EFFORTS TOWARDS UNDERSTANDING THE NICKEL CATALYZED CYCLOADDITION OF DIYNES AND NITRILES TO MAKE PYRIDINES

by

David Robert Thomas

A thesis submitted to the faculty of
The University of Utah
in partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemistry

The University of Utah

May 2014

The University of Utah Graduate School

STATEMENT OF THESIS APPROVAL

The thesis of **David Robert Thomas**

has been approved by the following supervisory committee members:

Janis Louie	, Chair	**12/13/2011** Date Approved
Ryan Looper	, Member	**12/13/2011** Date Approved
Ilya Zharov	, Member	**12/13/2011** Date Approved

and by **Cynthia J. Burrows**, Chair/Dean of the Department/College/School of **Chemistry**

and by David B. Kieda, Dean of The Graduate School.

ABSTRACT

Efforts towards understanding the nickel catalyzed cycloaddition of diynes and nitriles to make pyridines are described. During the course of this mechanistic study, a previously uncharacterized class of nickel-nitrile-NHC (N-heterocyclic carbene) dimers, which display cooperative η^1 and η^2 binding modes of the nitrile to nickel, were discovered. Crystal structures were obtained for select dimers. These dimers proved catalytically competent in the cycloaddition reaction. Pseudo first order kinetics revealed that the reaction was first order in dimer while being zero order in NHC ligand, nitrile, and diyne. While stoichiometric reactions with dimer and diyne in the absence of nitrile did give product, largely improved yields were observed in the presence of free nitrile. Stoichiometric competition studies utilizing various identities of free nitriles and dimers indicated a preference for incorporation of free nitrile into the product versus the dimer-bound nitrile. The results of this study suggest a mechanism involving partial dimer opening as the rate-determining step. This is then followed by nitrile binding, which precedes oxidative coupling with diyne.

Dedicated to my parents who have given me unwavering support and love throughout my life.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to first acknowledge Dr. Janis Louie. Her support, both in the form of facilities and supplies and in the form of encouragement and guidance, has been the cornerstone of my graduate career. She is a mentor with whom I could discuss not just chemistry, but life as well, and for that, I am very grateful.

I would also like to thank the other members of the Louie group, both past and present. True friends are among the most important treasures a person can have. In that respect, I have been extremely lucky due to the friendships I have developed while working in this lab. Though I cannot list everyone and how they have impacted my life, because it would double the length of this thesis, a special thanks to all of you. Also, a special thanks is due to Dr. Hung Duong, who pioneered this project and did significant work, as well as Ryan Stolley, who also contributed to the project.

Additionally, I would like to thank the University of Utah and in particular the Department of Chemistry for the opportunity to study here. Many individuals within the department have helped me along the way. While these are many, I would like to single out Dr. Greg Owens for his guidance and support. Additionally, I would like to thank Dr. Peter Flynn for the many hours of help with NMR-related issues. Similarly, I would like to thank Dennis Edwards and Dr. Atta Aarif for their help with NMR issues and obtaining crystal structures.

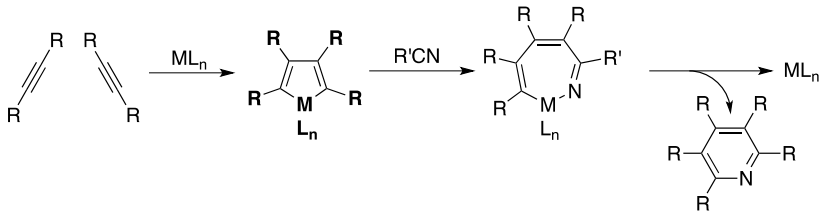
Lastly, and most importantly, I would like to thank my parents, Tom and Brenda Thomas, and my wife, Heather Thomas, for their love and support. They are my strength and the solid foundation for all that I do. Thank you for all the time and effort you have given to help me succeed.

Reproduced in part with permission from Stolley, R. M.; Duong, H. A.; Thomas, D. R.; Louie, J. *J. Am. Chem. Soc.*, **2012**, 134, 15154. Copyright 2014 American Chemical Society.

INTRODUCTION

The ability to synthesize structurally diverse pyridine-based molecules is an important tool in the synthesis of analogue scaffolds as the search continues for drugs that have both structural simplicity and high efficacy for their intended target. Transition-metal catalyzed methods to reach pyridine cores are becoming a preferred method as they hold the potential to access highly functionalized pyridines in a simplistic and atom economical fashion.[1] A handful of transition metals have demonstrated the ability to co-cyclize alkynes and nitriles to make pyridines catalytically. Specifically, Co,[2] Ru,[3] and Rh[4] have received considerable attention, and more recently, Ni[5] and Fe[6] have also shown the ability to catalyze pyridine formation.

Of these transition metals, the Co mechanistic pathway is the most thoroughly studied. It is believed that the Co catalyzed reaction goes through a homocoupling pathway, i.e., it undergoes a homo-oxidative coupling of the two

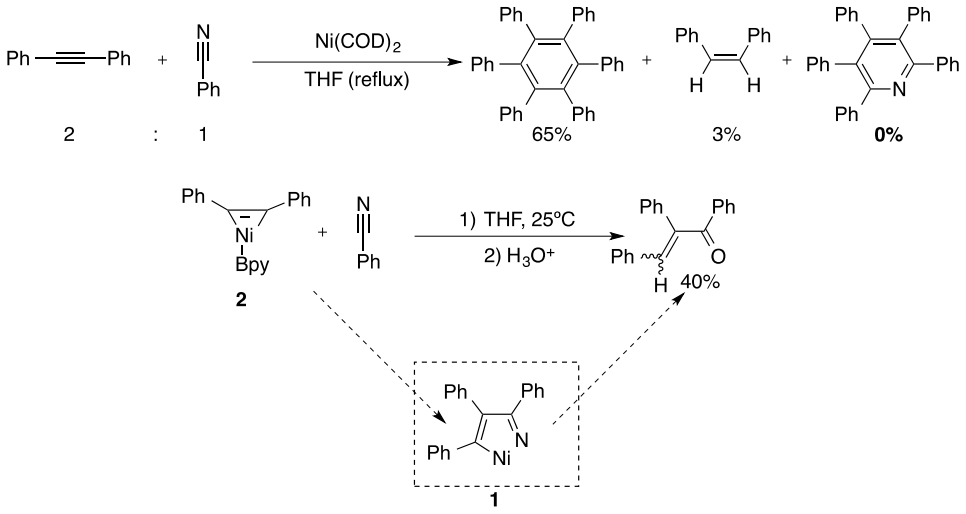


Scheme 1. Homocoupling pathway with a metallacyclopentadiene intermediate

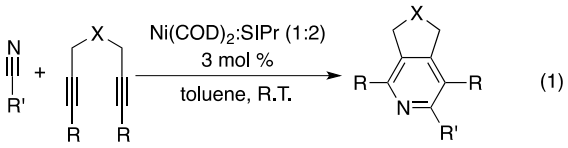
alkynes of the diyne before inserting the nitrile (Scheme 1).[2c,7] While less studied, the reactions catalyzed by Ru and Rh are believed to undergo a similar type of mechanism.[3a,3b,4a,7]

Much less is known about the Ni and Fe catalyzed reactions. The niche of information that is available about nickel's interactions with diynes and nitriles hint that Ni may "prefer" a heterocoupling pathway. Specifically, Eisch and coworkers demonstrated the difficulty of reaching a heterocoupled type intermediate (**1**) when both nitrile and alkyne are present.[8] Such an intermediate was only indicated after hydrolytic workup following subjection of benzonitrile to a previously isolated nickel-bound diphenyl acetylene complex (**2**) (Scheme 2).[8]

We recently reported a Ni/NHC catalyzed route to pyridines.[5] When diynes and nitriles are mixed in the presence of a catalytic amount of $Ni(COD)_2$ and 2 equiv NHC (N-heterocyclic carbene) ligand, pyridines are formed in good to excellent yields (eq 1).



Scheme 2. Difficult route to heterocoupled type intermediate

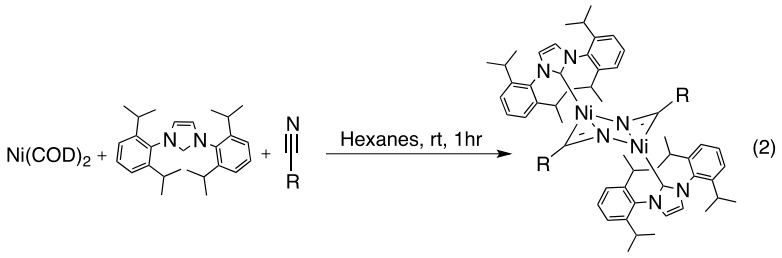


(1)

It is not obvious that a Ni-based catalyst should be able to perform such a transformation to make pyridines from diynes and nitriles. Jones and coworkers, as well as others, have extensively studied the ability of a Ni system to oxidatively add nitriles, both aryl and alkyl.[9] Additionally, it is known that Ni binds pyridines, which could potentially shut down or hinder a catalytic cycle. The ability of Ni to overcome these two documented interactions with nitriles, along with the fact that Ni initially appears to prefer an unexpected heterocoupling mechanism, make the investigation into mapping its catalytic pathway both highly interesting and synthetically necessary.

RESULTS AND DISCUSSION

To probe for species relevant to the reaction pathway, $Ni(COD)_2$ was mixed with IPr and diyne (**4**) in solution, but no product was observed. However, when $Ni(COD)_2$, IPr, and a nitrile were stirred in hexanes, a red to brown precipitate was formed (eq 2). This precipitate was found to be a Ni/NHC/nitrile dimer (**3**) where both nitriles display cooperative η^1 and η^2 binding between two different nickel atoms. Various dimers were synthesized using different nitriles and these are shown in Figure 1.[16]



(2)

A crystal structure was obtained for **3a** and is shown in Figure 2 along with important bond lengths and angles. Importantly, an N-C bond length of 1.226(3) Å was observed. This, along with a stretching frequency of 1757 cm^{-1}, is indicative of an N-C double bond of an η^2 bound nitrile.[9,10,11,12] The Ni-N and Ni-C bond lengths are similar to those of analogous phosphine-bound Ni-nitrile complexes.[11,12] However, the Ni-L bond length of **3a** is shortened (1.8677 Å vs. 2.1-2.2 Å). Interestingly, the nitriles bind two different nickel atoms, both in an η^1 and η^2

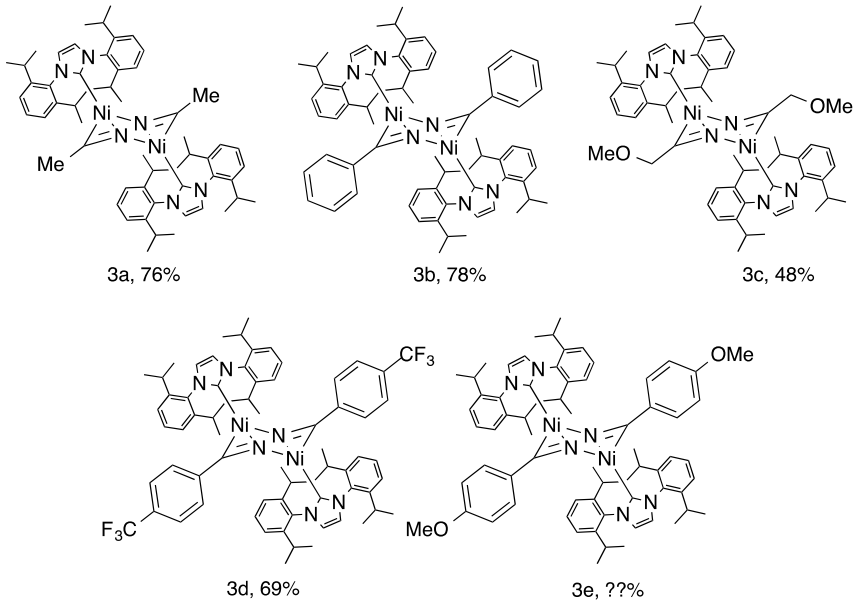


Figure 1. Various Ni/NHC/nitrile dimers synthesized

fashion. While this documented (albeit uncommon) binding mode of nitriles has been observed with select transition metals,[10] to the best of our knowledge, this binding mode has only been observed in nickel species that are tetranuclear.[10,11,12] Importantly, Signer analysis[13] confirmed that **3a** exists as a dimer in solution as well as the solid state (MW = cald. 978.7; obsd 961.9 ± 100). Additionally, a crystal structure was obtained for dimer 3d and is presented along with appropriate bond lengths and angles in Figure 3.

Dimer **3** was found to catalyze the cycloaddition of nitriles and diynes to form pyridines (eq 3). When 5 mol% **3a** was used in the presence of diyne **4** and MeCN, pyridine **5a** was formed in 71% yield. Similarly, when 5 mol% **3b** was used in the presence of **4** and PhCN, pyridine **5b** was formed in 95% yield. These are not largely different from those yields obtained from our originally reported $Ni(COD)_2$/NHC system (69% and 86%, respectively). [5]

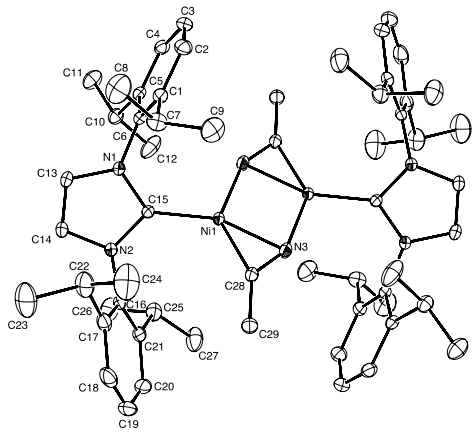


Figure 2. Ortep plot of **3a** at the 30% probability level. Hydrogen atoms omitted for clarity. Pertinent bond lengths include: Ni(1)-C(28): 1.854 Å, Ni(1)-C(15): 1.8677 Å, Ni(1)-N(3): 1.9523 Å, Ni(1)-N(3)_3: 1.9951, N(3)-C(28): 1.226. Pertinent bond angles include: C(28)-Ni(1)-C(15): 120.29°, C(28)-Ni(1)-N(3): 37.37°, C(15)-Ni(1)-N(3)_3: 132.83°, N(3)-Ni(1)-N(3)_3: 95.37°, N(3)-C(28)-C(29): 134.6°.

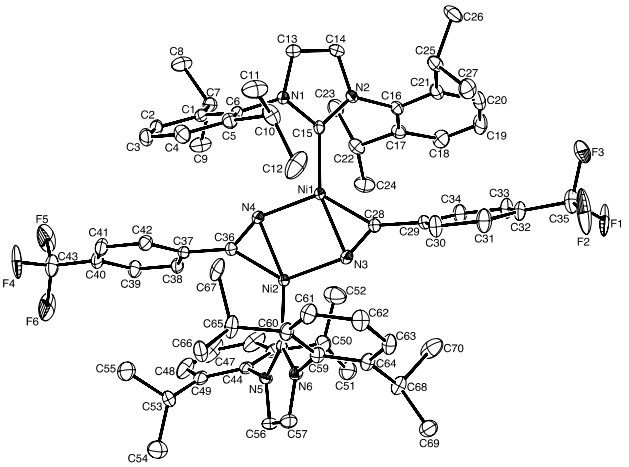
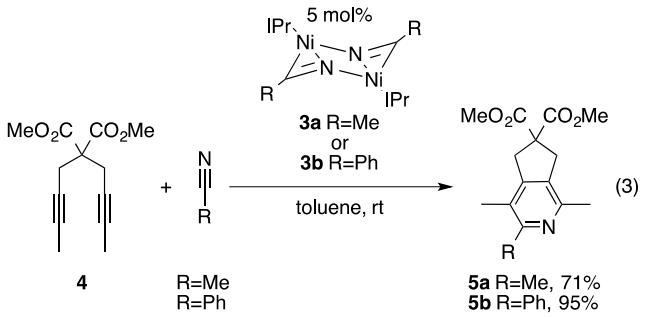
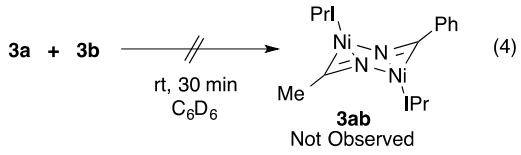
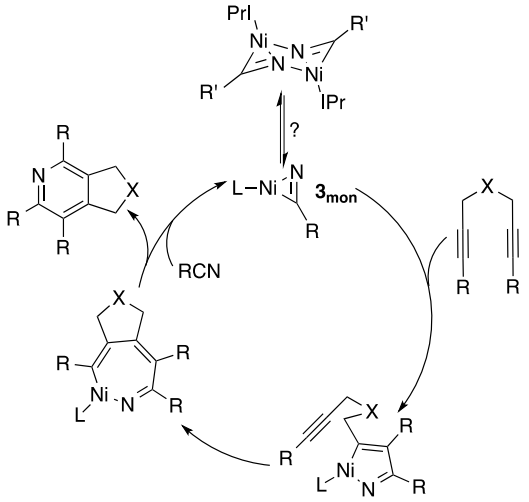


Figure 3. Ortep plot of **3d**. Hydrogen atoms are omitted for clarity. Pertinent bond lengths include: Ni(1)-C(28): 1.857 Å, Ni(1)-C(15): 1.895 Å, Ni(1)-N(3): 1.974 Å, Ni(1)-N(4): 1.982 Å, N(3)-C(28): 1.223 Å. Pertinent bond angles include: C(28)-Ni(1)-C(15): 119.48°, C(28)-Ni(1)-N(3): 37.08°, C(15)-Ni(1)-N(4): 109.50°, N(3)-Ni(1)-N(4): 93.93°, N(3)-C(28)-C(29): 136.1°.



It is easy to envision a mechanism where dimer dissociates to a monomer form (**3a**$_{\mathbf{mon}}$), which could then undergo subsequent oxidative coupling with diyne, followed by insertion and reductive elimination to give the pyridine product (Scheme 3). However, when **3a** and **3b** were mixed in solution using benzene-d_6 at r.t., no significant mixed dimer (i.e., **3ab**) was observed after 30 min (eq 4),[15a] indicating that dimer dissociation to monomer may not be a facile process.



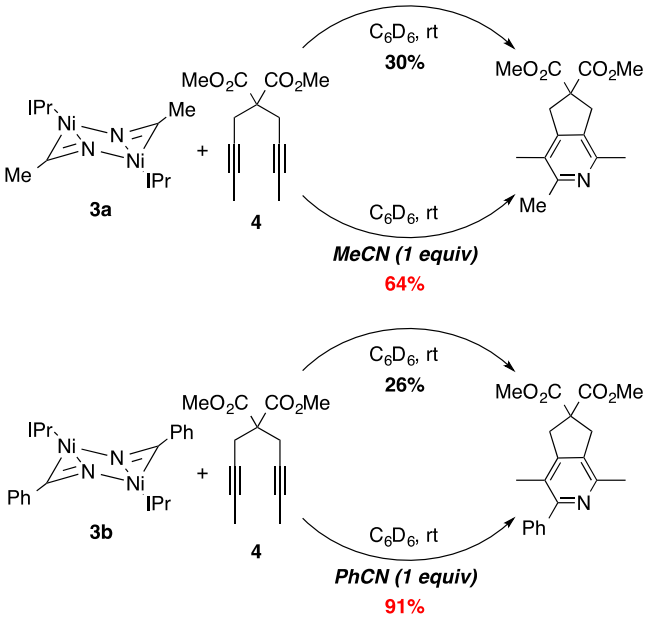


Scheme 3. Possible dimer-to-monomer dissociation

Additionally, and more importantly, stoichiometric reactions of **3a** and **3b** with diyne (**4**) in C_6D_6 at r.t. gave poor yields of pyridine product (30% with **3a**, 26% with **3b**). It was only in the presence of free nitrile that good yields were obtained (64% and 91%, respectively) (Scheme 4), strongly indicating the need for free nitrile in the reaction while discrediting a dimer to monomer mechanism.

Two reasonable pathways available to the dimer, other than dissociation to monomer, could occur through ligand loss or through a partial dimer opening. These pathways are depicted in Scheme 5 along with their corresponding rate laws. If ligand loss is reversible, then an inverse dependence on ligand (IPr) is expected. Additionally, a dependence on diyne (**4**) (pathway A) or MeCN (pathway B) and a dependence on dimer should be observed. Similarly, if partial dimer opening is reversible, a dependence on dimer and either **4** (pathway C) or MeCN (pathway D) is expected but without a dependence on ligand (IPr). In each of the above cases, binding of **4** or MeCN is assumed to be the rate-determining step. However, ligand loss or partial dimer opening could also be rate-determining (pathways E and F, respectively), and in each of these cases, a sole dependence on dimer would be expected.

Pseudo first order kinetic analysis was used to determine the dependence of the reaction on dimer (**3**), diyne (**4**), MeCN, and IPr (Figure 4). All kinetic reactions were run at 0° C in toluene-d_8. The reaction was found to be first order in **3** and 0 order in **4**, MeCN, and IPr, pointing to a mechanism resembling that of pathway E or F (Scheme 5).



