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Synthesis of Nickel Catalyst for use in Polymerization Reactions

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# Synthesis of Perfluoroalkylphosphine Nickel Complexes

Introduction

Perfluoroalkylphosphine, or PFAP, metal complexes have many applications and advantages as catalysts which has led to increased interest and development of these systems.[1] PFAP ligands are unique because of their strongly electron withdrawing nature in combination with their steric bulk.[2] There are many nickel complexes that are used as catalysts in many different reactions. Nickel is less expensive and less toxic than other metals, like palladium for example. Nickel phosphine complexes are useful catalysts in coupling reactions.[3] One goals of this research was to determine if certain perfluoroalkylphosphine nickel complex synthetic routes could be employed using different ligands. Here the synthesis of several basic PFAP nickel(0) complexes such as $(dfmp)_4Ni$ (dfmp = $(C_2F_5)_2PMe$), and $(dfepe)Ni(cod)$ (cod = 1,5-cyclodecatriene) wer attempted, with the end goal of synthesizing a hydride derivative. The other goal was to determine if other compounds like Ni(cdt) (cdt = trans, trans, trans-1, 5, 9-cyclododecatriene) and $Ni(1,5\text{-hexadiene})_2$ were labile enough to allow for perfluoroalkylphosphine ligands to bind, forming PFAP nickel(0) complexes. Several syntheses of PFAP nickel complexes were attempted, $(dfmp)_2Ni(\eta^2\text{-}C_{12}H_{18})$, $(dfepe)Ni(\eta^2\text{-}C_{12}H_{18})$ and $(dfebp)_2Ni(\eta^2\text{-}C_{12}H_{18})$ (dfebp = $(C_2F_5)_2P(^tBu)$) for Ni(cdt) and $(dfmp)_2Ni(\eta^2\text{-}C_6H_{10})$, $(dfepe)Ni(\eta^2\text{-}C_6H_{10})$ and $(dfebp)_2Ni(\eta^2\text{-}C_6H_{10})$ for $Ni(1,5\text{-hexadiene})_2$, adapting literature procedures.[3,4,5] Also, reactions with both Ni(cdt) and $Ni(1,5\text{-hexadiene})_2$ with ethylene to synthesize $Ni(C_2H_5)_3$ were attempted. This nickel ethylene compound if synthesized would then be examined to see if PFAP ligands will replace one or more of the ethylene ligands.

Experimental

General: All synthetic manipulations were performed under N_2 using Schlenk or high vacuum line and glove box techniques. The following chemical equations illustrate the desired outcomes and not what we have actually observed.

Attempted Synthesis of (dfmp)$_4$Ni

$$(acac)_2Ni \quad + \quad (^iBu)_3Al \xrightarrow[\text{Hexane/Toluene}]{MeP(C_2F_5)_2,\ C_4H_8} Ni(PMe(C_2F_5)_2)_4$$
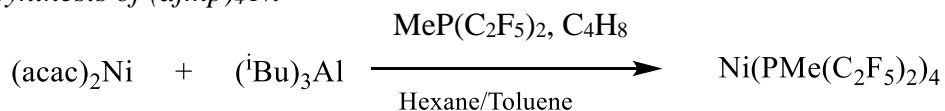
This synthesis was done following the procedure outlined in the synthesis of $(dfepe)_2Ni$, done by Roddick and associates only using dfmp in place of dfepe.[3] 15 mL of hexane/toluene (1:1) was added to $Ni(acac)_2$ (0.100 g, 0.389 mmol) by vacuum transfer. Then excess dfmp (1.5 g) containing some ether impurity was added to the solution using a syringe. The reaction mixture was cooled to -78 °C. 2.7 mL butadiene was vacuum transferred into the reaction flask. $Al(^iBu)_3$ (0.296 mL, 1.17 mmol) was next carefully added using a syringe. The stirred reaction mixture was then allowed to warm to room temperature. After 24 hours the solution went from the original amber color to a dark brown. The volatiles were then pulled off and hexane and petroleum ether were added. A fritted filter was then used to filter the solution, after which the solvents were then removed. A black precipitate remained in the reaction flask and orange

crystals formed in the filtrate flask. ^{31}P, ^{19}F and ^{1}H NMR were taken of the reaction. These showed shifts at [1]H δ 0.91 (s), [31]P δ 32.4 (s) and 29.3 (s) and for [19]F δ -80.46 (s) and -116.00 (s).

