheme. 1.11. a) $TESCF_3$ (2 eq.), KF (2 eq.) cat. $Pd(dba)_2$,

cat. Brettphos, dioxane, 80-100 ^oC

1.1.6. Studies for Trifluoromethyl Nickel Complexes

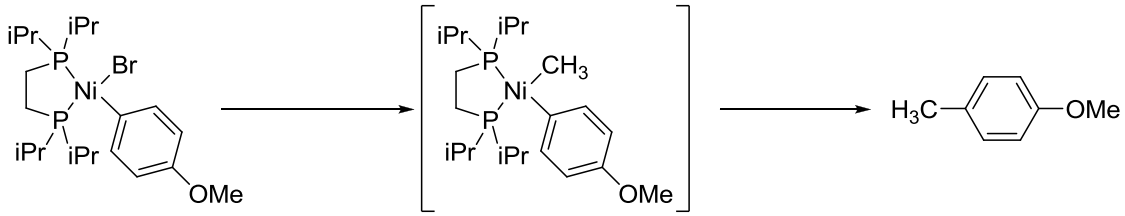
Nickel is a potentially good catalyst to perform aryl trifluoromethyl coupling reactions. There were few reports of Ni complexes bearing CF_3 group.[25] Vicic reported the first example of trifluoromethyl aryl nickel complexes.[26] [(dippe)Ni(Ar)(CF_3)] was obtained from [(dippe)Ni(Ar)(Br)] treated with Rupperts's reagent and CsF in 57-70% yield in similar manners of palladium as shown in Scheme 1.12. [(dippe)Ni(Ar)(CF_3)] did not undergo reductive elimination upon heating. Instead, [(dippe)Ni(Ar)(CF_3)] was readily decomposed, and [(dippe)Ni(CF_3)$_2$] and biaryl was obtained as a major byproducts (Scheme 1.12)

.



Scheme 1.12. a) $TMSCF_3$ (2 eq.), CsF (2 eq.), THF, rt, b) DCM, rt

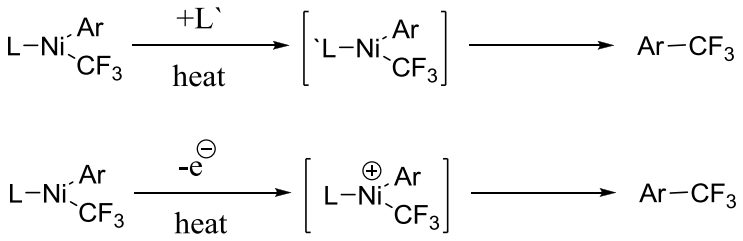
Vicic also found that [(dippe)Ni(Ar)(CH_3)] did reductive eliminate at room temperature to afford the corresponding Ar-CH_3 compounds as shown in Scheme 1.13. This was a similar result of [(dppbz)Pd(*o*-tol)CF_3]and [(dppbz)Pd(*o*-tol)CH_3] described earlier in section 1.1.5.



Scheme 1.13. a) MeLi, -30^{o}C to rt, THF, overnight

1.1.7. Objectives

Nickel has greatly succeeded in establishment of alkyl-alkyl and aryl-alkyl cross coupling reactions, whereas only a few trifluoromethyl nickel complexes have been isolated and investigated. Therefore, nickel could be considered as a potential catalyst for trifluoromethyl-aryl cross coupling reactions. For studies exploring the strength of Ni-CF_3 bonding, we decided to prepare bis-CF_3 complex bearing a bipyridine ligand because nickel bipyridine complexes have demonstrated significant roles in reductive elimination, polymer synthesis, and electrocatalytic coupling.[27-29] So it is promising that nickel bipyridine complex should induce reductive elimination of CF_3-CF_3. Moreover, we envisioned a new precursor for investigation of Ar-CF_3 reductive elimination as shown in Scheme 1.14. A new nickel precursor must have aryl group and trifluoromethyl group with a replaceable ligand so that a new nickel precursor would yield any trifluoromethyl nickel complexes just by addition of any ligands. A new precursor would simplify and accelerate optimizing conditions, ligand screens, or oxidation studies for aryl trifluoromethyl coupling reactions, and also allow us to study the fundamental chemistry of nickel CF_3 chemistry.

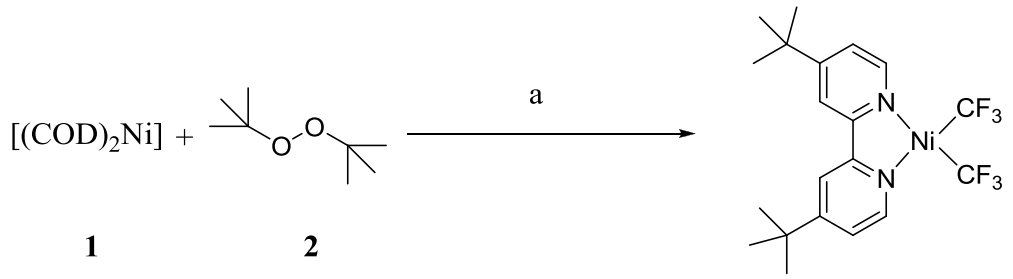


Scheme 1.14. The key step for nickel catalyzed cross coupling reactions

1.2. Results and Discussion

1.2.1. Preparation and Reactivity of a Nickel Bis-Alkoxide Complex

Our initial attempt to synthesize [(dtbpy)Ni(CF_3)$_2$] **3** was the reaction of [(COD)$_2$Ni] **1** with *t*-butyl peroxide **2** and $TMSCF_3$ and dtbpy. Ni (0) was oxidized by *t*-butyl peroxide to give Ni (II), and resulting Ni (II) was followed by substitution of CF_3 group to afford the desired [(dtbpy)Ni(CF_3)$_2$] **3** as shown in Scheme 1.15. However, only 8% yield was obtained after recrystallization of THF/pentane to perform furthermore purification. High yields may be achieved by use excess of oxidizing reagent and Ruppert's reagent presumably because [(COD)$_2$Ni] **1** was not fully oxidized by *t*-butyl peroxide. However, we decided to use another nickel source and methodology because of cost and safety issues.



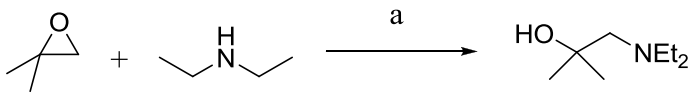
1 **2** **3**

8%

Scheme 1.15. a) $TMSCF_3$ (2 eq.), dtbpy, THF, reflux, 30 min

Many nickel (II) salts are insoluble in most organic solvents, which hinder reactivity with Ruppert's reagent. Therefore we decided to test a new pentane-soluble Ni (II) source towards its reactivity towards Ruppert's reagent. Very recently, Gyun reported in 2011, the nickel complex **8** which is readily soluble in most solvents (Scheme 1.18).[30] We decided to investigate whether the bis-alkoxide nickel complex **8** can serve as a precursor, [(dtbpy)Ni(CF_3)$_2$] **3** and any other perfluoroalkyl complexes. The aminioalcohol ligand was prepared by the reaction of epoxide **4**

with diethyl amine **5** in 5 M $LiClO_4$ (Scheme 1.16).[31] Fresh aminoalcohol **6** was obtained by distillation in 66 % yield.

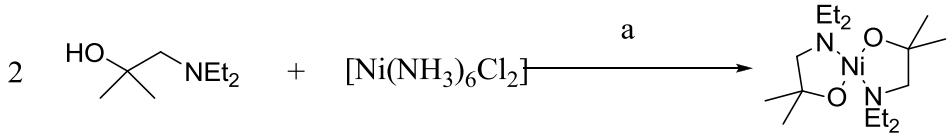


4 **5** **6**

66 %

Scheme 1.16. a) 5 M $LiClO_4$, diethyl ether, 30 min

The aminoalcohol **6** was dried over molecular sieves prior to use and was treated with NaH and $[Ni(NH_3)_6Cl_2]$ **7** under refluxing conditions to coordinate the ligand (Scheme 1.17). The resulting residue was then sublimed to give the desired nickel complex **8** in 73% yield.

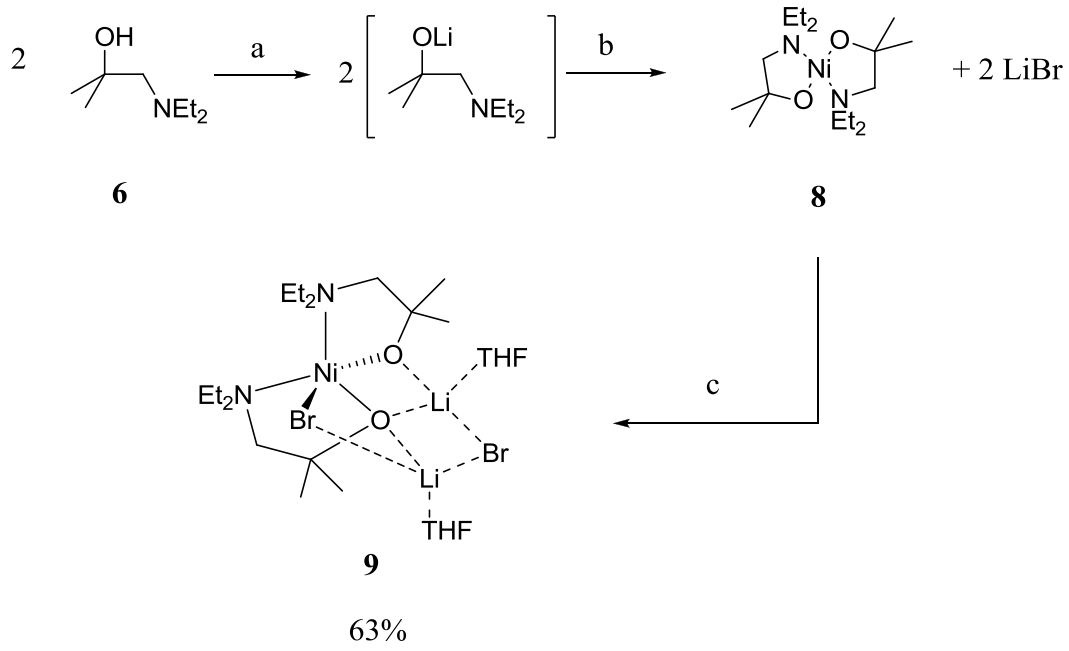


6 **7** **8**

73%

Scheme 1.17. a) NaH (2 eq.), toluene, 90 ^oC, 3 h

During the exploration of the synthesis of nickel complex **8**, we found that $(DME)NiBr_2$ reacted with lithium alkoxide to afford the desired complex **8**. However pentane extraction was not sufficient to purify the desired complex, because lithium bromide was slightly soluble in pentane. Pentane extract was cooled to - 30 ^oC for several days to give the trace amount of bis-LiBr crystals **9** as shown in Scheme 1.18.