Scheme 4. Stoichiometric reactions of **3** with and without added RCN

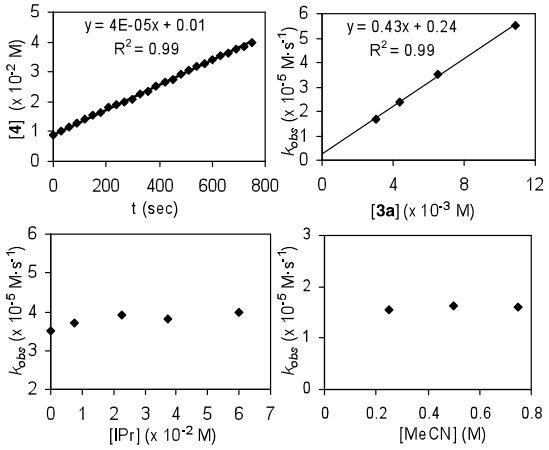
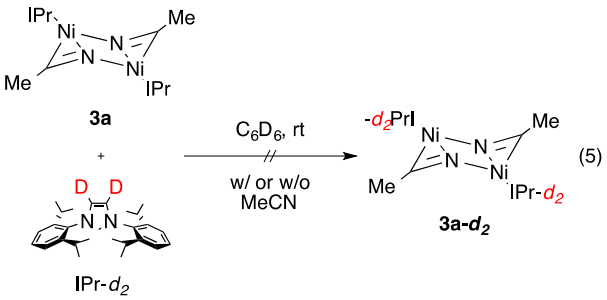
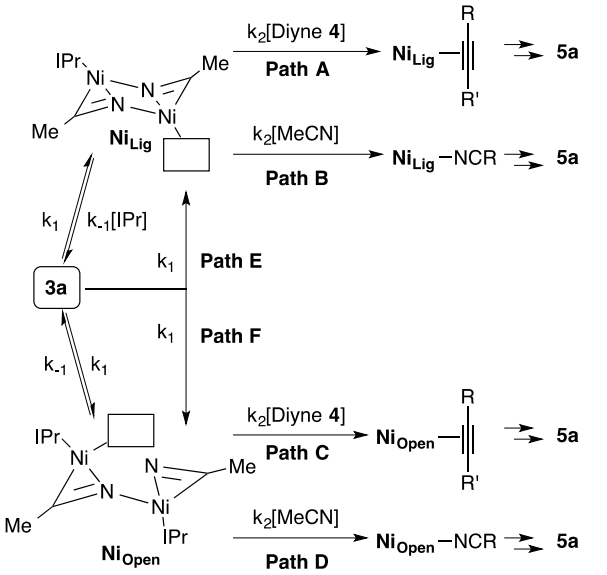


Figure 4. Plots of [**3a**] vs. time, k_{obs} vs. [IPr], and k_{obs} vs. [MeCN] for the cycloaddition of **4** at 0 °C in C_7D_8





Path A: $rate = \frac{k_1 k_2[\mathbf{3a}][\text{Diyne } \mathbf{4}]}{k_{-1}[\text{IPr}] + k_2[\text{Diyne } \mathbf{4}]}$

Path B: $rate = \frac{k_1 k_2[\mathbf{3a}][\text{MeCN}]}{k_{-1}[\text{IPr}] + k_2[\text{MeCN}]}$

Path C: $rate = \frac{k_1 k_2[\mathbf{3a}][\text{Diyne } \mathbf{4}]}{k_{-1} + k_2[\text{Diyne } \mathbf{4}]}$

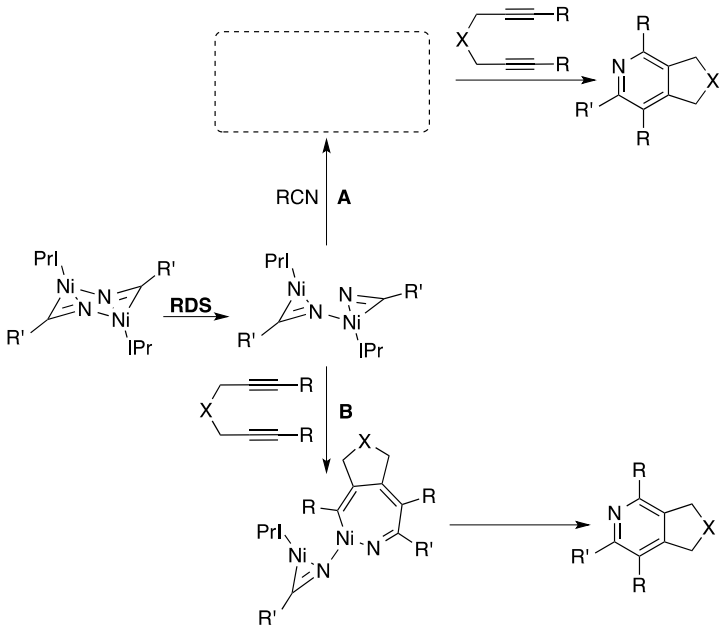
Path D: $rate = \frac{k_1 k_2[\mathbf{3a}][\text{MeCN}]}{k_{-1} + k_2[\text{MeCN}]}$

Path E and F: $rate = k_1[\mathbf{3a}]$

Scheme 5. Possible mechanistic pathways A-F

To differentiate between a rate-determining ligand loss (pathway E) and a rate-determining partial dimer opening (pathway F), ligand exchange experiments were employed. IPr-d_2 was mixed with **3a** in C_6D_6 at r.t., both in the presence and absence of free MeCN (eq 5). No substantial ligand exchange was observed, even after 30 min.[15a] Based on this, it is reasonable to assume a mechanism where dimer opening is the rate-determining step.

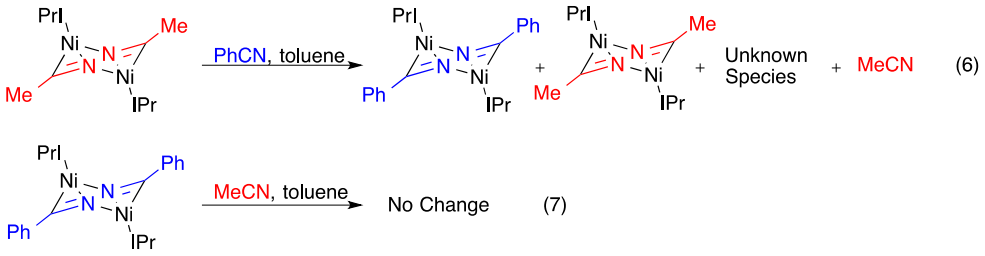
With a rate-determining step so early in the catalytic cycle, it is difficult to propose subsequent reaction steps or intermediates only from the kinetic data. However, it is likely that the reaction proceeds through one of two general pathways (Scheme 6). Pathway A involves interaction between the open dimer and nitrile



Scheme 6. General pathways available to open dimer

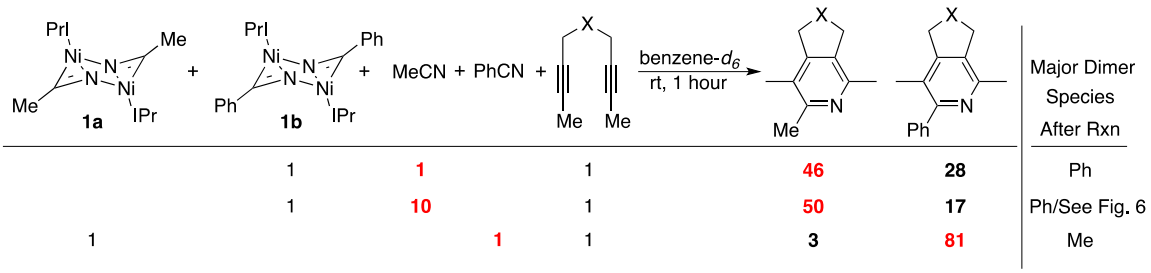
whereas pathway B involves interaction with diyne. If pathway B is operative, it is quite reasonable to visualize oxidative coupling of an alkyne with nitrile followed by insertion of the second alkyne, and finally reductive elimination to give product. Pathway A would be much less intuitive. In hopes of delineating between the two pathways, a series of competition studies were performed in which the identities of dimers and nitriles used were varied.

First, **3a** was placed in solution with free benzonitrile and within minutes at r.t. gave **3b, 3a,** and free acetonitrile along with peaks corresponding to unknown species (eq 6). Conversely, a solution of **3b** and acetonitrile exhibited almost no change under the same conditions and similar amount of time (eq 7), though substantial unknown peaks were observed after 3 h. This demonstrates an obvious preference for nitrile incorporation into the dimer, although whether the preference is electronically or sterically driven is unclear.



To understand whether it is free or bound nitrile that gets incorporated into product, the ratios of products were examined upon varying the identities of the free nitriles and dimers used, as well as their relative amounts. These results are displayed in Table 1.

Table 1. Competition study with Ph and Me dimers and nitriles



		1	1		1	46	28	Ph
		1	10		1	50	17	Ph/See Fig. 6
1				1	1	3	81	Me

Upon examination, the free nitrile that is used, or the one that is "external" to the dimer, appears to be the nitrile that is most widely incorporated into the product. However, it is also interesting that the internal nitrile is still incorporated into a significant amount of product in the case where the external nitrile is MeCN and the dimer used is **3b**. This is not observed when **3a** is subjected to free PhCN. It is also important to note that when the free MeCN is supplied in heavy excess (10 equiv.), the ratio of products observed changes only slightly. Importantly, this demonstrates that the appearance of Ph product cannot simply be explained as an artifact of decreasing concentration of free nitrile during the reaction. In addition to the product ratio, the identity of the dimer at the end of the reaction was monitored. As shown, the identity of the dimer at the end of the reaction is predominately the dimer initially employed for the reaction. However, it is interesting to note that in the case where MeCN in supplied in excess (10 equiv.), there are significant amounts of other species present as indicated by unknown peaks in the proton spectrum (Figure 5). Presumably, some of these belong to the mixed dimer (**3ab**), though attempts to isolate this mixed species thus far have been unsuccessful.

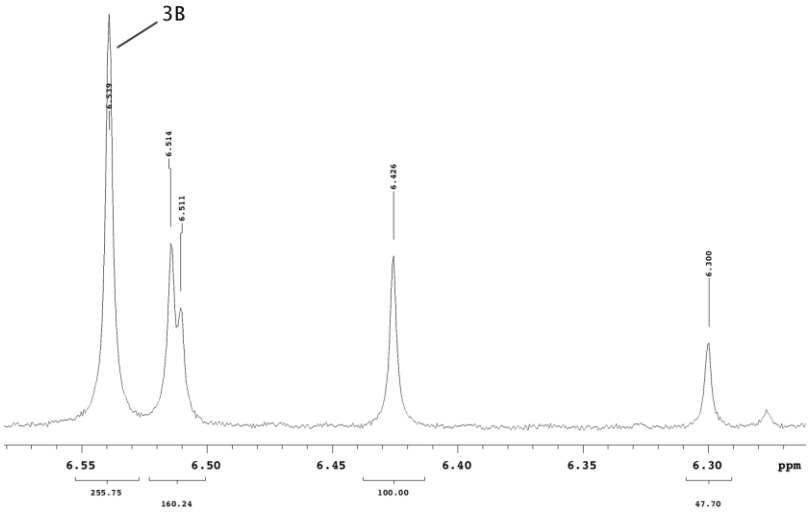
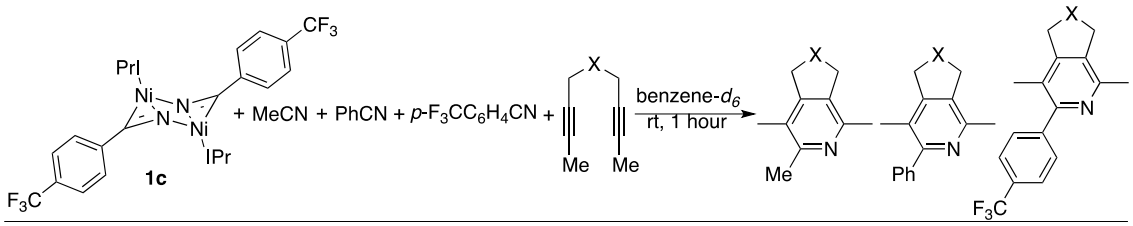


Figure 5. Backbone peak of dimer **3B** and unknown peaks after mixing **3B** (1 eq), **4** (1 eq), and MeCN (10eq) for 1 hr at R.T.

To further probe the reaction's dependence on electronics, other dimers were used in similar competition reactions. These reactions and their results are presented in Tables 2-4.[15b]

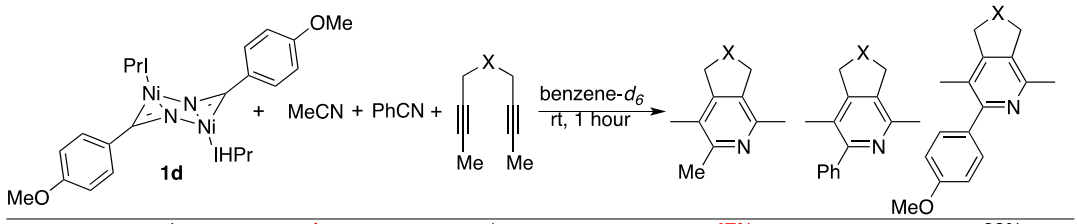
As is the case with the competition reactions involving MeCN and PhCN dimers given in Table 1, regardless of the dimers or nitriles employed, the major product in each reaction stems from incorporation of the external nitrile though some internally generated product is always present. In addition, the yields for product formation when the external nitrile has an aryl group are substantial better than for the alkyl MeCN. Also worth noting, as seen in Table 2 entry 3, when the CF_3 aryl nitrile and MeCN are both present, the aryl nitrile is selectively incorporated into product. The ratio of products from the above tables also demonstrates that when a more donating nitrile dimer (i.e., Me or MeO-aryl) is used with a less electron donating nitrile (i.e., Ph or CF_3-aryl), the product distribution more strongly

Table 2. Competition studies with introduction of CF_3 dimer and nitrile



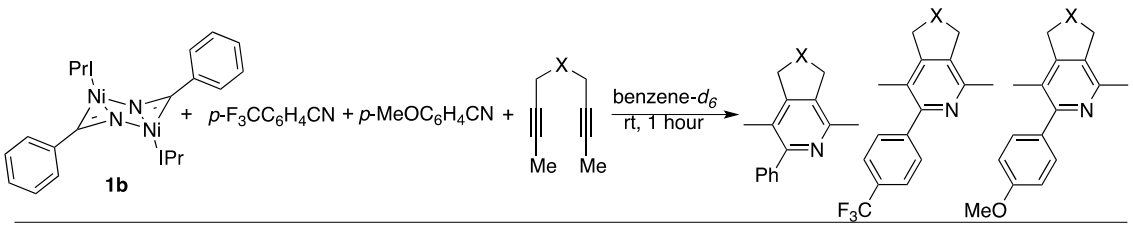
1	1			1	37%	26%
1	10			1	60%	31%
1	1		1	1		88%
1		1		1	78%	18%

Table 3. Competition studies with introduction of MeO aryl dimer



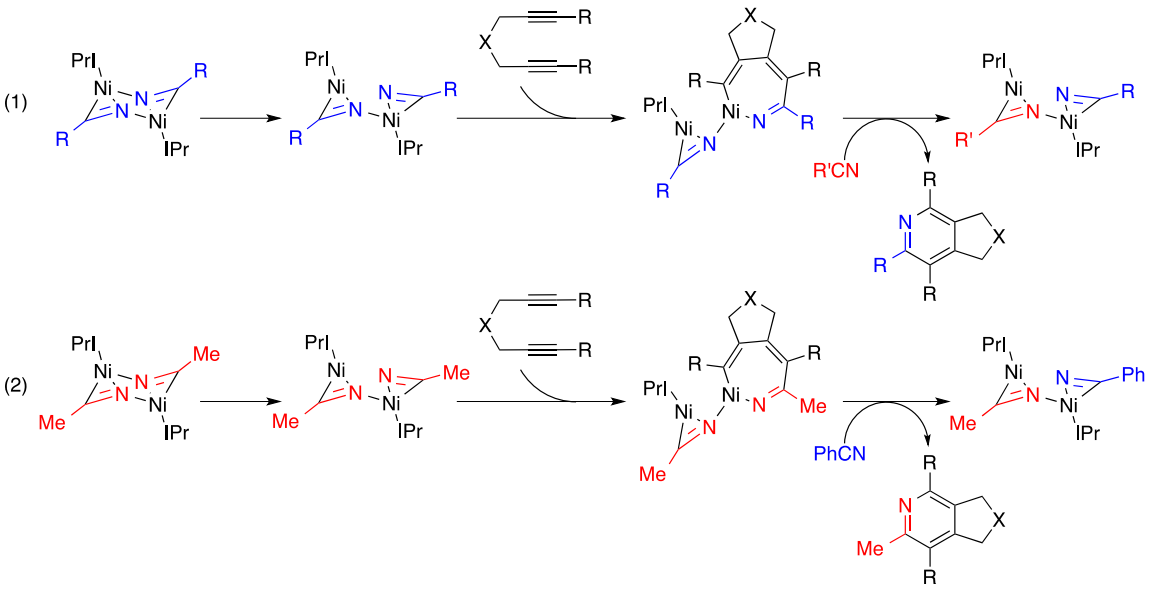
1	1	1	47%		22%
1		1	1	91%	8%

Table 4. Competition studies with Ph dimer and aryl nitriles

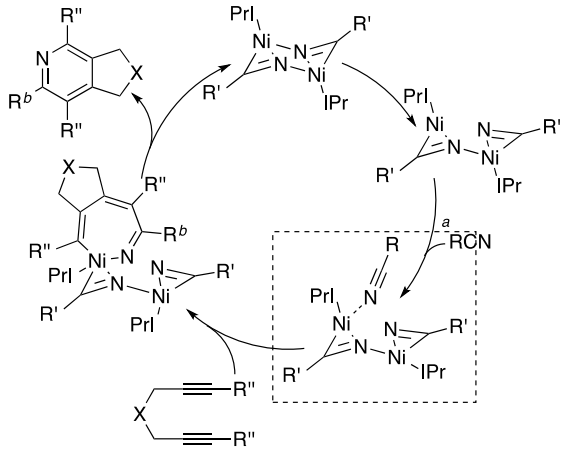


1	1		1	17%	76%
1		1	1	19%	76%

favors free nitrile incorporation to product (see Table 1, entry 3 and Table 3 entry 2). The opposite trend is also observed (see Table 2, entry 1 and Table 4, entry 2). Since the reactions above are stoichiometric, if pathway B (Scheme 4) were active, the major product would always originate from the internally held nitrile. This is illustrated in Scheme 7 for Ph and Me dimers (Table 1, entries 1 and 3). However, this is not observed for any of the above competition reactions. Therefore, pathway B can be ruled out as a possible mechanism, leaving pathway A (Scheme 4) as a likely candidate. One possible catalytic cycle for pathway A is illustrated in Scheme 8.



Scheme 7. Expected products when starting with (1) Ph Dimer (**3B**) OR (2) Me Dimer (**3A**)



Scheme 8. Possible catalytic pathway for pathway A.
[a]Suggested structure for additional nitrile binding. Other possible stuctures exist. Coinciding ligand loss would also be reasonable.
[b]Nitrile identity could vary depending on nitrile species used.

CONCLUSION

In summary, a new class of nickel/nitrile/NHC dimers have been isolated and characterized. The nickel centers demonstrate simultaneous η^1 and η^2 binding to two separate nitriles. These dimers proved to be catalytically competent in the cycloaddition of nitriles and diynes to form pyridines. Kinetic studies showed a dependence of the reaction solely on the dimer itself which, taken with a lack of dimer crossover and poor stoichiometric yields in the absence of free nitrile, has been interpreted as a partial dimer opening as the rate determining step. Competition studies were performed to gain information about the catalytic cycle after this initial rate-determining step. Product ratios of these reactions showed that external nitrile is preferentially incorporated into product. This points to a mechanism where, after opening, the dimer interacts first with nitrile instead of diyne before undergoing oxidative coupling and finally reductive elimination to give the pyridine product.

FUTURE WORK

Understanding the exact nature of the interaction of free nitrile with dimer (**3**) is critical for a full understanding of this mechanism. An initial attempt to characterize this interaction by IR suggests that this may indeed be a useful way to gain further insight, and it is suggested that the use of IR to monitor dimer (**3**) and nitrile be explored in depth. Additionally, computational studies should prove an invaluable tool for understanding the energetically feasible modes for this interaction.

Dimer (**3**) has demonstrated an ability to crossover with itself, creating a mixed dimer, albeit not on the reaction timescale (eq 4). This was observed for a variety of dimer species. Understanding exactly how this happens would be interesting, and useful on the way to fully realizing the potential of these dimer complexes. Furthermore, while met with little success to date, it would be interesting to put additional effort into synthesizing and isolating dimer species bearing other NHC ligands besides IPr, and then exploring their catalytic capabilities.

EXPERIMENTAL

General experimental. All reactions were conducted under an atmosphere of N_2 using standard Schlenk techniques or in a N_2 filled glove box unless otherwise noted. Toluene and Acetonitrile were dried over neutral alumina under N_2 using a Grubbs type solvent purification system. Acetonitrile was also used from a sure-sealed bottle purchased directly from Sigma-Aldrich. Benzonitrile was either distilled from CaH_2 prior to use or used from a sure-sealed bottle purchased directly from Sigma-Aldrich. Methoxyacetonitrile was degassed but not dried before use. Deuterated solvents were purchased from Cambridge and used without further purification. $Ni(COD)_2$ was purchased from Strem and used without further purification. Diyne **4** was prepared according to literature procedures.[17] All other reagents were purchased and used without further purification unless otherwise noted.

NMR. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 300 and 75 MHz, respectively, unless otherwise noted. The spectrum of **3d** and competition study spectra were referenced relative to ferrocene, which had in turn been referenced to residual solvent peaks. All other spectra are referenced directly to residual solvent peaks. The abbreviations s, d, dd, dt, dq, t, q, and quint stand for singlet, doublet, doublet of doublets, doublet of triplets, doublet of quartets, triplet, quartet, and quintet, in that order. All ^{13}C NMR

spectra were proton decoupled. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Gas chromatography was performed on an Agilent 6890 gas chromatograph with a 30 meter HP-5 column using the following conditions: initial oven temperature: 100 °C; temperature ramp rate 50 °C/min.; final temperature: 300 °C held for 7 min; detector temperature: 250 °C.

General procedure for synthesis of Ni/IPr/nitrile dimers. Dimers were synthesized by first stirring $Ni(COD)_2$ and IPr (1:1) in hexane or pentane for at least 10 min. The appropriate nitrile was then added and the resulting solution stirred for 1 h. The precipitate that formed, which was usually red to brown in color, was collected and dried to give the desired product. Dimers could be recrystallized from pentane if needed.

Preparation of [Ni(MeCN)(IPr)]$_2$ 3a. $Ni(COD)_2$ (163 mg, 0.59 mmol) and IPr (230 mg, 0.59 mmol) was dissolved in hexane (10 mL). After stirring the reaction for 10 min, acetonitrile (24.4 mg, 0.59 mmol) was added. After stirring the reaction for 1 h, the red precipitate was isolated and dried *in vacuo* to give **3a** (219 mg, 76 %). ^{1}H NMR (THF-d_8, ppm, 500 MHz) δ 7.13-7.25 (m, 12H), 6.81 (s, 4H), 3.03 (m, 8H), 1.24 (s, 24H), 1.05 (s, 24H), 0.61 (s, 6H). ^{13}C NMR (THF-d_8, ppm, 125 MHz) δ 199.8, 154.5, 146.9, 139.9, 129.2, 124.2, 123.4, 29.1, 24.9, 24.2, 9.0. IR (nujol, cm^{-1}) 1757. Analytically calculated for $C_{58}H_{78}N_6Ni_2$: C, 71.33; H, 8.05; N, 8.60, found C, 71.17; H, 7.95; N, 8.69.

Preparation of [Ni(PhCN)(IPr)]$_2$ 3b. $Ni(COD)_2$ (50 mg, 0.18 mmol) and IPr (70 mg, 0.18 mmol) was dissolved in hexane (5 mL). After stirring the reaction for 10 min, benzonitrile (22.2 mg, 0.22 mmol) was added. After stirring the reaction for

1 h, the brown precipitate was collected. Cooling the mother liquor to -40 ºC induced further precipitation. The combined brown solid was dried *in vacuo* to give **3b** (78mg, 78 %). ^{1}H NMR (THF-d_8, ppm, 500 MHz) δ 7.35–7.38 (m, 4H), 7.02–7.16 (m, 22H), 3.11 (m, 8H), 1.00 (d, J=6.5 Hz, 24H), 0.80 (d, J=6.5 Hz, 24H). ^{13}C NMR (THF-d_8, ppm, 125 MHz) δ 201.9, 157.7, 145.3, 137.4, 128.3, 127.5, 126.1, 125.9, 123.8, 122.7, 26.8, 24.0, 21.8. IR (nujol, cm^{-1}) 1758. Analytically calculated for $C_{68}H_{82}N_6Ni_2$: C, 74.19; H, 7.51; N, 7.63, found C, 74.29; H, 7.35; N, 7.36.

Preparation of [Ni(MeOCH$_2$CN)(IPr)]$_2$ 3c. Ni(COD)$_2$ (54 mg, 0.20 mmol) and IPr (79 mg, 0.20 mmol) was dissolved in hexane (5 mL). After stirring the reaction for 10 min, methoxyacetonitrile (17.2 mg, 0.24 mmol) was added. After stirring the reaction for 1 h, the solution was cooled down to -40 °C to induce precipitation. The solid obtained was further recrystallized from pentane at -40 °C to give **3c** as a red solid (49mg, 48 %). ^{1}H NMR (THF-d_8, ppm, 300 MHz) δ 7.16-7.28 (m, 12H), 6.38 (s, 4H), 3.16-3.26 (m, 12H), 2.97 (s, 6H), 1.39 (d, J=6.9 Hz, 24H), 1.12 (d, J=6.9 Hz, 24H). ^{13}C NMR (THF-d_8, ppm, 125 MHz) δ 201.9, 157.7, 147.1, 139.5, 129.1, 124.3, 123.7, 62.3, 57.4, 28.9, 25.2, 23.8. IR (nujol, cm^{-1}) 1768, 1739. Analytically calculated for $C_{60}H_{82}N_6Ni_2O_2$: C, 69.51; H, 7.97; N, 8.11, found C, 69.40; H, 7.94; N, 8.29.