Synthesis of (dfepe)Ni(cod)
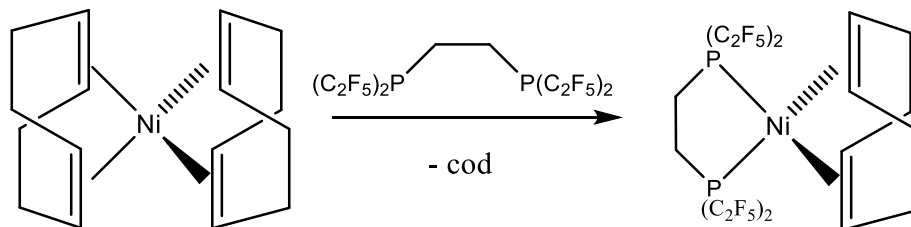
This synthesis was done following the procedure done by Roddick and colleagues on an increased scale.[3] Toluene (60 mL) was added to a flask containing Ni(cod)$_2$ (0.203 g, 0.726 mmol) at room temperature. Then using a syringe dfepe (0.965 g, 1.70 mmol) was added to the mixture. The mixture was then allowed to stir for 24 hours, after which the toluene was removed and 40 mL of methanol was added. This solution was then filtered and the collected precipitate was dried under vacuum. ^{31}P and ^{1}H NMR spectra were taken. ^{31}P NMR (C$_6$D$_6$): δ 67.89. ^{1}H NMR (C$_6$D$_6$) δ 4.18 (s) (cod), 2.28 (s) (cod), 1.93 (s) (cod), 1.68 (s) (dfepe). This confirmed the formation of our desired product and the next step could be started.

With (dfepe)Ni(cod) synthesized the next reaction to be done was to replace cod with other labile ligands. A 12 mg proportion of the product of the above synthesis was added to a NMR tube followed by benzene. This tube was then attached to the high vacuum line. Ethylene was then transferred into the tube while the tube was in a liquid nitrogen bath. The reaction tube was then allowed to warm to room temperature overnight. The ^{1}HNMR did not show any of the desired shifts so H$_2$(g) was added to the reaction tube. This too yielded no conclusive results so the tube was heated to 90˚C for 20 hours. Additionally, 15 mg of the product synthesized above was added to a round bottom flask to which 15 mL of diethyl ether was added. Then H$_2$(g) was added to the reaction flask and left exposed over night to collect the gas. NMR spectra were taken of both the reaction tube after heating and of the contents of the reaction flask. The spectra showed a single major species at δ 68.95.

Synthesis of Ni(cdt)