Scheme 1.18. a) nBuLi, THF, 0 ^{o}C; b) (DME)$NiBr_2$, THF, 0 ^{o}C; c) THF, 3 d

Salt free nickel complex **8** and LiBr were used for further studies of the bis-LiBr adduct **9**. When LiBr was added to complex **8** in THF solution, bis-LiBr adduct product **9** was obtained in 63% yield (Scheme 1.18). Structure analyzed by X-ray diffraction was shown in Figure 1.6. Amazingly, the nickel complex **9** was chiral in the solid state and crystallized in the $P2_12_12_1$ space group with the Flack parameter refining to -0.009(12) for the structureTo our knowledge, this was the first example of generation of an isolable chiral nickel complex just by addition of LiBr salt. Presumably, the solution of **9** from which the crystals were obtained was racemic, which contacting both enantiomers as would be expected from achiral starting material. As such, two crystal forms are likely. In the first, the crystals of **9** formed formed from pentane are a racemic conglomerate, i.e., a separable mixture of enantiomerically pure crystals of one enantiomer and the other. In the second, the crystals are twinned or a pseudoracemate, an agglomeration of homogenous domains of opposite chirality within a perfectly orientated lattice. Both cases could provide the $P2_12_12_1$ space group. One would expect that the two possibilities

could be distinguished through measurement of the optical activity, as the agglomeration crystals are racemic and those mechanically separated from the racemic conglomerate are enantiomerically pure.

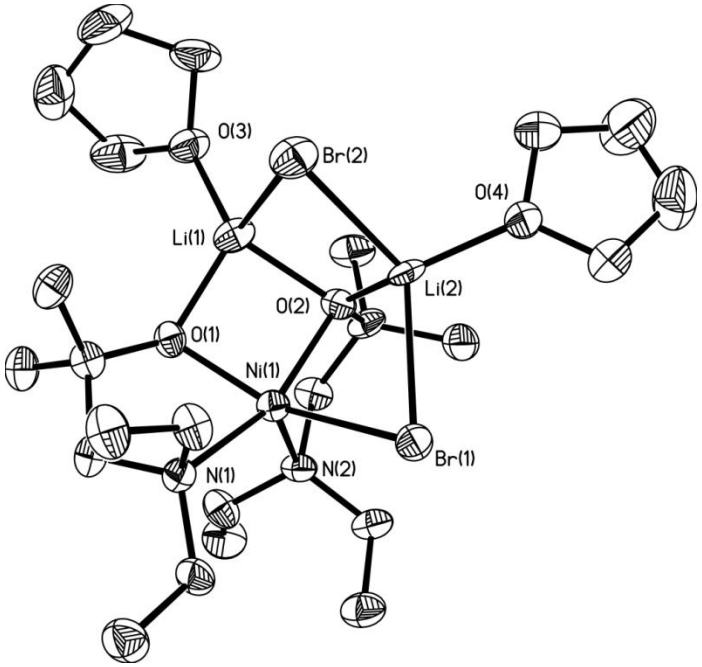
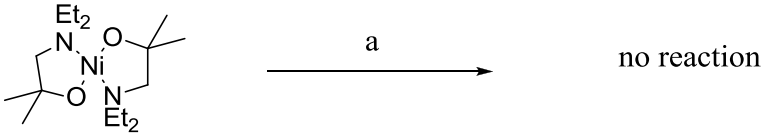


Figure 1.6. ORTEP diagram of **9**. Ellipsoids shown at 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Br(1)-Ni(1) 2.562(2); Br(2)-Li(1) 2.591(11); Br(2)-Li(2) 2.550(10); Br(1)-Li(2) 2.612(10); O(1)-Li(1) 1.892(11); Li(1)-O(3) 1.953(11); O(2)-Li(1) 1.966(11); O(4)-Li(2) 1.911(10); Li(2)-O(2) 1.887(11); Ni(1)-O(2) 2.047(4); Ni(1)-O(1) 1.948(4); Ni(1)-N(1) 2.187(5); Ni(1)-N(2) 2.126(5). Selected bond angles (°): O(2)-Ni(1)-O(1) 84.92(16); O(2)-Ni(1)-N(1) 156.23(16); O(1)-Ni(1)-N(1) 82.65(17); O(2)-Ni(1)-N(2) 85.97(17); O(1)-Ni(1)-N(2) 101.83(17); N(1)-Ni(1)-N(2); 116.38(18); O(2)-Ni(1)-Br(1) 88.63(11); O(1)-Ni(1)-Br(1) 153.90(12); N(1)-Ni(1)-Br(1) 93.69(13); N(2)-Ni(1)-Br(1) 102.91(14)

In this case, when dissolved in THF, solutions of complex **9** gave rise to no optical rotation,. While this data is consistent with twinning, i.e., the crystal structure contains both enantiomers, a similar results would be expected if the enantiomeric nickel complexes of **9** were fluxional in solution. Further experiments are needed to resolve these issues. These experiments could include examined multiple crystals by X-ray structure diffraction to rule out the racemic conglomerate. If chiral, we need to take an advantage of this chirality to perform further asymmetric reactions by using a chiral catalyst in the future studies. But chirality must be retained in solution to accomplish this last goal, because chirality was lost after dissolving in solution of THF. By taking a look at X-ray structure of **9**, Li^+ functioned as a Lewis acid and played an essential role to exhibit chirality of crystals. We proposed one idea. One is to use a stronger Lewis acid than Li^+ so that structure would be kept in original state.

The resulting complex **8** was soluble in pentane as previously reported. However, when **8** was treated with Ruppert's reagent, dtbpy and CsF, only trace amounts of **3** was obtained by ^{19}F NMR analysis. Crystals grown by THF/pentane also confirmed no formation of nickel complex **3** as shown in Scheme 1.19. Nickel complex **8** was highly soluble in any solvent, but nickel complex **8** was found out to be less reactive toward the combination of Ruppert's reagent and fluoride anion.

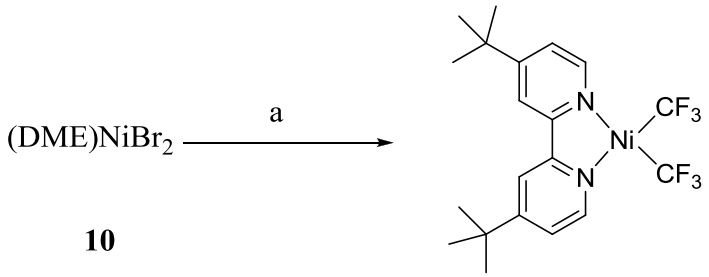


8

Scheme 1.19. a) $TMSCF_3$ (2 eq.), CsF (2 eq.), dtbpy, THF, rt, overnight

1.2.2. Synthesis of a Bis-Trifluoromethyl Nickel Complex

Our next attempt to prepare nickel complex **3** was by using [(dtbpy)NiX_2] treated with $TMSCF_3$ and CsF. However, when (DME)$NiCl_2$ was treated with $TMSCF_3$, dtbpy, and CsF in THF in the similar manner of palladium complexes, no nickel complex **3** was formed by means of ^{19}F NMR spectroscopy. This was because isolated [(dtbpy)$NiCl_2$] was insoluble in THF. After the investigation of solubility of isolated [(dtbpy)$NiCl_2$], DCM and DMF was found out to be a potentially good solvent.



Scheme 1.20. a) $TMSCF_3$ (4 eq.), CsF (4 eq.), dtbpy, rt, overnight

When (DME)$NiCl_2$ was treated with $TMSCF_3$, dtbpy, and CsF in DCM, the desired nickel complex **1** was obtained in 33% yield. In the case of (DME)$NiBr_2$ **10**, the nickel complex **3** was obtained in 66% when (DME)$NiBr_2$ **10** was treated with excess of Ruppert's reagent, and CsF in the presence of dtbpy in DCM (Scheme 1.20). Crystals can be grown by THF/pentane at -30 ^oC and the ORTEP was shown in Figure 1.7. A remarkable feature of the molecular geometry is the distortion from square planarity. The trans nitrogen−nickel−carbon bond angles were found to be 159.7(2) and 165.1(2) ° far from the ideal 180 ° whereas nitrogen-nickel-carbon bond angles of [(bpy)$Ni(Me)_2$] were reported to be 177.4 °.[32] Presumably, steric interactions of the fluorines

with the 6- and 6′-hydrogens of the bipyridine ligand caused this large distortion. The nickel−carbon distances in nickel complex **3** were Ni(1)−C(1) = 1.872(6) Å and Ni(1)−C(2) = 1.883(6) Å, while nickel−carbon distances of [bpyNi(Me)$_2$] were reported to be 1.923(4) Å. The nickel−nitrogen bond lengths were respectively 1.983(4) and 1.955(5) Å, whereas the nickel−nitrogen bond lengths in reported [(bpy)Ni(Me)$_2$] were 1.965(3) Å. This difference of bond length supports a stronger Ni-CF_3 bond and provides insight into the trans influencing of CF_3 group. Although large structural distortion of the isolated nickel complex **3** was revealed by X-ray analysis, the CF_3 complex **3** was found to be fairly air-stable. However, a solution of **3** decomposed when exposed to air in a day. We will discuss reductive elimination of nickel complex **3** later in section 1.2.6.

