RATIONAL DESIGN AND SYNTHESIZE STERICALLY LESS HINDERED PINCER-IRIDIUM CATALYSTS FOR ALKANE DEHYDROGENATION

by

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And approved by

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ABSTRACT OF THE THESIS

RATIONAL DESIGN AND SYNTHESIZE STERICALLY LESS HINDERED PINCER-IRIDIUM CATALYSTS FOR ALKANE DEHYDROGENATION

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Thesis Direction:

Professor Alan S. Goldman

Dehydrogenation of alkane, which can convert alkane to alkene effectively and atom economically, is one of the most important and challenge goal in modern catalysis since the dehydrogenation product, alkenes, are ubiquitous as reagents and intermediates for a variety of useful transformation. Our group focused on the development of PCP Iridium catalysts for alkane dehydrogenation in the last decades and made lots of significant breakthroughs. One of them was that we found the steric hindrance of the PCP ligand backbone can affect the activity of the catalysts for dehydrogenation of alkane observably. The work presented in this thesis studied one new sterically less hindered pincer-ligated Iridium complex, (^{tBu2}PCP^{Me2})IrH$_4$, as the perfection of the study of the steric effect of PCP Iridium complexes for alkane dehydrogenation.

(^{tBu2}PCP^{Me2})IrH$_4$ is the least steric PCP Iridium complex we have every made. It was expected to have all the advantage as another small steric complex (^{tBu2Me2}PCP)IrH$_4$, which had shown very high reactivity for alkane dehydrogenation but was hard to synthesis. (^{tBu2}PCP^{Me2})IrH$_4$ has the comparable satiric and electronic effects as

(^{tBu2Me2}PCP)IrH_4 and is relatively easier to synthesis compared with the latter. What's more, without the β-H in Me_2- side, the stability of complex may be improved due to the less chance undergoing Cyclometalation. As such, ($^{tBu2}PCP^{Me2}$)IrH_4 is a good complex to study the steric effect of PCP Iridium complexes for alkane dehydrogenation.

$^{tBu2}PCP^{Me2}$-H ligand was successfully synthesized by a revised procedure. The corresponding Iridium complexes ($^{tBu2}PCP^{Me2}$)IrH_4 and ($^{tBu2}PCP^{Me2}$)Ir(C_2H_4) were made as well. Addition of small molecules, H_2, N_2, CO, to ($^{tBu2}PCP^{Me2}$)IrH_4 and ($^{tBu2}PCP^{Me2}$)Ir(C_2H_4) was then studied to investigate the properties of such complexes. The alkane transfer dehydrogenation of cyclooctane by ($^{tBu2}PCP^{Me2}$)IrH_4 and ($^{tBu2}PCP^{Me2}$)Ir(C_2H_4) was studied to compare the activity of this new complex with our previous PCP Iridium catalysts. Finally, the effect of different acceptor and the effect of acceptor's concentration were also studied.

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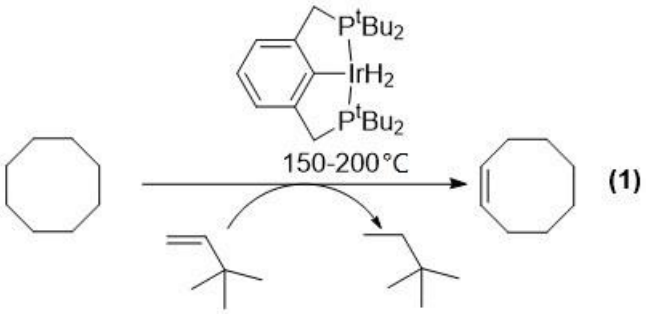
Chapter 1

Introduction

The development of catalysis system for functionalization of alkane is one of the most important and challenge goal in modern catalysis. One of the process is called "dehydrogenation", which can convert alkane to alkene effectively and atom economically. The dehydrogenation product, alkenes, are ubiquitous as reagents and intermediates for a variety of useful transformation. Because of this reason, the catalytic dehydrogenation of alkanes is a reaction with tremendous potential value and lots of progress has been made in the past two decades.

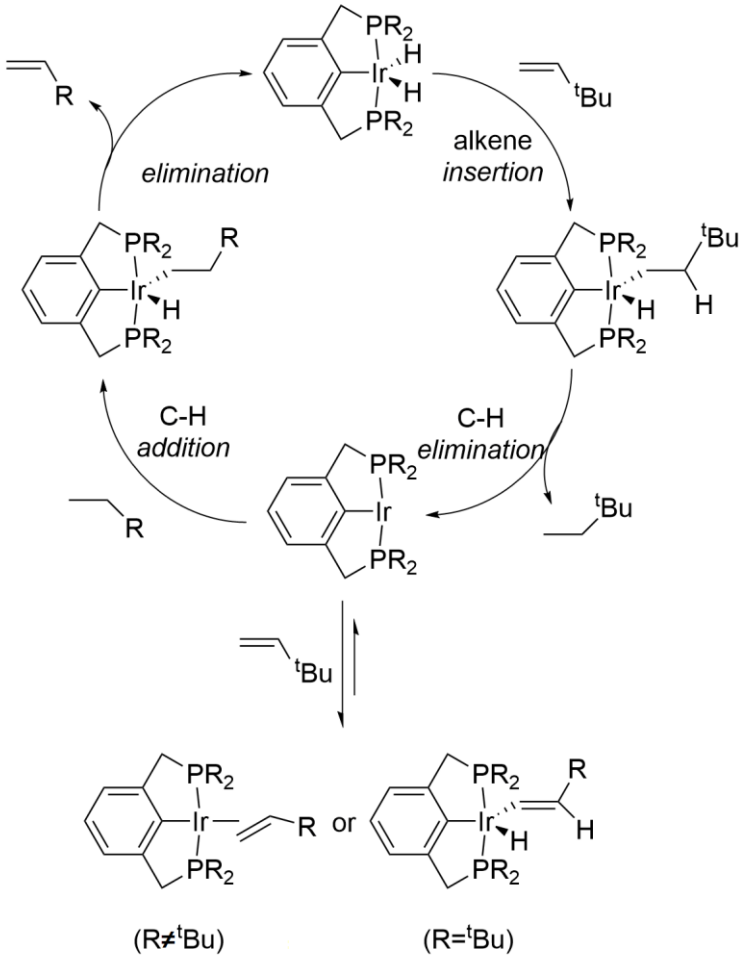
The research on homogeneous catalytic dehydrogenation was pioneered in as early as 1980s by Crabtree and Felkin[1]. Several catalytic systems were developed subsequently, although turnover number was limited due catalysts decomposition. In 1991, Goldman and coworkers[2] reported a new system using $Rh(PMe_3)_2Cl(CO)$ complex with significantly improved activity for transfer dehydrogenation. But more than one equivalent sacrificial acceptor was needed because of the presence of H_2 atmosphere. A key breakthrough was made by Jensen, Kaska and coworkers in 1996. They reported a very robust and active pincer-ligated iridium complex, (^{tBu4}PCP)IrH_2 as catalyst for alkane transfer-dehydrogenation (**eq. 1**).[3]



(1)

This complex can work at high temperature (200℃) for long term (more than 1 week).[4] Goldman and coworkers studied that such high temperatures are sufficiently high to overcome the positive enthalpy of dehydrogenation without using a sacrificial hydrogen acceptor. In 1997, they reported the first example of homogeneous catalytic dehydrogenation of alkanes under reflux without the need for a sacrificial hydrogen acceptor.[5]

The mechanism of transfer dehydrogenation of alkanes using (^{R4}PCP)IrH$_2$ complex has been studied experimently and computationaly by Goldman, Krogh-Jespersen and coworkers (**Scheme I-1**).[6]



Scheme I-1: Catalytic cycle of Transfer Dehydrogenation by (^{R4}PCP)IrH$_2$

The rigid pincer ligand backbone provides a good opportunity to exquisite control over electronic and steric properties without significant perturbation of the coordination geometry. This enables systematic investigation of electronic (X) and steric (R) effects and greatly facilitates optimization (**Figure I-1**). The steric properties of the pincer ligand clearly have a major impact on the activity of pincer iridium dehydrogenation catalysts. The presence of sterically bulky, robust, phosphinoalkyl groups (e.g., ^{t}Bu) could offer protection against cluster formation and bimolecular catalyst deactivation. However, it would seem likely that such groups also strongly contribute to the activation barriers to both C-H bond addition and the requisite β -H elimination of the resulting iridium alkyl intermediate. Thus, these bulky groups afford advantages and disadvantages.

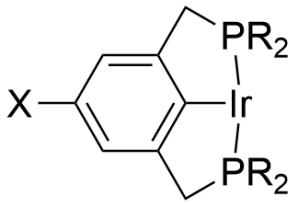


Figure I-1: PCP ligand backbone with Iridium

Attented to this steric effect, complexes (^{tBu4}PCP)IrH$_4$, (^{iPr4}PCP)IrH$_4$, (MeO-^{tBu4}PCP)IrH$_4$ and (MeO-^{iPr4}PCP)IrH$_4$ have been synthesized and fully studied by our group.[7,8] Complexes (^{tBu4}PCP)IrH$_4$ and (^{iPr4}PCP)IrH$_4$ have been compared by dehydrogenation of cyclooctane and it was found that complex (^{iPr4}PCP)IrH$_4$ with the isopropyl on phosphorous is a more efficient catalyst. On comparing complexes (MeO-^{tBu4}PCP)IrH$_4$ and (MeO-^{iPr4}PCP)IrH$_4$, it was again found that complex (MeO-^{iPr4}PCP)IrH$_4$ with the isopropyl on phosphorous is more active compared to the *tert*-butyl substituted analog. Based on these results, we supposed that less sterically hindered groups might improve the reactivity of the catalyst. On the other hand, if the substituted groups are too

less sterically hindered, it may impair the stability by catalyst dimerization and deactivation. The best choice seems to keep partial sterically bulky group *tert*-butyl and substitute others by less sterically bulky group, for example *Me* group.

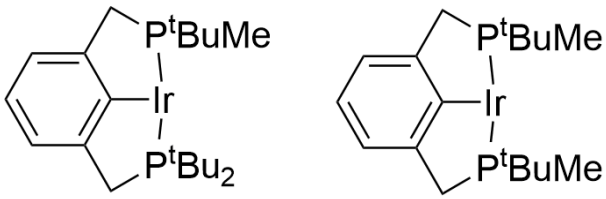


Figure I-2: (^{tBu3Me}PCP)Ir and (^{tBu2Me2}PCP)Ir catalyst precursor

Thus, we has designed and synthesized complex (^{tBu3Me}PCP)IrH_4 and (^{tBu2Me2}PCP)IrH_4 (**Figure I-2**) and studied their catalytic reactivity, combined with experimental and computational, separately.[9] DFT calculations showed that the substitution of a single methyl group for a *tert*-butyl group had a large favorable energetic effect on the alkyl hydride β-hydrogen elimination step, the rate-determining step in the calculated dehydrogenation cycle. Indeed, the catalysts' activity trend was (^{tBu3Me}PCP)IrH_4 > (^{iPr4}PCP)IrH_4 > (^{tBu4}PCP)IrH_4 no matter in alkane transfer or acceptorless hydrogenation, which support the computational prediction very well. (^{tBu2Me2}PCP)IrH_4 was synthesized and test for alkane transfer-dehydrogenation, using either NBE or TBE (0.2M) as an acceptor, with rates greater than that of (^{tBu4}PCP)IrH_4 but less than that of (^{tBu3Me}PCP)IrH_4. This lower catalytic activity may due to the reduced steric bulk of the (^{tBu2Me2}PCP)Ir unit (relative to (^{tBu4}PCP)Ir or even (^{tBu3Me}PCP)Ir), which resulting in strong binding of 1-alkene to (^{tBu2Me2}PCP)Ir or the formation of deactivated dinuclear species (**Figure I-3**). The actual reason was still not clear and under further investigation.