$$\text{Ni(acac)}_2 \quad + \quad 2\text{SmI}_2 \quad \xrightarrow[\text{THF, -20 °C}]{\text{2 eq}} \quad$$
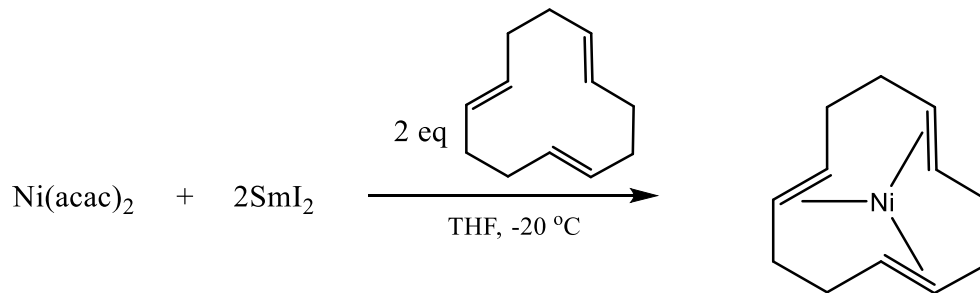
The procedure used in this synthesis followed the procedure by Ogoshi increased in scale and adapted to high vacuum line synthetic techniques.[4] To a round bottom flask of Ni(acac)$_2$ (0.22 g, 0.856 mmol) and trans, trans, trans-CDT (0.28 g, 1.72 mmol) was added 10 mL of THF. The solution was cooled to -28 ˚C using an ice, acetone and salt bath and SmI$_2$ (16.5 mL, 1.65 mmol) was added slowly dropwise. The dark blue color of the SmI$_2$ dissipated immediately into the green/blue of the solution. Once the addition of SmI$_2$ was complete the solution was allowed to warm to room temperature and then allowed to stir for an additional hour. At this point the solvent was removed and the remaining residue was allowed to dry completely. Then toluene was added to the reaction flask and then the solution was filtered. ^{1}H NMR spectra were taken for each product synthesized which led to the discovery that the SmI$_2$ reagent was not reactive. This synthesis was repeated four times before we realized the SmI$_2$ reagent was bad. All of the ^{1}H NMR spectra of isolated materials showed peaks at the chemical shifts of free cdt, δ 4.97 (s) and 1.99 (s). Once new SmI$_2$ was procured the synthesis was done four more times. All were done with the same procedure as before but using carbon tetrachloride as the cold bath solvent, which gives a temperature of -23 ˚C and then after the filtration with toluene petroleum ether was added (about 15 ml) while stirring and left for 1 hour. Afterwards this was filtered for and an NMR was taken of the collected solid. The ^{1}H NMR spectrum of the compound contained peaks at δ 1.98 (s) and 4.95 (s). These were not indicative of a successful reaction. The reaction was then conducted again without pet. ether. The ^{1}H NMR of the fourth attempt gave shifts at δ 1.58 (s) and 4.14 (s), which are very near the literature shift values.[4] The subsequent two reactions, to produce more compound, had shifts in their proton NMR spectra that coincided with this previous spectrum and the literature values.[4] were done to produce more of the compound for further use in PFAP reactions. In all of the spectra of the successful reactions there were peaks around δ 4.97 (s) and 1.99 (s), indicating free cdt. We did not however carry out any further purification to remove the unreacted cdt.

Attempted Reactions of Ni(cdt) with PFAPs

$$(dfebp)_2Ni(cdt)$$

$$^tBu\text{—}P\underset{C_2F_5}{\overset{C_2F_5}{<}}$$
dfebp

$$CH_3\text{—}P\underset{C_2F_5}{\overset{C_2F_5}{<}}$$
dfmp

$$(dfepe)_2Ni \xleftarrow{\quad dfepe \quad} Ni(cdt) \xrightarrow{\quad dfmp \quad} (dfmp)_2Ni(cdt)$$