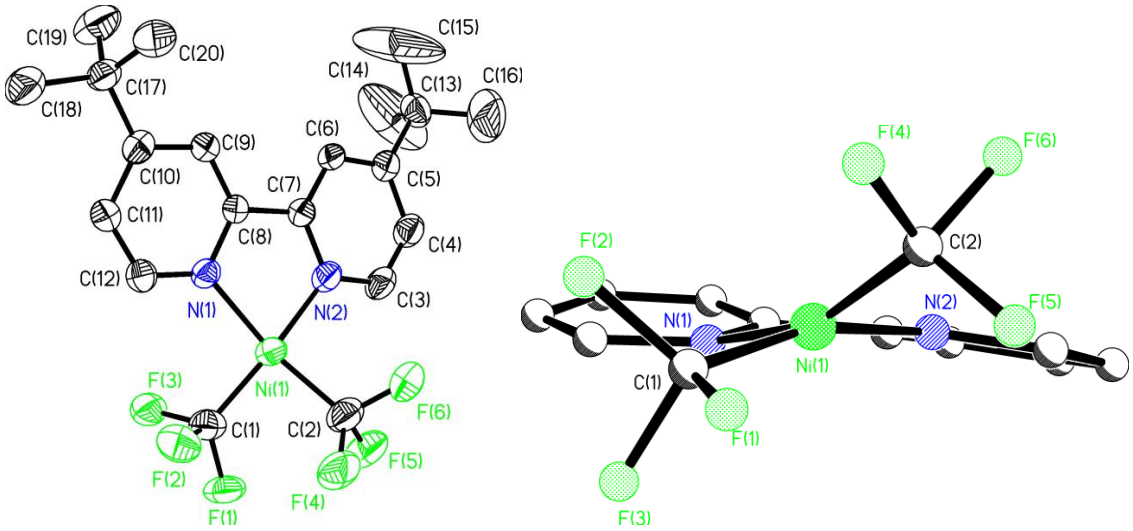
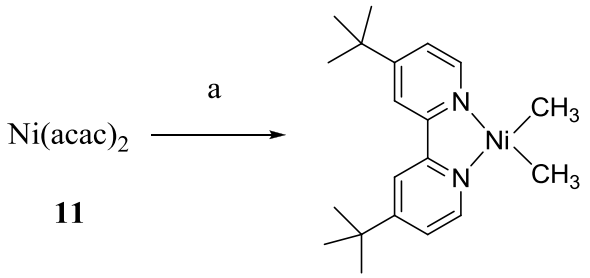


Figure 1.7. Left: ORTEP diagram of **3**. Ellipsoids shown at the 50% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å): Ni(1)-N(1) 1.983(4); Ni(1)-N(2) 1.955(5); Ni(1)-C(1) 1.872(6); Ni(1)-C(2) 1.883(6). Selected bond angles (°): N(1)-Ni(1)-N(2) 82.01(19); N(1)-Ni(1)-C(1) 97.1(2); N(1)-Ni(1)-C(2) 159.7(2); N(2)-Ni(1)-C(1) 165.1(2); N(2)-Ni(1)-C(2) 95.6(2) C(1)-Ni(1)-C(2) 90.3(3). Right: Ball and stick diagram of **1** showing the distortion of square planarity. *t*-Butyl groups and all hydrogens removed for clarity.

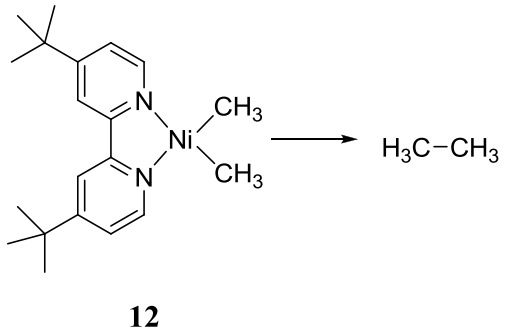
1.2.3. Synthesis of a Bis-Methyl Nickel Complex

We decided to prepare [(dtbpy)Ni(CH_3)$_2$] for reductive elimination comparisons. [dtbpyNi(CH_3)$_2$] was successively obtained by the reaction of Ni(acac)$_2$ **11** with two equivalents of MeMgCl in THF at – 20 ^oC to give nickel complex **12** in the same manner of previously reported [(bpy)Ni(CH_3)$_2$], a green powder as shown in Scheme 1.21.[26]



Scheme 1.21. a) MeMgCl (2 eq.), dtbpy, -20 ^oC, 30 min

While examining the purification, the decomposition of nickel complex **12** was occasionally encountered as shown in Scheme 1.22.



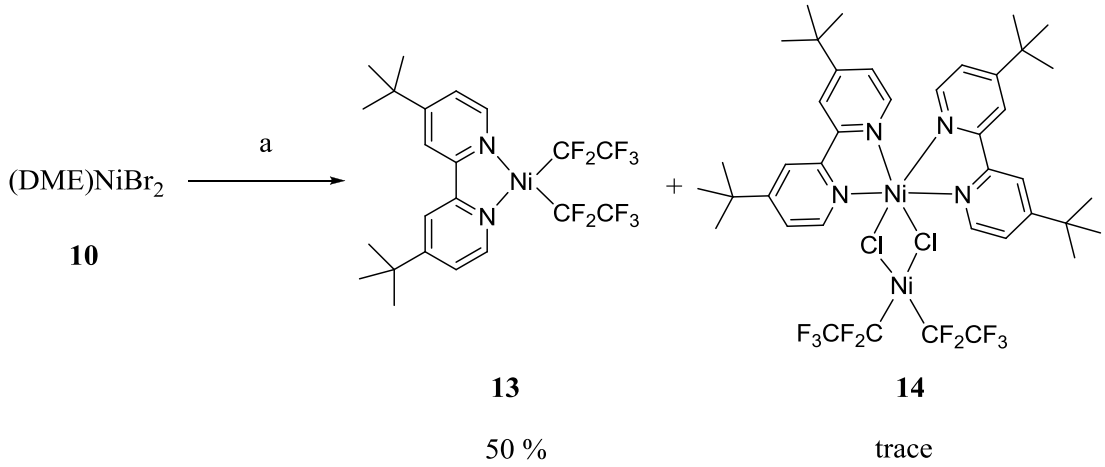
Scheme 1.22. Reductive elimination of **12**

After the careful analysis, the use of vacuum to remove the solvent at room temperature drove the reductive elimination of ethane from nickel complex **12**. When the decomposition of nickel

complex **12** was traced by ^{1}H NMR, the integration of the six hydrogen atoms at 0.98 ppm became gradually smaller. After placement under vacuum overnight, a red powder was obtained, and a paramagnetic signal was observed. Presumably, the paramagnetic signal was derived from the product of reductive elimination reaction. The final purification of the nickel complex **12** was achieved by the vacuum at 0 ^{o}C to give the desired nickel complex **12** in 86% yield. Nickel complex **12** was immediately decomposed upon exposure to air to give a red powder.

1.2.4. Synthesis of a Bis-Perfluoroethyl Nickel Complex

The synthesis of a bis-CF_2CF_3 nickel complex closely related to bis-CF_3 nickel complex was also investigated. We examined the $TMSCF_2CF_3$ and fluoride anion in the similar manner of $TMSCF_3$ (Scheme 1.21). When DCM was employed as solvent, [(dtbpy)Ni$(CF_2CF_3)_2$] **13** was obtained in 50% yield as a crude product. However, crystals grown by DCM /DMF suggested the presence of not the desired nickel complex **13**, but dinuclear nickel complex **14** as shown in Scheme 1.23 and Figure 1.8.