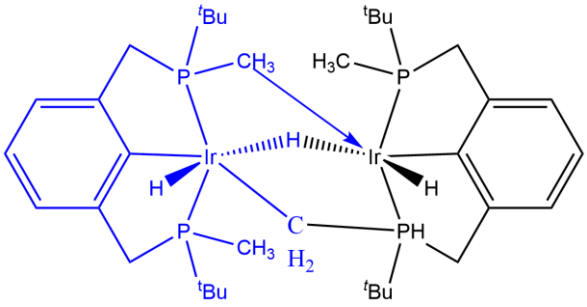


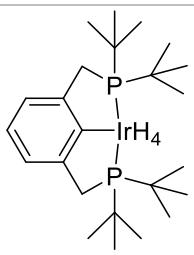
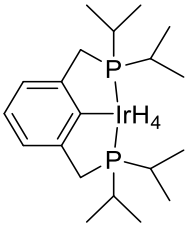
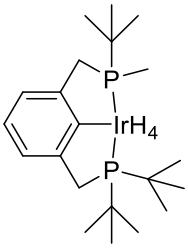
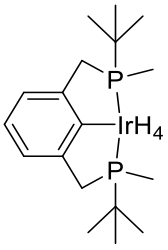
Figure I-3: Dinuclear species structure of (^{tBu2Me2}PCP)IrH$_4$

Recently, Dr. Akshai Kumar Alape Seetharam, in our group, found a surprising result that (^{tBu2Me2}PCP)IrH$_4$ showed much higher activity than (^{tBu3Me}PCP)IrH$_4$ and (^{tBu4}PCP)IrH$_4$ for *n*-pentane transfer-hydrogenation by using high concentration TBE (equimolar to *n*-alkane).[10] The result is listed in the **Table I-1**. This reversed catalytic activity may indicate that high concentration of acceptor may shift more catalyst to it's resting-state (^{tBu2Me2}PCP)Ir(olefin), which has an equilibrium to form (^{tBu2Me2}PCP)Ir complex, the expected "ture" catalyst for dehydrogenation. This accumulation of resting-state may prevent the totally deactivation of catalyst and thus shows higher activity than (^{tBu3Me}PCP)IrH$_4$ even there is stronger bonding of olefin to the less steric complex as DFT calculation predicated. What's more, this result may show some evidence against with the previous hypotheses that the lower activity of (^{tBu2Me2}PCP)IrH$_4$ is due to the energetics of the catalytic cycle (stronger bonding of 1-alkene to (^{tBu2Me2}PCP)Ir) and true reason is likely to be the dimerization of the catalyst.

Based on this, the (^{tBu2Me2}PCP)IrH$_4$ shows more promising for alkane transfer-dehydrogenation and other related reactions catalysis when using high concentration acceptor. Besides the high activity predicated by DFT calculation and supported by experiment, (^{tBu2Me2}PCP)IrH$_4$ also has advantage in DFT calculation than another less bulky catalyst, for example, (^{iPr4}PCP)IrH$_4$. Due to the quick rotate of the isopropyl group,

it is almost impossible to exactly calculate the energy of transformation and intermediate compounds when using (^{iPr4}PCP)IrH_4 as catalyst for alkane dehydrogenation. Sample substitution group, viz. *Me*, might simplify the calculation and provide a good opportunity to further understand the steric effect of the pincer-ligated Iridium catalyst.

Table-I-1: Transfer Dehydrogenation of n-Alkane Using TBE as Acceptor

Catalyst[a]	Temp. (℃)	Alkane	[TBE] (mM)	TON (mM)
	150	*n*-Octane	200	31
	200	*n*-Pentane	4300	58
	150	*n*-Octane	200	86
	200	*n*-Pentane	4300	729
	150	*n*-Octane	200	125
	200	*n*-Pentane	4300	113
	150	*n*-Octane	200	76
	200	*n*-Pentane	4300	467

[a][catalyst] = 1.0 mM. Product concentrations (mM) measured by GC.

However, synthesizing the (^{tBu2Me2}PCP)IrH_4 complex is not easy. Because of the different substituted group, ^{t}*Bu* and *Me*, on same phosphorous, ^{tBu2Me2}PCP-H ligand is obviously a mixture of meso- and *rac*-compound, which makes the study of the catalyst

complicated. Thus, in this thesis, we report to design and synthesize an new complex, (^{tBu2}PCP^{Me2})IrH$_4$ (**Figure I-4**), which is relatively easy to synthesis and needn't to consider chirality of ligand, as an alternative to study the less steric hindered pincer catalyst. This is the least steric complex we have every made, which is expected to have all the advantage as (^{tBu2Me2}PCP)IrH$_4$, such as high activity for alkane dehydrogenation due to the comparable satiric and electronic effects. Without β-H in *Me*$_2$- side, the stability of complex may be improved due to the less chance undergoing Cyclometalation. Cycloalkane or other even more steric alkane, which failed or not effectively catalyzed by (^{tBu4}PCP)Ir catalyst, may be favored by this less steric catalyst. What's more, because of the particular asymmetric structure of such complex, it might be potentially applied to other specific reaction, such as selective alkene isomerization and hydrogenation.

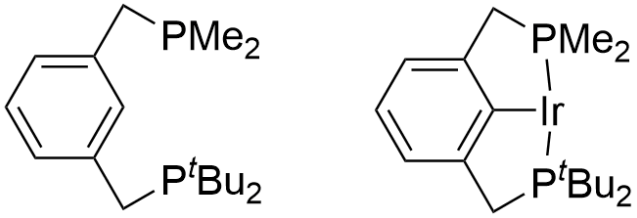


Figure I-4: A New PCP ligand and Iridium complex

Reference:

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10. Unpublished work by Dr. Akshai Kumar Alape Seetharam

Chapter 2

Synthesis and Reactivity of (^{tBu2}PCP^{Me2})Ir Complex

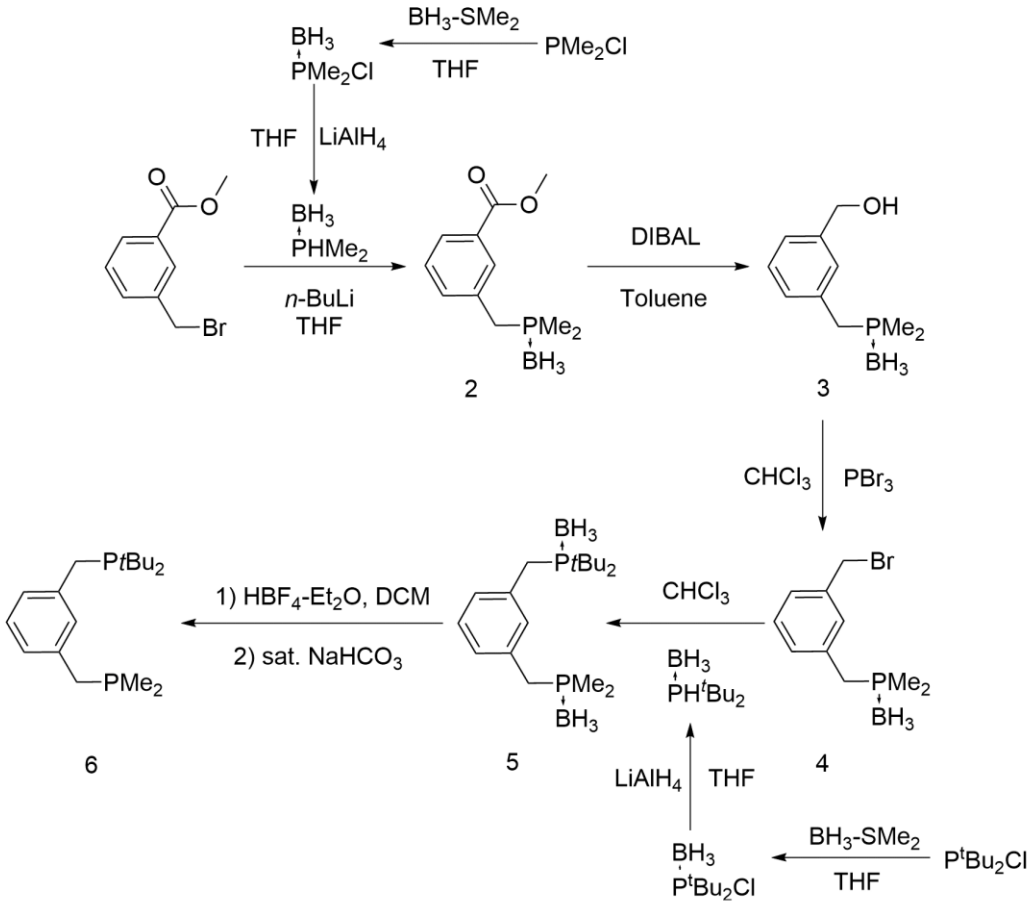
2.1 Revised Synthesis of ^{tBu2}PCP^{Me2}-H ligand

The Synthesis of ^{tBu4}PCP ligand was first reported by Shaw and coworkers in 1976,[1] which carried out by reacting HP^{t}Bu$_2$ with α,α-1,3-dibromoxylene and liberating the ^{tBu4}PCP from the salt by NaOAc. Our group also reported the similar synthesis route to obtain ^{tBu3Me}PCP-H and ^{tBu2Me2}PCP-H ligand.

Recently, Jensen at el. reported a synthesis scheme to generate unsymmetrical diphosphine pincer ligand starting from (2-chloromethyl) benzyl alcohol.[2] Although Jensen utilized this synthesis scheme to generate PCP pincer ligand with a diphenylphosphine moiety, this scheme can be easily adapt to the synthesis of asymmetric alkyl-phosphine pincer ligand. Our group once utilized a similar scheme to synthesize the asymmetrical pincer ligand *rac*-$^{(tBu3Me)}$PCP-H, as well as the (*S*,*S*)-$^{(tBu2Me2)}$PCP-H ligand, separately. Following these previous work, herein, we report a revised scheme to synthesize the new asymmetric pincer ligand ^{tBu2}PCP^{Me2}-H ligand (**Scheme II−1**)[3].

In contrast to the previous synthesis of $^{(tBu3Me)}$PCP-H ligand synthesis, our scheme utilized BH_3·$PHMe_2$ and (3-bromomethyl)benzyl benzoate as starting materials. Synthesis began with protecting $PClMe_2$ with BH_3 by treating BH_3·SMe_2 complex in THF solution. The BH_3·protected phosphine has the advantage of being stable in ambient condition and prevent side product in the next reduction step. In our group, we found that $LiAlH_4$ can effectively reduce PCl^{i}Pr$_2$ to PH^{i}Pr$_2$ with excellent yield. A similar procedure

was followed to synthesize $PHMe_2$. Along with the formation of $PHMe_2$, which appears at -98.2ppm in the ^{31}P spectrum, another product was formed as seen by ^{31}P at -57.5ppm. Based on previous work, we thought this product should be $Me_2P\text{-}PMe_2$, which probably formed by the reaction of $PClMe_2$ with $PHMe_2$. However, treatment of $BH_3{\cdot}PClMe_2$ with $LiAlH_4$ in THF, the reaction formed the only product $BH_3{\cdot}PHMe_2$, which showed a clean ^{31}P spectrum at -27ppm as quartet peaks.



Scheme II−1: Revised synthesis scheme for $^{tBu2}PCP^{Me2}$-H ligand

The next step is phosphonation of (3-bromomethyl)benzyl benzoate with $PHMe_2{\cdot}BH_3$. Treatment of $PHMe_2{\cdot}BH_3$ with *n*-BuLi in THF deprotonated it to $PLiMe_2{\cdot}BH_3$. It react with (3-bromomethyl)benzyl benzoate to form product **2**. Reaction

was quenched with water, extracted by DCM and solution was pumped off under vacuum. Column chromatograph afforded the product as a white solid.

The compound **2** was reduced by diisobutyl alumina hydride (DIBAL) to yield benzylic alcohol **3**. The reaction was allowed to stir slowly from 0℃ to room temperature and then quenched with water, 15% sodium hydroxide and water successively. Column chromatograph afforded the product as a white solid. Compound **3** can also be obtained in a one-pot reaction via the addition of DIBAL to the solution of compound **2** without isolation and purification of compound **2**. The yield of one-pot and two-step reaction is comparable.

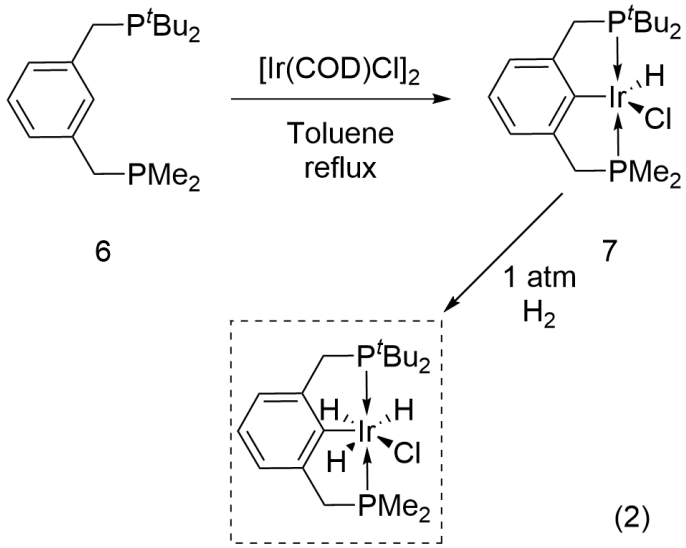
Treatment of compound **3** with PBr_3 afforded benzylic bromide **4**. The reaction processed very quickly (15 minutes), and was quenched with water. Column chromatograph afforded the product as a white solid.