Preparation of [Ni(CF$_3$C$_6$H$_4$CN)IPr]$_2$ 3d[16]. Ni(COD)$_2$ (55.6 mg, 0.202 mmol) and IPr (77.6 mg, 0.200 mmol) were dissolved in pentane (4 mL). After stirring the reaction for 10-15 min, 4-(triflouromethyl)benzonitrile (34.6 mg, 0.202 mmol), which had been dissolved in 0.5 ml pentane, was added. An additional 0.5 ml pentane was used to ensure complete transfer of nitrile to reaction mixture. After

stirring for 1 hr, the reaction mixture was cooled to -40 °C and allowed to sit overnight to induce maximum precipitation. The remaining pentane was decanted off and the precipitate dried under vacuum to give **3d** as a very dark solid (84.7 mg, 68.6%). ^{1}H NMR (C_6D_6, ppm, 400 MHz) δ 7.33 (d, J=7.9 Hz, 4H), 7.17 (t, J=7.7 Hz, 4H), 7.04 (d, J=7.7 Hz, 8H), 6.77 (d, J=7.9 Hz, 4H), 6.41 (s, 4H), 3.12 (sp, J=6.7 Hz, 8H), 1.02 (d, J=7.4 Hz, 24H), 1.01 (d, J=7.4 Hz, 24H). ^{13}C NMR (C_6D_6, ppm, 100 MHz) δ 200.4, 158.1, 146.0, 138.1, 130.7, 129.0, 127.6, 124.6 (q, 3.7 Hz), 124.2, 123.3, 28.4, 25.3, 23.3 (One carbon missing).

Preparation of [Ni(MeOC$_6$H$_4$CN)IPr]$_2$ 3e[16]. Yield and characterization data are still being collected for this compound.

Preparation of IPr·HCl-*d*$_3$ [18]. IPr·HCl (1.4992 g, 3.527 mmol) and K_2CO_3 (24.7 mg, 0.179 mmol) were added to a 50 mL roundbottom followed by ~ 6 ml D_2O. The reaction mixture was heated at 100 °C under N_2 for 24 h. After allowing the reaction to cool, remaining solvents were removed under reduced pressure. Once dry, the product was washed with hexanes before filtering to collect a white solid (1.3505 g, 89 % yield). 100 % deuteration of backbone observed with roughly 64 % deuteration of 2 position on imidazole ring. Theoretical yield assumes total deuteration of product. ^{1}H NMR ($CDCl_3$, ppm, 300 MHz) δ 10.12 (s, <1H), 7.58 (t, J=7.9 Hz, 2H), 7.36 (d, J=7.78 Hz, 4H), 2.46 (septet, J=6.7 Hz, 4H), 1.30 (d, J=6.7 Hz, 12 H), 1.25 (d, J=6.9 Hz, 12 H) ^{13}C NMR ($CDCl_3$, ppm, 100 MHz) δ 145.2, 132.3, 130.0, 128.5, 124.9, 29.3, 24.9, 23.9 (One carbon missing).[19]

Preparation of IPr-d_2. A suspension was created by adding 1.05 equiv IPr·HCl-d_3 (397 mg, 0.927 mmol) to 10 mL diethylether in a 20 mL, oven dried scintillation vial. To this was added 1.0 equiv KHMDS (183 mg, 0.89 mmol) which had been dissolved in 10 mL diethylether. The resulting mixture was stirred for 3 min before being filtered through celite followed by removal of solvent under vacuum. The resulting solid was recrystallized from diethylether to give 149.6 mg of white solid (43 % yield); < 3 proteated IPr remained (backbone position). Theoretical yield assumes total deuteration of product. ^{1}H NMR (C_6D_6, ppm, 300 MHz) δ 7.30 (dd, J=8.6, 6.7 Hz, 2H) 7.21-7.15 (m, 4H) 6.61 (s, <1H), 2.97 (septet, J=6.9 Hz, 4H), 1.30 (d, J=6.7 Hz, 12H) 1.19 (d, J=6.9 Hz, 12H) ^{13}C NMR (C_6D_6, ppm, 125 MHz) δ 220.7, 146.3, 139.0, 129.0, 123.7, 121.5 (m), 28.8, 24.8, 23.7.[19]

Cycloaddition catalyzed by 3a. A stock solution of **3a** was prepared by dissolving 28.4 mg (0.0290 mmol) in 1 ml toluene. Diyne **4** (59.2 mg, 0.251 mmol) was weighed into an oven dried vial equipped with a magnetic stir bar and dissolved in 4.6 ml of toluene. Acetonitrile (13.1 μL, 0.25 mmol) and the catalyst (**3a**) stock solution (431.0 μL, 0.0125 mmol) were sequentially added to the diyne solution via micropipette. The reaction mixture was stirred for 2 hrs at room temperature before being quenched by exposure to air and acetone. Remaining solvent was removed under vacuum and the pyridine product was purified via flash chromatography (1:1 ethyl acetate to hexanes) to give 49.2 mg **5a** (71 % yield).

For a full characterization of pyridine products made from diyne **4** and various nitriles, see reference 20.

Dimer exchange experiments. Dimer stock solutions: Dimers **3a** (27.7 mg, 0.028 mmol) and **3b** (14.6 mg, 0.013 mmol) were individually weighed into separate oven dried 5 mL vials. Benzene-d_6 (1 mL) was added to each vial and the solutions were stirred for 10-15 min. Benzene-d_6 (267 μL) was added to the NMR tube. The stock solutions of dimer **3a** (106 μL, 0.0030 mmol) and dimer **3b** (227 μL, 0.0030 mmol) were sequentially added to the NMR tube. The tube was sealed and then shaken and inverted to ensure proper mixing. ^{1}H NMR spectra were taken at 17 min and 29 min after mixing. No significant mixing of dimers was observed at either time point.

Kinetic studies with catalyst 3a (order in 3a). Stock solution #1 was prepared by dissolution of 213.2 mg (0.90 mmol) of **4** and 115.1 mg (0.68 mmol) of 1,3,5,-trimethoxybenzene in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #2 was prepared by dissolution of 298.6 mg (7.27 mmol) of acetonitrile in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #3 was prepared by dissolution of 34.8 mg (0.036 mmol) of **3a** in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Samples for each rate measurements were prepared by adding 33 μL of solution #1, 21 μL of solution #2, an appropriate volume of solution #3. An amount of toluene-d_8 was then added to make a total of 0.6 mL solution. Reactions were monitored at 0 ºC. The following pseudo-first-order rate constants were obtained at different concentrations of **3a** (k, [**3a**]): 1.6×10^{-5} M·s^{-1}, 3.0×10^{-3} M; 2.2×10^{-5} M·s^{-1}, 4.4×10^{-3} M; 3.5×10^{-5} M·s^{-1}, 6.5×10^{-3} M; 5.5×10^{-5} M·s^{-}, 10.9×10^{-3} M.

Kinetic studies with catalyst 3a (order in acetonitrile). Stock solution #1 was prepared by dissolution of 213.2 mg (0.90 mmol) of **4** and 115.1 mg (0.68

mmol) of 1,3,5,-trimethoxybenzene in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #2 was prepared by dissolution of 298.6 mg (7.27 mmol) of acetonitrile in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #3 was prepared by dissolution of 34.8 mg (0.036 mmol) of **3a** in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Samples for each rate measurements were prepared by adding 33 □L of solution #1, 50 □L of solution #3, an appropriate volume of solution #2. An amount toluene-d_8 was then added to make a total of 0.6 mL solution. Reactions were monitored at 0 ºC. The following pseudo-first-order rate constants were obtained at different concentrations of acetonitrile (k, [MeCN]): 1.7×10^{-5} M·s^{-1}, 0.25 M; 1.7×10^{-5} M·s^{-1}, 0.50 M; 1.7×10^{-5} M·s^{-1}, 0.75 M.

Kinetic studies with catalyst 3a (order in IPr). Stock solution #1 was prepared by dissolution of 213.2 mg (0.90 mmol) of **4** and 115.1 mg (0.68 mmol) of 1,3,5,-trimethoxybenzene in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #2 was prepared by dissolution of 298.6 mg (7.27 mmol) of acetonitrile in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #3 was prepared by dissolution of 34.8 mg (0.036 mmol) of **3a** in toluene-d_8 in a 1.00 ± 0.01 mL volumetric flask. Stock solution #4 was prepared by dissolution of 36.6 mg (0.094 mmol) of IPr in d^8-toluene in a 1.00 ± 0.01 mL volumetric flask. Samples for each rate measurements were prepared by adding 33 □L of solution #1, 21 □L of solution #2, 108 □L of solution #3 and an appropriate volume of solution #4. An amount of toluene-d_8 was then added to make a total of 0.6 mL solution. Reactions were monitored at 0 ºC. The following pseudo-first-order rate constants were obtained at different concentrations of IPr (k, [IPr]): 3.5×10^{-5} M·s^{-1}, 0.8×10^{-3} M; 3.8×10^{-5} M·s^{-1},

1.5×10^{-3} M; 3.9×10^{-5} M·s^{-1}, 2.3×10^{-3} M; 3.9×10^{-5} M·s^{-1}, 3.0×10^{-3} M; 4.0×10^{-5} M·s^{-1}, 3.8×10^{-3} M; 3.9×10^{-5} M·s^{-1}, 4.5×10^{-3} M; 3.8×10^{-5} M·s^{-1}, 6.8×10^{-3} M.

Deuterated IPr exchange reactions. A stock solution was prepared by dissolution of 19.6 mg (0.0200 mmol) of **3a** in benzene-d_6 in a 2.00 ± 0.01 mL volumetric flask. Similarly, a stock solution of deuterated IPr and ferrocene was prepared by dissolution of 80.5 mg (0.206 mmol) **IPr-*d*$_2$** followed by 10.2 mg (0.0548 mmol) of ferrocene in benzene-d_6 in a 2.00 ± 0.01 mL volumetric flask. A stock solution was prepared by dissolution of 50.0 µL (0.957 mmol) of MeCN in 450 µL of benzene-d_6 in a 5 mL oven dried vial. Solutions were added to two NMR tubes in the following order: 189 µL and 182.4 µL benzene-d_6 respectively, 117.2 µL **IPr-*d*$_2$**/ferrocene stock solution, 6.3 µL MeCN stock (to second tube only), and finally 294.1 µL dimer **3a** stock solution. The nmr tubes were equipped with septa caps before being shaken and inverted to ensure total mixing. Spectra were taken at 27 min and 21 min for with and without nitrile, respectively, and compared to an NMR sample made of only **IPr-*d*$_2$**/Ferrocene stock solution.

General procedure for competition reactions. Individual stock solutions were prepared of the required dimers (**3**) and nitriles in benzene-d_6. An additional stock solution of diyne (**4**) and ferrocene was also prepared. Appropriate amounts of the stock solutions to give 0.01 M reaction solutions were then added to oven-dried 5 mL scintillation vials via micropipette. Additional benzene-d_6 was added to give a total volume of the reaction mixtures of 600 µL. Dimer (**3**) stock was added last. After mixing, these solutions were later pipetted from their vials to NMR tubes

and NMR spectra were taken after more than 1 h from the final addition. Some spectra were obtained more than 2 h after final addition.

APPENDIX

Crystal structure report for $[Ni(MeCN)IPr]_2$ (3a). A red prism shaped crystal 0.30 x 0.28 x 0.20 mm in size was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 150(1)K with an oscillation range of *1* deg/frame and an exposure time of 20 sec/frame.[21] Indexing and unit cell refinement based on all observed reflection from those ten frames indicated a monoclinic ***P*** lattice. A total of 11677 reflections (Θ_{max} = 27.48°) were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC.[22] Postrefinement of the unit cell gave *a* = 14.3602(3) Å, b = 12.0810(2) Å, c = 15.8793(3) Å, β =100.8909(9), and V = 2705.21(9) Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in the monoclinic space group $\boldsymbol{P}2_1/n$.

The structure was solved by a combination of direct methods and heavy atom using SIR 97.[23]

All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were either refined isotropically or assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[24] The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 1.5746P]$ where $P = (F_o^2 + 2F_c^2$

)/3. The refinement converged to R1 = 0.0411, wR2 = 0.0976, and S = 1.025 for 4861 reflections with 1> 2σ(I), and R1 = 0.0606, wR2 = 0.1085, and S = 1.025 for 6184 unique reflections and 355 parameters.[25] The maximum Δ/σ in the final cycle of the least-squares was 0, and the residual peaks on the final difference-Fourier map ranged from -0.569 to 0.541 e/Å^3. Scattering factors were taken from the International Tables for Crystallography, Volume C.[26,27]

Table 5. Crystal data and structure refinement for $[Ni(MeCN)IPr]_2$.

Identification code	$[Ni(MeCN)IPr]_2$
Empirical formula	C58 H78 N6 Ni2
Formula weight	976.68
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 14.3602(3) Å ⟨= 90°.
	b = 12.0810(2) Å ®= 100.8909(9)°.
	c = 15.8793(3) Å © = 90°.
Volume	2705.21(9) $Å^3$
Z	2
Density (calculated)	1.199 Mg/m^3
Absorption coefficient	0.737 mm^{-1}
F(000)	1048
Crystal size	0.30 x 0.28 x 0.20 mm^3
Theta range for data collection	2.61 to 27.48°.
Index ranges	-18<=h<=18, -15<=k<=15, -20<=l<=20
Reflections collected	11677
Independent reflections	6184 [R(int) = 0.0318]
Completeness to theta = 27.48°	99.7 %
Absorption correction	Multi-scan
Max. and min. transmission	0.8665 and 0.8091
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6184 / 0 / 355
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0976
R indices (all data)	R1 = 0.0606, wR2 = 0.1085

Table 5 Continued.

Largest diff. peak and hole	0.541 and -0.569 e.Å^{-3}

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Ni(MeCN)IPr]_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	24(1)	-257(1)	4191(1)	21(1)
N(1)	1305(1)	291(1)	3012(1)	22(1)
N(2)	525(1)	-1193(1)	2626(1)	22(1)
N(3)	-941(1)	-499(2)	4888(1)	30(1)
C(1)	971(2)	2215(2)	3298(1)	27(1)
C(2)	1249(2)	3188(2)	3737(2)	34(1)
C(3)	2122(2)	3275(2)	4278(2)	35(1)
C(4)	2752(2)	2398(2)	4362(1)	31(1)
C(5)	2515(2)	1403(2)	3935(1)	24(1)
C(6)	1607(2)	1325(2)	3425(1)	23(1)
C(7)	21(2)	2166(2)	2682(2)	35(1)
C(8)	27(3)	2934(3)	1914(2)	66(1)
C(9)	-807(2)	2435(3)	3117(2)	55(1)
C(10)	3211(2)	437(2)	4017(2)	31(1)
C(11)	4234(2)	808(2)	4087(2)	44(1)
C(12)	3102(2)	-329(2)	4749(2)	59(1)
C(13)	1622(2)	-112(2)	2292(1)	29(1)
C(14)	1137(2)	-1033(2)	2057(1)	29(1)
C(15)	614(1)	-368(2)	3241(1)	20(1)
C(16)	-206(2)	-2024(2)	2477(1)	25(1)
C(17)	-943(2)	-1882(2)	1769(1)	34(1)
C(18)	-1604(2)	-2741(3)	1589(2)	51(1)
C(19)	-1539(2)	-3670(3)	2089(2)	56(1)
C(20)	-823(2)	-3773(2)	2798(2)	47(1)
C(21)	-133(2)	-2950(2)	3014(1)	31(1)

Table 6 Continued.

	x	y	z	U(eq)
C(22)	-1050(2)	-832(3)	1239(2)	48(1)
C(23)	-1051(3)	-1068(4)	293(2)	83(1)
C(24)	-1931(3)	-184(3)	1360(2)	82(1)
C(25)	672(2)	-3051(2)	3774(2)	37(1)
C(26)	1540(2)	-3556(2)	3485(2)	52(1)
C(27)	413(3)	-3719(2)	4518(2)	59(1)
C(28)	-1164(1)	-875(2)	4160(1)	25(1)
C(29)	-2005(2)	-1499(2)	3683(1)	33(1)

Table 7. Bond lengths [Å] and angles [°] for $[Ni(MeCN)IPr]_2$.

Ni(1)-C(28)	1.854(2)
Ni(1)-C(15)	1.8677(19)
Ni(1)-N(3)	1.9523(17)
Ni(1)-N(3)#1	1.9951(18)
Ni(1)-Ni(1)#1	2.6576(5)
N(1)-C(15)	1.375(2)
N(1)-C(13)	1.395(3)
N(1)-C(6)	1.439(3)
N(2)-C(15)	1.385(2)
N(2)-C(14)	1.387(3)
N(2)-C(16)	1.439(3)
N(3)-C(28)	1.226(3)
N(3)-Ni(1)#1	1.9951(18)
C(1)-C(2)	1.386(3)
C(1)-C(6)	1.401(3)
C(1)-C(7)	1.523(3)
C(2)-C(3)	1.384(4)
C(2)-H(2)	0.95(3)
C(3)-C(4)	1.383(3)
C(3)-H(3)	0.93(3)
C(4)-C(5)	1.391(3)
C(4)-H(4)	0.96(3)
C(5)-C(6)	1.402(3)
C(5)-C(10)	1.525(3)
C(7)-C(9)	1.519(4)
C(7)-C(8)	1.533(4)
C(7)-H(7)	0.92(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800

Table 7 Continued.

C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.517(3)
C(10)-C(11)	1.520(3)
C(10)-H(10)	0.99(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.328(3)
C(13)-H(13)	0.90(3)
C(14)-H(14)	0.92(3)
C(16)-C(21)	1.399(3)
C(16)-C(17)	1.401(3)
C(17)-C(18)	1.399(4)
C(17)-C(22)	1.514(4)
C(18)-C(19)	1.367(5)
C(18)-H(18)	0.95(3)
C(19)-C(20)	1.379(5)
C(19)-H(19)	0.95(4)
C(20)-C(21)	1.399(3)
C(20)-H(20)	0.97(3)
C(21)-C(25)	1.510(3)
C(22)-C(24)	1.530(4)
C(22)-C(23)	1.530(4)

Table 7 Continued.

C(22)-H(22)	0.93(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(27)	1.533(3)
C(25)-C(26)	1.534(3)
C(25)-H(25)	0.98(2)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.502(3)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(28)-Ni(1)-C(15)	120.29(8)
C(28)-Ni(1)-N(3)	37.47(8)
C(15)-Ni(1)-N(3)	157.68(8)
C(28)-Ni(1)-N(3)#1	132.83(8)
C(15)-Ni(1)-N(3)#1	106.77(8)
N(3)-Ni(1)-N(3)#1	95.37(7)
C(28)-Ni(1)-Ni(1)#1	85.83(6)
C(15)-Ni(1)-Ni(1)#1	153.65(6)

Table 7 Continued.

N(3)-Ni(1)-Ni(1)#1	48.37(5)
N(3)#1-Ni(1)-Ni(1)#1	47.00(5)
C(15)-N(1)-C(13)	112.22(17)
C(15)-N(1)-C(6)	123.53(16)
C(13)-N(1)-C(6)	124.05(17)
C(15)-N(2)-C(14)	111.99(17)
C(15)-N(2)-C(16)	125.77(16)
C(14)-N(2)-C(16)	121.48(16)
C(28)-N(3)-Ni(1)	66.93(12)
C(28)-N(3)-Ni(1)#1	151.53(16)
Ni(1)-N(3)-Ni(1)#1	84.63(7)
C(2)-C(1)-C(6)	117.4(2)
C(2)-C(1)-C(7)	119.6(2)
C(6)-C(1)-C(7)	122.88(19)
C(3)-C(2)-C(1)	121.2(2)
C(3)-C(2)-H(2)	119.6(15)
C(1)-C(2)-H(2)	119.1(15)
C(4)-C(3)-C(2)	120.1(2)
C(4)-C(3)-H(3)	121.1(16)
C(2)-C(3)-H(3)	118.8(16)
C(3)-C(4)-C(5)	121.3(2)
C(3)-C(4)-H(4)	121.7(15)
C(5)-C(4)-H(4)	116.9(15)
C(4)-C(5)-C(6)	117.0(2)
C(4)-C(5)-C(10)	121.5(2)
C(6)-C(5)-C(10)	121.42(19)
C(1)-C(6)-C(5)	122.80(19)
C(1)-C(6)-N(1)	118.00(18)
C(5)-C(6)-N(1)	119.19(18)

Table 7 Continued.

C(9)-C(7)-C(1)	112.5(2)
C(9)-C(7)-C(8)	110.8(2)
C(1)-C(7)-C(8)	110.4(2)
C(9)-C(7)-H(7)	105.0(15)
C(1)-C(7)-H(7)	109.4(15)
C(8)-C(7)-H(7)	108.7(15)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	111.2(2)
C(12)-C(10)-C(5)	111.8(2)
C(11)-C(10)-C(5)	112.9(2)
C(12)-C(10)-H(10)	108.0(16)
C(11)-C(10)-H(10)	104.1(17)
C(5)-C(10)-H(10)	108.4(16)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5

Table 7 Continued.

H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-N(1)	106.75(19)
C(14)-C(13)-H(13)	130.5(16)
N(1)-C(13)-H(13)	122.7(16)
C(13)-C(14)-N(2)	107.26(18)
C(13)-C(14)-H(14)	130.5(17)
N(2)-C(14)-H(14)	122.2(17)
N(1)-C(15)-N(2)	101.79(15)
N(1)-C(15)-Ni(1)	129.19(14)
N(2)-C(15)-Ni(1)	128.81(14)
C(21)-C(16)-C(17)	123.0(2)
C(21)-C(16)-N(2)	119.32(19)
C(17)-C(16)-N(2)	117.62(19)
C(18)-C(17)-C(16)	117.0(2)
C(18)-C(17)-C(22)	121.0(2)
C(16)-C(17)-C(22)	122.0(2)
C(19)-C(18)-C(17)	121.4(3)
C(19)-C(18)-H(18)	119.6(18)
C(17)-C(18)-H(18)	119.0(18)
C(18)-C(19)-C(20)	120.4(3)
C(18)-C(19)-H(19)	120(2)
C(20)-C(19)-H(19)	119(2)
C(19)-C(20)-C(21)	121.3(3)

Table 7 Continued.

C(19)-C(20)-H(20)	119.0(18)
C(21)-C(20)-H(20)	119.7(19)
C(20)-C(21)-C(16)	116.8(2)
C(20)-C(21)-C(25)	122.5(2)
C(16)-C(21)-C(25)	120.6(2)
C(17)-C(22)-C(24)	111.0(3)
C(17)-C(22)-C(23)	111.7(3)
C(24)-C(22)-C(23)	111.8(3)
C(17)-C(22)-H(22)	107.9(18)
C(24)-C(22)-H(22)	107.5(19)
C(23)-C(22)-H(22)	106.7(19)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(21)-C(25)-C(27)	113.5(2)
C(21)-C(25)-C(26)	109.6(2)
C(27)-C(25)-C(26)	110.5(2)
C(21)-C(25)-H(25)	107.8(14)
C(27)-C(25)-H(25)	106.2(14)
C(26)-C(25)-H(25)	109.2(14)

Table 7 Continued.