$$(C_2F_5)_2P\text{—} \atop (C_2F_5)_2P\text{—}$$

Ethylene

$$H_2C=CH_2$$

$$Ni(C_2H_4)_3$$
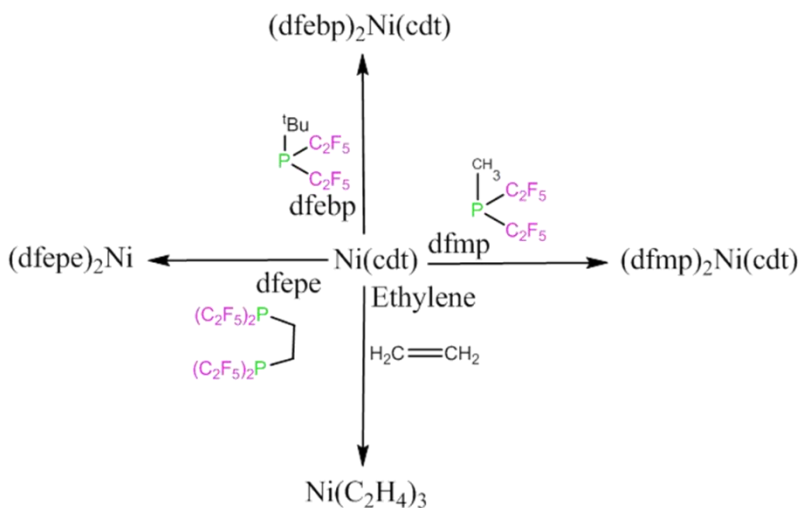
       Once the Ni(cdt) was successfully synthesized with active SmI_2, four reactions were attempted with the Ni(cdt) compound. These four reactions followed reactions done by Pörschke and colleagues, though using fluorinated alkyl phosphine ligands.[5] The reactions that were attempted included three perfluoroalkylphosphine ligands, dfepe, dfebp and dfmp, and then a reaction with ethylene gas. For all of the reactions that used a PFAP ligand the same general procedure was used. An amount of Ni(cdt), about 10 – 15 mg, was dissolved into deuterated benzene then was added to a NMR tube. To each of the tube one of the PFAP ligands was added in a small excess, about 2-3 drops. These mixtures were then allowed to react for a minimum of 24 hours, after which an NMR was taken. For the ethylene reaction a similar procedure was done. An amount Ni(cdt) was again dissolved in deuterated benzene but then the NMR flask was attached to the vacuum line and the line was filled with ethylene gas. Then after freezing the benzene Ni(cdt) reaction solution using liquid nitrogen, the ethylene gas was allowed to condense into the tube will still under liquid nitrogen. A sufficient amount of ethylene was condensed so there would be excess and the charged NMR tube was then taken off the line and let sit for 24 hours at room temperature. An NMR was taken the after this period.

Synthesis of Ni(1,5-Hexadiene)₂

$$Ni(acac)_2 \;+\; 2SmI_2 \xrightarrow[\text{THF, -20 °C}]{\text{2 eq}} \text{[Ni(1,5-hexadiene)}_2\text{]}$$
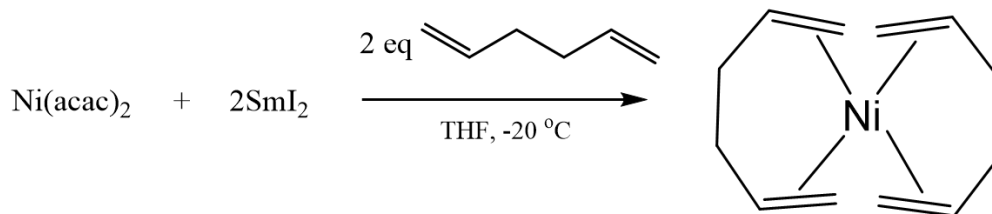
       The synthesis procedure for the synthesis of Ni(1,5-hexadiene)₂ follows the same procedure as the synthesis of Ni(cdt). To a round bottom flask containing Ni(acac)₂ (0.21 g, 0.845 mmol), 1,5-hexadiene (0.3 ml, 2.53 mmol) was added. The flask was then attached to the line and 15 ml of THF was then transferred into the flask. The mixture was then cooled to -23°C using a carbon tetrachloride and liquid nitrogen bath. Then, while under nitrogen, SmI_2 (20 ml,

45.6 mmol) was added drop wise into the reaction mixture. Once all of the SmI_2 had been added the reaction was let stir in the cold bath for 15 minutes, after which the bath was removed and the flask was allowed to warm to room temperature. At this point the solvent was removed and the remaining residue was allowed to dry. Toluene was then added to the flask and the solution was filtered. The solvent was removed from the filtrate and an ^{1}H NMR spectrum was taken, first in deuterated benzene then in a 60% deuterated dichloromethane 40% dichloromethane, to determine if the desired product had been synthesized. This reaction was then done again using only 16.5 ml (37.7 mmol) of SmI_2 instead. A ^{1}H NMR was taken in deuterated dichloromethane and gave shifts at δ 5.22 (s), 2.34 (s) and 0.11 (s). The flasks containing synthesized Ni(1,5-hexadiene)$_2$ were capped and placed in a freezer at - 33˚C for storage.