The second phosphination reaction was achieved by reacting another lithiated BH_3-protected phosphine $BH_3{\cdot}PLitBu_2$, which came from treating $PCltBu_2$ with $BH_3{\cdot}SMe_2$ complex in THF and reduced to $BH_3{\cdot}PHtBu_2$ by the similar procedure as formation of $BH_3{\cdot}PHMe_2$, with benzylic bromide **4** to form the $BH_3{\cdot}$protected ligand **5**. Reaction was quenched with 1M HCl and extracted with diethyl ether and ethyl acetate. Column chromatograph afforded product as a white solid.

Deprotection of the phosphine under the conditions reported by Jensen afforded the desired $^{tBu2}PCP^{Me2}$-H pincer ligand **6**. Compound **5** was treated with HBF_4/Et_2O in the CH_2Cl_2 gave compound **6**. Reaction was quenched with aqueous $NaHCO_3$ and extracted with *n*-hexane. After washing and drying, *n*-hexane was removed under vacuum to give pasty liquid. ^{31}P spectrum showed two doublet peaks around 34.4ppm and -44.8ppm.

2.2 Synthesis of (^{tBu2}PCP^{Me2})IrHCl and (^{tBu2}PCP^{Me2})IrH$_4$ complex

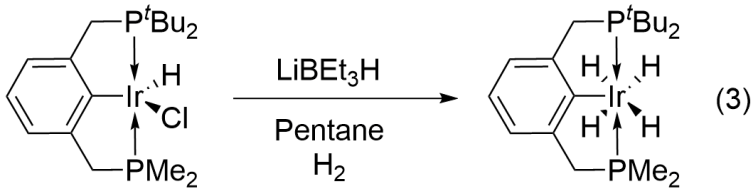
The metallation of the ligand onto Iridium to yield hydride chloride complex **7** (**eq. 2**). The procedure to synthesize complex **7** is similar to ^{tBu3Me}PCPIrHCl, which made by our group previously. Ligand **6** was treated with [Ir(COD)Cl]$_2$ in toluene and stirred at 165℃ for 2 days under hydrogen atmosphere. Pentane was used to extract product and then pumped off afforded a red solid. By ^{31}P and ^{1}H spectrum, the product could be a mixture of several compounds, which were not characterized. In the ^{31}P spectrum, four major broad peaks appears at 72ppm, 70ppm, 21ppm, 19ppm, as well as other peaks appears at 68ppm, 66ppm, 64ppm, 61ppm, 9ppm, 7ppm, 5ppm. In the ^{1}H spectrum, one broad hydride peaks appears at -38ppm. When the solution was charged with H_2 (1 atm), we found that in the ^{1}H spectrum, two new quartet peaks appears around -18ppm and -27ppm. These new peaks may indicate the coordination of H_2 to the central metal.



(2)

The procedure to attempt synthesizing ^{tBu2}PCP^{Me2}IrH$_4$ is similar to ^{tBu3Me}PCPIrH$_4$ (**eq. 3**). Treatment of ^{tBu2}PCP^{Me2}IrHCl **7** with LiBEt$_3$H in pentane under hydrogen atmosphere to generate compound **8**. The product was extracted with pentane and then

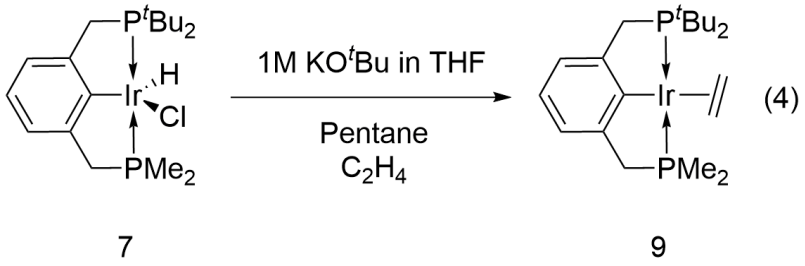
the solution was pumped off under vacuum. In the ^{31}P spectrum, two major doublet peaks appears at 74.50ppm, 72.45ppm (d, J_{PP}=332.98 Hz), -11.32ppm, -13.38ppm (d, J_{PP}=332.98 Hz). Other peaks appears around 86ppm, 84ppm, 62ppm, 59ppm, -4ppm, -6ppm, -7ppm, which may indicate the product of oxidative addition of benzene to the central metal. In the ^{1}H spectrum, several new peaks appears from -5ppm to -17ppm, while typically triplet hydride peaks appears at -9ppm after charge with H_2.



7 8 (3)

2.3 Synthesis of (^{tBu2}PCP^{Me2})Ir(C_2H_4) complex

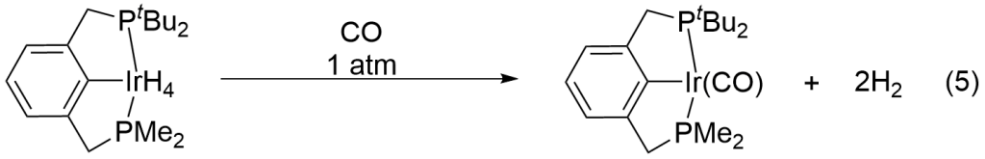
The procedure to attempt synthesizing ^{tBu2}PCP^{Me2}Ir(C_2H_4) is similar to ^{tBu3Me}PCPIr(C_2H_4) (**eq. 4**). Treatment of ^{tBu2}PCP^{Me2}IrHCl **7** with KO^{t}Bu in pentane in JY-NMR tube under C_2H_4 atmosphere to generate compound **9**. The product was extracted with pentane and then the solution was pumped off under vacuum. In the ^{31}P spectrum, two major doublet peaks appears at 73.39ppm, 71.86ppm (d, J_{PP}=309.1 Hz), 12.46ppm, 10.94ppm (d, J_{PP}=309.0 Hz). In the ^{1}H spectrum, triplet hydride peaks appears at 2.79ppm indicates the coordination of the C_2H_4 to the central metal. Addition of 1atm C_2H_4 to NMR tube provides two new doublet peaks at 1.43ppm, 0.08ppm (d, J_{PP}=303.7 Hz), -31.8ppm, -33.3ppm (d, J_{PP}=303.8 Hz) in ^{31}P spectrum, which indicates the appearance of ^{tBu2}PCP^{Me2}Ir(C_2H_4)$_n$ complex. Such kind of Iridium complex is too stable and showed no reactivity in transfer alkane dehydrogenation reaction.



7 9

2.4 Addition of CO to (^{tBu2}PCP^{Me2})IrH$_4$

To further understanding of the complex **8** propriety and getting the X-ray quality crystal easier, complex **8** was tried to react with several small molecule. Addition of 1 atm of CO to the (^{tBu2}PCP^{Me2})IrH$_4$ complex generated the complex (^{tBu2}PCP^{Me2})Ir(CO) **10** (**eq. 5**), which is analogy with the known reaction of ^{tBu4}PCPIrH$_4$[4]. In the ^{31}P spectrum, two major doublet peaks appears around 85.01ppm, 84.18ppm (d, J_{PP}=134.28 Hz), -0.75ppm, -0.08ppm (d, J_{PP}=134.66 Hz). Crystals were attempt to obtaining from the hexane solution after solvent removed.

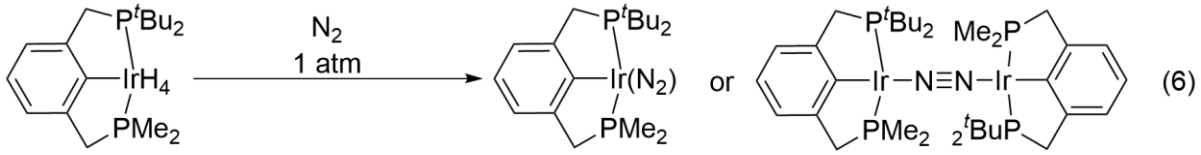


8 10

2.5 Addition of N$_2$ to (^{tBu2}PCP^{Me2})IrH$_4$

Since we had a lot experience that our PCP Iridium complex was easily killed by N_2, the complex **8** was also tested to react with N_2. Addition of 1 atm of N_2 gave (^{tBu2}PCP^{Me2})Ir(N_2) **11** (**eq. 6**), which is analogy with the known reaction of ^{tBu4}PCPIrH$_4$. In the ^{31}P spectrum, three major doublet peaks appears around 67.99ppm, 66.02ppm (d,

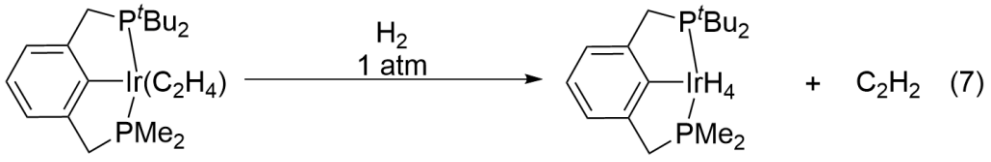
J_{PP}=319.67 Hz), 2.08ppm, 0.12ppm (d, J_{PP}=317.00 Hz) 1.09ppm, -0.88ppm (d, J_{PP}=318.53 Hz). The latter two doublet peaks (2.08ppm, 1.09ppm, 0.12ppm, -0.88ppm), belonging to -*PMe*$_2$ group, may indicate the actual structure of the nitrogen complex is dinuclear instead the mono one. Crystals were attempt to obtaining from the hexane solution after solvent removed.



8 11 (6)

2.6 Addition of H_2 to (^{tBu2}PCP^{Me2})Ir(C_2H_4)

Addition of 1 atm of H_2 to the (^{tBu2}PCP^{Me2})IrH_4 complex generated the complex (^{tBu2}PCP^{Me2})IrH_4 **10** (**eq. 6**). This go-back product had the same properties as the complex (^{tBu2}PCP^{Me2})IrH_4 that we synthesized from (^{tBu2}PCP^{Me2})IrHCl (**eq. 3**). In the ^{31}P spectrum (202 MHz, Toluene-d_8), two major doublet peaks appeared around 79.33ppm, 77.67ppm (d, J_{PP}=332.98 Hz), -6.37ppm, -8.03ppm (d, J_{PP}=332.98 Hz). In the hydride region of ^{1}H spectrum, the triplet peaks at -9.02ppm indicated the formation of Iridium hydride complex.



8 12 (7)

2.7 Transfer dehydrogenation of cyclooctane by high concentrated 3,3-Dimethyl-1-butene (TBE) with different catalysts

The catalyst precursor (^{tBu2}PCP^{Me2})IrH$_4$ **8** was studied for dehydrogenation of cyclooctane (COA). Based on our hypothesis, under high concentration of acceptor, the transfer alkane dehydrogenation should be catalyzed more effectively by sterically less hindered PCP-Iridium catalyst. Thus, (^{tBu2}PCP^{Me2})IrH$_4$ **8** was studied for transfer-dehydrogenation of cyclooctane (COA) by using the equal molar of 3,3-Dimethyl-1-butene (TBE) as acceptor and the reactivity of the reaction was compared with other PCP-Iridium catalysts we knew already. Table II-1 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{tBu2}PCP^{Me2})IrH$_4$ **8** with 3.8 M TBE (equal molar to cyclooctane). In a typical experiment, 0.51mL COA (3.8M), 1 mM catalyst precursor **8** and 0.49mL TBE (3.8M) were charged into a vial and then transferred into separate glass tubes connected with a high-vacuum head by rubber hose. The tube was freezed by liquid nitrogen and sealed under vacuum. Then the tube was moved into a 150℃ oven for heating and analyzed by GC periodically. Table II-2 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{tBu4}PCP)IrH$_4$ with 3.8 M TBE. Table II-3 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{iPr4}PCP)Ir(C$_2$H$_4$) with 3.8M TBE. Figure II-1 shows a plot of concentration of cyclooctene verse time for these three catalysts. It shows that complex (^{iPr4}PCP)Ir(C$_2$H$_4$) is more effective than complex (^{tBu4}PCP)IrH$_4$ and (^{tBu2}PCP^{Me2})IrH$_4$ **8**. In 30 min, 286mM cyclooctene was produced for (^{iPr4}PCP)Ir(C$_2$H$_4$). However, only 38mM cyclooctene was produced for the complex (^{tBu2}PCP^{Me2})IrH$_4$ **8**. This result is against our initial hypothesis and the reason caused the low activity of complex (^{tBu2}PCP^{Me2})IrH$_4$ **8** will be further studied separately.