C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(3)-C(28)-C(29)	134.6(2)
N(3)-C(28)-Ni(1)	75.60(13)
C(29)-C(28)-Ni(1)	149.76(16)
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table 8. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[Ni(MeCN)IPr]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	21(1)	24(1)	19(1)	-4(1)	8(1)	-4(1)
N(1)	24(1)	23(1)	21(1)	-2(1)	9(1)	-2(1)
N(2)	24(1)	23(1)	21(1)	-3(1)	8(1)	-2(1)
N(3)	25(1)	40(1)	28(1)	-7(1)	13(1)	-9(1)
C(1)	30(1)	25(1)	29(1)	1(1)	10(1)	-1(1)
C(2)	36(1)	24(1)	45(1)	-2(1)	12(1)	2(1)
C(3)	43(1)	26(1)	39(1)	-9(1)	16(1)	-10(1)
C(4)	29(1)	35(1)	28(1)	-2(1)	6(1)	-11(1)
C(5)	25(1)	26(1)	24(1)	2(1)	9(1)	-5(1)
C(6)	26(1)	21(1)	23(1)	-1(1)	11(1)	-4(1)
C(7)	31(1)	31(1)	41(1)	1(1)	0(1)	4(1)
C(8)	64(2)	86(2)	45(2)	23(2)	0(1)	6(2)
C(9)	32(1)	64(2)	68(2)	5(2)	9(1)	8(1)
C(10)	26(1)	34(1)	35(1)	2(1)	8(1)	1(1)
C(11)	28(1)	52(2)	54(2)	12(1)	9(1)	2(1)
C(12)	49(2)	51(2)	86(2)	36(2)	38(2)	19(1)
C(13)	30(1)	34(1)	27(1)	-2(1)	16(1)	-5(1)
C(14)	30(1)	34(1)	27(1)	-7(1)	15(1)	-4(1)
C(15)	19(1)	22(1)	20(1)	-1(1)	5(1)	-2(1)
C(16)	24(1)	26(1)	26(1)	-10(1)	11(1)	-5(1)
C(17)	28(1)	49(1)	27(1)	-13(1)	6(1)	-2(1)
C(18)	33(2)	76(2)	46(2)	-35(2)	9(1)	-15(1)
C(19)	49(2)	55(2)	73(2)	-37(2)	32(2)	-29(2)
C(20)	59(2)	28(1)	66(2)	-16(1)	37(2)	-14(1)
C(21)	35(1)	23(1)	40(1)	-7(1)	20(1)	1(1)

Table 8 Continued.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(22)	43(2)	71(2)	26(1)	0(1)	-1(1)	7(2)
C(23)	99(3)	120(3)	28(1)	4(2)	8(2)	12(3)
C(24)	82(3)	97(3)	69(2)	21(2)	21(2)	41(2)
C(25)	47(2)	28(1)	39(1)	6(1)	17(1)	9(1)
C(26)	46(2)	57(2)	57(2)	14(1)	19(1)	21(1)
C(27)	88(2)	45(2)	54(2)	16(1)	38(2)	20(2)
C(28)	22(1)	29(1)	25(1)	-3(1)	9(1)	-2(1)
C(29)	27(1)	39(1)	32(1)	-9(1)	7(1)	-9(1)

Table 9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Ni(MeCN)IPr]_2$.

	x	y	z	U(eq)
H(8A)	548	2726	1627	99
H(8B)	114	3701	2115	99
H(8C)	-577	2868	1510	99
H(9A)	-807	1923	3596	82
H(9B)	-1403	2358	2703	82
H(9C)	-746	3196	3333	82
H(11A)	4283	1304	3609	66
H(11B)	4639	160	4067	66
H(11C)	4440	1201	4631	66
H(12A)	2437	-550	4691	89
H(12B)	3305	56	5296	89
H(12C)	3496	-989	4733	89
H(23A)	-1103	-370	-27	125
H(23B)	-1591	-1545	60	125
H(23C)	-460	-1442	238	125
H(24A)	-2497	-637	1169	122
H(24B)	-1977	499	1022	122
H(24C)	-1882	0	1968	122
H(26A)	1735	-3078	3051	78
H(26B)	1378	-4291	3240	78
H(26C)	2061	-3621	3979	78
H(27A)	-152	-3398	4685	89
H(27B)	943	-3699	5008	89
H(27C)	283	-4488	4337	89
H(29A)	-2130	-1271	3080	49

Table 9 Continued.

	x	y	z	U(eq)
H(29B)	-2562	-1338	3937	49
H(29C)	-1873	-2295	3721	49
H(2)	818(18)	3790(20)	3683(15)	38(7)
H(3)	2283(19)	3940(20)	4568(16)	42(7)
H(4)	3369(18)	2450(20)	4718(16)	36(7)
H(7)	-89(17)	1460(20)	2484(15)	30(6)
H(10)	3080(20)	10(20)	3480(19)	46(8)
H(13)	2057(19)	250(20)	2050(17)	38(7)
H(14)	1158(19)	-1510(20)	1608(17)	46(7)
H(18)	-2100(20)	-2680(20)	1106(18)	50(8)
H(19)	-2000(20)	-4240(30)	1960(20)	72(10)
H(20)	-790(20)	-4440(30)	3146(19)	56(9)
H(22)	-530(20)	-390(20)	1434(19)	54(9)
H(25)	831(17)	-2300(20)	3998(15)	31(6)

Table 10. Torsion angles [°] for $[Ni(MeCN)IPr]_2$.

C(15)-Ni(1)-N(3)-C(28)	-6.0(3)
N(3)#1-Ni(1)-N(3)-C(28)	-178.65(17)
Ni(1)#1-Ni(1)-N(3)-C(28)	-178.65(17)
C(28)-Ni(1)-N(3)-Ni(1)#1	178.65(17)
C(15)-Ni(1)-N(3)-Ni(1)#1	172.65(19)
N(3)#1-Ni(1)-N(3)-Ni(1)#1	0.0
C(6)-C(1)-C(2)-C(3)	0.0(3)
C(7)-C(1)-C(2)-C(3)	-177.6(2)
C(1)-C(2)-C(3)-C(4)	2.8(4)
C(2)-C(3)-C(4)-C(5)	-2.4(3)
C(3)-C(4)-C(5)-C(6)	-0.7(3)
C(3)-C(4)-C(5)-C(10)	179.3(2)
C(2)-C(1)-C(6)-C(5)	-3.3(3)
C(7)-C(1)-C(6)-C(5)	174.2(2)
C(2)-C(1)-C(6)-N(1)	176.56(18)
C(7)-C(1)-C(6)-N(1)	-5.9(3)
C(4)-C(5)-C(6)-C(1)	3.6(3)
C(10)-C(5)-C(6)-C(1)	-176.39(19)
C(4)-C(5)-C(6)-N(1)	-176.25(17)
C(10)-C(5)-C(6)-N(1)	3.8(3)
C(15)-N(1)-C(6)-C(1)	-69.2(2)
C(13)-N(1)-C(6)-C(1)	105.2(2)
C(15)-N(1)-C(6)-C(5)	110.6(2)
C(13)-N(1)-C(6)-C(5)	-74.9(3)
C(2)-C(1)-C(7)-C(9)	-58.3(3)
C(6)-C(1)-C(7)-C(9)	124.2(2)
C(2)-C(1)-C(7)-C(8)	66.0(3)
C(6)-C(1)-C(7)-C(8)	-111.5(3)
C(4)-C(5)-C(10)-C(12)	90.8(3)

Table 10 Continued.

C(6)-C(5)-C(10)-C(12)	-89.2(3)
C(4)-C(5)-C(10)-C(11)	-35.5(3)
C(6)-C(5)-C(10)-C(11)	144.5(2)
C(15)-N(1)-C(13)-C(14)	-0.1(3)
C(6)-N(1)-C(13)-C(14)	-175.15(19)
N(1)-C(13)-C(14)-N(2)	0.2(3)
C(15)-N(2)-C(14)-C(13)	-0.2(3)
C(16)-N(2)-C(14)-C(13)	170.4(2)
C(13)-N(1)-C(15)-N(2)	0.0(2)
C(6)-N(1)-C(15)-N(2)	175.07(17)
C(13)-N(1)-C(15)-Ni(1)	175.09(16)
C(6)-N(1)-C(15)-Ni(1)	-9.9(3)
C(14)-N(2)-C(15)-N(1)	0.1(2)
C(16)-N(2)-C(15)-N(1)	-169.97(18)
C(14)-N(2)-C(15)-Ni(1)	-174.99(16)
C(16)-N(2)-C(15)-Ni(1)	14.9(3)
C(28)-Ni(1)-C(15)-N(1)	156.72(17)
N(3)-Ni(1)-C(15)-N(1)	160.94(19)
N(3)#1-Ni(1)-C(15)-N(1)	-26.7(2)
Ni(1)#1-Ni(1)-C(15)-N(1)	-31.5(3)
C(28)-Ni(1)-C(15)-N(2)	-29.5(2)
N(3)-Ni(1)-C(15)-N(2)	-25.3(3)
N(3)#1-Ni(1)-C(15)-N(2)	147.09(17)
Ni(1)#1-Ni(1)-C(15)-N(2)	142.30(13)
C(15)-N(2)-C(16)-C(21)	-79.6(3)
C(14)-N(2)-C(16)-C(21)	111.2(2)
C(15)-N(2)-C(16)-C(17)	103.0(2)
C(14)-N(2)-C(16)-C(17)	-66.2(3)
C(21)-C(16)-C(17)-C(18)	-2.6(3)

Table 10 Continued.

N(2)-C(16)-C(17)-C(18)	174.66(19)
C(21)-C(16)-C(17)-C(22)	175.1(2)
N(2)-C(16)-C(17)-C(22)	-7.7(3)
C(16)-C(17)-C(18)-C(19)	0.9(4)
C(22)-C(17)-C(18)-C(19)	-176.8(2)
C(17)-C(18)-C(19)-C(20)	1.2(4)
C(18)-C(19)-C(20)-C(21)	-1.6(4)
C(19)-C(20)-C(21)-C(16)	0.0(3)
C(19)-C(20)-C(21)-C(25)	-178.6(2)
C(17)-C(16)-C(21)-C(20)	2.2(3)
N(2)-C(16)-C(21)-C(20)	-175.02(19)
C(17)-C(16)-C(21)-C(25)	-179.2(2)
N(2)-C(16)-C(21)-C(25)	3.5(3)
C(18)-C(17)-C(22)-C(24)	66.1(3)
C(16)-C(17)-C(22)-C(24)	-111.4(3)
C(18)-C(17)-C(22)-C(23)	-59.4(4)
C(16)-C(17)-C(22)-C(23)	123.0(3)
C(20)-C(21)-C(25)-C(27)	-31.0(3)
C(16)-C(21)-C(25)-C(27)	150.5(2)
C(20)-C(21)-C(25)-C(26)	93.0(3)
C(16)-C(21)-C(25)-C(26)	-85.5(3)
Ni(1)-N(3)-C(28)-C(29)	178.8(3)
Ni(1)#1-N(3)-C(28)-C(29)	176.0(2)
Ni(1)#1-N(3)-C(28)-Ni(1)	-2.8(4)
C(15)-Ni(1)-C(28)-N(3)	177.37(13)
N(3)#1-Ni(1)-C(28)-N(3)	1.8(2)
Ni(1)#1-Ni(1)-C(28)-N(3)	1.01(13)
C(15)-Ni(1)-C(28)-C(29)	-0.9(4)
N(3)-Ni(1)-C(28)-C(29)	-178.3(4)

Table 10 Continued.

N(3)#1-Ni(1)-C(28)-C(29)	-176.5(3)
Ni(1)#1-Ni(1)-C(28)-C(29)	-177.3(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1

Crystal structure report for $[Ni(CF_3C_6H_4CN)IPr]_2$ (3d). A red plate shaped crystal 0.33 x 0.30 x 0.05 mm in size was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 150(1) K with an oscillation range of *1* deg/frame and an exposure time of 20 sec/frame.[21] Indexing and unit cell refinement based on all observed reflection from those ten frames, indicated a triclinic ***P*** lattice. A total of 26684 reflections (Θ_{max} = 27.510000000000002°) were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC.[22] Postrefinement of the unit cell gave *a* = 11.2679(2) Å, b = 12.7149(3) Å, c = 23.5803(5) Å, α=103.0033(12), β =93.2032(13), γ=99.1686(11), and V = 3234.86(12) Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in the triclinic space group ***P*** $\bar{1}$.

The structure was solved by a combination of direct methods and heavy atom using SIR 97.[23]

All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[24] Three isopropyl and CF3 groups exhibit orientation disorder. The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 2.3091P]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to R1 = 0.0486, wR2 = 0.0968, and S = 1.022 for 10096 reflections with $1 > 2\sigma(I)$, and R1 = 0.090, wR2 = 0.1126, and S = 1.022 for 14731 unique reflections and 835

parameters.[25] The maximum Δ/σ in the final cycle of the least-squares was 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.571 to 0.557 e/Å^3. Scattering factors were taken from the International Tables for Crystallography, Volume C.[26,27]

Table 11. Crystal data and structure refinement for $[Ni(CF_3C_6H_4CN)IPr]_2$.

Identification code	[Ni(CF3C6H4CN)IPr]2	
Empirical formula	C70 H80 F6 N6 Ni2	
Formula weight	1236.82	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	***P***	
Unit cell dimensions	a = 11.2679(2) Å	⟨= 103.0033(12)°.
	b = 12.7149(3) Å	®= 93.2032(13)°.
	c = 23.5803(5) Å	© = 99.1686(11)°.
Volume	3234.86(12) $Å^3$	
Z	2	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.644 mm^{-1}	
F(000)	1304	
Crystal size	0.33 x 0.30 x 0.05 mm^3	
Theta range for data collection	2.13 to 27.51°.	
Index ranges	-14<=h<=14, -16<=k<=16, -30<=l<=30	
Reflections collected	26684	
Independent reflections	14731 [R(int) = 0.0420]	
Completeness to theta = 27.51°	98.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9685 and 0.8155	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14731 / 6 / 835	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.0968	
R indices (all data)	R1 = 0.0900, wR2 = 0.1126	
Largest diff. peak and hole	0.557 and -0.571 $e.Å^{-3}$	

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $[Ni(CF_3C_6H_4CN)IPr]_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	-136(1)	-975(1)	2142(1)	22(1)
Ni(2)	313(1)	1118(1)	2781(1)	21(1)
F(1)	-4517(3)	-1234(3)	-741(1)	75(1)
F(2)	-5808(2)	-1711(5)	-191(1)	108(2)
F(3)	-4692(4)	-2786(3)	-571(2)	118(2)
F(4)	4160(3)	1466(4)	5797(1)	79(1)
F(5)	5620(4)	1251(4)	5255(2)	102(2)
F(6)	5016(5)	2787(3)	5489(2)	115(2)
F(1A)	-5259(10)	-790(9)	-362(5)	85(3)
F(2A)	-5449(9)	-2348(8)	-281(4)	51(2)
F(3A)	-4273(10)	-1934(11)	-791(5)	83(3)
F(4A)	4529(10)	859(9)	5617(5)	78(3)
F(5A)	5668(10)	1824(8)	5286(5)	51(3)
F(6A)	4504(11)	2540(12)	5671(6)	84(4)
N(1)	27(2)	-3152(2)	2344(1)	23(1)
N(2)	26(2)	-3198(2)	1434(1)	24(1)
N(3)	-688(2)	374(2)	2040(1)	30(1)
N(4)	912(2)	-222(2)	2869(1)	32(1)
N(5)	867(2)	3560(2)	3216(1)	23(1)
N(6)	-1023(2)	2910(2)	3049(1)	25(1)
C(1)	1198(2)	-2539(2)	3295(1)	26(1)
C(2)	1198(3)	-2245(2)	3904(1)	34(1)
C(3)	140(3)	-2217(2)	4164(1)	38(1)
C(4)	-965(3)	-2483(2)	3832(1)	37(1)
C(5)	-1032(2)	-2793(2)	3224(1)	29(1)
C(6)	62(2)	-2797(2)	2972(1)	24(1)
C(7)	2372(2)	-2598(2)	3012(1)	31(1)
C(8)	3026(3)	-3453(2)	3196(2)	47(1)
C(9)	3227(3)	-1495(2)	3149(2)	45(1)
C(10)	-2250(2)	-3132(3)	2856(1)	40(1)

Table 12 Continued.

	x	y	z	U(eq)
C(11)	-3191(3)	-3822(3)	3121(2)	51(1)
C(12)	-2754(3)	-2138(3)	2749(2)	68(1)
C(13)	155(2)	-4203(2)	2067(1)	29(1)
C(14)	158(2)	-4235(2)	1495(1)	30(1)
C(15)	-44(2)	-2488(2)	1960(1)	22(1)
C(16)	-24(2)	-2949(2)	865(1)	27(1)
C(17)	938(2)	-2232(2)	732(1)	31(1)
C(18)	885(3)	-2063(3)	166(1)	41(1)
C(19)	-72(3)	-2597(3)	-242(1)	48(1)
C(20)	-1004(3)	-3299(3)	-101(1)	41(1)
C(21)	-1015(2)	-3500(2)	460(1)	33(1)
C(22)	2003(2)	-1676(2)	1182(1)	35(1)
C(23)	2880(3)	-2467(3)	1228(1)	45(1)
C(24)	2665(3)	-617(3)	1070(2)	51(1)
C(25)	-2053(2)	-4282(2)	604(1)	36(1)
C(26)	-2099(15)	-5415(14)	253(7)	51(3)
C(27)	-3296(8)	-3917(8)	488(3)	43(2)
C(26A)	-3013(11)	-3691(9)	833(6)	116(5)
C(27A)	-2480(18)	-5314(17)	119(9)	113(8)
C(28)	-1129(2)	-442(2)	1659(1)	26(1)
C(29)	-2036(2)	-700(2)	1151(1)	26(1)
C(30)	-3254(2)	-878(3)	1234(1)	38(1)
C(31)	-4118(2)	-1173(3)	759(1)	44(1)
C(32)	-3764(2)	-1298(2)	197(1)	33(1)
C(33)	-2557(2)	-1104(2)	115(1)	37(1)
C(34)	-1693(2)	-807(2)	591(1)	34(1)
C(35)	-4685(3)	-1694(3)	-311(1)	47(1)
C(36)	1317(2)	599(2)	3259(1)	27(1)
C(37)	2162(2)	856(2)	3791(1)	27(1)
C(38)	3312(2)	1445(2)	3795(1)	31(1)
C(39)	4110(2)	1698(2)	4293(1)	36(1)
C(40)	3757(3)	1376(2)	4791(1)	36(1)

Table 12 Continued.

	x	y	z	U(eq)
C(41)	2610(3)	797(2)	4793(1)	38(1)
C(42)	1813(2)	535(2)	4292(1)	33(1)
C(43)	4620(3)	1691(3)	5331(1)	51(1)
C(44)	2166(2)	3677(2)	3292(1)	26(1)
C(45)	2795(2)	3468(2)	2797(1)	33(1)
C(46)	4043(3)	3585(3)	2889(2)	57(1)
C(47)	4633(3)	3931(3)	3441(2)	74(1)
C(48)	4002(3)	4163(3)	3917(2)	61(1)
C(49)	2749(3)	4041(2)	3863(1)	39(1)
C(50)	2184(3)	3178(2)	2177(1)	40(1)
C(51)	2677(3)	4024(3)	1837(1)	58(1)
C(52)	2319(4)	2033(3)	1852(2)	66(1)
C(53)	2078(3)	4302(3)	4405(1)	53(1)
C(54)	2016(8)	5476(5)	4702(3)	67(2)
C(55)	2149(8)	3619(6)	4865(3)	60(2)
C(54A)	3124(6)	4928(6)	4930(3)	57(2)
C(55A)	1435(5)	3337(5)	4529(2)	37(1)
C(56)	266(2)	4446(2)	3360(1)	31(1)
C(57)	-915(2)	4033(2)	3256(1)	35(1)
C(58)	83(2)	2583(2)	3017(1)	22(1)
C(59)	-2168(2)	2179(2)	2885(1)	27(1)
C(60)	-2579(2)	1515(2)	3260(1)	31(1)
C(61)	-3703(2)	842(2)	3099(1)	36(1)
C(62)	-4386(2)	838(3)	2591(1)	38(1)
C(63)	-3952(2)	1497(2)	2229(1)	36(1)
C(64)	-2835(2)	2189(2)	2369(1)	30(1)
C(65)	-1851(3)	1565(3)	3832(1)	42(1)
C(66)	-2617(6)	1854(6)	4345(2)	43(2)
C(67)	-1594(7)	364(7)	3826(3)	40(2)
C(66A)	-2057(7)	2637(7)	4313(3)	66(2)
C(67A)	-1966(10)	617(8)	4062(4)	79(3)
C(68)	-2357(2)	2898(2)	1957(1)	35(1)

Table 12 Continued.

	x	y	z	U(eq)
C(69)	-3245(3)	3621(2)	1829(1)	41(1)
C(70)	-2073(3)	2178(3)	1383(1)	58(1)

Table 13. Bond lengths [Å] and angles [°] for $[Ni(CF_3C_6H_4CN)IPr]_2$.

Ni(1)-C(28)	1.857(2)
Ni(1)-C(15)	1.895(2)
Ni(1)-N(3)	1.974(2)
Ni(1)-N(4)	1.982(2)
Ni(1)-Ni(2)	2.6999(4)
Ni(2)-C(36)	1.848(2)
Ni(2)-C(58)	1.883(2)
Ni(2)-N(4)	1.979(2)
Ni(2)-N(3)	1.979(2)
F(1)-C(35)	1.288(4)
F(2)-C(35)	1.310(4)
F(3)-C(35)	1.385(5)
F(4)-C(43)	1.310(4)
F(5)-C(43)	1.340(5)
F(6)-C(43)	1.352(5)
F(1A)-C(35)	1.430(11)
F(2A)-C(35)	1.116(9)
F(3A)-C(35)	1.241(12)
F(4A)-C(43)	1.371(11)
F(5A)-C(43)	1.181(11)
F(6A)-C(43)	1.221(14)
N(1)-C(15)	1.376(3)
N(1)-C(13)	1.384(3)
N(1)-C(6)	1.445(3)
N(2)-C(15)	1.376(3)
N(2)-C(14)	1.388(3)
N(2)-C(16)	1.447(3)
N(3)-C(28)	1.223(3)
N(4)-C(36)	1.229(3)
N(5)-C(58)	1.373(3)
N(5)-C(56)	1.392(3)
N(5)-C(44)	1.444(3)
N(6)-C(58)	1.376(3)
N(6)-C(57)	1.384(3)

Table 13 Continued.

N(6)-C(59)	1.442(3)
C(1)-C(2)	1.398(4)
C(1)-C(6)	1.404(3)
C(1)-C(7)	1.519(4)
C(2)-C(3)	1.373(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.384(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.395(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.397(4)
C(5)-C(10)	1.528(4)
C(7)-C(9)	1.527(4)
C(7)-C(8)	1.531(4)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.520(4)
C(10)-C(12)	1.529(5)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.339(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(16)-C(17)	1.399(4)

Table 13 Continued.

C(16)-C(21)	1.406(4)
C(17)-C(18)	1.398(4)
C(17)-C(22)	1.521(4)
C(18)-C(19)	1.381(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.373(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.403(4)
C(20)-H(20)	0.9500
C(21)-C(25)	1.516(4)
C(22)-C(24)	1.517(4)
C(22)-C(23)	1.534(4)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(26A)	1.472(12)
C(25)-C(26)	1.482(17)
C(25)-C(27A)	1.52(2)
C(25)-C(27)	1.573(9)
C(25)-H(25)	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(26A)-H(26D)	0.9800
C(26A)-H(26E)	0.9800
C(26A)-H(26F)	0.9800
C(27A)-H(27D)	0.9800

Table 13 Continued.