Scheme 1.23. a) $TMSCF_2CF_3$ (4 eq.), CsF (4 eq.), dtbpy, DCM, rt, overnight

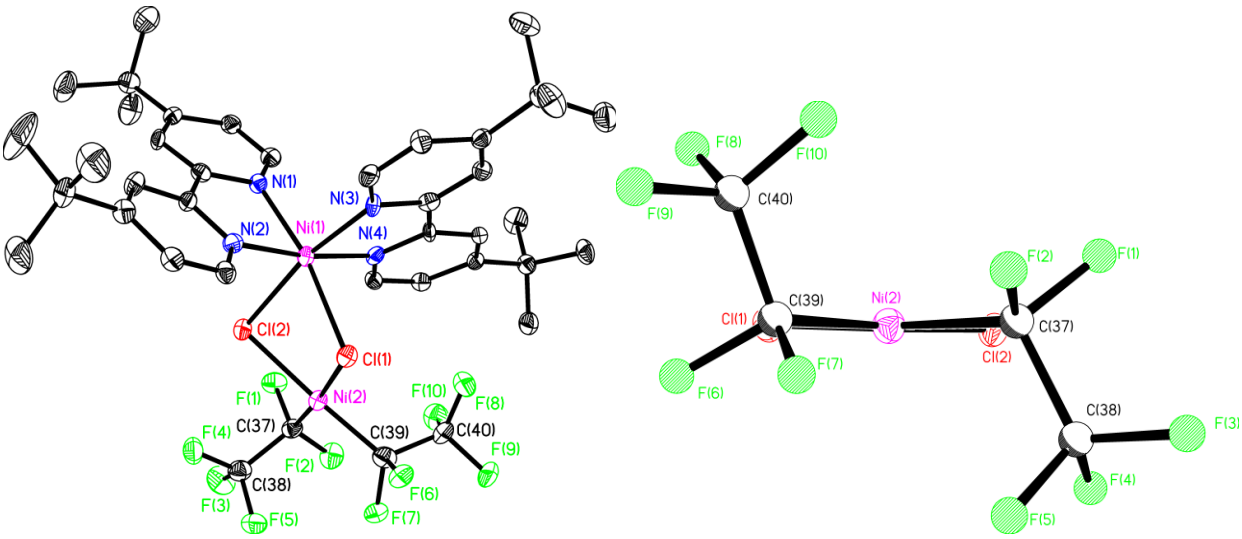
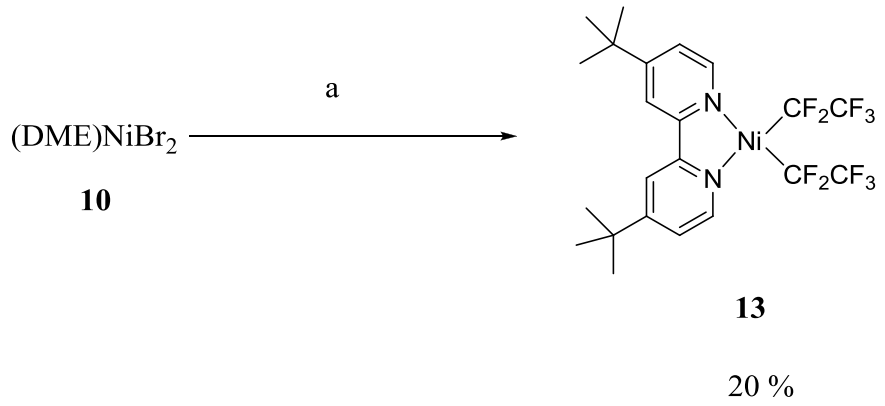


Figure 1.6. Left: ORTEP diagram of **14**. Ellipsoids shown at the 50 % level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å): Ni(1)-N(3) 2.047(4); Ni(1)-N(2) 2.053(5); Ni(1)-N(4) 2.057(4); Ni(1)-N(1) 2.080(4); Ni(1)-Cl(2) 2.4258(15), Ni(1)-Cl(1) 2.4269(15), Ni(2)-C(39) 1.919(6), Ni(2)-C(37) 1.930(5), Ni(2)-Cl(2) 2.2746(15), Ni(2)-Cl(1) 2.2753(15). N(3)-Ni(1)-N(2) 95.78(17). Selected bond angles (°): N(3)-Ni(1)-N(4) 79.66(17); N(2)-Ni(1)-N(4) 172.02(18); N(3)-Ni(1)-N(1) 98.75(17); N(2)-Ni(1)-N(1) 78.43(17); N(4)-Ni(1)-N(1) 95.69(17); N(3)-Ni(1)-Cl(2) 169.43(13); N(2)-Ni(1)-Cl(2) 89.02(13); N(4)-Ni(1)-Cl(2) 96.58(13); N(1)-Ni(1)-Cl(2) 91.44(12); N(3)-Ni(1)-Cl(1) 91.52(13); N(2)-Ni(1)-Cl(1) 98.01(13); N(4)-Ni(1)-Cl(1) 88.70(13); N(1)-Ni(1)-Cl(1) 169.40(13); Cl(2)-Ni(1)-Cl(1) 78.46(5); C(39)-Ni(2)-C(37) 93.2(2); C(39)-Ni(2)-Cl(2) 175.88(18); C(37)-Ni(2)-Cl(2) 90.75(17); C(39)-Ni(2)-Cl(1) 91.15(17); C(37)-Ni(2)-Cl(1) 175.13(18); Cl(2)-Ni(2)-Cl(1) 84.83(5); Ni(2)-Cl(1)-Ni(1) 90.72(5); Ni(2)-Cl(2)-Ni(1) 90.77(5). Right: Ball and stick diagram showing the square-planar coordination around Ni2.

To avoid the formation of dinuclear nickel complex **14**, other solvent systems were furthermore explored. THF/DMF was found out to be a good solvent to afford nickel complex **13** in 20% yield as shown in Scheme 1.24.



Scheme 1.24. a) $TMSCF_2CF_3$ (4 eq.), CsF (4 eq.), dtbpy, THF/DMF, rt, overnight

The yield of **13** in THF/DMF was lower than that in DCM, but it was pure and crystals grown by THF/pentane confirmed its structure (Figure 1.9). X-ray structure analysis revealed nickel complex **13** has more distorted square planarity than nickel complex **3**. Carbon−nickel−nitrogen bond angles of nickel complex **13** were found to be 152.2(2) °. The nickel−carbon distances of nickel complex **13** were found to be longer than those in **1** at 1.910 (6) and 1.911(6) Å. Although nickel complex **13** was more distorted structure than other two nickel complexes, nickel complex **13** was as air-stable as nickel complex **3**. Similarly, solution of nickel complex **13** was decomposed in air from hours to one day.

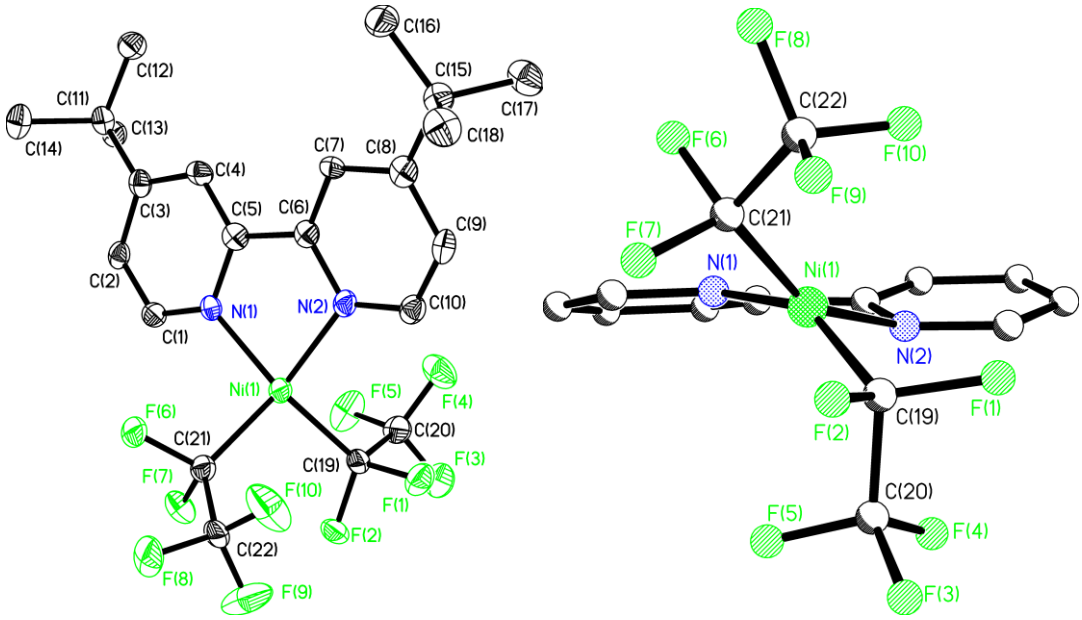


Figure 1.9. Left: ORTEP diagram of **13**. Ellipsoids shown at the 50 % level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å): Ni(1)-C(21) 1.910(6), Ni(1)-C(19) 1.911(6), Ni(1)-N(1) 1.941(5), Ni(1)-N(2) 1.960(5), C(19)-C(20) 1.530(9). Selected bond angles (°): C(21)-Ni(1)-C(19) 94.0(3), C(21)-Ni(1)-N(1) 96.7(2), C(19)-Ni(1)-N(1) 152.2(2), C(21)-Ni(1)-N(2) 152.2(2), C(19)-Ni(1)-N(2) 100.0(2), N(1)-Ni(1)-N(2) 81.8(2). Right: Ball and stick diagram of **5** showing the distortion of square planarity. *t*-Butyl groups and all hydrogens removed for clarity.

1.2.5. Visible Spectrum of New Nickel Complexes

Solutions of nickel complex **3** were yellow, and those of nickel complex **14** were orange while those of nickel complex **12**, and reported [(bpy)Ni(CH_3)$_2$], were dark green. The visible spectrum of all three compounds was shown in Figure 1.10.