Table II-1: Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with TBE (3.8M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	3834
10	24	3817
20	34	3806
30	38	3801
60	47	3788
120	59	3774
720	-	-

Table II-2: Transfer-dehydrogenation of COA by (^{tBu4}PCP)IrH$_4$ with TBE (3.8M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	3813
10	39	3765
20	59	3747
30	64	3736
60	82	3719
120	96	3710
720	111	3700

Table II-3: Transfer-dehydrogenation of COA by (^{iPr4}PCP)Ir(C_2H_4) with TBE (3.8M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	3859
10	159	3693
20	232	3619
30	286	3565
60	439	3416
120	731	3119
720	1474	2376

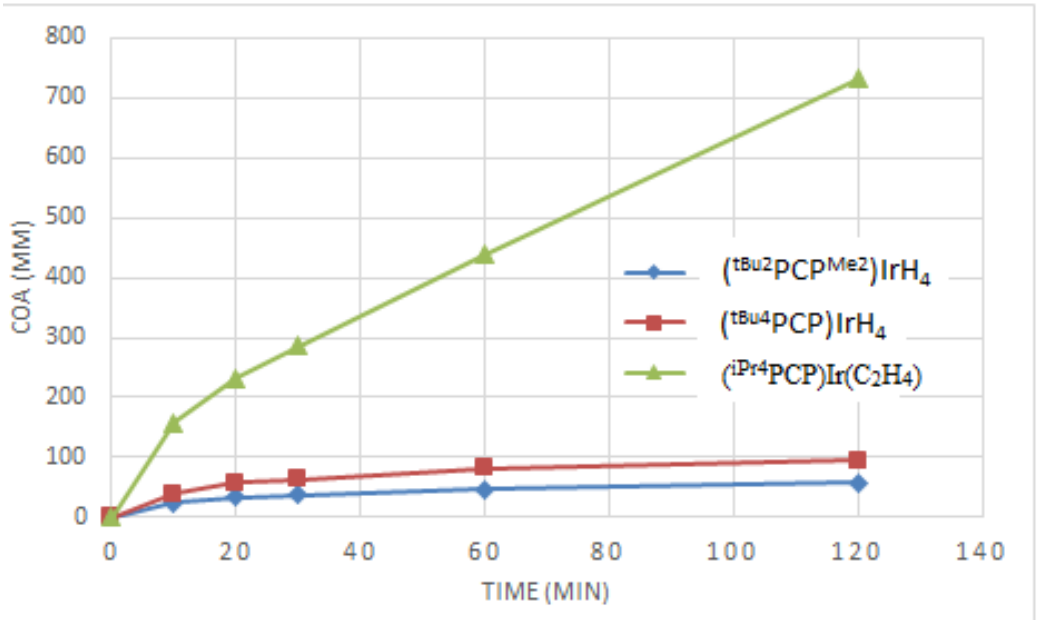


Figure II-1: Comparison on of (^{tBu2}PCP ^{Me2})IrH$_4$, (^{tBu4}PCP)IrH$_4$ and (^{iPr4}PCP)Ir(C_2H_4)

2.8 (^{tBu2}PCP^{Me2})IrH$_4$ catalyzed transfer-dehydrogenation of cyclooctane by different concentration of 3,3-Dimethyl-1-butene (TBE)

(^{tBu2}PCP^{Me2})IrH$_4$ **8** was then studied for transfer-dehydrogenation of cyclooctane (COA) by using different concentration of 3,3-Dimethyl-1-butene (TBE) for investigating the effect of acceptor's concentration. The reaction conditions were similar to the transfer dehydrogenation of cyclooctane. Table II-4 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{tBu2}PCP^{Me2})IrH$_4$ **8** with different concentration of 3,3-Dimethyl-1-butene (TBE) (from 0.2M to 1.1M). Figure II-2 shows a plot of concentration of cyclooctene verse concentration of TBE for (^{tBu2}PCP^{Me2})IrH$_4$ **8**. The result shows that the complex (^{tBu2}PCP^{Me2})IrH$_4$ **8** is most effective with 1.1M TBE as acceptor. The activity of the catalyst increased with the increasing of acceptor's concentration in low concentration region while it decreased when the acceptor's concentration is too high. This interesting result need further study to explain it.

Table II-4: Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with TBE (0.2M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	195.7
10	13.9	92.9
20	12.2	89.1
30	21.6	67.8
60	18.5	79.1
120	31	75.2
720	44.6	80.6

Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with TBE (0.45M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	448.9
10	23.0	205.7
20	36.5	175.9
30	44.8	189.1
60	51.0	173.6
120	65.8	189.2
720	87.1	119.1

Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with TBE (1.1M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	1112.3
10	26.3	405.0
20	37.8	396.8
30	51.4	370.2
60	66.3	357.6
120	83.2	310.6
720	111.4	280.1

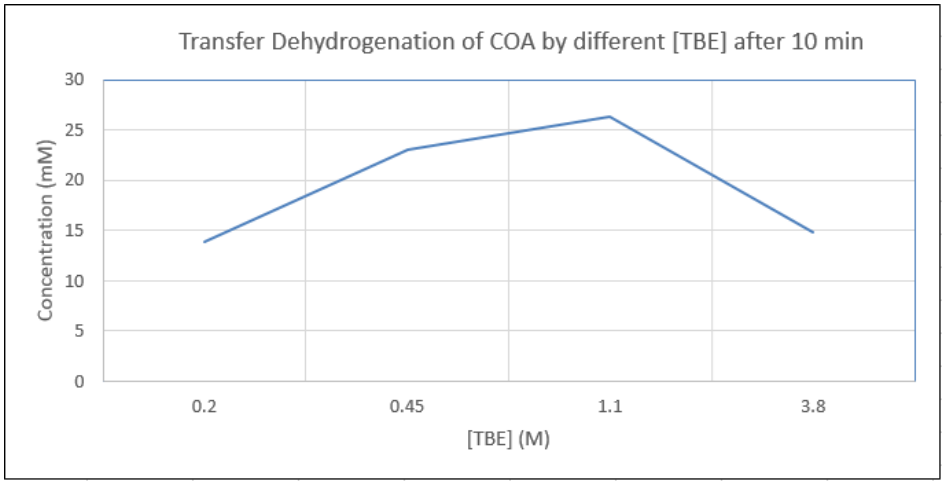


Figure II-2: Comparison on of transfer-dehydrogenation of COA by (^{tBu2}PCP ^{Me2})IrH$_4$ with different concentration of TBE

2.9 (^{tBu2}PCP^{Me2})IrH$_4$ catalyzed transfer-dehydrogenation of cyclooctane by bicyclo[2.2.1]hept-2-ene (NBE)

The catalyst precursor (^{tBu2}PCP^{Me2})IrH$_4$ **8** was also studied for dehydrogenation of cyclooctane (COA) with bicyclo[2.2.1]hept-2-ene NBE (0.2M or 0.45M). The reaction was carried out under same conditions as the reactions with TBE. Table II-5 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{tBu2}PCP^{Me2})IrH$_4$ **8**. In 10 min, 45mM cyclooctene was produced for TBE (0.45M) and only 3.8mM cyclooctene was produced for NBE (0.45M). And after the reaction solution was heated for 10 min at 150 ℃, a brown pasty compound that looked like polymer was found in the reaction vessel. On heating longer, more of the polymerized material was observed along with dehydrogenation products. The acceptor NBE was probably polymerized in the presence of the catalyst.

Table II-5: Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with NBE (0.2M)

Time (min)	Cyclooctene (mM)	NBE (mM)
0	0	193.4
10	4.5	109.1
20	5.6	105.3
30	7.8	115.9
60	7.0	125.7
120	10.4	98.0
720	16.8	94.4

Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})IrH$_4$ with NBE (0.45M)

Time (min)	Cyclooctene (mM)	NBE (mM)
0	0	432.1
10	2.1	283.5
20	2.8	243.4
30	3.8	305.2
60	3.8	265.5
120	4.3	212.0
720	9.0	256.9

2.10 (^{tBu2}PCP^{Me2})Ir(C_2H_4) catalyzed transfer-dehydrogenation of cyclooctane by 3,3-Dimethyl-1-butene (TBE)

The catalyst precursor (^{tBu2}PCP^{Me2})Ir(C_2H_4) **11** was also studied for dehydrogenation of cyclooctane (COA) by 3,3-Dimethyl-1-butene (TBE) (3.8M). The reaction was carried out under same conditions as the reactions with (^{tBu2}PCP^{Me2})IrH_4 **8**. Table II-6 lists the results of cyclooctane transfer dehydrogenation catalyzed by (^{tBu2}PCP^{Me2})Ir(C_2H_4) **11**. Figure II-3 shows a plot of concentration of cyclooctene verse time for two complexes (^{tBu2}PCP^{Me2})IrH_4 **8** and (^{tBu2}PCP^{Me2})Ir(C_2H_4) **11**. The result should that there was no cyclooctene produced after 30 min. The complex (^{tBu2}PCP^{Me2})Ir(C_2H_4) **11** was probably too stable to catalyze the alkane dehydrogenation reaction.

Table II-6: Transfer-dehydrogenation of COA by (^{tBu2}PCP^{Me2})Ir(C_2H_4) with TBE (3.8M)

Time (min)	Cyclooctene (mM)	TBE (mM)
0	0	3788.9
10	0	3786.3
20	0	3785.5
30	0	3784.1
60	0	3779.3
120	0	3769.1
720	0	3760.6

2.11 Summary

A revised synthesis scheme for the synthesis of $^{tBu2}PCP^{Me2}$-H ligand was developed. This scheme was found to be amenable for the synthesis of variety of asymmetric pincer ligand. With the $^{tBu2}PCP^{Me2}$-H ligand, ($^{tBu2}PCP^{Me2}$)IrH_4 **8** and ($^{tBu2}PCP^{Me2}$)$Ir(C_2H_4)$ **11** complexes were obtained. Addition of small molecules, CO and N_2, were tested to added to ($^{tBu2}PCP^{Me2}$)IrH_4 **8** complex formed ($^{tBu2}PCP^{Me2}$)Ir(CO) **9**, ($^{tBu2}PCP^{Me2}$)$Ir(N_2)$ **10**. H_2 was added to complex ($^{tBu2}PCP^{Me2}$)$Ir(C_2H_4)$ **11** to form the reversed complex ($^{tBu2}PCP^{Me2}$)IrH_4 **8**. The activity of ($^{tBu2}PCP^{Me2}$)IrH_4 **8** was compared with other two known PCP-Iridium catalyst systems ((^{tBu4}PCP)IrH_4 and (^{iPr4}PCP)$Ir(C_2H_4)$) by alkane transfer dehydrogenation of cyclooctane by high concentrated 3,3-Dimethyl-1-butene (TBE). The result showed that ($^{tBu2}PCP^{Me2}$)IrH_4 **8** do not have higher activity with high concentration of acceptor than more bulky PCP-Iridium as expected. The study of effect of different concentration of acceptor indicated that the activity of the complex ($^{tBu2}PCP^{Me2}$)IrH_4 **8** increased with the increasing of acceptor's concentration in low concentration region while it decreased when the acceptor's concentration is too high. NBE was also tested as acceptor for ($^{tBu2}PCP^{Me2}$)IrH_4 **8** catalyzed transfer dehydrogenation of cyclooctane (COA). It did not show better result than TBE but was probably polymerized in the presence of the catalyst. ($^{tBu2}PCP^{Me2}$)$Ir(C_2H_4)$ **11** was also studied for alkane transfer dehydrogenation of cyclooctane (COA) by 3,3-Dimethyl-1-butene (TBE). No alkane dehydrogenation product was found in this reaction, which may be caused by the high stability of such olefin coordinated complex.

Reference:

1. Moulton, C. J.; Shaw, B. L. J. *Chem. Soc. Dalton Trans.* **1976**, 1020-1024.
2. Naghipour, Ali; Sabounchei, Seyyed Javad; Morales-Morales, David; Hernandez-Ortega, Simon; Jensen, Craig M. *J. Organomet. Chem.* **2004**, *689*, 2494
3. Dr. David Yu-Ber Wang's PhD dissertation
4. Krogh-Jespersen, K.;Czerw,M.;Zhu, K.; Singh,B.;Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797–10809.