C(27A)-H(27E)	0.9800
C(27A)-H(27F)	0.9800
C(28)-C(29)	1.472(3)
C(29)-C(34)	1.380(4)
C(29)-C(30)	1.387(4)
C(30)-C(31)	1.384(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.387(4)
C(31)-H(31)	0.9500
C(32)-C(33)	1.375(4)
C(32)-C(35)	1.480(4)
C(33)-C(34)	1.386(4)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(36)-C(37)	1.473(3)
C(37)-C(38)	1.388(4)
C(37)-C(42)	1.392(4)
C(38)-C(39)	1.383(4)
C(38)-H(38)	0.9500
C(39)-C(40)	1.387(4)
C(39)-H(39)	0.9500
C(40)-C(41)	1.381(4)
C(40)-C(43)	1.495(4)
C(41)-C(42)	1.386(4)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(44)-C(45)	1.396(4)
C(44)-C(49)	1.407(4)
C(45)-C(46)	1.391(4)
C(45)-C(50)	1.520(4)
C(46)-C(47)	1.373(5)
C(46)-H(46)	0.9500
C(47)-C(48)	1.364(6)
C(47)-H(47)	0.9500

Table 13 Continued.

C(48)-C(49)	1.390(4)
C(48)-H(48)	0.9500
C(49)-C(53)	1.520(5)
C(50)-C(52)	1.519(4)
C(50)-C(51)	1.535(4)
C(50)-H(50)	1.0000
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-C(55A)	1.420(6)
C(53)-C(54)	1.514(7)
C(53)-C(55)	1.540(6)
C(53)-C(54A)	1.628(6)
C(53)-H(53)	1.0000
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(54A)-H(54D)	0.9800
C(54A)-H(54E)	0.9800
C(54A)-H(54F)	0.9800
C(55A)-H(55D)	0.9800
C(55A)-H(55E)	0.9800
C(55A)-H(55F)	0.9800
C(56)-C(57)	1.337(4)
C(56)-H(56)	0.9500
C(57)-H(57)	0.9500
C(59)-C(64)	1.398(3)
C(59)-C(60)	1.402(3)

Table 13 Continued.

C(60)-C(61)	1.391(4)
C(60)-C(65)	1.522(4)
C(61)-C(62)	1.386(4)
C(61)-H(61)	0.9500
C(62)-C(63)	1.380(4)
C(62)-H(62)	0.9500
C(63)-C(64)	1.391(4)
C(63)-H(63)	0.9500
C(64)-C(68)	1.530(3)
C(65)-C(67A)	1.420(8)
C(65)-C(66)	1.538(6)
C(65)-C(67)	1.596(8)
C(65)-C(66A)	1.623(8)
C(65)-H(65)	1.0000
C(66)-H(66A)	0.9800
C(66)-H(66B)	0.9800
C(66)-H(66C)	0.9800
C(67)-H(67A)	0.9800
C(67)-H(67B)	0.9800
C(67)-H(67C)	0.9800
C(66A)-H(66D)	0.9800
C(66A)-H(66E)	0.9800
C(66A)-H(66F)	0.9800
C(67A)-H(67D)	0.9800
C(67A)-H(67E)	0.9800
C(67A)-H(67F)	0.9800
C(68)-C(69)	1.524(4)
C(68)-C(70)	1.536(4)
C(68)-H(68)	1.0000
C(69)-H(69A)	0.9800
C(69)-H(69B)	0.9800
C(69)-H(69C)	0.9800
C(70)-H(70A)	0.9800
C(70)-H(70B)	0.9800

Table 13 Continued.

C(70)-H(70C)	0.9800
C(28)-Ni(1)-C(15)	119.48(10)
C(28)-Ni(1)-N(3)	37.08(9)
C(15)-Ni(1)-N(3)	156.56(9)
C(28)-Ni(1)-N(4)	131.01(10)
C(15)-Ni(1)-N(4)	109.50(9)
N(3)-Ni(1)-N(4)	93.93(9)
C(28)-Ni(1)-Ni(2)	84.05(8)
C(15)-Ni(1)-Ni(2)	156.40(7)
N(3)-Ni(1)-Ni(2)	46.99(6)
N(4)-Ni(1)-Ni(2)	46.97(6)
C(36)-Ni(2)-C(58)	118.58(10)
C(36)-Ni(2)-N(4)	37.27(10)
C(58)-Ni(2)-N(4)	155.60(9)
C(36)-Ni(2)-N(3)	131.13(10)
C(58)-Ni(2)-N(3)	110.22(9)
N(4)-Ni(2)-N(3)	93.87(9)
C(36)-Ni(2)-Ni(1)	84.33(8)
C(58)-Ni(2)-Ni(1)	156.54(7)
N(4)-Ni(2)-Ni(1)	47.07(6)
N(3)-Ni(2)-Ni(1)	46.83(6)
C(15)-N(1)-C(13)	112.53(19)
C(15)-N(1)-C(6)	125.1(2)
C(13)-N(1)-C(6)	122.20(19)
C(15)-N(2)-C(14)	112.5(2)
C(15)-N(2)-C(16)	126.4(2)
C(14)-N(2)-C(16)	121.1(2)
C(28)-N(3)-Ni(1)	66.29(15)
C(28)-N(3)-Ni(2)	152.37(19)
Ni(1)-N(3)-Ni(2)	86.17(8)
C(36)-N(4)-Ni(2)	65.60(14)
C(36)-N(4)-Ni(1)	151.54(19)
Ni(2)-N(4)-Ni(1)	85.96(8)

Table 13 Continued.

C(58)-N(5)-C(56)	112.2(2)
C(58)-N(5)-C(44)	125.00(19)
C(56)-N(5)-C(44)	122.7(2)
C(58)-N(6)-C(57)	112.2(2)
C(58)-N(6)-C(59)	124.5(2)
C(57)-N(6)-C(59)	123.3(2)
C(2)-C(1)-C(6)	116.2(2)
C(2)-C(1)-C(7)	120.8(2)
C(6)-C(1)-C(7)	123.0(2)
C(3)-C(2)-C(1)	121.3(2)
C(3)-C(2)-H(2)	119.4
C(1)-C(2)-H(2)	119.4
C(2)-C(3)-C(4)	121.0(2)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.7(3)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	116.8(2)
C(4)-C(5)-C(10)	121.0(2)
C(6)-C(5)-C(10)	122.2(2)
C(5)-C(6)-C(1)	124.0(2)
C(5)-C(6)-N(1)	118.4(2)
C(1)-C(6)-N(1)	117.5(2)
C(1)-C(7)-C(9)	112.8(2)
C(1)-C(7)-C(8)	111.3(2)
C(9)-C(7)-C(8)	109.2(2)
C(1)-C(7)-H(7)	107.8
C(9)-C(7)-H(7)	107.8
C(8)-C(7)-H(7)	107.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5

Table 13 Continued.

H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(5)	113.1(2)
C(11)-C(10)-C(12)	108.9(2)
C(5)-C(10)-C(12)	111.7(3)
C(11)-C(10)-H(10)	107.6
C(5)-C(10)-H(10)	107.6
C(12)-C(10)-H(10)	107.6
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-N(1)	106.8(2)
C(14)-C(13)-H(13)	126.6
N(1)-C(13)-H(13)	126.6
C(13)-C(14)-N(2)	106.5(2)
C(13)-C(14)-H(14)	126.7
N(2)-C(14)-H(14)	126.7
N(2)-C(15)-N(1)	101.64(19)
N(2)-C(15)-Ni(1)	130.76(17)

Table 13 Continued.

N(1)-C(15)-Ni(1)	127.54(17)
C(17)-C(16)-C(21)	123.4(2)
C(17)-C(16)-N(2)	119.0(2)
C(21)-C(16)-N(2)	117.5(2)
C(18)-C(17)-C(16)	117.0(2)
C(18)-C(17)-C(22)	121.7(2)
C(16)-C(17)-C(22)	121.3(2)
C(19)-C(18)-C(17)	120.9(3)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(20)-C(19)-C(18)	120.9(3)
C(20)-C(19)-H(19)	119.6
C(18)-C(19)-H(19)	119.6
C(19)-C(20)-C(21)	121.3(3)
C(19)-C(20)-H(20)	119.3
C(21)-C(20)-H(20)	119.3
C(20)-C(21)-C(16)	116.5(2)
C(20)-C(21)-C(25)	120.2(2)
C(16)-C(21)-C(25)	123.3(2)
C(24)-C(22)-C(17)	113.4(2)
C(24)-C(22)-C(23)	110.6(2)
C(17)-C(22)-C(23)	110.8(2)
C(24)-C(22)-H(22)	107.2
C(17)-C(22)-H(22)	107.2
C(23)-C(22)-H(22)	107.2
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5

Table 13 Continued.

C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26A)-C(25)-C(26)	131.6(8)
C(26A)-C(25)-C(21)	110.7(5)
C(26)-C(25)-C(21)	111.0(8)
C(26A)-C(25)-C(27A)	115.1(9)
C(26)-C(25)-C(27A)	21.7(9)
C(21)-C(25)-C(27A)	113.9(9)
C(26A)-C(25)-C(27)	31.2(6)
C(26)-C(25)-C(27)	108.9(6)
C(21)-C(25)-C(27)	111.2(4)
C(27A)-C(25)-C(27)	88.5(8)
C(26A)-C(25)-H(25)	79.9
C(26)-C(25)-H(25)	108.6
C(21)-C(25)-H(25)	108.6
C(27A)-C(25)-H(25)	124.0
C(27)-C(25)-H(25)	108.6
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(26A)-H(26D)	109.5
C(25)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26E)	109.5
C(25)-C(26A)-H(26F)	109.5

Table 13 Continued.

H(26D)-C(26A)-H(26F)	109.5
H(26E)-C(26A)-H(26F)	109.5
C(25)-C(27A)-H(27D)	109.5
C(25)-C(27A)-H(27E)	109.5
H(27D)-C(27A)-H(27E)	109.5
C(25)-C(27A)-H(27F)	109.5
H(27D)-C(27A)-H(27F)	109.5
H(27E)-C(27A)-H(27F)	109.5
N(3)-C(28)-C(29)	136.1(2)
N(3)-C(28)-Ni(1)	76.63(15)
C(29)-C(28)-Ni(1)	147.08(19)
C(34)-C(29)-C(30)	119.4(2)
C(34)-C(29)-C(28)	121.0(2)
C(30)-C(29)-C(28)	119.6(2)
C(31)-C(30)-C(29)	120.3(2)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8
C(30)-C(31)-C(32)	119.8(3)
C(30)-C(31)-H(31)	120.1
C(32)-C(31)-H(31)	120.1
C(33)-C(32)-C(31)	119.9(2)
C(33)-C(32)-C(35)	120.4(3)
C(31)-C(32)-C(35)	119.7(3)
C(32)-C(33)-C(34)	120.2(2)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9
C(29)-C(34)-C(33)	120.3(2)
C(29)-C(34)-H(34)	119.8
C(33)-C(34)-H(34)	119.8
F(2A)-C(35)-F(3A)	109.9(8)
F(2A)-C(35)-F(1)	127.0(5)
F(3A)-C(35)-F(1)	44.4(5)
F(2A)-C(35)-F(2)	45.2(5)
F(3A)-C(35)-F(2)	129.5(6)

Table 13 Continued.

F(1)-C(35)-F(2)	108.6(3)
F(2A)-C(35)-F(3)	58.6(5)
F(3A)-C(35)-F(3)	60.9(6)
F(1)-C(35)-F(3)	102.3(3)
F(2)-C(35)-F(3)	101.8(4)
F(2A)-C(35)-F(1A)	103.8(7)
F(3A)-C(35)-F(1A)	102.5(7)
F(1)-C(35)-F(1A)	59.3(5)
F(2)-C(35)-F(1A)	60.7(5)
F(3)-C(35)-F(1A)	142.0(5)
F(2A)-C(35)-C(32)	117.0(5)
F(3A)-C(35)-C(32)	114.8(6)
F(1)-C(35)-C(32)	116.0(3)
F(2)-C(35)-C(32)	115.6(3)
F(3)-C(35)-C(32)	110.9(3)
F(1A)-C(35)-C(32)	107.1(5)
N(4)-C(36)-C(37)	136.0(2)
N(4)-C(36)-Ni(2)	77.13(15)
C(37)-C(36)-Ni(2)	146.9(2)
C(38)-C(37)-C(42)	119.7(2)
C(38)-C(37)-C(36)	119.5(2)
C(42)-C(37)-C(36)	120.8(2)
C(39)-C(38)-C(37)	120.0(2)
C(39)-C(38)-H(38)	120.0
C(37)-C(38)-H(38)	120.0
C(38)-C(39)-C(40)	120.1(3)
C(38)-C(39)-H(39)	120.0
C(40)-C(39)-H(39)	120.0
C(41)-C(40)-C(39)	120.3(2)
C(41)-C(40)-C(43)	120.5(3)
C(39)-C(40)-C(43)	119.2(3)
C(40)-C(41)-C(42)	119.7(2)
C(40)-C(41)-H(41)	120.2
C(42)-C(41)-H(41)	120.2

Table 13 Continued.

C(41)-C(42)-C(37)	120.3(2)
C(41)-C(42)-H(42)	119.9
C(37)-C(42)-H(42)	119.9
F(5A)-C(43)-F(6A)	102.6(8)
F(5A)-C(43)-F(4)	122.6(6)
F(6A)-C(43)-F(4)	70.4(6)
F(5A)-C(43)-F(5)	31.9(5)
F(6A)-C(43)-F(5)	128.0(7)
F(4)-C(43)-F(5)	108.8(3)
F(5A)-C(43)-F(6)	73.7(5)
F(6A)-C(43)-F(6)	35.9(6)
F(4)-C(43)-F(6)	103.8(4)
F(5)-C(43)-F(6)	105.0(4)
F(5A)-C(43)-F(4A)	99.5(7)
F(6A)-C(43)-F(4A)	109.5(8)
F(4)-C(43)-F(4A)	42.0(4)
F(5)-C(43)-F(4A)	73.1(5)
F(6)-C(43)-F(4A)	134.9(6)
F(5A)-C(43)-C(40)	119.3(6)
F(6A)-C(43)-C(40)	114.3(7)
F(4)-C(43)-C(40)	114.7(3)
F(5)-C(43)-C(40)	112.4(3)
F(6)-C(43)-C(40)	111.4(3)
F(4A)-C(43)-C(40)	110.6(5)
C(45)-C(44)-C(49)	122.7(2)
C(45)-C(44)-N(5)	118.8(2)
C(49)-C(44)-N(5)	118.4(2)
C(46)-C(45)-C(44)	117.0(3)
C(46)-C(45)-C(50)	119.8(3)
C(44)-C(45)-C(50)	123.1(2)
C(47)-C(46)-C(45)	121.4(3)
C(47)-C(46)-H(46)	119.3
C(45)-C(46)-H(46)	119.3
C(48)-C(47)-C(46)	120.5(3)

Table 13 Continued.

C(48)-C(47)-H(47)	119.8
C(46)-C(47)-H(47)	119.8
C(47)-C(48)-C(49)	121.6(3)
C(47)-C(48)-H(48)	119.2
C(49)-C(48)-H(48)	119.2
C(48)-C(49)-C(44)	116.7(3)
C(48)-C(49)-C(53)	120.0(3)
C(44)-C(49)-C(53)	123.3(3)
C(52)-C(50)-C(45)	111.5(3)
C(52)-C(50)-C(51)	110.3(2)
C(45)-C(50)-C(51)	111.2(3)
C(52)-C(50)-H(50)	107.9
C(45)-C(50)-H(50)	107.9
C(51)-C(50)-H(50)	107.9
C(50)-C(51)-H(51A)	109.5
C(50)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(50)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(50)-C(52)-H(52A)	109.5
C(50)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(50)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(55A)-C(53)-C(54)	126.9(4)
C(55A)-C(53)-C(49)	111.8(3)
C(54)-C(53)-C(49)	120.8(4)
C(55A)-C(53)-C(55)	41.5(4)
C(54)-C(53)-C(55)	110.0(4)
C(49)-C(53)-C(55)	119.1(4)
C(55A)-C(53)-C(54A)	110.9(4)
C(54)-C(53)-C(54A)	63.0(4)

Table 13 Continued.

C(49)-C(53)-C(54A)	104.9(4)
C(55)-C(53)-C(54A)	69.7(4)
C(55A)-C(53)-H(53)	61.3
C(54)-C(53)-H(53)	100.7
C(49)-C(53)-H(53)	100.7
C(55)-C(53)-H(53)	100.7
C(54A)-C(53)-H(53)	154.2
C(53)-C(54)-H(54A)	109.5
C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(53)-C(55)-H(55A)	109.5
C(53)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(53)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(53)-C(54A)-H(54D)	109.5
C(53)-C(54A)-H(54E)	109.5
H(54D)-C(54A)-H(54E)	109.5
C(53)-C(54A)-H(54F)	109.5
H(54D)-C(54A)-H(54F)	109.5
H(54E)-C(54A)-H(54F)	109.5
C(53)-C(55A)-H(55D)	109.5
C(53)-C(55A)-H(55E)	109.5
H(55D)-C(55A)-H(55E)	109.5
C(53)-C(55A)-H(55F)	109.5
H(55D)-C(55A)-H(55F)	109.5
H(55E)-C(55A)-H(55F)	109.5
C(57)-C(56)-N(5)	106.4(2)
C(57)-C(56)-H(56)	126.8
N(5)-C(56)-H(56)	126.8

Table 13 Continued.

C(56)-C(57)-N(6)	107.1(2)
C(56)-C(57)-H(57)	126.5
N(6)-C(57)-H(57)	126.5
N(5)-C(58)-N(6)	102.1(2)
N(5)-C(58)-Ni(2)	132.95(17)
N(6)-C(58)-Ni(2)	124.91(18)
C(64)-C(59)-C(60)	122.9(2)
C(64)-C(59)-N(6)	118.5(2)
C(60)-C(59)-N(6)	118.5(2)
C(61)-C(60)-C(59)	117.2(2)
C(61)-C(60)-C(65)	121.4(2)
C(59)-C(60)-C(65)	121.3(2)
C(62)-C(61)-C(60)	121.1(2)
C(62)-C(61)-H(61)	119.5
C(60)-C(61)-H(61)	119.5
C(63)-C(62)-C(61)	120.3(3)
C(63)-C(62)-H(62)	119.8
C(61)-C(62)-H(62)	119.8
C(62)-C(63)-C(64)	121.1(2)
C(62)-C(63)-H(63)	119.4
C(64)-C(63)-H(63)	119.4
C(63)-C(64)-C(59)	117.3(2)
C(63)-C(64)-C(68)	120.4(2)
C(59)-C(64)-C(68)	122.2(2)
C(67A)-C(65)-C(60)	119.1(5)
C(67A)-C(65)-C(66)	77.1(5)
C(60)-C(65)-C(66)	109.7(3)
C(67A)-C(65)-C(67)	28.4(4)
C(60)-C(65)-C(67)	108.3(4)
C(66)-C(65)-C(67)	105.5(4)
C(67A)-C(65)-C(66A)	111.9(5)
C(60)-C(65)-C(66A)	108.6(3)
C(66)-C(65)-C(66A)	41.1(3)
C(67)-C(65)-C(66A)	137.4(4)

Table 13 Continued.

C(67A)-C(65)-H(65)	122.6
C(60)-C(65)-H(65)	111.1
C(66)-C(65)-H(65)	111.1
C(67)-C(65)-H(65)	111.1
C(66A)-C(65)-H(65)	74.1
C(65)-C(66)-H(66A)	109.5
C(65)-C(66)-H(66B)	109.5
H(66A)-C(66)-H(66B)	109.5
C(65)-C(66)-H(66C)	109.5
H(66A)-C(66)-H(66C)	109.5
H(66B)-C(66)-H(66C)	109.5
C(65)-C(67)-H(67A)	109.5
C(65)-C(67)-H(67B)	109.5
H(67A)-C(67)-H(67B)	109.5
C(65)-C(67)-H(67C)	109.5
H(67A)-C(67)-H(67C)	109.5
H(67B)-C(67)-H(67C)	109.5
C(65)-C(66A)-H(66D)	109.5
C(65)-C(66A)-H(66E)	109.5
H(66D)-C(66A)-H(66E)	109.5
C(65)-C(66A)-H(66F)	109.5
H(66D)-C(66A)-H(66F)	109.5
H(66E)-C(66A)-H(66F)	109.5
C(65)-C(67A)-H(67D)	109.5
C(65)-C(67A)-H(67E)	109.5
H(67D)-C(67A)-H(67E)	109.5
C(65)-C(67A)-H(67F)	109.5
H(67D)-C(67A)-H(67F)	109.5
H(67E)-C(67A)-H(67F)	109.5
C(69)-C(68)-C(64)	111.8(2)
C(69)-C(68)-C(70)	109.9(2)
C(64)-C(68)-C(70)	110.6(2)
C(69)-C(68)-H(68)	108.1
C(64)-C(68)-H(68)	108.1

Table 13 Continued.