Attempted Reactions of Ni(1,5-Hexadiene)$_2$ with PFAPs
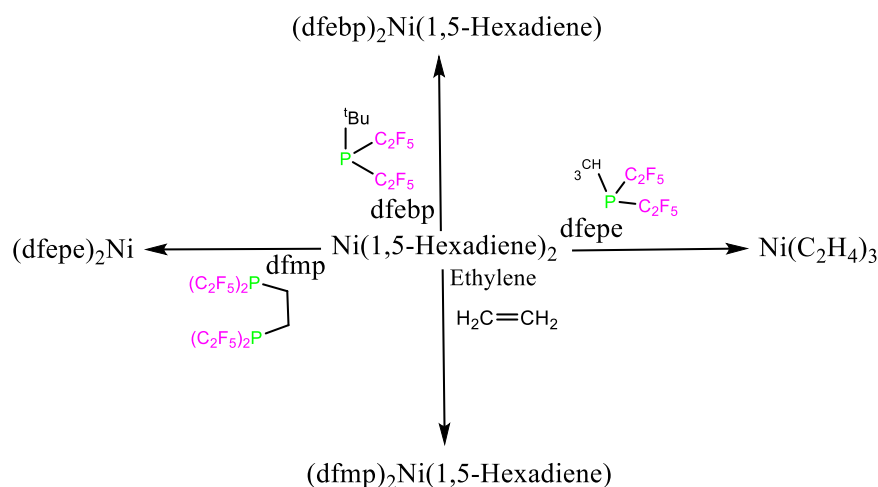
Once Ni(1,5-hexadiene)$_2$ had been successfully synthesized the next step was to determine if the PFAP ligands could displace one of the 1,5-hexadiene and bind to the nickel. These reactions followed reactions done by Pörschke and colleagues, though using perfluoroalkylphosphine ligands.[5] Just as with the Ni(cdt) the same three PFAP ligands were used, dfepe, dfebp, and dfmp. Also, hexadiene displacement with ethylene gas was attempted too. As done with the Ni(cdt) reactions, about 10-15 mg of Ni(1,5-hexadiene)$_2$ was added to an NMR deuterated solvent as well as the appropriate PFAP ligand. In the cases of theses reactions, the solvent was 60:40 deuterated dichloromethane instead of benzene. In the case of the ethylene reaction the NMR tube was again attached to the vacuum line and then ethylene gas added to the tube. All of the reactions were allowed to react for 24 hours and then ^{31}P and ^{1}H NMR spectra were taken to determine if the reaction was successful.

Results and Discussion

(dfmp)$_4$Ni

This reaction yielded a black precipitate from the dark brown solution. A black precipitate does not bode well since it tends to point toward degraded nickel compounds. ^{31}P, ^{19}F and ^{1}H NMR spectra were taken. The proton NMR spectrum of the precipitate in deuterated benzene showed a prominent peak at δ 0.915 (s) which is indicative of the methyl shift of free

dfmp. Also, the ^{19}F NMR spectrum illustrates free dfmp with shifts at δ -80.46 (s) and -116.00 (s).

This along with the black precipitate pointed toward an unsuccessful reaction. Though the dfmp reagent used contained some amount of ether this should not have caused the reaction to be completely unsuccessful. This was also compensated for by using a larger amount of the ligand.

(dfepe)Ni(cod)

The synthesis of (dfepe)Ni(cod) from Ni(cod)$_2$ worked well. ^{31}P and ^1H NMR spectra were taken in deuterated benzene. The ^{31}P spectra contained a shift at δ 67.8 (s) and the ^1H spectrum contained peaks at δ 1.93 (s), 2.27 (s) and 4.77 (s). Both spectra contained shifts very near that of the expected shifts. After determining the synthesis was successful the next step was the removal of the remaining cod. This was attempted using ethylene and H$_2$, separate and together. Neither of these attempts were successful even upon heating of the reaction mixtures to increases temperatures. All NMR spectra taken of the reaction mixtures yielded shifts corresponding to the starting reactants.