Experimental

General

All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures.[1] The following compounds were purchased from Aldrich or Stream and used without further purification HP^tBu_2, $ClPMe_2$, $BH_3{\cdot}SMe_2$ in THF, (3-bromomethyl)benzyl benzoate, diisobutyl alumina hydride (DIBAL), PBr_3, $HBF_4{\cdot}Et_2O$, *n*-BuLi, $LiAlH_4$, $[Ir(COD)Cl]_2$, $LiBEt_3H$, $NaHCO_3$. ^1H, ^{13}C and ^{31}P NMR spectra were recorded with Varian Mercury and Inova spectrometers operating at 300, 400 or 500 MHz respectively.

Synthesis of compound **6** was prepared from compound **5** using the deprotection procedure detailed by Jensen *et. al*.[2] Me_2PH preparation was followed the similar procedure for ^{t}BuMePH reported by our group.[3] BH_3 protection of $^tBu_2PH$ and Me_2PH was performed as reported by Higham *et. al*.[4]

Representative procedure for the formation of lithiated phosphine-boranes ($Li^tBu_2P{\cdot}BH_3$*,* $LiMe_2P{\cdot}BH_3$*).* A solution of $^tBu_2PH{\cdot}BH_3$ (0.731g, 5.0mmol) in 5ml THF was cooled to 0℃. A solution of *n*-BuLi in THF (2.0M, 2.875mL, 5.75mmol) was added via syringe. The reaction solution was allowed to war to room temperature and stirred for 3 hours.

Synthesis procedure followed the **Scheme 2**. Details is similar as the revised procedure in David Yu-Ber Wang's PhD dissertation.[5]

Compound 2.

Methyl-3-(bromomethyl)benzoate (1.091g, 4.762mmol) was dissolved in 3.6mL THF and cooled to 0℃. This solution was transferred via cannula to a flask charged with a solution of $Li^tMe_2P{\cdot}BH_3$ (5.0mmol) in 7.2mL of THF that was prepared separately and cooled to 0℃. After 90 min, 7.2mL water was added. The aqueous layer was extracted with dichloromethane (3 x 3.6mL), and the combined organic layers were dried over magnesium sulfate, filtered and concentrated. Column chromatography (5:1 hexanes:ethyl acetate) afforded the product as a white solid (0.767g, 3.424mmol) in 72% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 7.36 (q). ^1H NMR ($CDCl_3$, 500MHz): δ 7.96 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.46 – 7.37 (m, 2H), 3.92 (s, 3H), 3.08 (d, *J* = 10.7 Hz, 2H), 1.23 (d, *J* = 10.1 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 166.82 (s), 134.16 (d, *J* = 3.8 Hz), 133.25 (d, *J* = 7.6 Hz), 130.77 (d, *J* = 2.2 Hz), 130.41 (d, *J* = 3.9 Hz), 128.97 (d, *J* = 2.5 Hz), 128.51 (d, *J* = 2.7 Hz), 52.43 (s), 34.45 (d, *J* = 31.5 Hz), 10.47 (d, *J* = 36.9 Hz).

Compound 3.

A flask was charged with compound **2** (0.767g, 3.424mmol) and 13.0mL of toluene and cooled to 0℃. This solution was transferred via cannula to a flask containing a solution of di-isobutyl alumina hydride (7.2mL, 1.0M in cyclohexane, 7.2mmol) that was diluted with 7.0mL of toluene and cooled to 0℃. The reaction solution was allowed to slowly warm to room temperature and stir for 6h. Diethyl ether (27.5mL) was added, and the reaction solution was cooled to 0℃. Water (0.34mL), a 15% sodium hydroxide solution (0.34mL), and a second portion of water (0.86mL) were added successively. The

reaction mixture was then allowed to warm to room temperature and stir for an additional 15 min. The reaction mixture was dried over magnesium sulfate, filtered and concentrated. Column chromatography (5:1 hexanes:ethyl acetate) afforded the product as a white solid (0.616g, 3.142mmol) in 93.3% yield. Compound **3** can also be obtained in a one-pot reaction via the addition of DIBAL to the solution of compound **2** without isolation and purification of compound **2**. The yield of one-pot and two-step reaction is comparable. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 6.67 (q). ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.09 (s, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 4.61 (s, 2H), 2.96 (d, *J* = 10.6 Hz, 2H), 1.89 (s, 1H), 1.15 (d, *J* = 10.1 Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 141.56 (d, *J* = 2.5 Hz), 133.01 (d, *J* = 7.9 Hz), 128.95 (d, *J* = 2.5 Hz), 128.76 (d, *J* = 4.0 Hz), 128.04 (d, *J* = 4.1 Hz), 125.73 (d, *J* = 2.8 Hz), 65.00 (s), 34.47 (d, *J* = 31.8 Hz), 10.42 (d, *J* = 37.0 Hz).

Compound 4.

Compound **3** (0.616g, 3.142mmol) was dissolved in 30.0mL of chloroform and cooled to 0℃. Phosphorus tribromide (0.354mL, 3,77mmol) was added, and the reaction mixture was allowed to stir for 15 min. Water (0.73mL) was added. The reaction mixture was then dried over magnesium sulfate, filtered, and concentrated. Column chromatography (5:1 hexanes:ethyl acetate) afforded the product as a white solid (0.371g, 1.433mmol) in 45.6% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 7.02(q). ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.23 (d, *J* = 6.1 Hz, 2H), 7.11 (s, 1H), 7.04 – 7.00 (m, 1H), 4.40 (s, 2H), 2.96 (d, *J* = 10.6 Hz, 2H), 1.15 (d, *J* = 10.1 Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 138.44 (d, *J* = 2.6 Hz), 133.42 (d, *J* = 8.0 Hz), 130.21 (d, *J* = 4.1 Hz), 129.59

(d, *J* = 4.0 Hz), 129.20 (d, *J* = 2.5 Hz), 127.79 (d, *J* = 2.8 Hz), 34.36 (d, *J* = 31.4 Hz), 33.17 (s), 10.37 (d, *J* = 37.0 Hz).

Compound 5.

Compound **4** (0.492g, 1.433mmol) was dissolved in 6.7mL of THF cooled to 0℃. This solution was transferred via cannula to a flask that was charged with a solution of compound $LiMe_2P{\cdot}BH_3$ (1.873mmol) in 13.4mL of THF and cooled to 0℃. The reaction was stirred at 0℃ for 1 h and then warmed to room temperature. An aqueous solution hydrochloric acid (1M, 6.7mL) was added. The aqueous layer was extracted with diethyl ether (3 x 6.7mL) and ethyl acetate (6.7mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Column chromatography (10:1 hexanes:ethyl acetate) afforded the product as a white solid (0.400g, 1.183mmol) in 82.6% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 47.91 (br d, *J* = 72.0 Hz), 7.33 (br d, *J* = 71.1 Hz). ^1H NMR ($CDCl_3$, 500MHz): δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.12 (d, *J* = 12.1 Hz, 2H), 3.00 (d, *J* = 10.6 Hz, 2H), 1.26 (d, *J* = 12.5 Hz, 18H), 1.22 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 135.72 – 135.64 (m), 132.97 (dd, *J* = 8.0, 1.8 Hz), 131.79 (t, *J* = 3.9 Hz), 129.61 (dd, *J* = 4.2, 2.7 Hz), 128.63 (t, *J* = 2.1 Hz), 128.13 (dd, *J* = 4.1, 2.2 Hz), 34.56 (d, *J* = 31.8 Hz), 33.09 (d, *J* = 25.0 Hz), 28.49 (d, *J* = 1.1 Hz), 26.04 (d, *J* = 24.5 Hz), 10.69 (d, *J* = 37.2 Hz).

Compound 6.

Compound **5** (0.400g, 1.183mmol) was dissolved in degassed dichloromethane (11.0mL). The solution was cooled to -5℃. 54 w% HBF_4 in diethyl ether (1.62mL) was

added dropwise by a syringe. Then the reaction mixture was warmed to room temperature and stirred overnight. The reaction was diluted with degassed anhydrous diethyl ether (20.0mL) and the solution was added to degassed, saturated solution of sodium bicarbonate in water (62.0mL). The reaction mixture was stirred under argon for 10 minutes. Then the organic layer was separated and the aqueous layer was extracted with anhydrous diethyl ether (20.0mL). The organic portion was combined and washed with degassed water, brine and dried with Na_2SO_4. Then the solvent was removed and the product was obtained as a colorless pasty liquid (0.233g, 0.75mmol) in 63.5% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 34.36 (s) , -44.82 (s). ^1H NMR ($CDCl_3$, 500MHz): δ 6.98 (d, *J* = 11.6 Hz, 1H), 6.86 (q, *J* = 7.5, 6.9 Hz, 2H), 6.62 (d, *J* = 7.5 Hz, 1H), 2.46 (d, *J* = 2.3 Hz, 2H), 2.25 (d, *J* = 2.3 Hz, 2H), 0.79 (d, *J* = 10.6 Hz, 18H), 0.52 (d, *J* = 3.4 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 142.03 (d, *J* = 13.8 Hz), 138.24 (d, *J* = 3.1 Hz), 130.86 (dd, *J* = 8.8, 5.3 Hz), 128.45 (s), 127.50 (dd, *J* = 8.7, 2.2 Hz), 126.55 (dd, *J* = 5.2, 2.1 Hz), 39.06 (d, *J* = 15.4 Hz), 31.79 (d, *J* = 24.3 Hz), 29.98 (d, *J* = 13.5 Hz), 29.08 (d, *J* = 25.6 Hz), 13.65 (d, *J* = 16.5 Hz).

Compound 7.

Compound **6** (50.0mg, 0.161mmol) and $[Ir(COD)Cl]_2$ (54.1mg, 0.08mmol) were dissolved in toluene (13.0mL) and hydrogen bubbled into this solution. The solution was refluxed under hydrogen atmosphere for 2 days. Toluene was then removed under vacuum and the residue was extracted with pentane (3 x 10.0mL). The pentane washings were collected and the solvent evaporated under vacuum. A red solid was obtained (50.5mg, 0.094mmol) in 58.1% yield. By NMR data (^{31}P, ^1H), the product could be a

mixture of several compounds. In the ^{31}P spectrum, four major broad peaks appears at 72ppm, 70ppm, 21ppm, 19ppm, as well as other peaks appears at 68ppm, 66ppm, 64ppm, 61ppm, 9ppm, 7ppm, 5ppm. In the ^{1}H spectrum, one broad hydride peaks appears at -38ppm. When the solution was charged with H_2 (1 atm), two new quartet peaks appears around -18ppm and -27ppm in ^{1}H spectrum. These compounds are not characterized so far.

Compound 8.

Compound **7** (50.5mg, 0.094mmol) was dissolved in pentane (15.0mL) and hydrogen was bubbled into the solution for two hours. Solution turned from red to yellow. A 1 M solution of $LiBEt_3H$ in THF (0.094mL, 0.094mmol) was added dropwise into the solution under hydrogen atmosphere. The solution was stirred for 7 hours and filtered out by a cannula filter. The filtrate was collected and pentane was removed under vacuum. The product was an orange solid (40.0mg, 0.079mmol) in 85.0% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 73.20 (d, J = 335.7 Hz), -12.17 (d, J = 335.7 Hz).

Compound 9.

Compound **7** (50.0mg, 0.093mmol) was dissolved in pentane (15.0mL) and ethylene was bubbled into the solution for two hours. Solution turned from red to yellow. A 1 M solution of KO^tBu in THF (0.093mL, 0.093mmol) was added dropwise into the solution under ethylene atmosphere. The solution was stirred for 7 hours and filtered out by a cannula filter. The filtrate was collected and pentane was removed under vacuum.

The product was a brown solid (38.4mg, 0.073mmol) in 78.1% yield. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 72.62 (d, *J* = 309.1 Hz), 11.70 (d, *J* = 309.0 Hz).

Addition of CO to ($^{tBu2}PCP^{Me2}$)IrH_4

To a p-xylene-d_{10} solution of 5 mg of ($^{tBu2}PCP^{Me2}$)IrH_4 (**8**; 10 μmol) in a *J*-Young NMR tube was added 1 atm of CO. An immediate color change from red to yellow was observed. The reaction was monitored by ^{31}P NMR. The reaction was stopped when all the peaks of ($^{tBu2}PCP^{Me2}$)IrH_4 disappeared. The solvent was removed and the complex was redissolved in p-xylene-d_{10} solution. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 84.59 (d, *J* = 134.5 Hz), 0.34 (d, *J* = 134.7 Hz).