C(70)-C(68)-H(68)	108.1
C(68)-C(69)-H(69A)	109.5
C(68)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(68)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
C(68)-C(70)-H(70A)	109.5
C(68)-C(70)-H(70B)	109.5
H(70A)-C(70)-H(70B)	109.5
C(68)-C(70)-H(70C)	109.5
H(70A)-C(70)-H(70C)	109.5
H(70B)-C(70)-H(70C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Ni(CF_3C_6H_4CN)IPr]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	25(1)	20(1)	19(1)	3(1)	-4(1)	3(1)
Ni(2)	23(1)	20(1)	21(1)	3(1)	-4(1)	4(1)
F(1)	66(2)	105(3)	44(2)	52(2)	-39(1)	-44(2)
F(2)	17(1)	252(5)	38(2)	15(2)	-12(1)	6(2)
F(3)	158(4)	60(2)	103(3)	-19(2)	-104(3)	15(2)
F(4)	53(2)	151(3)	20(1)	25(2)	-17(1)	-20(2)
F(5)	83(2)	156(4)	60(2)	-13(3)	-44(2)	73(3)
F(6)	159(4)	73(3)	78(2)	29(2)	-89(3)	-61(3)
N(1)	24(1)	22(1)	21(1)	6(1)	-1(1)	4(1)
N(2)	31(1)	21(1)	19(1)	2(1)	-1(1)	1(1)
N(3)	33(1)	28(1)	29(1)	8(1)	-7(1)	7(1)
N(4)	40(1)	24(1)	29(1)	5(1)	-12(1)	8(1)
N(5)	23(1)	20(1)	25(1)	3(1)	1(1)	5(1)
N(6)	22(1)	28(1)	26(1)	7(1)	2(1)	8(1)
C(1)	30(1)	22(1)	27(1)	9(1)	-1(1)	2(1)
C(2)	40(2)	33(2)	28(1)	11(1)	-7(1)	1(1)
C(3)	52(2)	38(2)	22(1)	8(1)	1(1)	1(1)
C(4)	40(2)	40(2)	30(1)	9(1)	12(1)	0(1)
C(5)	29(1)	28(1)	29(1)	7(1)	3(1)	0(1)
C(6)	30(1)	20(1)	20(1)	7(1)	-2(1)	3(1)
C(7)	27(1)	30(2)	34(1)	6(1)	-5(1)	6(1)
C(8)	41(2)	33(2)	70(2)	16(2)	2(2)	11(1)
C(9)	32(2)	34(2)	72(2)	16(2)	9(2)	7(1)
C(10)	26(1)	53(2)	34(2)	-1(1)	4(1)	0(1)
C(11)	32(2)	36(2)	86(3)	16(2)	4(2)	2(1)
C(12)	39(2)	89(3)	89(3)	59(2)	-7(2)	-2(2)
C(13)	33(1)	22(1)	31(1)	7(1)	2(1)	3(1)
C(14)	36(1)	20(1)	31(1)	0(1)	2(1)	4(1)
C(15)	20(1)	25(1)	19(1)	5(1)	-3(1)	2(1)
C(16)	34(1)	28(1)	19(1)	2(1)	4(1)	8(1)

Table 14 Continued.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(17)	34(1)	30(2)	27(1)	4(1)	8(1)	6(1)
C(18)	44(2)	50(2)	35(2)	16(1)	15(1)	9(2)
C(19)	56(2)	69(2)	21(1)	13(2)	8(1)	19(2)
C(20)	46(2)	52(2)	21(1)	1(1)	-3(1)	8(2)
C(21)	36(2)	35(2)	24(1)	0(1)	1(1)	6(1)
C(22)	31(1)	36(2)	33(1)	1(1)	8(1)	1(1)
C(23)	37(2)	46(2)	48(2)	9(2)	-6(1)	-1(1)
C(24)	46(2)	37(2)	66(2)	8(2)	10(2)	0(2)
C(25)	38(2)	31(2)	32(1)	0(1)	-4(1)	-1(1)
C(26)	59(6)	33(5)	48(7)	-11(4)	-12(4)	1(4)
C(27)	29(3)	52(5)	45(4)	8(4)	-3(3)	7(3)
C(26A)	95(10)	53(7)	211(16)	36(10)	92(11)	7(6)
C(27A)	150(20)	68(12)	76(12)	-21(7)	10(11)	-58(12)
C(28)	27(1)	25(1)	23(1)	4(1)	-3(1)	5(1)
C(29)	28(1)	24(1)	24(1)	3(1)	-6(1)	3(1)
C(30)	30(2)	59(2)	23(1)	9(1)	0(1)	5(1)
C(31)	25(1)	70(2)	34(2)	15(2)	-2(1)	2(1)
C(32)	28(1)	45(2)	25(1)	11(1)	-9(1)	2(1)
C(33)	34(2)	56(2)	22(1)	11(1)	-1(1)	7(1)
C(34)	24(1)	47(2)	30(1)	9(1)	-2(1)	4(1)
C(35)	35(2)	65(2)	35(2)	15(2)	-8(1)	-6(2)
C(36)	31(1)	25(1)	24(1)	5(1)	-6(1)	4(1)
C(37)	32(1)	22(1)	24(1)	2(1)	-8(1)	9(1)
C(38)	32(1)	36(2)	25(1)	7(1)	-3(1)	6(1)
C(39)	29(1)	44(2)	34(2)	11(1)	-5(1)	1(1)
C(40)	38(2)	41(2)	27(1)	9(1)	-10(1)	5(1)
C(41)	42(2)	42(2)	29(1)	15(1)	-7(1)	-1(1)
C(42)	33(1)	29(2)	34(1)	9(1)	-10(1)	-4(1)
C(43)	44(2)	71(3)	35(2)	18(2)	-12(2)	-1(2)
C(44)	26(1)	19(1)	32(1)	8(1)	-2(1)	0(1)
C(45)	30(1)	32(2)	42(2)	17(1)	7(1)	7(1)
C(46)	30(2)	67(2)	91(3)	52(2)	20(2)	9(2)

Table 14 Continued.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(47)	26(2)	84(3)	123(4)	71(3)	-14(2)	-12(2)
C(48)	50(2)	48(2)	79(3)	34(2)	-39(2)	-20(2)
C(49)	51(2)	21(1)	41(2)	10(1)	-14(1)	-3(1)
C(50)	47(2)	47(2)	31(2)	11(1)	15(1)	14(1)
C(51)	86(3)	55(2)	41(2)	21(2)	17(2)	19(2)
C(52)	94(3)	50(2)	58(2)	12(2)	35(2)	14(2)
C(53)	87(3)	38(2)	27(2)	-2(1)	-15(2)	16(2)
C(54)	104(6)	45(4)	54(4)	11(4)	11(4)	18(4)
C(55)	92(6)	59(5)	40(4)	21(4)	24(4)	27(4)
C(54A)	72(5)	45(4)	39(3)	-4(3)	-18(3)	-3(3)
C(55A)	34(3)	54(4)	17(3)	1(3)	1(2)	5(3)
C(56)	38(2)	21(1)	34(1)	4(1)	3(1)	11(1)
C(57)	36(2)	33(2)	38(2)	7(1)	6(1)	17(1)
C(58)	22(1)	26(1)	18(1)	6(1)	-1(1)	6(1)
C(59)	20(1)	35(2)	28(1)	8(1)	3(1)	8(1)
C(60)	27(1)	42(2)	26(1)	11(1)	4(1)	10(1)
C(61)	31(2)	48(2)	35(2)	19(1)	8(1)	5(1)
C(62)	25(1)	50(2)	39(2)	13(1)	4(1)	1(1)
C(63)	28(1)	53(2)	29(1)	13(1)	0(1)	9(1)
C(64)	23(1)	41(2)	29(1)	13(1)	4(1)	9(1)
C(65)	34(2)	67(2)	28(1)	21(2)	0(1)	9(2)
C(66)	49(4)	54(4)	23(3)	5(3)	-3(3)	8(3)
C(67)	36(4)	71(5)	29(4)	33(4)	17(3)	21(3)
C(66A)	61(5)	99(7)	39(4)	11(4)	1(4)	28(5)
C(67A)	90(8)	91(8)	58(6)	56(6)	-23(5)	-23(6)
C(68)	29(1)	45(2)	35(2)	21(1)	3(1)	8(1)
C(69)	45(2)	40(2)	43(2)	14(1)	7(1)	14(1)
C(70)	74(2)	71(2)	55(2)	40(2)	37(2)	40(2)

Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Ni(CF_3C_6H_4CN)IPr]_2$.

	x	y	z	U(eq)
H(2)	1945	-2062	4141	41
H(3)	167	-2011	4578	45
H(4)	-1686	-2454	4021	44
H(7)	2168	-2832	2579	37
H(8A)	3775	-3476	3006	71
H(8B)	2505	-4176	3079	71
H(8C)	3217	-3255	3622	71
H(9A)	3964	-1576	2954	68
H(9B)	3434	-1243	3572	68
H(9C)	2830	-957	3008	68
H(10)	-2120	-3586	2466	48
H(11A)	-3949	-4017	2866	77
H(11B)	-3326	-3403	3507	77
H(11C)	-2903	-4493	3160	77
H(12A)	-3530	-2386	2509	102
H(12B)	-2184	-1725	2545	102
H(12C)	-2869	-1665	3124	102
H(13)	226	-4790	2247	34
H(14)	236	-4846	1192	36
H(18)	1516	-1574	60	50
H(19)	-87	-2477	-626	57
H(20)	-1654	-3656	-388	49
H(22)	1673	-1486	1570	42
H(23A)	3553	-2096	1523	68
H(23B)	3192	-2698	849	68
H(23C)	2455	-3111	1342	68
H(24A)	3333	-297	1375	77
H(24B)	2105	-100	1074	77
H(24C)	2985	-770	687	77
H(25)	-1929	-4281	1028	43

Table 15 Continued.

	x	y	z	U(eq)
H(26A)	-2776	-5904	353	77
H(26B)	-1342	-5662	336	77
H(26C)	-2210	-5426	-164	77
H(27A)	-3283	-3177	728	64
H(27B)	-3949	-4429	591	64
H(27C)	-3432	-3919	74	64
H(26D)	-3676	-4209	922	175
H(26E)	-3313	-3337	539	175
H(26F)	-2687	-3132	1190	175
H(27D)	-3148	-5780	241	170
H(27E)	-1811	-5717	39	170
H(27F)	-2755	-5108	-236	170
H(30)	-3497	-797	1619	46
H(31)	-4951	-1290	817	52
H(33)	-2315	-1174	-269	45
H(34)	-860	-677	532	41
H(38)	3551	1673	3455	37
H(39)	4900	2093	4294	43
H(41)	2370	580	5135	46
H(42)	1025	136	4291	40
H(46)	4498	3421	2563	68
H(47)	5488	4010	3493	88
H(48)	4428	4414	4295	73
H(50)	1303	3188	2201	48
H(51A)	2576	4756	2049	87
H(51B)	2234	3843	1448	87
H(51C)	3537	4014	1797	87
H(52A)	1911	1869	1456	99
H(52B)	1954	1497	2060	99
H(52C)	3178	1997	1830	99
H(53)	1224	4030	4232	63
H(54A)	1552	5486	5042	100

Table 15 Continued.

	x	y	z	U(eq)
H(54B)	1620	5814	4427	100
H(54C)	2835	5887	4830	100
H(55A)	2189	2861	4669	90
H(55B)	1431	3631	5080	90
H(55C)	2873	3931	5138	90
H(54D)	3550	5594	4837	85
H(54E)	3699	4442	4973	85
H(54F)	2754	5127	5297	85
H(55D)	1017	3536	4880	55
H(55E)	2003	2857	4595	55
H(55F)	843	2952	4198	55
H(56)	624	5195	3503	37
H(57)	-1558	4434	3314	41
H(61)	-4009	378	3342	44
H(62)	-5156	379	2491	46
H(63)	-4423	1477	1879	43
H(65)	-1080	2104	3885	50
H(66A)	-2146	1885	4712	64
H(66B)	-3345	1292	4294	64
H(66C)	-2850	2569	4357	64
H(67A)	-1129	380	4193	60
H(67B)	-1132	119	3497	60
H(67C)	-2362	-143	3787	60
H(66D)	-1961	3275	4140	98
H(66E)	-1461	2776	4652	98
H(66F)	-2872	2509	4437	98
H(67D)	-1443	776	4428	119
H(67E)	-1726	14	3779	119
H(67F)	-2807	406	4136	119
H(68)	-1590	3386	2152	42
H(69A)	-2906	4067	1568	62
H(69B)	-3393	4103	2195	62

Table 15 Continued.

	x	y	z	U(eq)
H(69C)	-4008	3159	1641	62
H(70A)	-1762	2646	1127	87
H(70B)	-2811	1681	1189	87
H(70C)	-1465	1749	1467	87

Table 16. Torsion angles [°] for $[Ni(CF_3C_6H_4CN)IPr]_2$.

C(28)-Ni(1)-Ni(2)-C(36)	-179.38(11)
C(15)-Ni(1)-Ni(2)-C(36)	4.7(2)
N(3)-Ni(1)-Ni(2)-C(36)	-177.98(12)
N(4)-Ni(1)-Ni(2)-C(36)	-0.54(12)
C(28)-Ni(1)-Ni(2)-C(58)	12.42(19)
C(15)-Ni(1)-Ni(2)-C(58)	-163.5(2)
N(3)-Ni(1)-Ni(2)-C(58)	13.8(2)
N(4)-Ni(1)-Ni(2)-C(58)	-168.7(2)
C(28)-Ni(1)-Ni(2)-N(4)	-178.84(12)
C(15)-Ni(1)-Ni(2)-N(4)	5.3(2)
N(3)-Ni(1)-Ni(2)-N(4)	-177.44(13)
C(28)-Ni(1)-Ni(2)-N(3)	-1.39(12)
C(15)-Ni(1)-Ni(2)-N(3)	-177.3(2)
N(4)-Ni(1)-Ni(2)-N(3)	177.44(13)
C(15)-Ni(1)-N(3)-C(28)	-0.4(3)
N(4)-Ni(1)-N(3)-C(28)	-179.57(17)
Ni(2)-Ni(1)-N(3)-C(28)	-177.70(19)
C(28)-Ni(1)-N(3)-Ni(2)	177.70(19)
C(15)-Ni(1)-N(3)-Ni(2)	177.3(2)
N(4)-Ni(1)-N(3)-Ni(2)	-1.87(9)
C(36)-Ni(2)-N(3)-C(28)	7.2(5)
C(58)-Ni(2)-N(3)-C(28)	-169.6(4)
N(4)-Ni(2)-N(3)-C(28)	6.4(4)
Ni(1)-Ni(2)-N(3)-C(28)	4.5(4)
C(36)-Ni(2)-N(3)-Ni(1)	2.66(16)
C(58)-Ni(2)-N(3)-Ni(1)	-174.18(8)
N(4)-Ni(2)-N(3)-Ni(1)	1.88(9)
C(58)-Ni(2)-N(4)-C(36)	-10.0(3)
N(3)-Ni(2)-N(4)-C(36)	179.02(17)
Ni(1)-Ni(2)-N(4)-C(36)	-179.1(2)
C(36)-Ni(2)-N(4)-Ni(1)	179.1(2)
C(58)-Ni(2)-N(4)-Ni(1)	169.15(19)
N(3)-Ni(2)-N(4)-Ni(1)	-1.87(9)
C(28)-Ni(1)-N(4)-C(36)	3.2(5)

Table 16 Continued.

C(15)-Ni(1)-N(4)-C(36)	-176.1(4)
N(3)-Ni(1)-N(4)-C(36)	3.6(4)
Ni(2)-Ni(1)-N(4)-C(36)	1.7(4)
C(28)-Ni(1)-N(4)-Ni(2)	1.53(16)
C(15)-Ni(1)-N(4)-Ni(2)	-177.76(8)
N(3)-Ni(1)-N(4)-Ni(2)	1.87(9)
C(6)-C(1)-C(2)-C(3)	0.1(4)
C(7)-C(1)-C(2)-C(3)	-178.3(2)
C(1)-C(2)-C(3)-C(4)	0.3(4)
C(2)-C(3)-C(4)-C(5)	0.4(4)
C(3)-C(4)-C(5)-C(6)	-1.3(4)
C(3)-C(4)-C(5)-C(10)	177.5(3)
C(4)-C(5)-C(6)-C(1)	1.8(4)
C(10)-C(5)-C(6)-C(1)	-177.1(2)
C(4)-C(5)-C(6)-N(1)	177.9(2)
C(10)-C(5)-C(6)-N(1)	-1.0(4)
C(2)-C(1)-C(6)-C(5)	-1.2(4)
C(7)-C(1)-C(6)-C(5)	177.2(2)
C(2)-C(1)-C(6)-N(1)	-177.3(2)
C(7)-C(1)-C(6)-N(1)	1.1(3)
C(15)-N(1)-C(6)-C(5)	86.4(3)
C(13)-N(1)-C(6)-C(5)	-98.6(3)
C(15)-N(1)-C(6)-C(1)	-97.3(3)
C(13)-N(1)-C(6)-C(1)	77.8(3)
C(2)-C(1)-C(7)-C(9)	-61.9(3)
C(6)-C(1)-C(7)-C(9)	119.7(3)
C(2)-C(1)-C(7)-C(8)	61.2(3)
C(6)-C(1)-C(7)-C(8)	-117.2(3)
C(4)-C(5)-C(10)-C(11)	-39.6(4)
C(6)-C(5)-C(10)-C(11)	139.2(3)
C(4)-C(5)-C(10)-C(12)	83.8(3)
C(6)-C(5)-C(10)-C(12)	-97.4(3)
C(15)-N(1)-C(13)-C(14)	-0.5(3)
C(6)-N(1)-C(13)-C(14)	-176.1(2)

Table 16 Continued.

N(1)-C(13)-C(14)-N(2)	-0.3(3)
C(15)-N(2)-C(14)-C(13)	1.0(3)
C(16)-N(2)-C(14)-C(13)	-179.1(2)
C(14)-N(2)-C(15)-N(1)	-1.2(3)
C(16)-N(2)-C(15)-N(1)	178.9(2)
C(14)-N(2)-C(15)-Ni(1)	176.13(18)
C(16)-N(2)-C(15)-Ni(1)	-3.8(4)
C(13)-N(1)-C(15)-N(2)	1.0(3)
C(6)-N(1)-C(15)-N(2)	176.5(2)
C(13)-N(1)-C(15)-Ni(1)	-176.44(17)
C(6)-N(1)-C(15)-Ni(1)	-1.0(3)
C(28)-Ni(1)-C(15)-N(2)	42.1(3)
N(3)-Ni(1)-C(15)-N(2)	42.4(4)
N(4)-Ni(1)-C(15)-N(2)	-138.5(2)
Ni(2)-Ni(1)-C(15)-N(2)	-142.56(16)
C(28)-Ni(1)-C(15)-N(1)	-141.19(19)
N(3)-Ni(1)-C(15)-N(1)	-140.9(2)
N(4)-Ni(1)-C(15)-N(1)	38.2(2)
Ni(2)-Ni(1)-C(15)-N(1)	34.1(3)
C(15)-N(2)-C(16)-C(17)	68.8(3)
C(14)-N(2)-C(16)-C(17)	-111.1(3)
C(15)-N(2)-C(16)-C(21)	-115.0(3)
C(14)-N(2)-C(16)-C(21)	65.1(3)
C(21)-C(16)-C(17)-C(18)	0.5(4)
N(2)-C(16)-C(17)-C(18)	176.4(2)
C(21)-C(16)-C(17)-C(22)	-178.6(2)
N(2)-C(16)-C(17)-C(22)	-2.7(4)
C(16)-C(17)-C(18)-C(19)	-0.8(4)
C(22)-C(17)-C(18)-C(19)	178.2(3)
C(17)-C(18)-C(19)-C(20)	0.7(5)
C(18)-C(19)-C(20)-C(21)	-0.1(5)
C(19)-C(20)-C(21)-C(16)	-0.2(4)
C(19)-C(20)-C(21)-C(25)	-179.8(3)
C(17)-C(16)-C(21)-C(20)	0.1(4)

Table 16 Continued.

N(2)-C(16)-C(21)-C(20)	-175.9(2)
C(17)-C(16)-C(21)-C(25)	179.6(3)
N(2)-C(16)-C(21)-C(25)	3.6(4)
C(18)-C(17)-C(22)-C(24)	25.1(4)
C(16)-C(17)-C(22)-C(24)	-155.9(3)
C(18)-C(17)-C(22)-C(23)	-100.1(3)
C(16)-C(17)-C(22)-C(23)	79.0(3)
C(20)-C(21)-C(25)-C(26A)	-90.4(7)
C(16)-C(21)-C(25)-C(26A)	90.0(7)
C(20)-C(21)-C(25)-C(26)	64.4(6)
C(16)-C(21)-C(25)-C(26)	-115.1(6)
C(20)-C(21)-C(25)-C(27A)	41.1(8)
C(16)-C(21)-C(25)-C(27A)	-138.4(8)
C(20)-C(21)-C(25)-C(27)	-56.9(4)
C(16)-C(21)-C(25)-C(27)	123.5(4)
Ni(1)-N(3)-C(28)-C(29)	175.7(4)
Ni(2)-N(3)-C(28)-C(29)	170.7(3)
Ni(2)-N(3)-C(28)-Ni(1)	-5.0(4)
C(15)-Ni(1)-C(28)-N(3)	179.80(15)
N(4)-Ni(1)-C(28)-N(3)	0.6(2)
Ni(2)-Ni(1)-C(28)-N(3)	1.69(14)
C(15)-Ni(1)-C(28)-C(29)	5.3(4)
N(3)-Ni(1)-C(28)-C(29)	-174.5(5)
N(4)-Ni(1)-C(28)-C(29)	-173.9(3)
Ni(2)-Ni(1)-C(28)-C(29)	-172.8(4)
N(3)-C(28)-C(29)-C(34)	102.0(4)
Ni(1)-C(28)-C(29)-C(34)	-85.8(4)
N(3)-C(28)-C(29)-C(30)	-80.5(4)
Ni(1)-C(28)-C(29)-C(30)	91.8(4)
C(34)-C(29)-C(30)-C(31)	0.7(4)
C(28)-C(29)-C(30)-C(31)	-176.9(3)
C(29)-C(30)-C(31)-C(32)	0.4(5)
C(30)-C(31)-C(32)-C(33)	-1.5(5)
C(30)-C(31)-C(32)-C(35)	175.4(3)

Table 16 Continued.

C(31)-C(32)-C(33)-C(34)	1.4(5)
C(35)-C(32)-C(33)-C(34)	-175.5(3)
C(30)-C(29)-C(34)-C(33)	-0.8(4)
C(28)-C(29)-C(34)-C(33)	176.8(3)
C(32)-C(33)-C(34)-C(29)	-0.2(4)
C(33)-C(32)-C(35)-F(2A)	138.2(7)
C(31)-C(32)-C(35)-F(2A)	-38.7(8)
C(33)-C(32)-C(35)-F(3A)	7.1(8)
C(31)-C(32)-C(35)-F(3A)	-169.8(8)
C(33)-C(32)-C(35)-F(1)	-42.3(5)
C(31)-C(32)-C(35)-F(1)	140.8(4)
C(33)-C(32)-C(35)-F(2)	-171.1(4)
C(31)-C(32)-C(35)-F(2)	12.0(6)
C(33)-C(32)-C(35)-F(3)	73.7(4)
C(31)-C(32)-C(35)-F(3)	-103.1(4)
C(33)-C(32)-C(35)-F(1A)	-105.9(6)
C(31)-C(32)-C(35)-F(1A)	77.2(6)
Ni(2)-N(4)-C(36)-C(37)	-179.7(4)
Ni(1)-N(4)-C(36)-C(37)	178.4(3)
Ni(1)-N(4)-C(36)-Ni(2)	-1.9(4)
C(58)-Ni(2)-C(36)-N(4)	175.33(15)
N(3)-Ni(2)-C(36)-N(4)	-1.3(2)
Ni(1)-Ni(2)-C(36)-N(4)	0.65(15)
C(58)-Ni(2)-C(36)-C(37)	-5.1(4)
N(4)-Ni(2)-C(36)-C(37)	179.6(5)
N(3)-Ni(2)-C(36)-C(37)	178.3(3)
Ni(1)-Ni(2)-C(36)-C(37)	-179.7(4)
N(4)-C(36)-C(37)-C(38)	105.9(4)
Ni(2)-C(36)-C(37)-C(38)	-73.5(4)
N(4)-C(36)-C(37)-C(42)	-75.4(4)
Ni(2)-C(36)-C(37)-C(42)	105.1(4)
C(42)-C(37)-C(38)-C(39)	0.8(4)
C(36)-C(37)-C(38)-C(39)	179.5(2)
C(37)-C(38)-C(39)-C(40)	-0.8(4)

Table 16 Continued.