Ni(cdt)

This synthesis was conducted six times due to the use of dead SmI$_2$ and a need for more Ni(cdt) for more reactions. The first reaction yielded different a color than expected and NMR did not show the expected shifts, just the reactant shifts. The second reaction yielded similar results. Both reactions when filtered, gave a black precipitate. The first attempt had a black filtrate, which was most likely due to the decomposition of nickel complexes, while the second had a pink filtrate. Using the precipitate filtered off from the second reaction the removal of the cdt ligands with dfmp and dfepe was attempted, even though in retrospect the initial reaction did not work. Both of these reactions were done on a small scale, NMR tube reactions. The proton NMR spectra for these two reactions showed the same two shifts of about δ 1.99 (s) and 4.97 (s). These shifts corresponded to the shifts of free cdt ligand which lead us to suspect that the initial Ni(cdt) reaction was not working. We first looked at the SmI$_2$ since it was previously improperly stored. We tested each of the bottles that we had by adding an amount to water and see if it reacted. For both bottles there was no substantial reactivity and a new bottle was obtained. With this the initial Ni(cdt) synthesis reaction was done a fourth time. Once filtrated and after the solvent was removed an orange precipitate was seen, which is what the is expected if the reaction is successful. Proton NMR of the reaction before filtration showed a few new shifts though they are not exactly the expected shifts of Ni(cdt). After the proton NMR of both the precipitate that was filtered off and the orange precipitate gave peaks at δ 4.99 (s) and 1.99 (s). These are not the expected peaks though they are very close and this along with the color points toward a semi-successful reaction. The NMR also told us that further drying was needed to completely remove all of the toluene due to the presence of toluene shifts. The reaction was then attempted again using petroleum ether to extracted the product since it is insoluble in the solvent. This yield the same results of previous attempts so extraction with pet. ether was dropped. The reaction was then attempted again this time having a yellow/light brown colored precipitate with some larger clear crystals at the near the top of the flaks. These clear crystals are believed to be unreacted cdt, thought this was never test or confirmed. The ^1H NMR contained two broad peaks at δ 4.17 (s) and 1.56 (s) that have an integration ratio of 1:1. These two peaks are believed to be the peaks of the bound cdt, though each are shifted a bit lower than the paper reported (δ 4.30 (s) and 1.66 (s)). These shifts were not they shifts we had been seeing of free cdt. With this we concluded that

we had synthesized the product and could now attempt reactions with this product and the PFAP ligands.

Reactions with Ni(cdt)

The precise stoichiometry of reactants for all four of these reactions was not needed because these were only attempts to see if the reactions worked. The first reaction done was done in benzene and used dfmp as the PFAP ligand. The Ni(cdt) did not seem fully soluble in the benzene. Within the clear orange solution there were dark brown solids. Both ^{31}P and ^{1}H NMR spectra were taken of the reaction mixture. With the excess dfmp, if the reaction was successful there should have been two peaks within the ^{31}P spectrum, one for the free dfmp and one for bound dfmp. The ^{31}P spectrum showed only one peak, corresponding to free dfmp. The ^{1}H spectrum also point toward unsuccessful reaction with a very large peak indicating free dfmp. Since there was some undissolved solid when using benzene, the solvent for the reaction of Ni(cdt) with dfepe and ethylene were both done in 60% deuterated dichloromethane. This seemed to dissolve the Ni(cdt) better but still not completely and there was still some dark brown solid within the clear orange solution. For the dfepe only a ^{31}P NMR spectrum was taken. Further proton NMR would be taken if the ^{31}P spectrum illustrated a successful reaction. Again within the spectrum there should be two peaks due to the excess dfepe but again only the free ligand peak seen. A proton NMR was taken of the ethylene reaction. The spectrum only showed large peaks at the shifts of free ethylene, indicating no reaction with Ni(cdt). The last ligand attempted was dfebp. This reaction was done in benzene. A ^{31}P spectrum was taken and as with the previous reactions there was only one peak of free dfebp indicating no reaction. Since, none of the reactions worked with Ni(cdt) a more labile precursor is needed. We then looked into 1,5-hexadiene since Pörschke was able to successfully synthesize nickel non-PFAP ligand complexes using 1,5-hexadiene.