Addition of N_2 to ($^{tBu2}PCP^{Me2}$)IrH_4

To a p-xylene-d_{10} solution of 5 mg of ($^{tBu2}PCP^{Me2}$)IrH_4 (**8**; 10 μmol) in a *J*-Young NMR tube was added 1 atm of N_2. An immediate color change from red to yellow was observed. The reaction was monitored by ^{31}P NMR. The reaction was stopped when all the peaks of ($^{tBu2}PCP^{Me2}$)IrH_4 disappeared. The solvent was removed and the complex was redissolved in p-xylene-d_{10} solution. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 500MHz): δ 67.01 (d, *J* = 321.2 Hz), 1.10 (d, *J* = 317.4 Hz), 0.10 (d, *J* = 319.1 Hz).

Addition of H_2 to ($^{tBu2}PCP^{Me2}$)$Ir(C_2H_4)$

To a p-xylene-d_{10} solution of 5 mg of ($^{tBu2}PCP^{Me2}$)$Ir(C_2H_4)$ (**9**; 10 μmol) in a *J*-Young NMR tube was added 1 atm of H_2. An immediate color change from brown to orange was observed. The reaction was monitored by ^{31}P NMR. The reaction was

stopped when all the peaks of (^{tBu2}PCP^{Me2})Ir(C_2H_4) disappeared. The solvent was removed and the complex was redissolved in p-xylene-d_{10} solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 500MHz): δ 78.50 (d, *J* = 334.9 Hz), -7.20 (d, *J* = 336.3 Hz).

Transfer dehydrogenation of cyclooctane by high concentrated 3,3-Dimethyl-1-butene (TBE) with different catalysts

General procedure for transfer dehydrogenation:

(^{tBu2}PCP^{Me2})IrH_4 (**8**) (1 mg, 0.002 mmol) was dissolved in the cyclooctane (2 mL). 0.51mL solution was taken and added into a small vial. Then 3,3-dimethyl-1-butene TBE (0.49mL, 3.8M) were added into that vial. The solution in the vial was transferred to separate glass tubes, which was then connected by rubber hose with high-vacuum head. Then the solution was cooled under liquid nitrogen and the glass tube was sealed under vacuum. Then the tube was kept in a preheated oven at 150 ℃. The reaction was monitored by GC. The reaction was continued until 12 hours.

The procedure for transfer dehydrogenation by (^{tBu4}PCP)IrH_4 and (^{iPr4}PCP)Ir(C_2H_4) was similar to the procedure mentioned above.

(^{tBu2}PCP^{Me2})IrH_4 catalyzed transfer-dehydrogenation of cyclooctane by different concentration of 3,3-Dimethyl-1-butene (TBE)

General procedure for transfer dehydrogenation:

(^{tBu2}PCP^{Me2})IrH_4 (**8**) (1 mg, 0.002 mmol) was dissolved in the cyclooctane (2 mL). 0.51mL solution was taken and added into a small vial. Then 3,3-dimethyl-1-butene TBE (0.49mL, 3.8M) were added into that vial. The solution in the vial was transferred to

separate glass tubes, which was then connected by rubber hose with high-vacuum head. Then the tube was kept in a preheated oven at 150 ℃. The reaction was monitored by GC. The reaction was continued until 12 hours.

The procedure for transfer dehydrogenation by different concentration (0.2M, 0.45M, 1.1M) of TBE was similar to the procedure mentioned above.

(^{tBu2}PCP^{Me2})IrH$_4$ catalyzed transfer-dehydrogenation of cyclooctane by bicyclo[2.2.1]hept-2-ene (NBE)

General procedure for transfer dehydrogenation:

(^{tBu2}PCP^{Me2})IrH$_4$ (**8**) (1 mg, 0.002 mmol) was dissolved in the cyclooctane (2 mL). 1mL solution was taken and added into a small vial. Then bicyclo[2.2.1]hept-2-ene (NBE) (18.8mg, 0.2M or 42.4mg, 0.45M) were added into that vial. The solution in the vial was transferred to separate glass tubes, which was then connected by rubber hose with high-vacuum head. Then the solution was cooled under liquid nitrogen and the glass tube was sealed under vacuum. Then the tube was kept in a preheated oven at 150 ℃. The reaction was monitored by GC. The reaction was continued until 12 hours.

(^{tBu2}PCP^{Me2})Ir(C$_2$H$_4$) catalyzed transfer-dehydrogenation of cyclooctane by 3,3-Dimethyl-1-butene (TBE)

General procedure for transfer dehydrogenation:

(^{tBu2}PCP^{Me2})IrH$_4$ (**8**) (1 mg, 0.002 mmol) was dissolved in the cyclooctane (2 mL). 0.51mL solution was taken and added into a small vial. Then 3,3-dimethyl-1-butene TBE (0.49mL, 3.8M) were added into that vial. The solution in the vial was transferred to

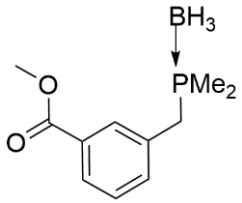
separate glass tubes, which was then connected by rubber hose with high-vacuum head. Then the solution was cooled under liquid nitrogen and the glass tube was sealed under vacuum. Then the tube was kept in a preheated oven at 150 ℃. The reaction was monitored by GC. The reaction was continued until 12 hours.

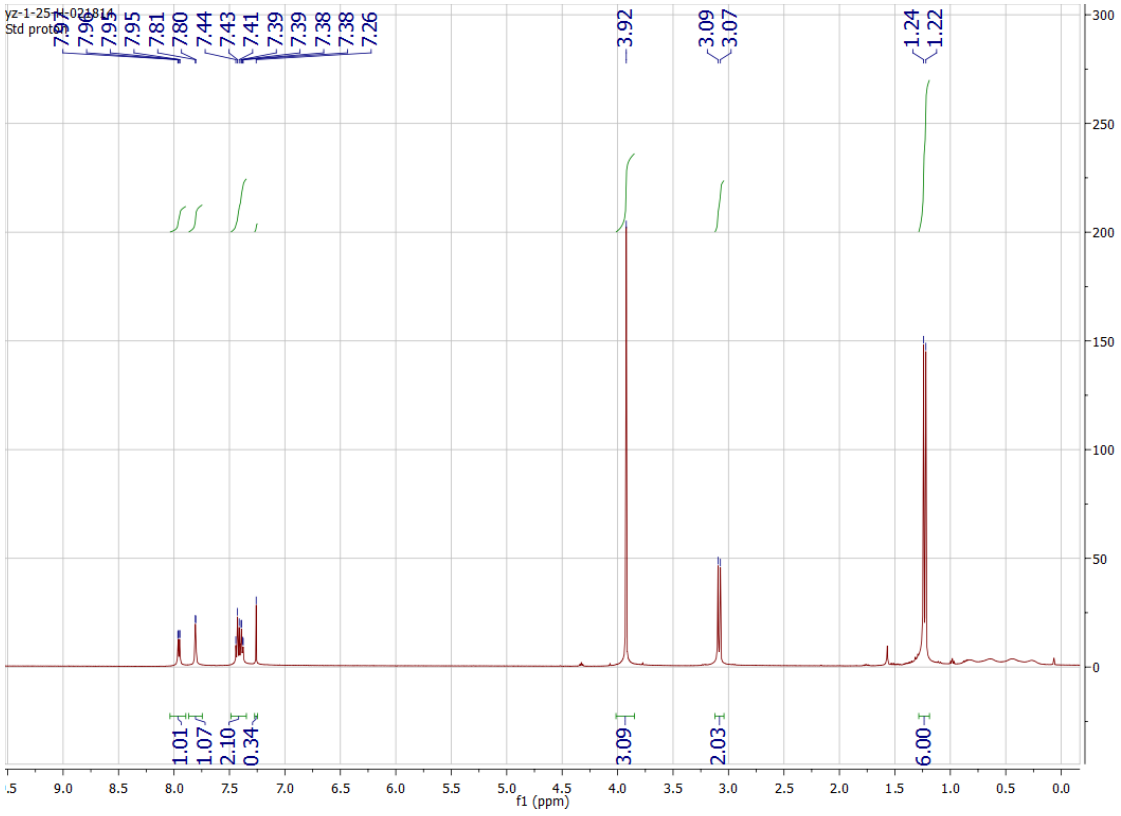
Reference:

1. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals, 2nd edition*, Pergamon Press, **1980**.
2. Naghipour, Ali; Sabounchei, Seyyed Javad; Morales-Morales, David; Hernandez-Ortega, Simon; Jensen, Craig M. *J. Organomet. Chem.* **2004**, *689*, 2494
3. Sabuj Kundu, Yuriy Choliy, Gao Zhuo, Ritu Ahuja, Thomas J. Emge, Ralf Warmuth, Maurice Brookhart, Karsten Krogh-Jespersen, and Alan S. Goldman *Organometallics* **2009**, *28*, 5432–5444
4. Higham, Lee J.; Heslop, Katie; Pringle, Paul G.; Orpen, A. Guy, *J. Organomet. Chem.* **2004**, *689*, 2975
5. Dr. David Yu-Ber Wang's PhD dissertation