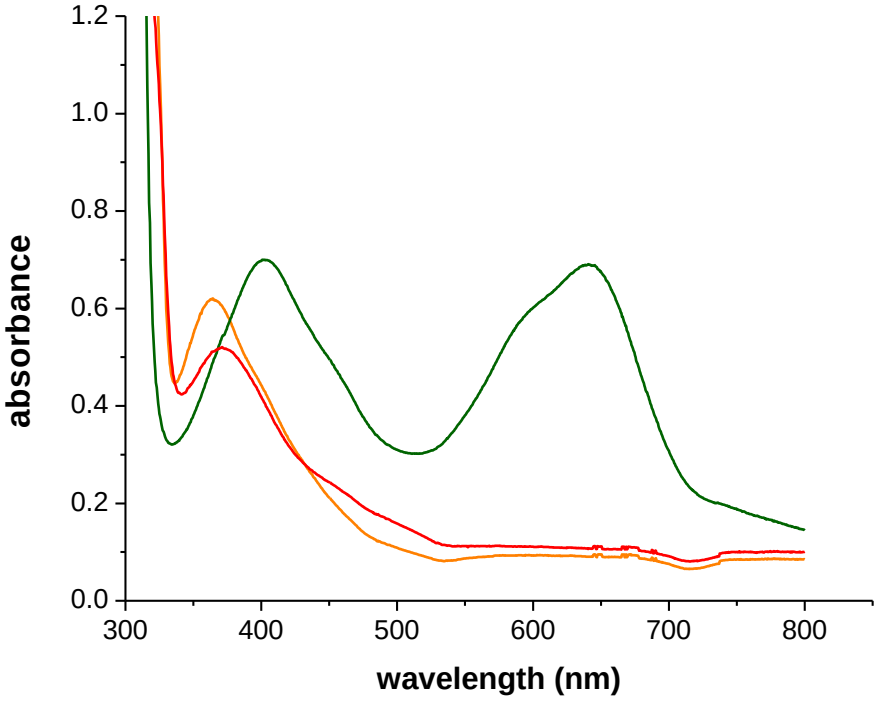


Figure 1.10. Experimental UV-vis spectra in THF. Complex **3** (orange), ε_{364} = 2484 $M^{-1}\cdot cm^{-1}$; Complex **14** (red), ε_{372} = 2078 $M^{-1}\cdot cm^{-1}$; Complex **12** (green), ε_{402} = 2800 $M^{-1}\cdot cm^{-1}$.

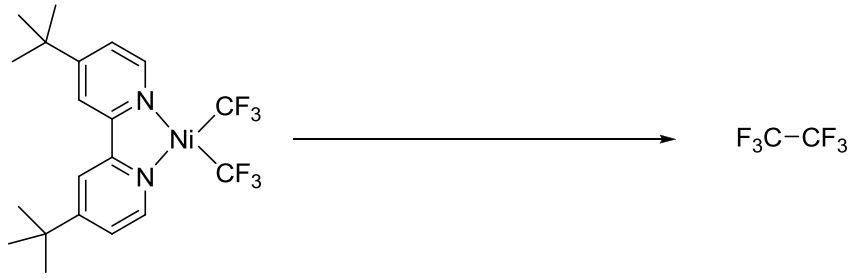
Two broad absorption bands at 402 and 640 nm were observed in a bis-CH_3 nickel complex **12**. We can assign two broad absorption bands at 402 and 640 nm to a metal-to-ligand charge transfer excitation in good agreement with previous works.[33] However, nickel complexes **3** and **14** showed no absorption bands from 600 to 700 nm, but absorption at 370 nm was still present.

This plausible explanation is that this observed behavior was mixed character contributed from metal-to-ligand charge transfer, $d_{(Ni)}$-$\pi^*_{(dtbpy)}$ and the Ni-CF_3 σ bonds. Both the nickel complexes **3** and **14** exhibit similar absorption bands from 600 to 700 nm in THF, but a thorough loss of intensity at a low-energy band clarified only the high energy π-π^* transitions are analogous characters whereas the corresponding absorption at long-wavelength principally varies in character, when replacing CH_3 by CF_3.

1.2.6. Studies for Reductive Elimination of a Bis-Trifluoromethyl Nickel Complex

We found that nickel complex **12** underwent facile reductive elimination, but **3** did not. Here in, we decided to further investigate the reductive elimination of nickel complex **3** as shown in Table 1.1.

Table 1.1. Attempts of reductive elimination of **3**



3

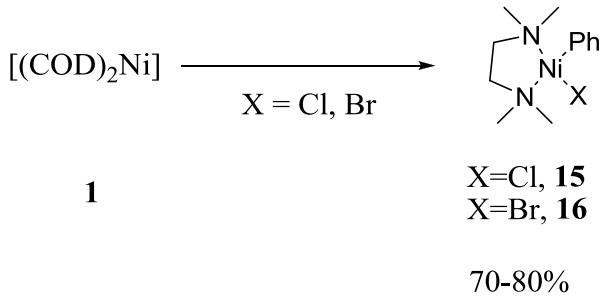
entry	additive (eq.)	condition	yield[a] (%)
1	none	toluene, 90 °C, 2 d	0
2	none	PhI, 90 °C, 1 d	0
3	*o*-dinitrobenzene(10)	toluene, 90 °C, 1 d	0
4	benzyl isocyanide (6)	toluene, 90 °C, 1 d	0
5	*t*-butyl isocyanide (10)	toluene, 90 °C, 1 d	0
6	TCNE (10)	toluene, 90 °C, 1 d	0
7	PPh_3 (10)	toluene, 90 °C, 1 d	0
8	IPr (5)	toluene, 90 °C, 1 d	0
9	SIPr (5)	toluene, 90 °C, 1 d	0
10	$Cp_2Fe \cdot PF_6$ (1)	DCM, rt, 1 d	0
11	AgOTf (1)	DCM, rt, 1 d	0

[a] Reactions and yields were monitered by ^{19}F NMR

It was reported by Murakami that the reductive elimination of [(bpy)$NiPh_2$] was promoted by the π coordination of electron accepting aromatic compounds such as nitrobenzene.[34] Our first attempt was heating of toluene solution for 2 days (Table 1.1, entry 1). No changes were observed by NMR spectroscopy. This result indicated that nickel complex **3** was thermally very stable. Iodobenzene and dinitrobenzene which induced reductive elimination of [(bpy)$NiPh_2$] were employed (Table 1.1, entry 2-3). Even in this condition, no reductive elimination was found. These results demonstrated again the strength of Ni-CF_3 bond. We decided to make a furthermore investigation by using other electron accepting ligand. TCNE, and isocyanide upon heating in toluene at 90 ^oC. Benzyl isocyanide, and *t*-butyl isocyanide were also employed (Table 1.1, entry 4-5), no reductive elimination was seen. TCNE did not promote reductive elimination as well (Table 1.1, entry 6). Electron donor ligands were then examined. Neither the PPh_3 electron donating ligand, nor the IPr and SIPr carbenes, included reductive elimination of C_2F_6 from nickel complex **3** (Table 1.1, entry 7-9). Oxidizing reagents, AgOTf and $Cp_2Fe{\cdot}PF_6$ also did not promote the reductive elimination (Table 1.1, entry 10-11). In summary, [(dtbpy)Ni$(CF_3)_2$] **3** was pretty air-stable, and thermally stable. In addition, [(dtbpy)Ni$(CF_3)_2$] **3** was very stable toward electron withdrawing group, electron donating group and oxidizing reagent.

1.2.7. Synthesis of the Key Intermediate for Aryl Trifluoromethyl Nickel Complex to Explore the Possibility of Ar-CF_3 Reductive Elimination, as opposed to CF_3-CF_3 Reductive Elimination

We decided to prepare an aryl trifluoromethyl nickel complex bearing a readily exchangeable ligand as shown (Scheme 1.12). The tmeda ligand was chosen as a first choice, because it was an exchangeable ligand which could be purchased at a moderate price. The oxidative addition of PhCl to [$(COD)_2$Ni] **1** in the presence of tmeda gave desired [(tmeda)Ni(Ph)Cl] **15** in 76% yield reported by Grushin.[35] [(tmeda)Ni(Ph)Br] **16** was also prepared in the similar manner as shown in Scheme 1.25.



1

X=Cl, **15**
X=Br, **16**

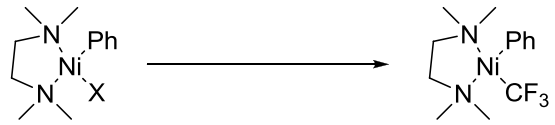
70-80%

Scheme 1.25. a) tmeda, PhX, rt, 6 h

Trifluoromethylation of these two complexes was examined by the treatment of Ruppert's reagent and cesium fluoride as shown in Table 1.2. It was reported by Grushin that [(tmeda)Ni(Ph)Cl] **15** in chlorinated solvents such as DCM was decomposed, but found that [(tmeda)Ni(Ph)Cl] **15** was easily decomposed in THF and biphenyl was obtained as a byproduct. Additionaly, no desired trifluoromethyl complex of [(tmeda)Ni(Ph)Cl] **15** was obtained (Table 1.2, entry 1). When [(tmeda)Ni(Ph)Cl] **15** was treated with Ruppert's reagent in DCM, the desired [(tmeda)Ni(Ph)CF_3] **17** was obtained (Table 1.2, entry 2-3). However, obtained yield was

only 20% yield.

Table 1.2. Failed attempts to prepare a phenyl trifluoromethyl nickel complex with an exchangeable ligand



X=Cl, **15**
X=Br, **16**

17

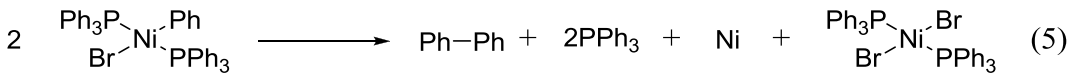
entry	X	reagent (eq.)	condition	Concentration (M)	yield[a] (%)
1	Cl	$TMSCF_3$ (2), CsF (2)	DCM, rt, 1 d	0.05	0
2	Cl	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.05	10-20
3	Cl	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.1	10-20
4	Cl	$TMSCF_3$ (1), AgF (1)	CH_3CN, rt. 1 d	0.1	10-20
5	Br	$TMSCF_3$ (2), CsF (2)	DCM, rt, 1 d	0.1	10-20
6	Br	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.05	10-20
7	Br	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.1	10-20
8	Br	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.2	10-20
9	Br	$TMSCF_3$ (1), AgF (1)	CH_3CN, rt. 1 d	0.05	10-20
10	Br	$TMSCF_3$ (1), AgF (1)	CH_3CN, rt. 1 d	0.1	10-20

[a] Yields were monitered by ^{19}F NMR

The combination of Ruppert's reagent and AgF, resulting in the formation of $AgCF_3$, was reacted with [(tmeda)Ni(Ph)Cl] **15** to give the desired phenyl trifluoromethyl nickel complex **17** in extremely low yield (Table 1.2, entry 4). [(tmeda)Ni(Ph)Br] **16** in THF or DCM was fairly stable compared to [(tmeda)Ni(Ph)Cl] **15** solution, but desired [(tmeda)Ni(Ph)CF_3] **17** was obtained in less than 20% yield according to this protocol (Table 1.2, entry 5-8). [(tmeda)Ni(Ph)Br] was reacted with $AgCF_3$, but the desired complex was obtained in so low yield as other entries (Table

1.2, entry 9-10).One of the explanations for obtained low yield was that biphenyl was obtained during the reaction as result of dimerisation. Biphenyl can be removed by washing with pentane, but the resulting residue was obtained only 20% yield (Table 1.2 2-5 entries). Concentration was a big factor to affect the reaction rate and yield, but it was found that concentration was not so important to affect the transmetalation reactions (Table 1.2 2-3 and 6-10 entries).