Ni(1,5-Hexadiene)$_2$

This synthesis was done two times due to a discrepancy that was found in Ogoshi's paper.[4] This error was that moles and the volume of the SmI$_2$ used do not equal one another. We did not know which of the two values were the correct value. We first did the reaction using about 23 ml of SmI$_2$. After filtration, a proton NMR was taken and gave shifts corresponding to free 1,5-hexadiene, about δ 6.01 (s), 4.20 (s) and 2.11 (s). These were not far shifted from free 1,5-hexadiene at about δ 5.59 (s), 4.80 (s) and 2.15 (s). This reaction is believed to have not gone to completion because of an over use of the reducing agent. Because of this calculation we used redid the reaction using less SmI$_2$, 16.5 ml. After, reducing the amount of SmI$_2$ the reaction went to completion without any problems. Before taking pulling off the THF a crude proton NMR was taken using an acetone capillary. The spectrum shows shifts of δ 2.10 (s), 4.61 (s) and 5.48 (s). though they were a bit shadowed by the THF shifts but are still shifted off the free 1,5-hexadiene. This indicates that the 1,5-hexadiene has bound to the nickel. After this the solution was filtered a light yellow brown precipitate was left. This then had a proton NMR spectrum taken of it which was initially dissolved in deuterated benzene but when not all of the solid dissolved 60% deuterated dichloromethane was added. The shifts seen was a group centered at δ 5.22 (s), 2.34 (s) and 0.11 (s). Those these are slightly different from the crude NMR a different solvent was used and the THF greatly shadowed possible peaks. These peaks do indicate bounded 1,5-hexadiene. Now that Ni(1,5-Hexadiene)$_2$ had been synthesized reaction with PFAP ligands could been attempted.

Reactions with Ni(1,5-Hexadiene)$_2$

      Again the exact amount of the reaction was not needed because these reactions were only attempts to see if the synthesis worked and the stoichiometric ratios were not believed to be important to the reaction's success. All of these reactions were attempted in the same time frame. Since Ni(1,5-hexadiene)$_2$ was determined to be more soluble in dichloromethane than benzene all of the reactions we done in 60% deuterated dichloromethane. All of the solutions within the NMR tubes were a transparent yellow-brown in color. All reactions were allowed to sit for 24 hours after the addition of all the reagents. The first reaction done was with dfepe. A ^{31}P and ^{1}H NMR spectrum were taken. Since excess of the ligand was added, in all four reactions, therefore in the ^{31}P spectrum there should be two peaks if the reaction was successful. The ^{31}P spectrum only showed one peak indicating that the reaction was not successful. The ^{1}H spectrum confirmed the ^{31}P spectrum with no shifts for unbound 1,5-hexadiene which would have occurred if the dfepe was bound to the nickel. Because of this for the other two PFAP ligands, dfmp and dfebp, reactions only ^{31}P spectra were taken. For both the dfmp and dfebp ^{31}P spectra, each only showed one shift for the free ligand, indicating that both of the reactions were unsuccessful. For the ethylene reaction a ^{1}H spectrum was taken which, like all previous reactions, showed shifts that indicate free unreacted ethylene.

Summary

      Multiple synthesizes were undertaken to see if methods previously done to form nickel complexes would work for the formation of PFAP nickel complexes or with alternative PFAP ligand. First, attempted reactions were done to see if the synthetic routes could be done with different PFAP ligands. Next, the reactions were done following synthetic routes that lead to nickel complexes containing non-fluorinated ligands. The reaction to form Ni(cdt) was being done with a dead reagent, SmI$_2$. Once the workable SmI$_2$ was obtained the reaction preceded to work on the basis of color and NMR shifts. With the synthesis of Ni(cdt) further reactions can be done to form PFAP complexes. The synthesis of Ni(1,5-heaxadiene)$_2$ was done following the same method as Ni(cdt). Once synthesized, the same reactions were attempted in an attempt determine if this compound could be used to form PFAP nickel complexes. The four reactions done with both the Ni(cdt) and Ni(1,5-hexadiene)$_2$ did not yield to any successful results. None of the ligands bound to the nickel compounds. This is likely due to the ligands that are already bound to the nickel are not labile enough to allow the electron deficient phosphorus center to bind to the metal. The next step would be to find a more labile precursor compound. With more research in the area of PFAP metal complexes better and more applicable synthesis methods can be developed which has the potential to extend the applications of these complexes as catalysts. We were unable to get the attempted nickel PFAP reactions to work.

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