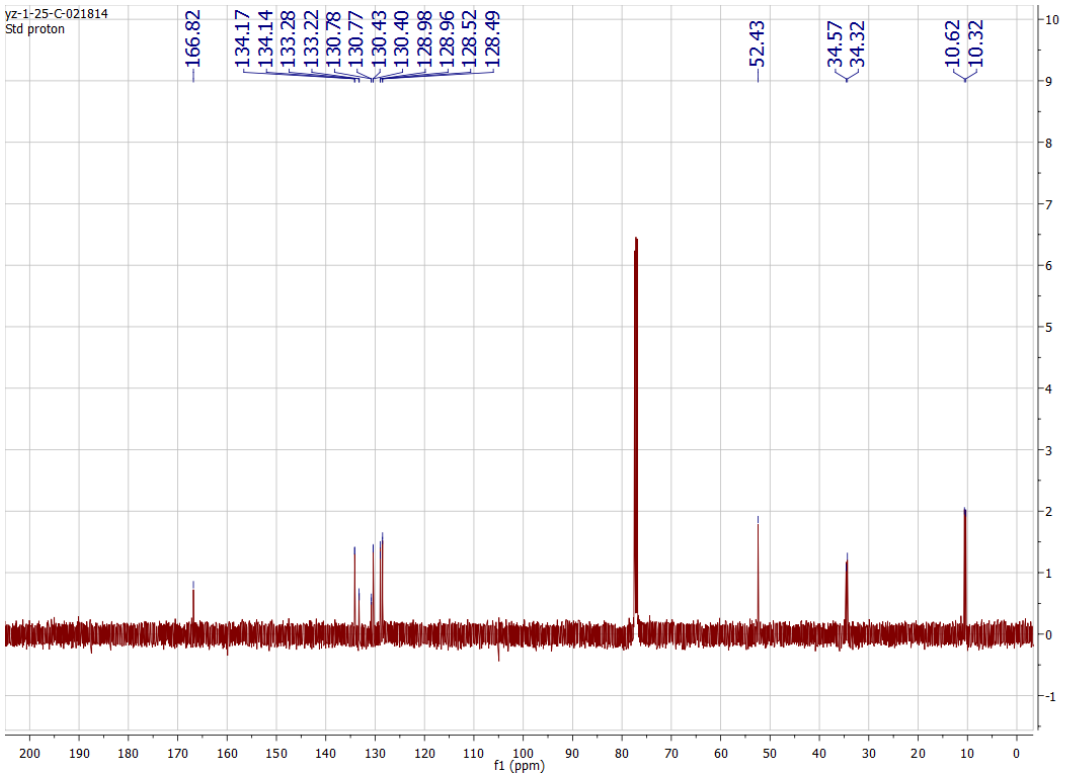
Selected NMR Spectrums

Compound **2**

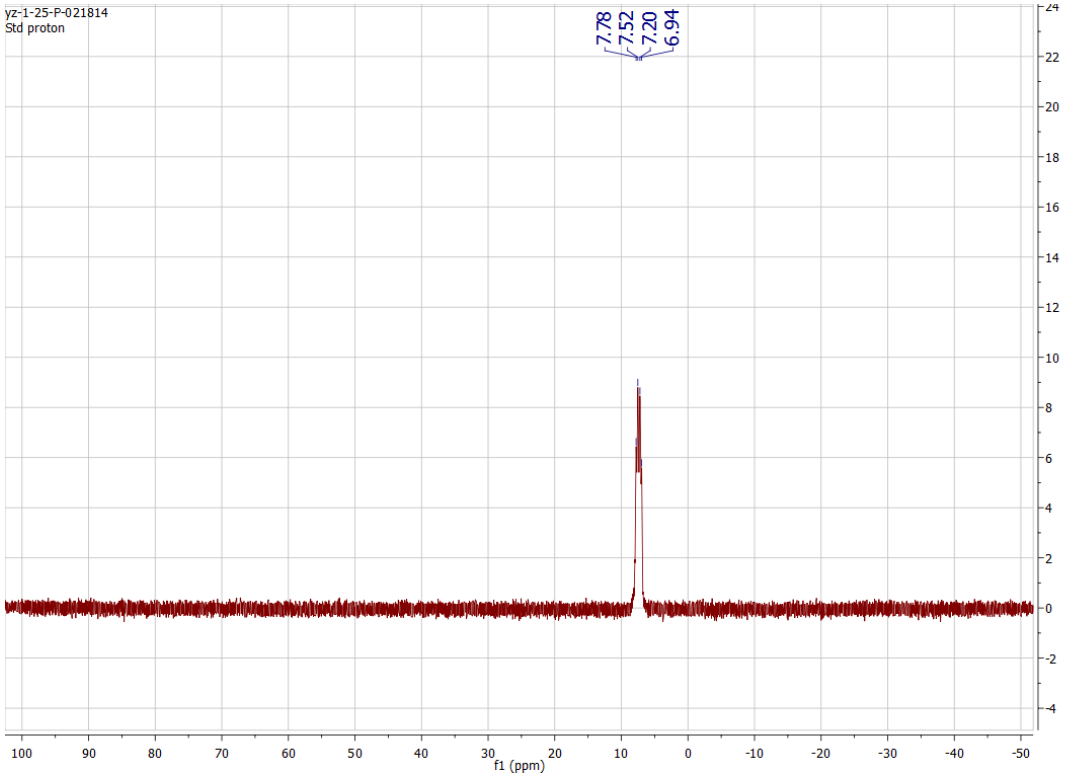




^{1}H spectrum of compound **2**

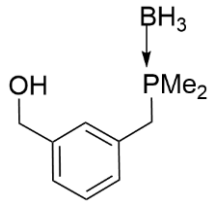


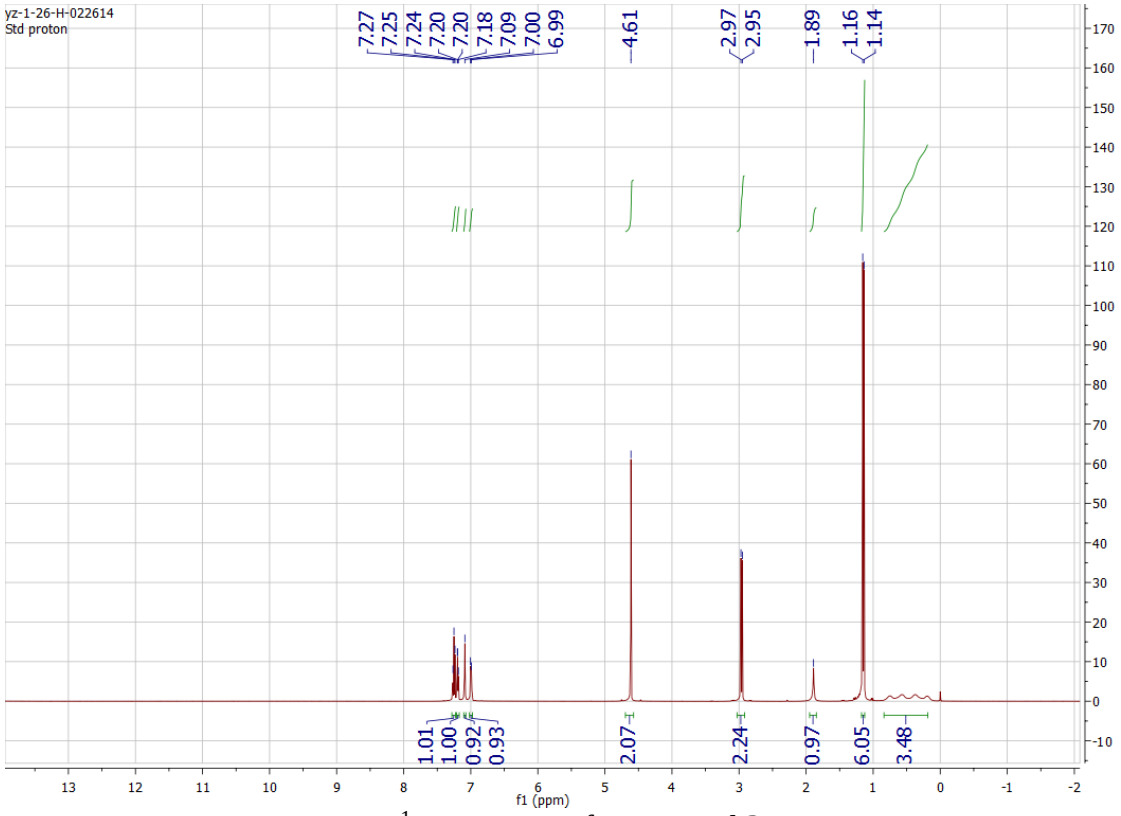
^{13}C spectrum of compound **2**



^{31}P spectrum of compound **2**

Compound **3**





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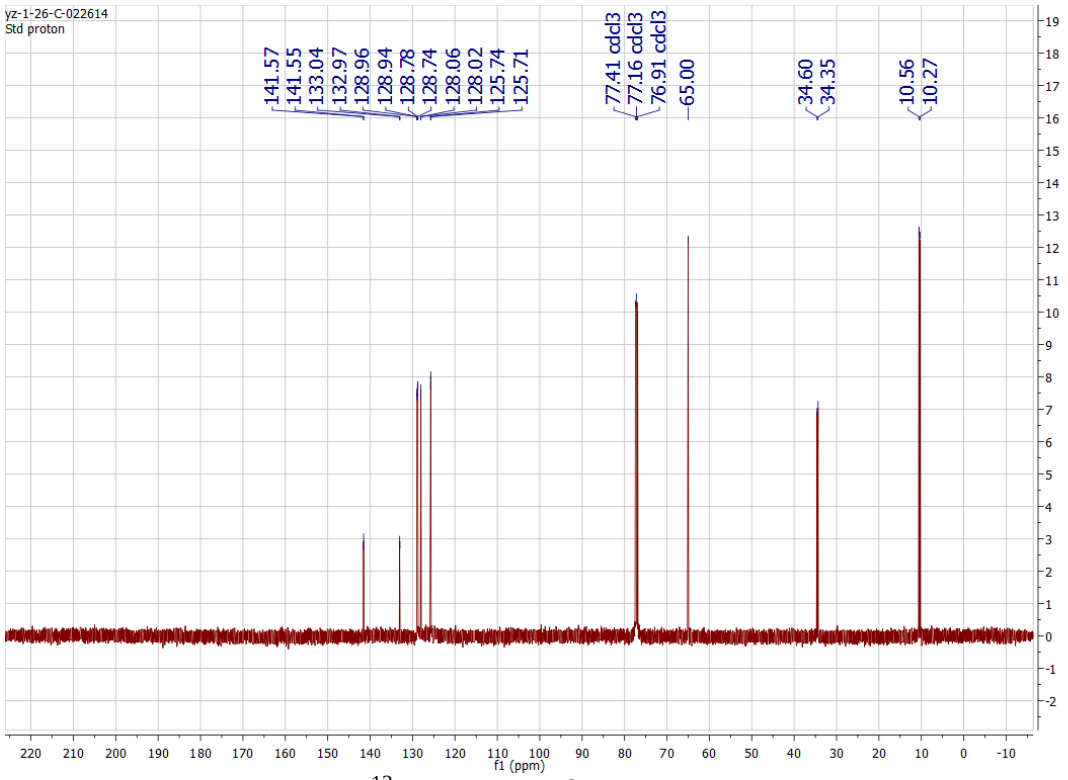

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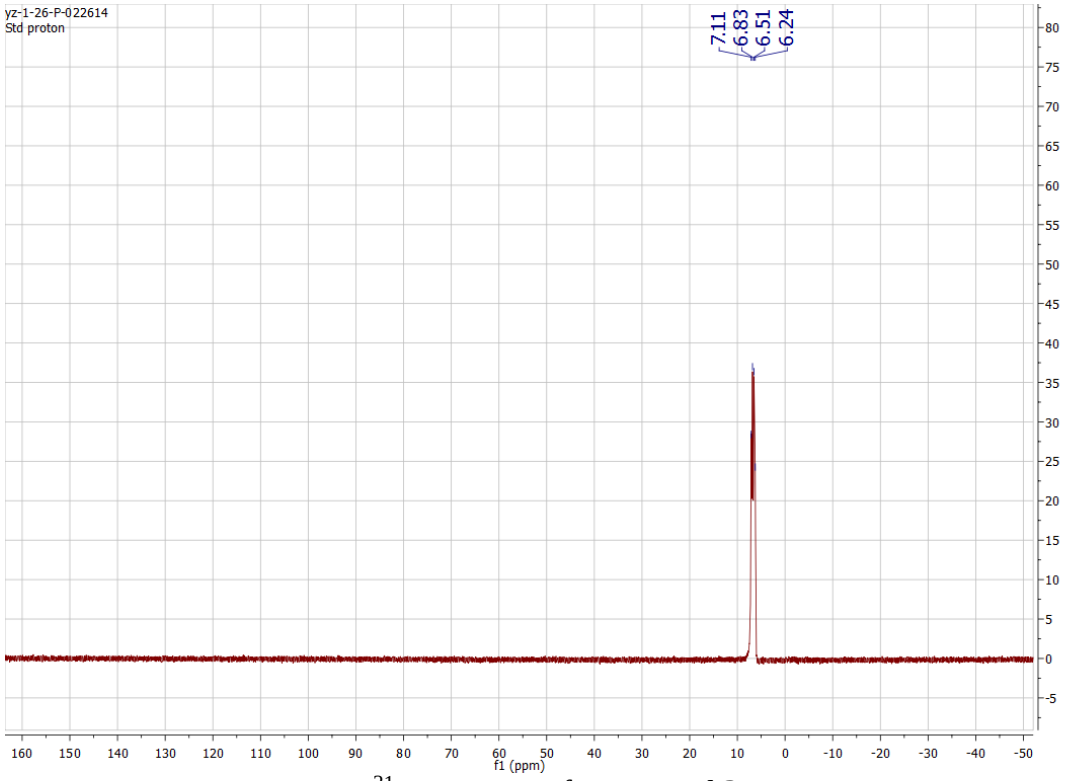
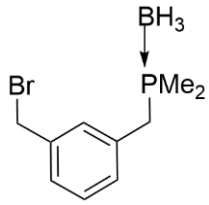
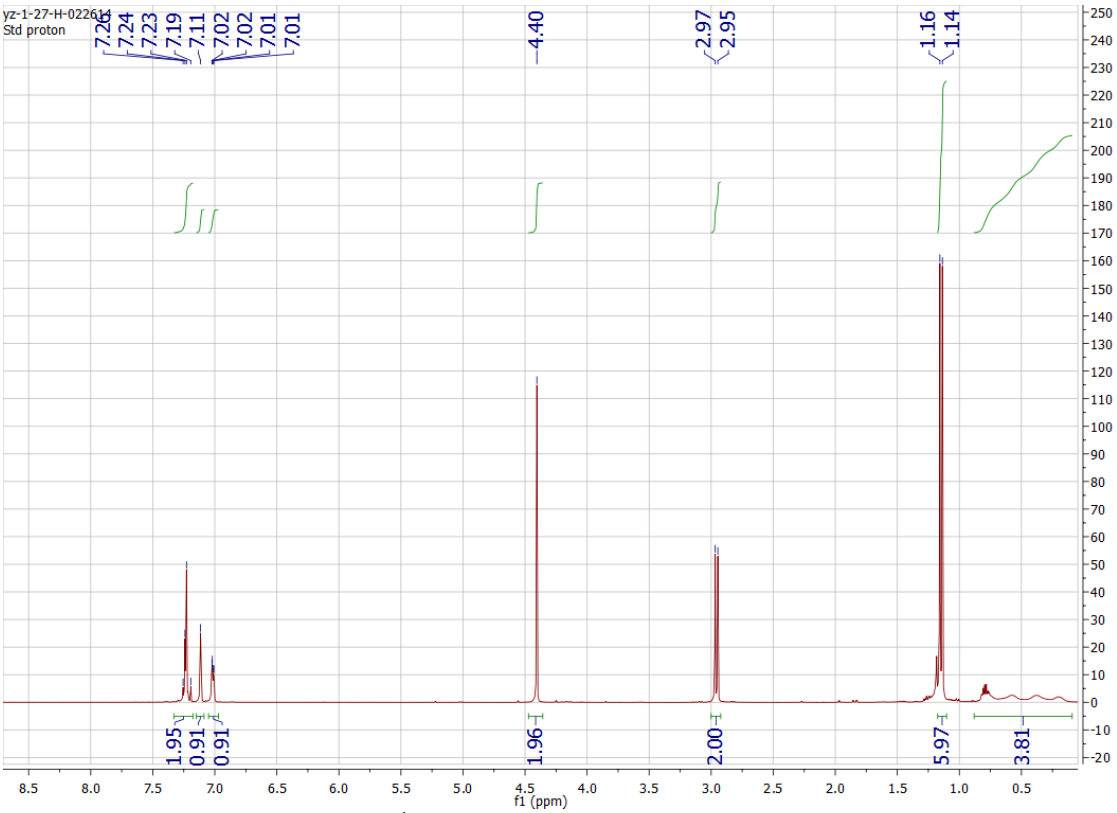