C(38)-C(39)-C(40)-C(41)	0.3(5)
C(38)-C(39)-C(40)-C(43)	-178.0(3)
C(39)-C(40)-C(41)-C(42)	0.2(5)
C(43)-C(40)-C(41)-C(42)	178.5(3)
C(40)-C(41)-C(42)-C(37)	-0.2(4)
C(38)-C(37)-C(42)-C(41)	-0.3(4)
C(36)-C(37)-C(42)-C(41)	-179.0(3)
C(41)-C(40)-C(43)-F(5A)	153.6(6)
C(39)-C(40)-C(43)-F(5A)	-28.1(7)
C(41)-C(40)-C(43)-F(6A)	-84.7(8)
C(39)-C(40)-C(43)-F(6A)	93.6(8)
C(41)-C(40)-C(43)-F(4)	-6.1(5)
C(39)-C(40)-C(43)-F(4)	172.2(4)
C(41)-C(40)-C(43)-F(5)	118.9(4)
C(39)-C(40)-C(43)-F(5)	-62.8(5)
C(41)-C(40)-C(43)-F(6)	-123.6(4)
C(39)-C(40)-C(43)-F(6)	54.7(5)
C(41)-C(40)-C(43)-F(4A)	39.3(7)
C(39)-C(40)-C(43)-F(4A)	-142.4(6)
C(58)-N(5)-C(44)-C(45)	69.1(3)
C(56)-N(5)-C(44)-C(45)	-113.2(3)
C(58)-N(5)-C(44)-C(49)	-113.5(3)
C(56)-N(5)-C(44)-C(49)	64.2(3)
C(49)-C(44)-C(45)-C(46)	3.0(4)
N(5)-C(44)-C(45)-C(46)	-179.7(2)
C(49)-C(44)-C(45)-C(50)	-174.1(2)
N(5)-C(44)-C(45)-C(50)	3.1(4)
C(44)-C(45)-C(46)-C(47)	-2.5(4)
C(50)-C(45)-C(46)-C(47)	174.8(3)
C(45)-C(46)-C(47)-C(48)	0.5(5)
C(46)-C(47)-C(48)-C(49)	1.1(5)
C(47)-C(48)-C(49)-C(44)	-0.6(4)
C(47)-C(48)-C(49)-C(53)	179.6(3)
C(45)-C(44)-C(49)-C(48)	-1.5(4)

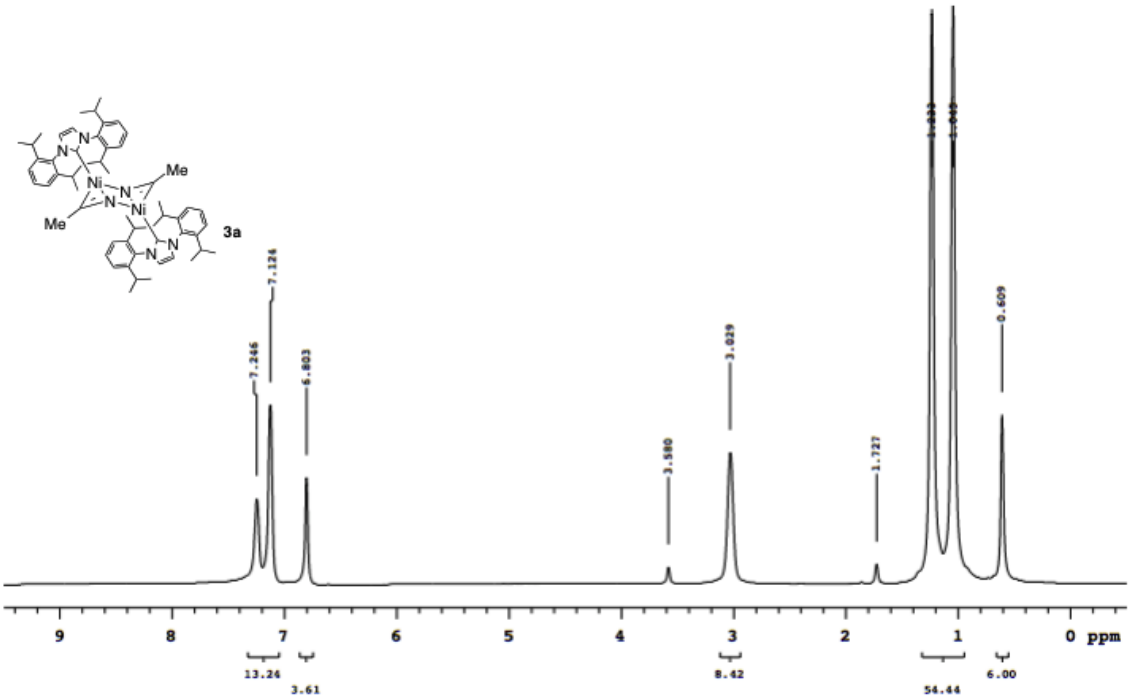
Table 16 Continued.

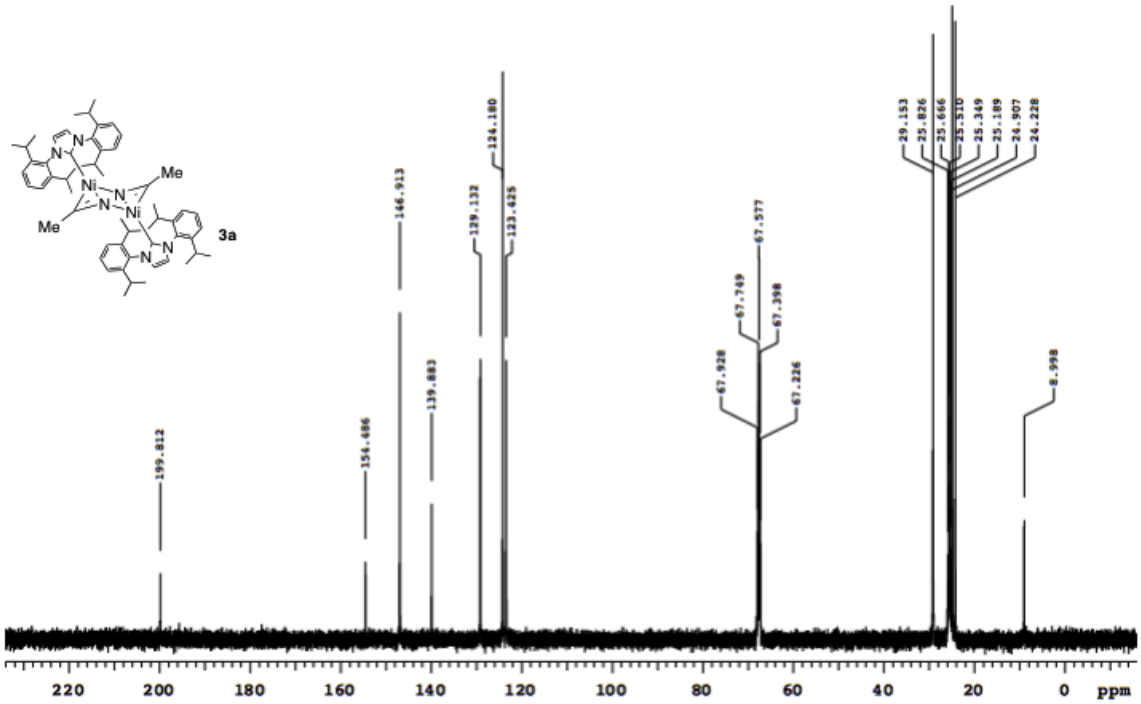
N(5)-C(44)-C(49)-C(48)	-178.8(2)
C(45)-C(44)-C(49)-C(53)	178.2(3)
N(5)-C(44)-C(49)-C(53)	0.9(4)
C(46)-C(45)-C(50)-C(52)	66.0(4)
C(44)-C(45)-C(50)-C(52)	-116.9(3)
C(46)-C(45)-C(50)-C(51)	-57.6(4)
C(44)-C(45)-C(50)-C(51)	119.6(3)
C(48)-C(49)-C(53)-C(55A)	-108.7(4)
C(44)-C(49)-C(53)-C(55A)	71.6(4)
C(48)-C(49)-C(53)-C(54)	78.8(5)
C(44)-C(49)-C(53)-C(54)	-101.0(5)
C(48)-C(49)-C(53)-C(55)	-63.2(5)
C(44)-C(49)-C(53)-C(55)	117.1(5)
C(48)-C(49)-C(53)-C(54A)	11.6(4)
C(44)-C(49)-C(53)-C(54A)	-168.1(3)
C(58)-N(5)-C(56)-C(57)	0.5(3)
C(44)-N(5)-C(56)-C(57)	-177.5(2)
N(5)-C(56)-C(57)-N(6)	-0.3(3)
C(58)-N(6)-C(57)-C(56)	0.1(3)
C(59)-N(6)-C(57)-C(56)	-179.6(2)
C(56)-N(5)-C(58)-N(6)	-0.4(2)
C(44)-N(5)-C(58)-N(6)	177.6(2)
C(56)-N(5)-C(58)-Ni(2)	-177.82(18)
C(44)-N(5)-C(58)-Ni(2)	0.1(3)
C(57)-N(6)-C(58)-N(5)	0.2(3)
C(59)-N(6)-C(58)-N(5)	179.9(2)
C(57)-N(6)-C(58)-Ni(2)	177.88(17)
C(59)-N(6)-C(58)-Ni(2)	-2.4(3)
C(36)-Ni(2)-C(58)-N(5)	48.9(3)
N(4)-Ni(2)-C(58)-N(5)	55.7(4)
N(3)-Ni(2)-C(58)-N(5)	-133.8(2)
Ni(1)-Ni(2)-C(58)-N(5)	-144.52(16)
C(36)-Ni(2)-C(58)-N(6)	-128.07(19)
N(4)-Ni(2)-C(58)-N(6)	-121.2(2)

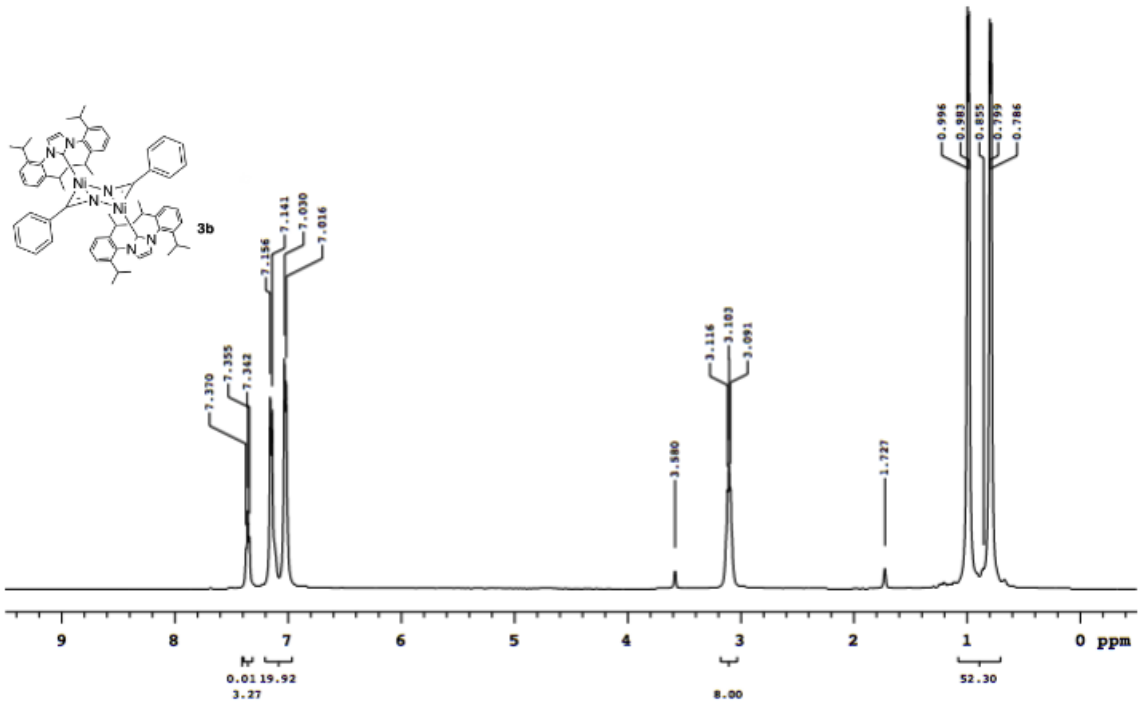
Table 16 Continued.

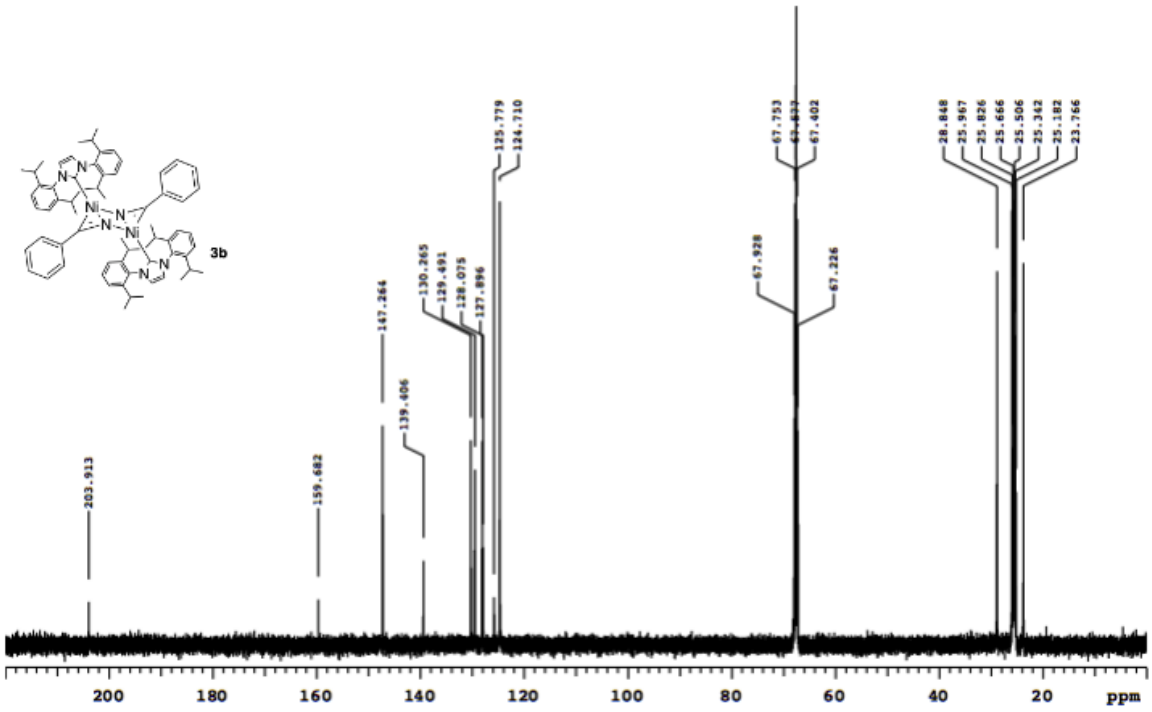
N(3)-Ni(2)-C(58)-N(6)	49.2(2)
Ni(1)-Ni(2)-C(58)-N(6)	38.5(3)
C(58)-N(6)-C(59)-C(64)	-107.3(3)
C(57)-N(6)-C(59)-C(64)	72.4(3)
C(58)-N(6)-C(59)-C(60)	74.6(3)
C(57)-N(6)-C(59)-C(60)	-105.7(3)
C(64)-C(59)-C(60)-C(61)	0.1(4)
N(6)-C(59)-C(60)-C(61)	178.1(2)
C(64)-C(59)-C(60)-C(65)	-177.3(3)
N(6)-C(59)-C(60)-C(65)	0.7(4)
C(59)-C(60)-C(61)-C(62)	-0.3(4)
C(65)-C(60)-C(61)-C(62)	177.0(3)
C(60)-C(61)-C(62)-C(63)	0.7(5)
C(61)-C(62)-C(63)-C(64)	-0.9(5)
C(62)-C(63)-C(64)-C(59)	0.7(4)
C(62)-C(63)-C(64)-C(68)	178.9(3)
C(60)-C(59)-C(64)-C(63)	-0.3(4)
N(6)-C(59)-C(64)-C(63)	-178.3(2)
C(60)-C(59)-C(64)-C(68)	-178.4(3)
N(6)-C(59)-C(64)-C(68)	3.6(4)
C(61)-C(60)-C(65)-C(67A)	30.9(7)
C(59)-C(60)-C(65)-C(67A)	-151.9(6)
C(61)-C(60)-C(65)-C(66)	-55.0(5)
C(59)-C(60)-C(65)-C(66)	122.2(4)
C(61)-C(60)-C(65)-C(67)	59.6(4)
C(59)-C(60)-C(65)-C(67)	-123.2(4)
C(61)-C(60)-C(65)-C(66A)	-98.6(5)
C(59)-C(60)-C(65)-C(66A)	78.6(4)
C(63)-C(64)-C(68)-C(69)	55.5(4)
C(59)-C(64)-C(68)-C(69)	-126.4(3)
C(63)-C(64)-C(68)-C(70)	-67.3(3)
C(59)-C(64)-C(68)-C(70)	110.7(3)

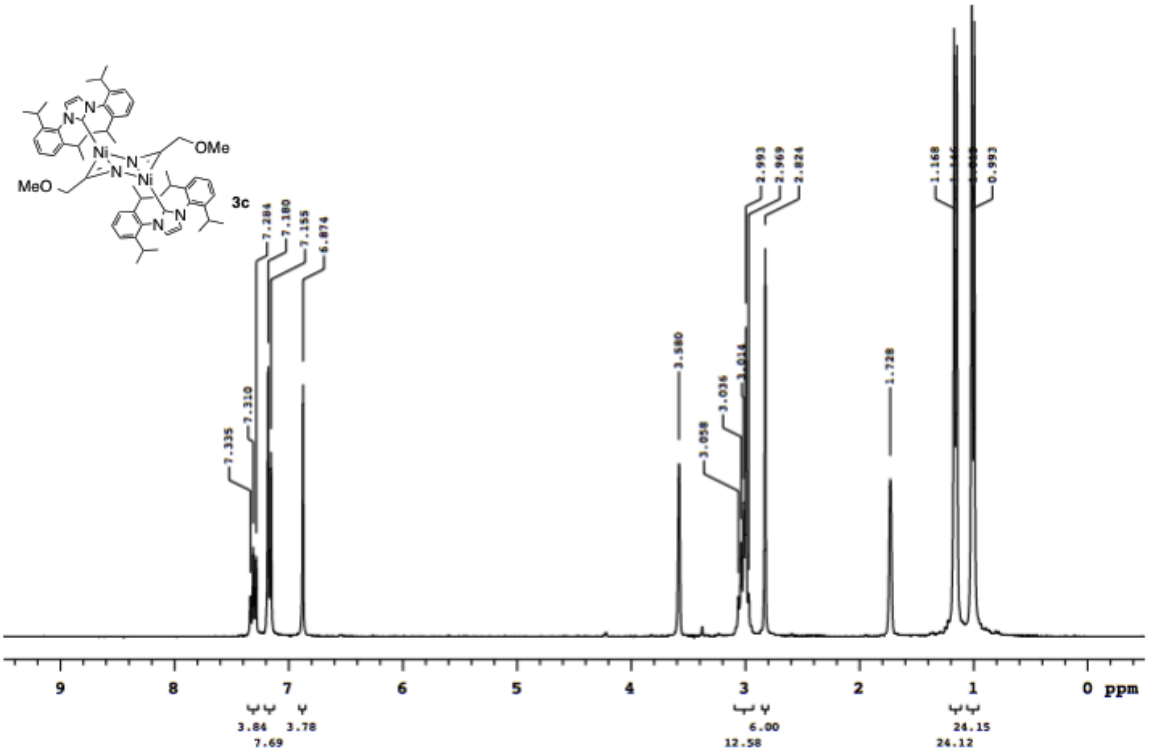
Symmetry transformations used to generate equivalent atoms:

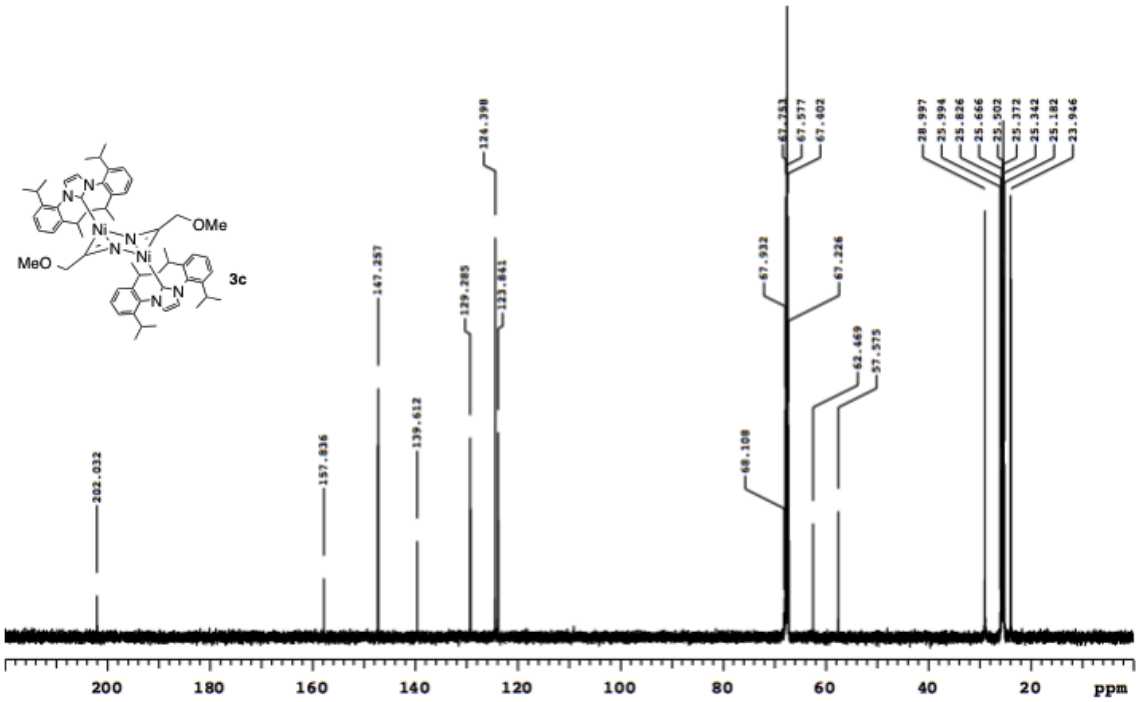

Me
Ni
N
Ni
Me
3a
7.246
7.124
6.803
3.580
3.029
1.727
0.609
9
8
7
6
5
4
3
2
1
0 ppm
13.24
3.61
8.42
54.44
6.00

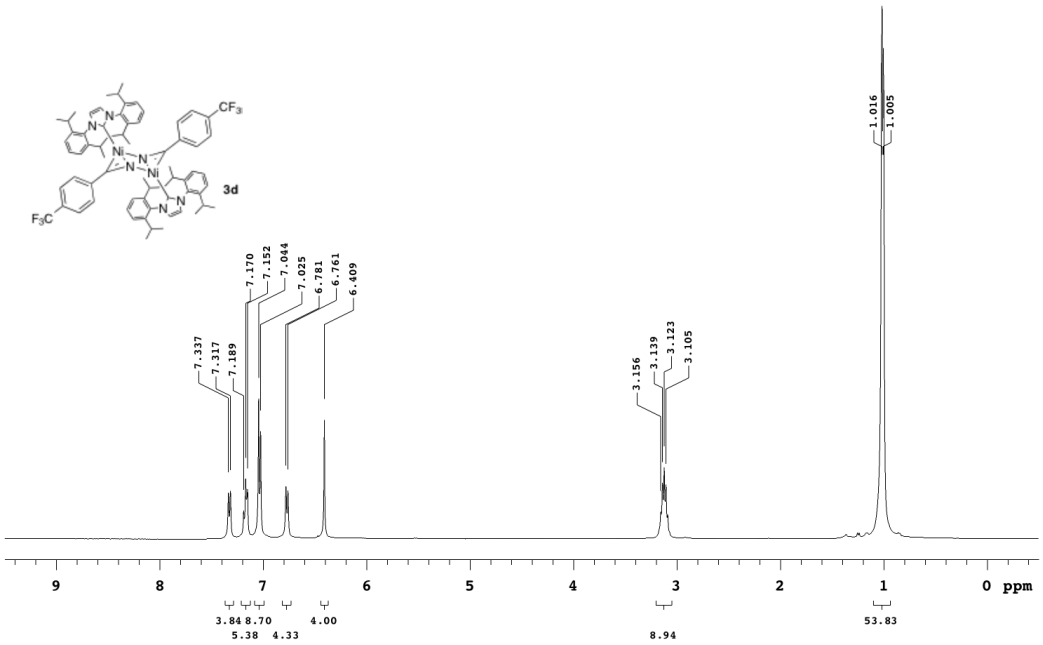

Me
Ni
N
Ni
Me
3a
199.812
154.486
146.913
139.883
129.132
124.180
123.425
67.928
67.749
67.577
67.398
67.226
29.153
25.826
25.666
25.510
25.349
25.189
24.907
24.228
8.998
220
200
180
160
140
120
100
80
60
40
20
0 ppm