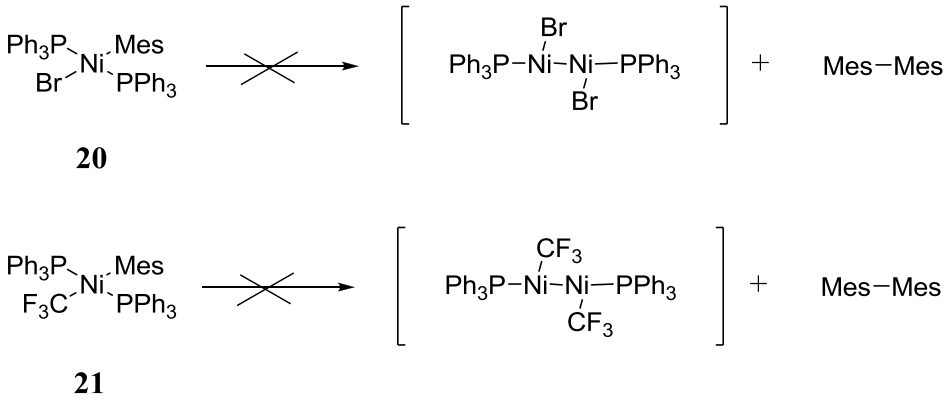
Triphenyl phosphine was chosen as a next target ligand for furthermore investigation. Several synthetic pathways of $[(PPh_3)_2Ni(Ar)Br]$ were reported.[36] $[(PPh_3)_2Ni(Ph)Br]$ **19** in the solid state was air-stable, but it was unstable in solution state. $[(PPh_3)_2Ni(Ph)Br]$ **19** was easily decomposed to give biphenyl as a major byproduct reported by Koeckelberghs (eq 5).[36]



(5)

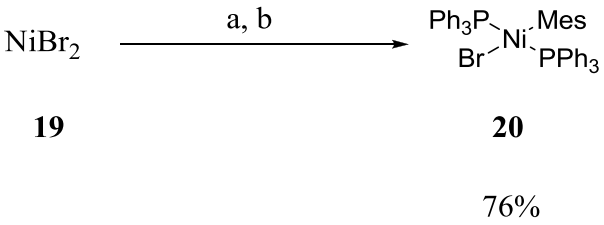
18

In my hands, the same result was obtained. Then $[(PPh_3)_2Ni(Mes)Br]$ **20** was chosen because of robust stability in solution state. Moreover, the resulting $[(PPh_3)_2Ni(Mes)CF_3]$ **21** was certainly stable toward dimerization because biaryl was obtained via the formation of the dinuclear complex and highly bulky Mes substituent hinders the formation of a Ni-Ni bond (Scheme1.26).



Scheme 1.26. Stability of Mes nickel complexes toward dimerisation.

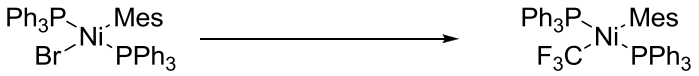
[$(PPh_3)_2$Ni(Mes)Br] **20** was obtained from the mixture of $NiBr_2$ **19** and PPh_3 in THF treated with MesMgBr in 76% yield as shown in Scheme 1.27.



Scheme 1.27. a) PPh_3 (2 eq), THF, rt, overnight, b) MesMgBr (1 eq), 0 ^oC, 30 min

The reactivity of [$(PPh_3)_2$Ni(Mes)Br] **20** was examined. The reaction of Ruppert's reagent and CsF with [$(PPh_3)_2$Ni(Mes)Br] **20** did not give the desired complex **21** (Table 1.3, entry 1-3). $AgCF_3$, also was not reacted with [$(PPh_3)_2$Ni(Mes)Br] **20** (Table 1.3, entry 4-5). Concentration did not affect the reaction yield (Table1.3, entry 2-5). Presumably, trifluoromethylation was prevented by highly bulky PPh_3 ligand from nucleophilic substitution attack. [$(PPh_3)_2$Ni(Mes)Br] **20** was extremely stable, but it was found that [$(PPh_3)_2$Ni(Mes)Br] **20** was inert toward Ruppert's reagent activated fluoride anion and $AgCF_3$.

Table 1.3. Failed attempts to prepare an aryl trifluoromethyl nickel complex

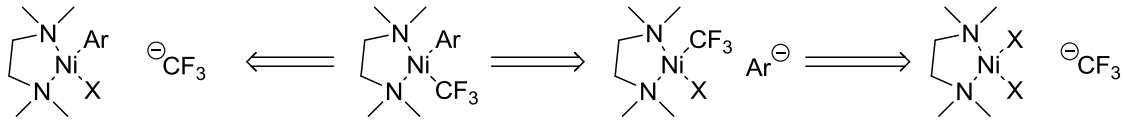


20 **21**

entry	reagent (eq.)	condition	Concentration (M)	yield[a] (%)
1	$TMSCF_3$ (2), CsF (2)	DCM, rt, 1 d	0.05	0
2	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.05	0
3	$TMSCF_3$ (2), CsF (2)	THF, rt, 1 d	0.2	0
4	$TMSCF_3$ (1), AgF (1)	CH_3CN, rt. 1 d	0.05	0
5	$TMSCF_3$ (1), AgF (1)	CH_3CN, rt. 1 d	0.1	0

[a] Yields were monitered by ^{19}F NMR

Then, another synthetic pathway was considered as shown in Scheme 1.28.

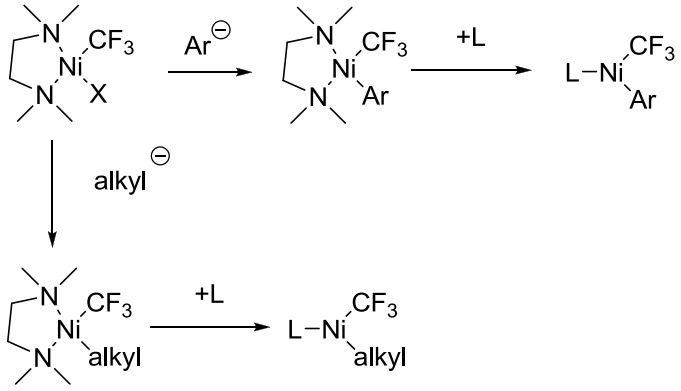


Path 1 Path 2

Scheme 1.28. Synthetic pathway for an aryl trifluoromethy nickel complex

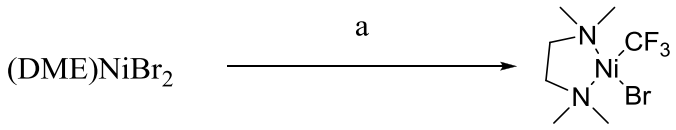
Path 1 was rather reliable pathway to make the desired metal complex such as palladium and nickel complexes as described section 1.1.5 and 1.1.6. In path 2, aryl Grignard reagent or aryl lithium reagent would be used to introduce Ar group after following the introduction of mono trifluoromethyl group of [(tmeda)NiX_2]. If the key intermediate [(tmeda)Ni(CF_3)X] were isolated, it would have a good access to not only aryl trifluoromethyl nickel complexes, but also alkyl trifluoromethyl nickel complexes. The reaction of a variety of Grignard reagent or lithium reagent and trifluoromethyl nickel complex with an exchangeable ligand would yield any

trifluoromethyl nickel complexes. In addition, these complexes would give us more detailed information of trifluoromethyl nickel chemistry.



Scheme 1.29. Synthetic pathway for a variety of trifluoromethyl nickel complexes

The key step of introduction of mono trifluoromethyl group was pretty successful. [(tmeda)$NiBr_2$] was reacted with $AgCF_3$ in CH_3CN at rt for 2 days to afford the desired [(tmeda)Ni(CF_3)Br] **22** in 60 % yield in a good accord with theoretical elemental analysis. In the synthesis of [(tmeda)Ni(CF_3)Br] **22**, a nickel dibromide complex was not found by ^1H NMR and ^{19}F NMR, because [(tmeda)$NiBr_2$] showed paramagnetic behavior.



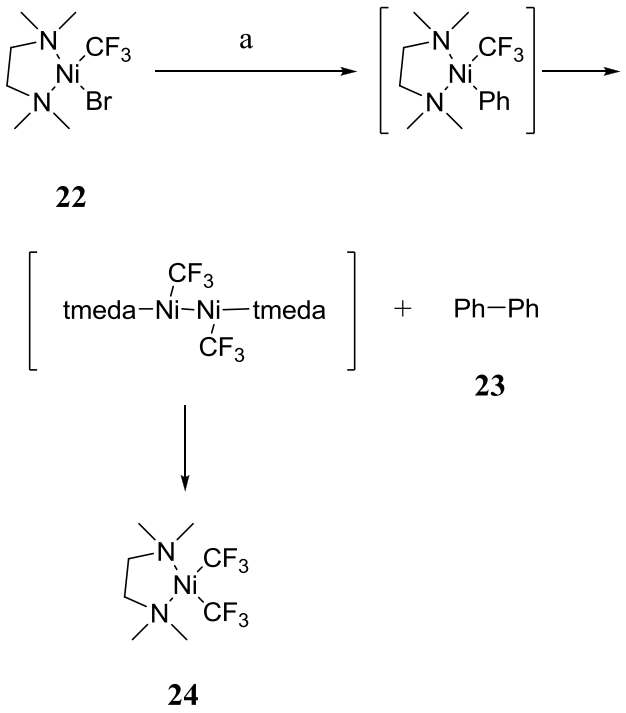
10 **22**

60%

Scheme 1.30. a) $TMSCF_3$ (1 eq.), AgF (1 eq.), CH_3CN, rt, 2 d

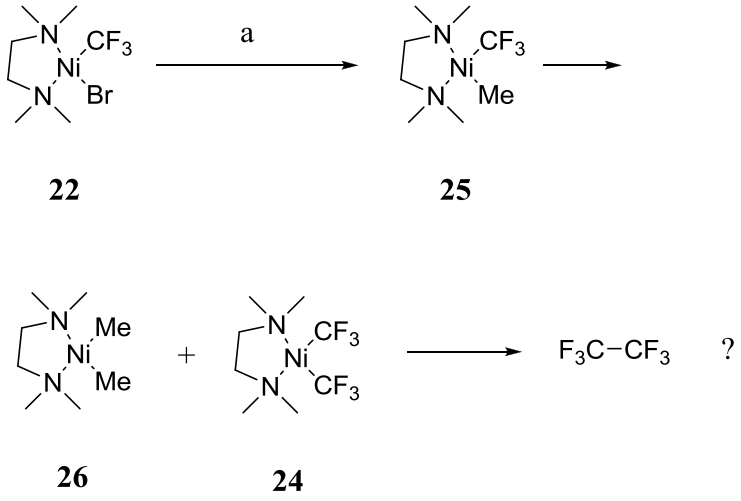
1.2.8. Studies for Aryl and Methyl Trifluoromethyl Nickel Complex

As final route to introduce aryl group into [(tmeda)Ni(CF_3)Br] was investigated as shown in Scheme 1.27. Phenyl Grignard reagent was used to make the desired [(tmeda)Ni(CF_3)Ar] complex, but the desired complex was not found in ^{1}H NMR and ^{13}C NMR analysis. Instead of the desired complex, bipheny and [(tmeda)Ni(CF_3)$_2$] were obtained by means of TLC and ^{19}F NMR spectroscopy. When phenyl Grignard reagent was added into THF solution of **22**, pink color changed immediately brown color. However, TLC analysis showed one spot, biphenyl **23** and the other yellow spot, [(tmeda)Ni(CF_3)$_2$] **24**. Presumably, [(tmeda)Ni(CF_3)Ph] was obtained as intermediate and immediately underwent disproportionation to yield dinuclear species. The formation of a Ni-Ni bond caused the dimerization, yielding to [(tmeda)Ni(CF_3)$_2$] **24** and biphenyl **23** as a major byproduct.



Scheme 1.31. a) PhMgCl (1eq.), THF, - 30 ^{o}C, 15 min

Methyl Grignard reagent was employed for further investigation of reactivity towards nickel complex **22**. One eq. of methyl Grignard was reacted with nickel complex **22** at -30 ^{o}C for 15 min, and the desired complex was apparently formed as shown in Scheme 1.32.



Scheme 1.32. a) MeMgCl (1eq.), THF, - 30 ^{o}C, 15 min

However, ^{1}H NMR indicated two tmeda singals and ^{19}F NMR showed the presence of CF_3-CF_3 as a trace amount of impurity. Presumably, the desired complex [(tmeda)Ni(CF_3)Me] **25** was obtained similar to the reaction of phenyl Grignard reagent and nickel complex **22**. A trace amount of desired complex underwent dimerization to give a bis-CF_3 complex **24** and [(tmeda)Ni($Me)_2$] **26**. Interestingly, this bis-CF_3 complex did reductive elimination to afford CF_3-CF_3 as an impurity confirmed by ^{19}F NMR. We were not sure what triggered the reductive elimination of this bis-CF_3 complex **24**. To get pure [(tmeda)Ni(CF_3)Me] **25**, specific work-up and caution will have to be done for future studies.

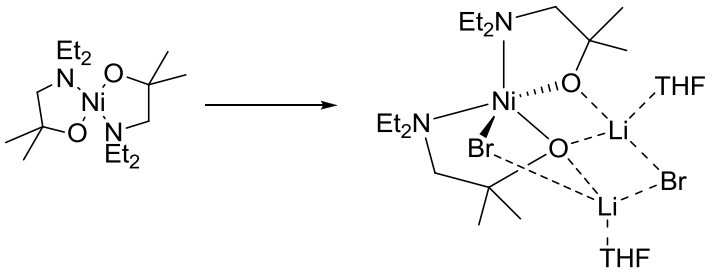
In both cases, the desired complexes were obtained as intermediates. However, to isolate pure complexes, work-up, and reaction conditions, and other lithium reagents must be examined in the future studies.

1.3 Conclusion

We have demonstrated the synthesis of [(dtbpy)Ni(CF_3)$_2$] **3** and [(dtbpy)Ni(CF_2CF_3)$_2$] **13** in moderated yields. We also succeeded in isolation of the key intermediate nickel complex, [(tmeda)Ni(CF_3)Br] **22** in good yield. This key intermediate has a potentially good access to a variety of nickel complexes such as [LNi(CF_3)(Ar)] and [LNi(CF_3)(alkyl)] in the future studies. These complexes would experimentally simplify optimizing conditions and ligand screens for aryl and alkyl trifluoromethyl cross-coupling reactions and also allow us to investigate the fundamental chemistry of trifluoromethyl nickel complexes. With these complexes, we can explore the possibilities of both Ar-CF_3 and alkyl-CF_3 reductive eliminations at nickel. We also discovered an unusual reaction where a chiral-at-metal complex can be precipitated. This chiral nickel complex is a potentil catalyst for asymmetric reactions in future studies.

1.4. Experimental Section

General Considerations. All manipulations were performed using standard Schlenk and high vacuum techniques or in a nitrogen filled glovebox. Solvents were distilled from Na/benzophenone or CaH_2. DMF was distilled over BaO under reduced pressure. All reagents were used as received from commercial vendors, unless otherwise noted. Elemental analyses were performed by Columbia Analytical Services. ^{1}H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent signals. ^{13}C NMR spectra were recorded on the Varian Oxford spectrometers operating 75 MHz or 126 MHz and referenced to solvent signals. ^{19}F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz and were referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7). UV-vis absorption spectra were recorded in 1 cm quartz cells using a Varian Cary 50 Scan photospectrometer.



8 **9**

Preparation of compound 9: LiBr (40 mg, 0.46 mmol) was added to the suspension of complex **8** (79 mg, 0.23 mmol) in THF 3 mL. This reaction mixture was stirred for 3 days at room temperature to yield an orange brown residue. The volatiles were then removed under the reduced pressure. The residue was dissolved in a minimum amount of THF and then layered with pentane and stored at -35 °C. Orange crystals precipitated, which were washed with cold (-35 °C) pentane, and dried in vacuo to yield the bis-LiBr·THF adduct (96 mg, 63% yield). Compound **3** is NMR silent. Loss of THF prohibited good elemental analyses: Anal. Calcd (found) for $C_{24}H_{52}Br_2Li_2N_2NiO_4$: C, 43.34 (38.50); H, 7.88 (7.18).

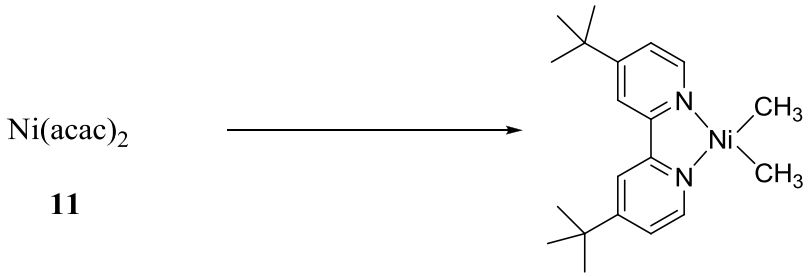
Table 1.4. Crystal data and structure refinement parameters for **9**

Compound	**9**
chemical formula	$C_{24}H_{52}Br_2Li_2N_2NiO_4$
formula weight	665.08
crystal dimensions (mm)	0.35 x 0.22 x 0.14
color, habit	orange, prism
crystal system	orthorhombic
wavelength, Å	0.7107
space group, Z	$P2_12_12_1$, 4
a, Å	11.276(11)
b, Å	13.736(13)
c, Å	20.651(20)
α (deg)	90
β (deg)	90
γ (deg)	90
vol, $Å^3$	3199(5)
ρ_{calc}, g cm^{-3}	1.381
temp, K	173
Residuals: R1 [I>2sigma(I)]	0.0464
R indices [all data]	0.0914, 0.1086
goodness of fit	0.899
θ range, deg	1.78-27.49
number of data collected	30110
number of unique data	7212
R_{int}	0.1011