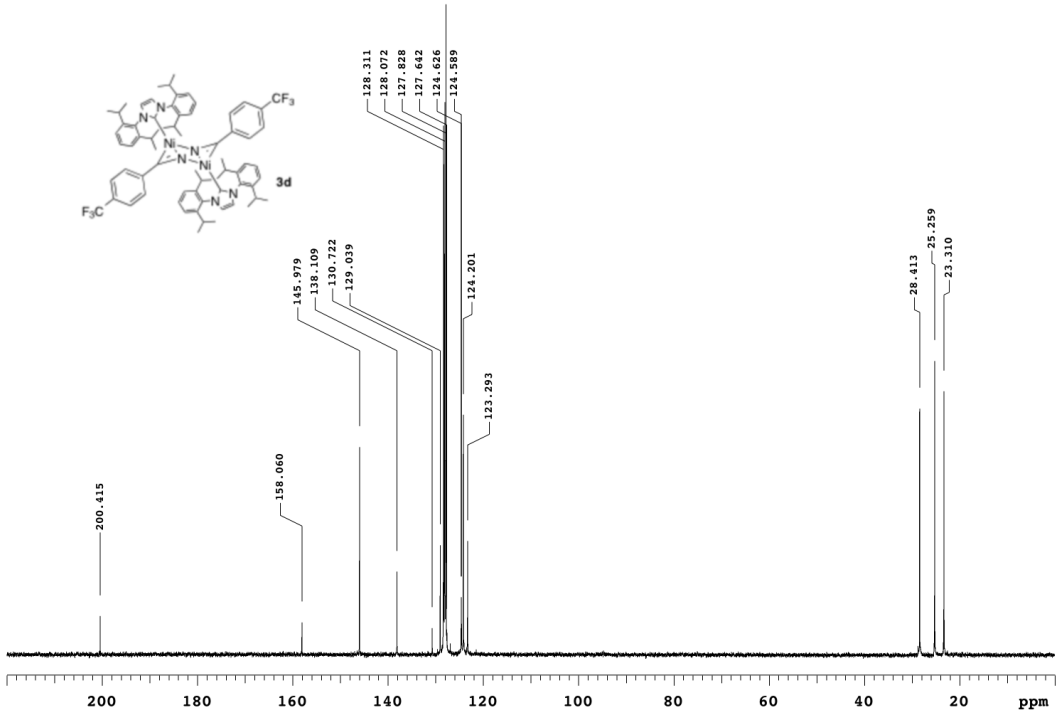

3b
7.370
7.355
7.342
7.156
7.141
7.030
7.016
3.580
3.116
3.103
3.091
1.727
0.996
0.983
0.855
0.799
0.786
9
8
7
6
5
4
3
2
1
0 ppm
0.01 19.92
3.27
8.00
52.30

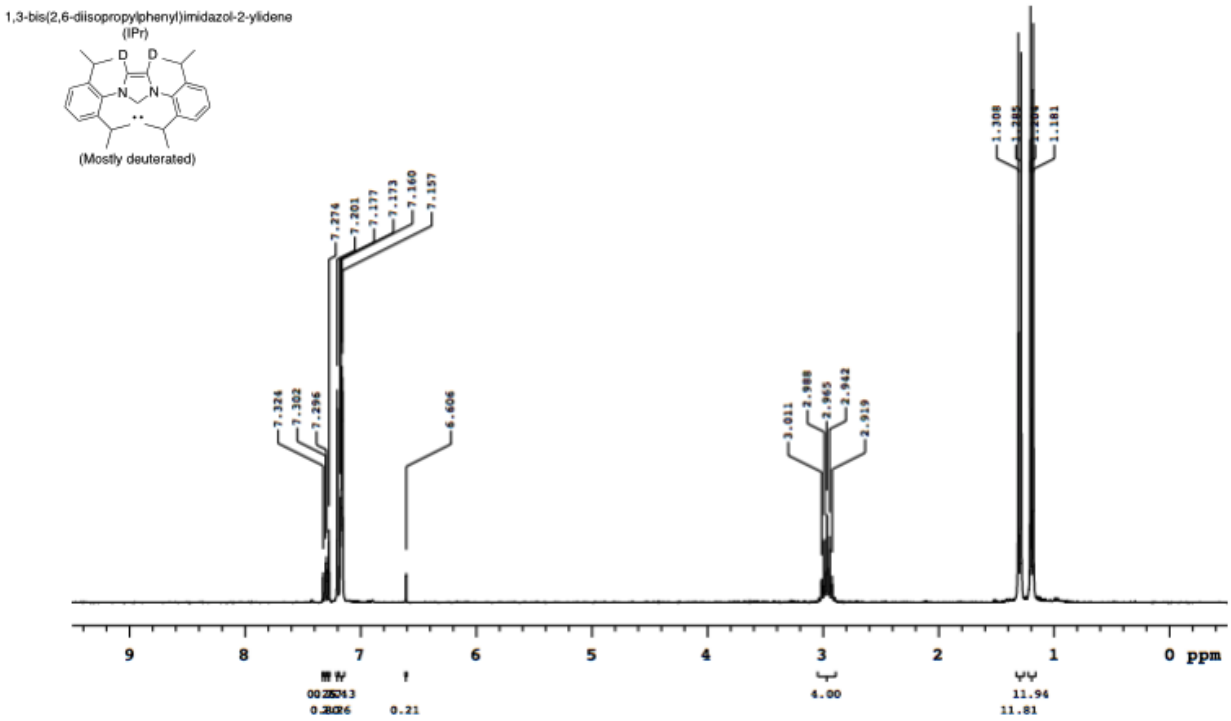

3b
203.913
159.682
147.264
139.406
130.265
129.491
128.075
127.896
125.779
124.710
67.753
67.632
67.402
67.928
67.226
28.848
25.967
25.826
25.666
25.506
25.342
25.182
23.766
200
180
160
140
120
100
80
60
40
20
ppm

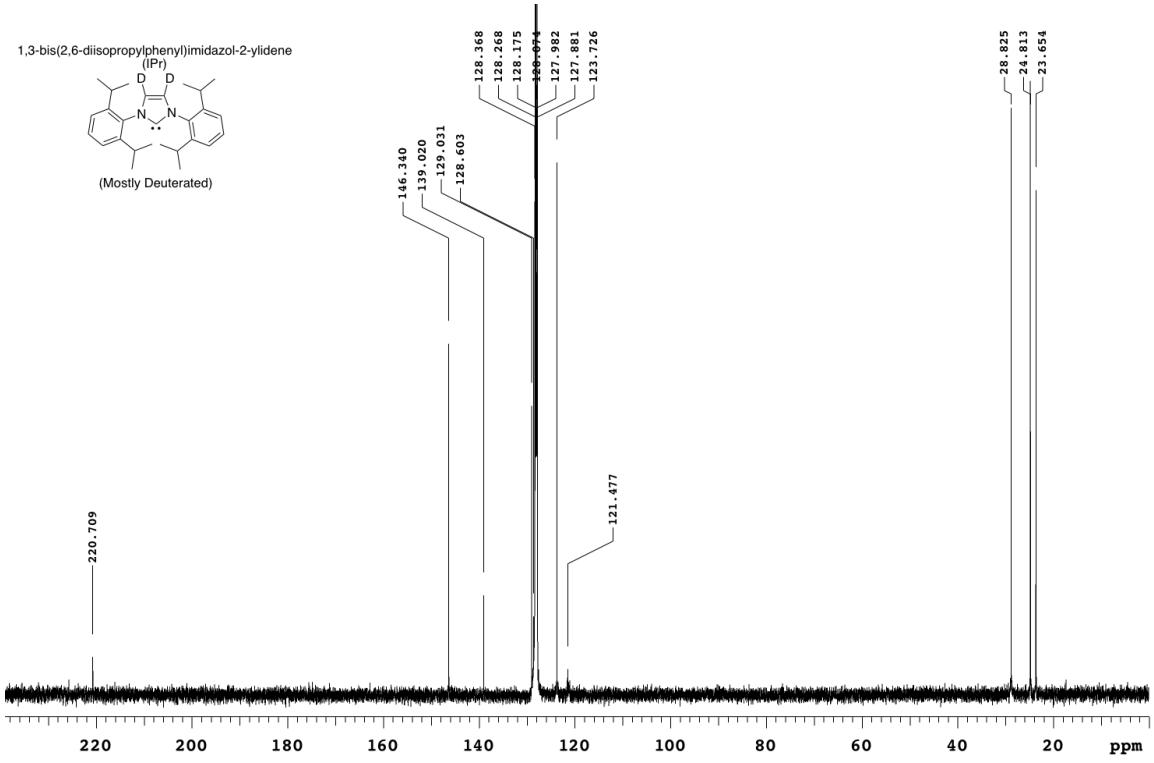

3c
MeO
OMe
Ni
N
7.335
7.310
7.284
7.180
7.155
6.874
3.580
3.058
3.036
3.014
2.993
2.969
2.824
1.728
1.168
0.993
9
8
7
6
5
4
3
2
1
0 ppm
3.84
3.78
7.69
6.00
12.58
24.15
24.12

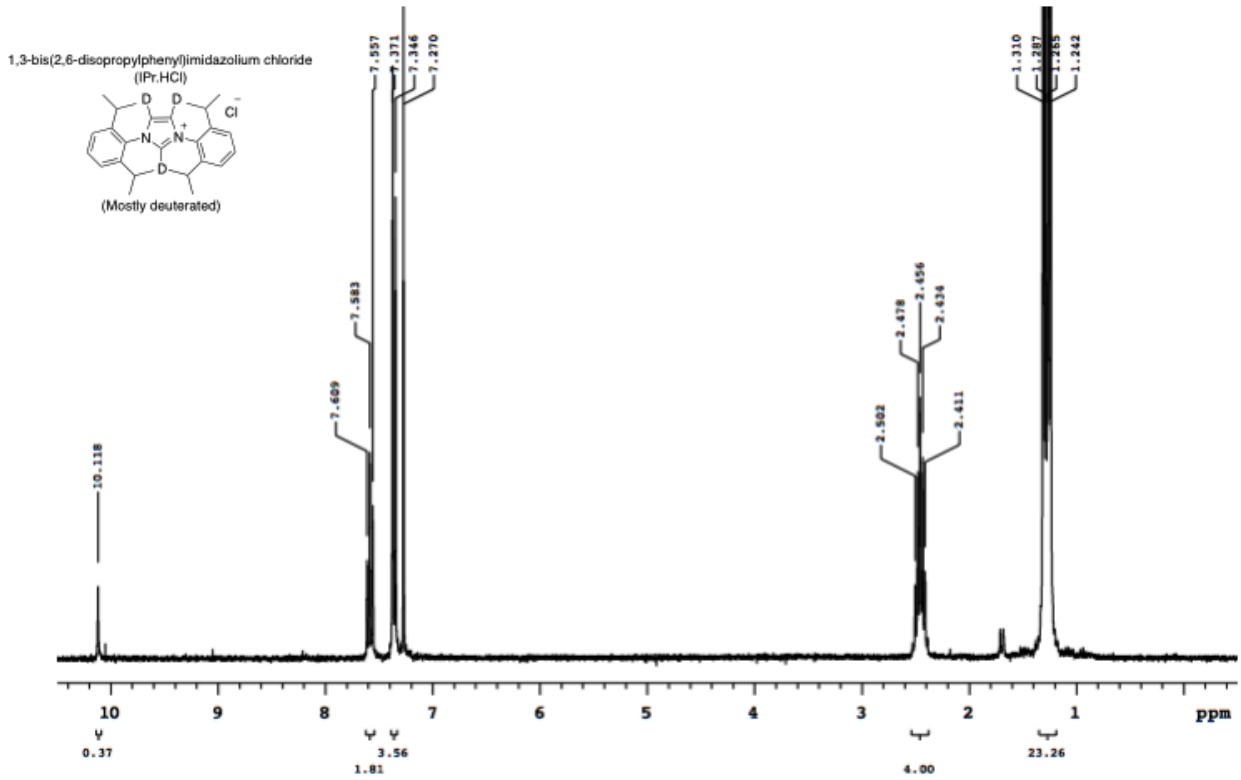

3c
MeO
OMe
Ni
N
202.032
157.836
147.257
139.612
129.285
124.398
123.841
68.108
67.932
67.577
67.403
67.226
62.469
57.575
28.997
25.994
25.826
25.666
25.502
25.372
25.342
25.182
23.946
200
180
160
140
120
100
80
60
40
20
ppm

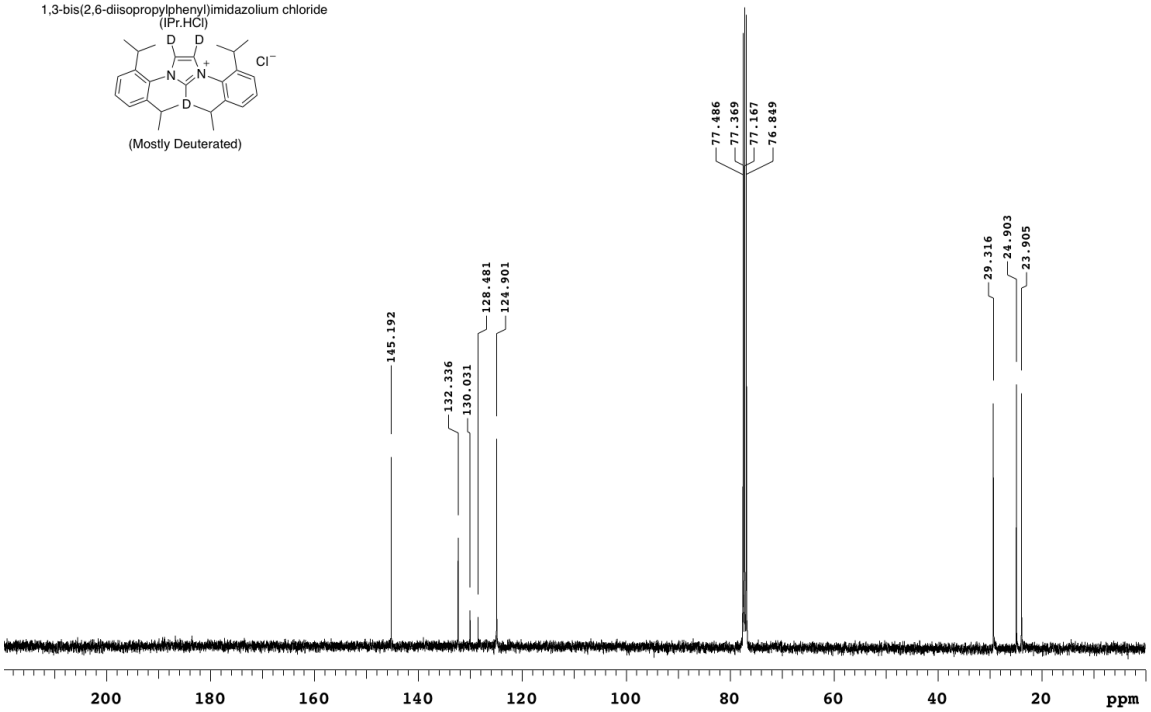

3d
7.337
7.317
7.189
7.170
7.152
7.044
7.025
6.781
6.761
6.409
3.156
3.139
3.123
3.105
1.016
1.005
9
8
7
6
5
4
3
2
1
0 ppm
3.84
8.70
4.00
5.38
4.33
8.94
53.83


3d
128.311
128.072
127.828
127.642
124.626
124.589
145.979
138.109
130.722
129.039
124.201
123.293
158.060
200.415
28.413
25.259
23.310
200
180
160
140
120
100
80
60
40
20
ppm


1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
(IPr)
D
D
N
N
(Mostly deuterated)
7.324
7.302
7.296
7.274
7.201
7.177
7.173
7.160
7.157
6.606
3.011
2.988
2.965
2.942
2.919
1.308
1.285
1.181
9
8
7
6
5
4
3
2
1
0 ppm
0.21
4.00
11.96
11.81


1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
(IPr)
D
D
N
N
(Mostly Deuterated)
220.709
146.340
139.020
129.031
128.603
128.368
128.268
128.175
128.074
127.982
127.881
123.726
121.477
28.825
24.813
23.654
220
200
180
160
140
120
100
80
60
40
20
ppm


1,3-bis(2,6-disopropylphenyl)imidazolium chloride
(IPr.HCl)
(Mostly deuterated)
10.118
7.609
7.583
7.557
7.371
7.346
7.270
2.502
2.478
2.456
2.434
2.411
1.310
1.287
1.265
1.242
ppm
0.37
1.81
3.56
4.00
23.26


1,3-bis(2,6-diisopropylphenyl)imidazolium chloride
(IPr.HCl)
(Mostly Deuterated)
145.192
132.336
130.031
128.481
124.901
77.486
77.369
77.167
76.849
29.316
24.903
23.905
ppm

REFERENCES

(1) (a) Varela, J.A.; Saá, C. *Synlett.* **2008**, 17, 2571. (b) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085. (c) Henry, G. D. *Tetrahedron.* **2004**, 60, 6043. (d) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787.

(2) (a) Kase, K.; Goswami, A.; Ohtaki, K.; Tanabe, E.; Saino, N.; Okamoto, S. *Org. Lett.* **2007**, 9, 931. (b) Wakatsuki, Y.; Yamazaki, H. *J.C.S. Chem. Comm.* **1973**, 8, 280. (c) Wakatsuki, Y.; Yamazaki, H. *J.C.S. Dalton* **1978**, 10, 1278. (d) Bonnemann, H.; Brinkmann, R.; Schenkluhn, H. *Synthesis*. **1974**, 8, 575. (e) Naiman, A.; Vollhardt, K. P. C. *Angew. Chem.* **1977**, 89, 758.

(3) (a) Yamamoto, Y.; Kinpara, K.; Ogawa, R.; Nishiyama, H.; Itoh, K. *Chem. Eur. J.* **2006**, 12, 5618. (b) Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Takagishi, H.; Okuda, S.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 605. (c) Yamamoto, Y.; Kinpara, K.; Nishiyama, H.; Itoh, K. *Adv. Synth. Catal.* **2005**, 347, 1913. (d) Yamamoto, Y.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6189. (e) Yamamoto, Y.; Okuda, S.; Itoh, K. *Chem. Commun*. **2001**,1102. (f) Varela, J. A.; Castedo, L.; Saá, C. *J. Org. Chem.* **2003**, *68*, 8595.

(4) (a) Diversi, P.; Ermini, L.; Ingrosso, C.; Lucherini, A. *J. Organomet. Chem.* **1993**, *447*, 291. (b) Tanaka, K.; Suzuki, N.; Nishida, G. *Eur. J. Org. Chem.* 2006, 3917 (c) Tanaka, K.; Hara, H.; Nishida, G.; Hirano, M. *Org. Lett.* **2007**, 9, 1907. (d) Wada, A.; Noguchi, K.; Hirano, M.; Tanaka, K. *Org. Lett.* **2007**, 9, 1295.

(5) (a) McCormick, M. M.; Duong, H. A.; Zuo, G.; Louie, J. *J. Am. Chem. Soc.* **2005**, *127*, 5030. (b) Tekavec, T. N.; Zuo, G.; Simon, K.; Louie, J. *J. Org. Chem.* **2006**, *71*, 5834.

(6) (a) D'Souza, B. R.; Lane, T. K.; Louie, J. *Org. Lett.* **2011**, 13, 2936. (b) Knoch, F.; Kremer, F.; Schmidt, U.; Zenneck, U. *Organometallics* **1996**, 15, 2713.

(7) Dazinger, G.; Torres-Rodrigues, M.; Kirchner, K.; Calhorda, M. J.; Costa, P. J. *J. Organomet. Chem.* **2006**, *691*, 4434.

(8) Eisch, J. J.; Ma, X.; Han, K. I., Gitua, J. N.; Kruger, C. *Eur. J. Inorg. Chem.* **2001**, *1*, 77.

(9) (a) García, J. J.; Jones, W. D.; *Organometallics* **2000**, *19*, 5544. (b) García, J. J.; Brunkan, N. M.; Jones, W. D.; *J. Am. Chem. Soc.* **2002**, *124*, 9547. (c) García, J. J.; Arévalo, A.; Brunkan, N. M.; Jones, W. D. *Organometallics* **2004**, *23*, 3997. (d) Ateşin, T. A.; Li, T.; Lachaize, S.; García, J. J.; Jones, W. D. *Organometallics* **2008**, *27*, 3811. (e) Schaub, T.; Döring, C.; Radius, U. *Dalton Trans.* **2007,** 20, 1993.

(10) Michelin, R.A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299.

(11) Bassi, I.W.; Benedicenti, C.; Calcaterra, M.; Intrito, R.; Rucci, G.; Santini, C.; *J. Organomet. Chem.* **1978**, *144*, 225.

(12) Walther, D.; Schonberg, H.; Dinjus, E.; *J. Organomet. Chem.* **1987**, *334*, 377.

(13) Zoellner, R. W. *J. Chem. Educ.* **1990**, *67*, 714.

(14) **2ab** could be generated through the addition of MeCN of PhCN to $Ni(COD)_2$ and IPr.

(15) (a) Dimer **2** catalyzed cycloaddition reactions are complete after only 15 min at rt. (b) CF_3 and MeO aryl pyridine products need to be isolated and NMR spectra obtained in benzene-d_6 to confirm beyond doubt the identities of these products in the competition studies

(16) Dimer species are still being fully characterized.

(17) Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc. Perkin Trans. 1*, **1986**, 1215.

(18) Dieter, K. M.; Dymek, Jr., C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, 110, 2723

(19) Better C^{13} spectra should be obtained for d^2-IPr and d^3-IPr.HCl for clarification of peaks and deuterium-carbon coupling constants.

(20) McCormick, M. M.; Duong, H. A.; Zuo, G.; Louie, J. *J. Am. Chem. Soc.* **2005**, *127*, 5030.

(21) COLLECT Data Collection Software. Nonius B.V. 1998.

(22) Otwinowski, Z.; Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods Enzymol. 1997, 276, 307-326.

(23) SIR97 (Release 1.02) - A program for automatic solution and refinement of crystal structure. A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. G. Moliteni, G. Polidori, and R. Spagna.

(24) SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Sheldrick, G. M. (1997).

Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany.

(25) R1 = $\Sigma(|| F_o | - |F_c ||) / \Sigma |F_o|$, wR2 = $[\Sigma(w(F_o^2 - F_c^2)2) / \Sigma(F_o^2)^2]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\Sigma(w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

(26) Maslen, E. N.; Fox, A. G.; O'Keefe, M. A., International Tables for Crystallography: Mathemetical, Physical and Chemical Tables, Vol. C, Chapter 6, Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 476-516.

(27) Creagh, D. C.; McAuley, W. J., International Tables for Crystallography: mathematical, Physical and Chemical tables, Vol. C, Chapter 4 Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 206-222.

(28) ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565.

(29) WinGX A Windows Program for Crystal Structure Analysis. L. J. Farrugia, University of Glasgow, Glasgow, 1998