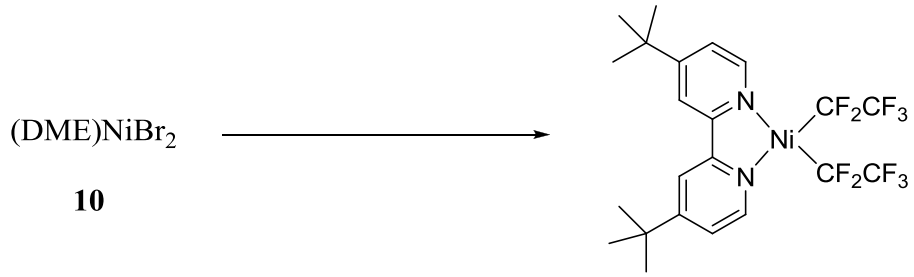
Preparation of [(dtbpy)Ni(CF_3)$_2$] 3: A 100 mL round-bottom flask was charged with (DME)$NiBr_2$ **10** (0.202 g, 0.65 mmol), dtbpy (0.201 g, 0.75 mmol), and THF (10 mL). Within a few minutes, the solution had turned green. After stirring at room temperature for 10 min, DMF (5 mL) and CsF (0.451 g, 2.97 mmol) were added to the flask. After 5 min, a DMF solution of Me_3SiCF_3 (0.430 g, 3.02 mmol in 3 mL of DMF) was added dropwise. The reaction mixture was stirred for overnight, and then the volatiles were removed under reduced pressure. The residue was redissolved in Et_2O (40 mL), the solution was passed through a celite pad on a glass filter. After removing the volatiles, the residual solid was washed with hexane (10 mL x 2) and dried in vacuo to yield [(dtbpy)Ni(CF_3)$_2$] as a yellow powder (0.033 g, 0.071 mmol, 11%). Suitable single crystals for X-ray analysis were obtained by recrystallization from THF/pentane at -35 °C. ^{1}H NMR (300MHz, THF-d_8): 8.60 (d, J = 6.0 Hz, 2H, dtbpy), 8.19 (s, 2H, dtbpy), 7.66 (d, J = 6.0 Hz, 2H, dtbpy), 1.41 (s, 18H, CH_3). ^{13}C NMR (126 MHz, THF-d_8); 165.5 (s, dtbpy), 155.8 (s, dtbpy), 153.1 (s, dtbpy), 131.3 (quartet, $^1J_{CF}$ = 369.1 Hz, CF_3), 124.5 (s, dtbpy), 119.2 (s, dtbpy), 36.3 (s, $C(CH_3)_3$), 30.3 (s, $C(CH_3)_3$). ^{19}F NMR (282 MHz, THF-d_8): -28.7. Anal. Calcd (found) for $C_{20}H_{24}F_6N_2Ni$: C, 51.65 (51.13); H, 5.20 (5.79); N, 6.02 (5.99).

Table 1.5. Crystal data and structure refinement parameters for **3**

Compound	**3**
chemical formula	$C_{24}H_{32}F_6N_2NiO$
formula weight	537.22
crystal dimensions (mm)	0.40 x 0.10 x 0.10
color, habit	orange, prism
crystal system	monoclinic
wavelength, Å	0.71075
space group, Z	C2/c
a, Å	21.386(18)
b, Å	12.908(11)
c, Å	18.422(15)
α (deg)	90
β (deg)	90
γ (deg)	90
vol, $Å^3$	5077(7)
ρ_{calc}, g cm^{-3}	1.405
temp, K	173
Residuals: R1 [I>2sigma(I)]	0.0832
R indices [all data]	0.1513,0.2823
goodness of fit	1.026
θ range, deg	0.696 - 0.921
number of data collected	24010
number of unique data	5648
R_{int}	0.098



Preparation of [(dtbpy)NiMe$_2$] 12: dtbpy (0.358 g, 1.33 mmol) was added to Ni(acac)$_2$ **11** (0.327 g., 1.27 mmol) dissolved in 10 mL (THF). This suspension was stirred over 1 hour at -20 ^{o}C. MeMgCl (3.0 M in ether, 869 *u*L, 2.61 mmol) was dropwised to this suspension which turned immediately dark green solution. After stirring 1 hour at -20 ^{o}C, the reaction mixture was passed through a glass filter. The volatiles of this resulting dark green solution were removed under the reduced pressure. The residue was extracted with toluene and then filtered through a glass filter. After the removal of solvent, the residual solid was washed with pentane and dried in vacuo at 0 ^{o}C to give the desired [NiMe$_2$(dtbpy)] as a black powder (0.374 g, 1.06 mmol, 83%). ^{1}H NMR (300MHz, benzene-d_6): 9.04 (d, J = 6.0 Hz, 2H, dtbpy), 7.43 (s, 2H, dtbpy), 6.72 (d, J = 6.0 Hz, 2H, dtbpy), 1.01 (s, 18H, CH_3), 0.98 (s, 6H, CH_3). ^{13}C NMR (126 MHz, benzene-d_6): 158.3 (s, dtbpy), 154.8 (s, dtbpy), 147.6 (s, dtbpy), 123.3 (s, dtbpy), 116.4 (s, dtbpy), 34.9 (s, $C(CH_3)_3$), 29.9 (s, $C(CH_3)_3$), -4.5 (s, CH_3).

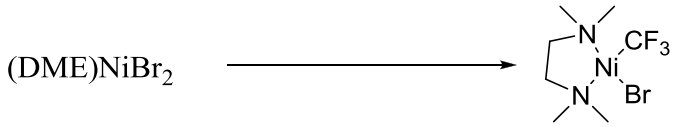


13

Preparation of [(dtbpy)Ni(CF_2CF_3)$_2$] 13: This complex was obtained from (DME)$NiBr_2$ **10** (0.201 g, 0.65 mmol), dtbpy (0.181 g, 0.67 mmol), CsF (0.450 g, 2.96 mmol), $Me_3SiCF_2CF_3$ (0.502 g, 2.61 mmol), THF (10 mL), and DMF (8 mL) in the same manner as that for [Ni(CF_3)$_2$(dtbpy)]. The complex was isolated as an orange powder (0.071 g, 0.13 mmol, 20%). Suitable single crystals for X-ray analysis were obtained by recrystallization from THF/pentane at -35 °C. ^{1}H NMR (300MHz, THF-d_8): 8.61 (d, J = 6.3 Hz, 2H, dtbpy), 8.17 (d, J = 1.8 Hz, 2H, dtbpy), 7.66 (dd, J = 6.3, 1.8 Hz, 2H, dtbpy), 1.41 (s, 18H, CH_3). ^{13}C NMR (126 MHz, THF-d_8); 165.5 (s, dtbpy), 155.6 (s, dtbpy), 153.1 (s, dtbpy), 124.3 (s, dtbpy), 119.5 (s, dtbpy), 36.3 (s, $C(CH_3)_3$), 30.2 (s, $C(CH_3)_3$). Although the signals assignable to CF_2CF_3 carbons were observed at 117 ~ 126 ppm, the chemical shifts for them were not able to be determined due to overlapping with the signals of dtbpy and complicated C-F couplings. ^{19}F NMR (282 MHz, THF-d_8): -79.0 (CF_3), -102.6 (CF_2). Anal. Calcd (found) for $C_{22}H_{24}F_{10}N_2Ni$: C, 46.67 (46.97); H, 4.28 (4.47); N, 4.96 (4.86).

Table 1.6. Crystal data and structure refinement parameters for **13**

Compound	**13**
chemical formula	$C_{22}H_{24}F_{10}N_2Ni$
formula weight	565.14
crystal dimensions (mm)	0.30 x 0.12 x 0.10
color, habit	orange, rod
crystal system	morphology
wavelength, Å	0.71073
space group, Z	*P21/c*
a, Å	13.355(3)
b, Å	9.754(2)
c, Å	17.601(4)
α (deg)	90
β (deg)	90
γ (deg)	90
vol, Å^3	2288.9(9)
ρ_{calc}, g cm^{-3}	1.64
temp, K	173
Residuals: R1 [I>2sigma(I)]	0.0765
R indices [all data]	0.1130, 0.1912
goodness of fit	1.12
θ range, deg	1.53-27.48
number of data collected	50084
number of unique data	5262
R_{int}	0.1186



10 **22**

Preparation of [(tmeda)Ni(Br)(CF_3)] 22: $TMSCF_3$ (260mg, 1.8 mmol) and AgF (233mg, 1.8 mmol) were added into 35 mL of dry CH_3CN. After stirring for 1 hour at room temperature, $(DME)NiBr_2$ **10** (564mg, 1.8 mmol) was added. *N,N,N,N*-tetramethylethane-1,2-diamine (212mg, 99%, 1.8 mmol) was added over 1 hour. The reaction mixture was stirred for 2 days, and then filtered. The volatiles were removed under reduced pressure. The residue was extracted by THF, and filtered. Then filtrate was redissolved in THF. Pentane was added into this solution, which was stirred for 30 more minutes at room temperature. The resulting precipitate was washed with pentane, and dried on a vaccum line to yield a pink powder (353mg, 60%) ^{1}H NMR (300MHz, dichloromethane-d_2): 2.57 (s, 12H, tmeda), 2.38 (s, 4H, tmeda). ^{13}C NMR (126MHz, dichloromethane-d_2): 126.4 (quartet, $^1J_{CF}$=365.4 Hz, CF_3), 61.3 (s, tmeda), 49.1 (s, tmeda). ^{19}F NMR (282 MHz, dichloromethane-d_2): -28.3. Anal. Calcud (found) for $C_7H_{16}BrF_3N_2Ni$: C, 25.96 (25.82); H, 4.98 (4.95); N, 8.65 (8.67).

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