^{31}P spectrum of compound **3**

Compound **4**





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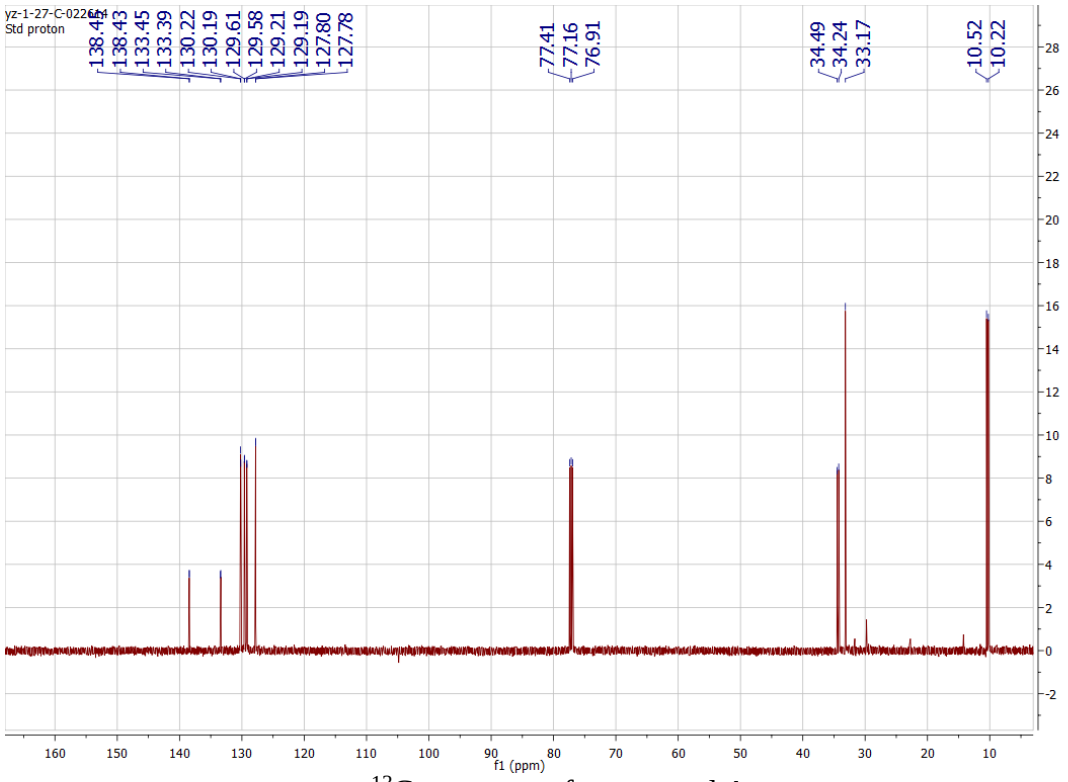
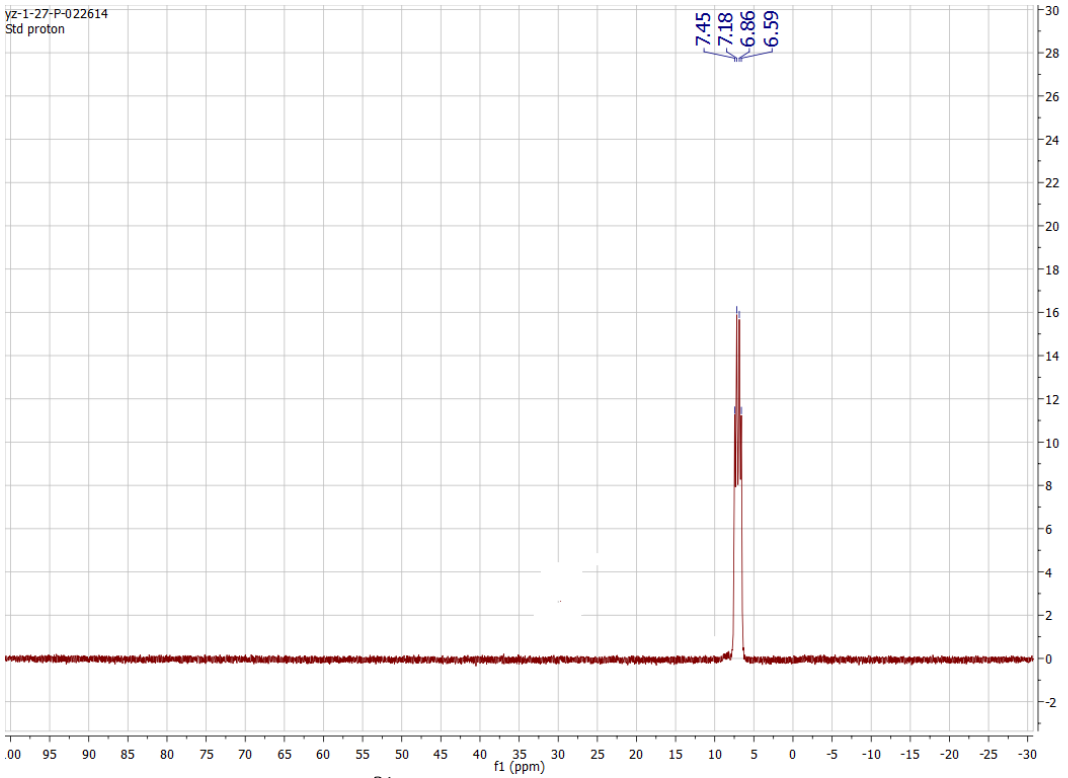
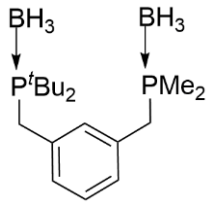


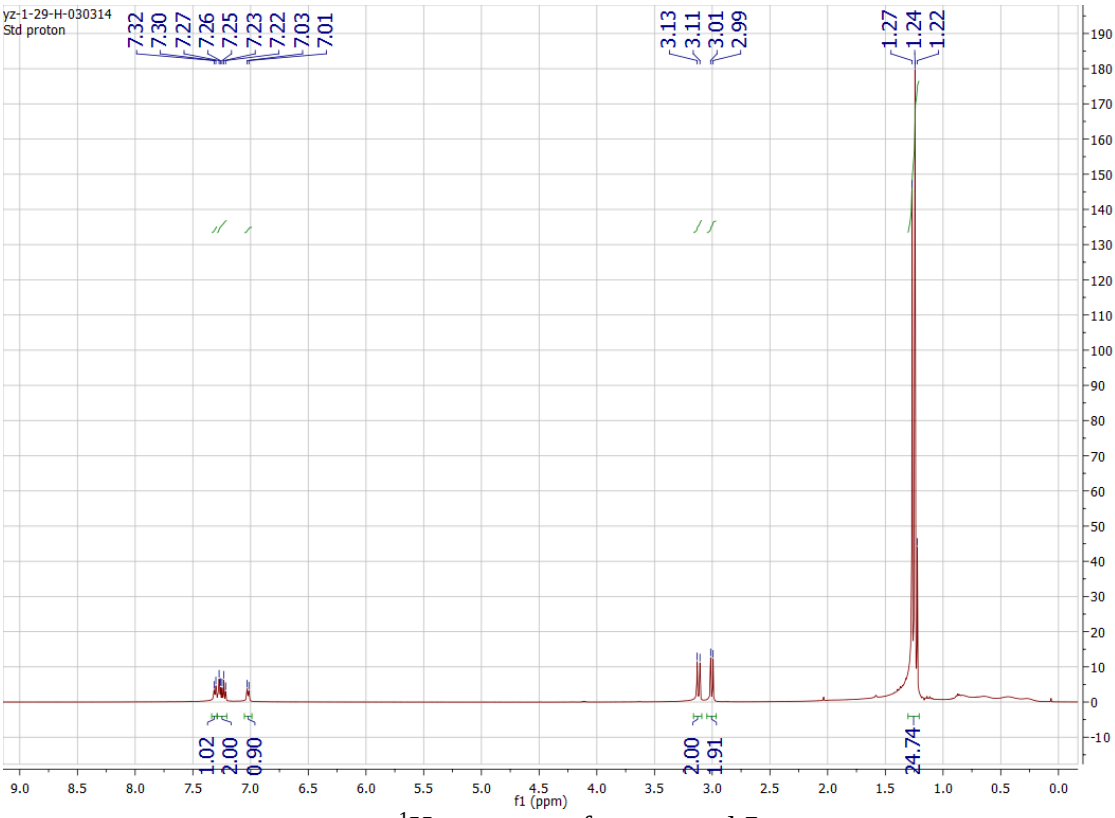
^{13}C spectrum of compound **4**



^{31}P spectrum of compound **4**

Compound **5**





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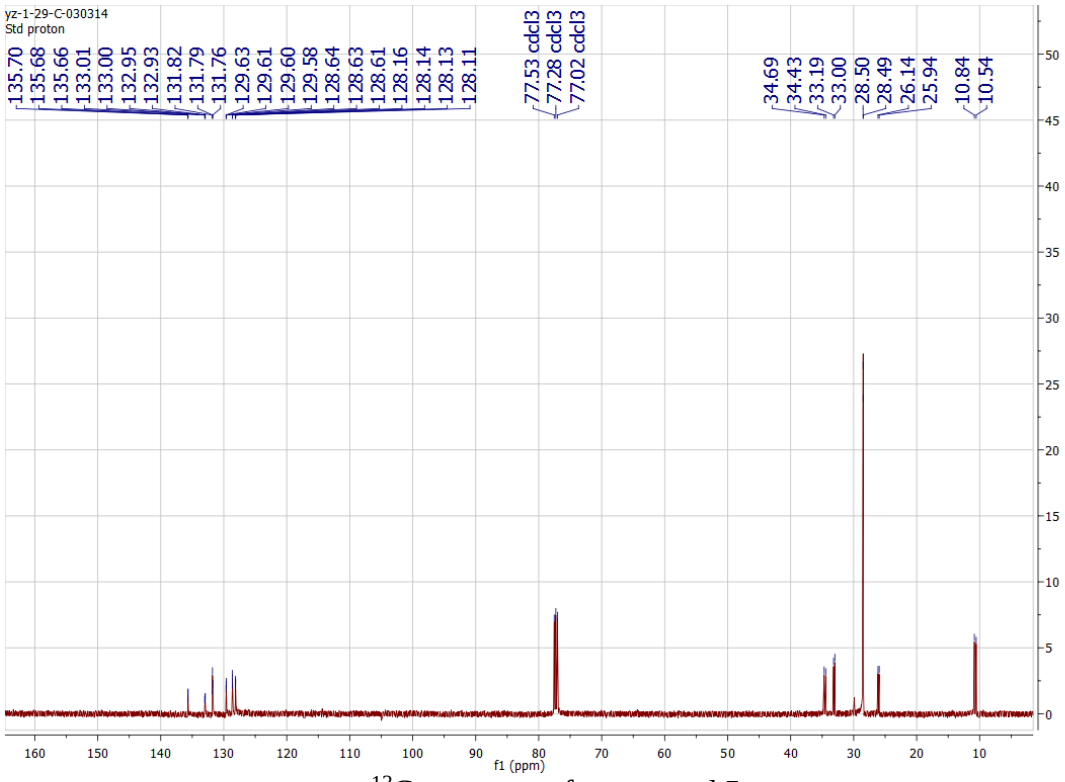

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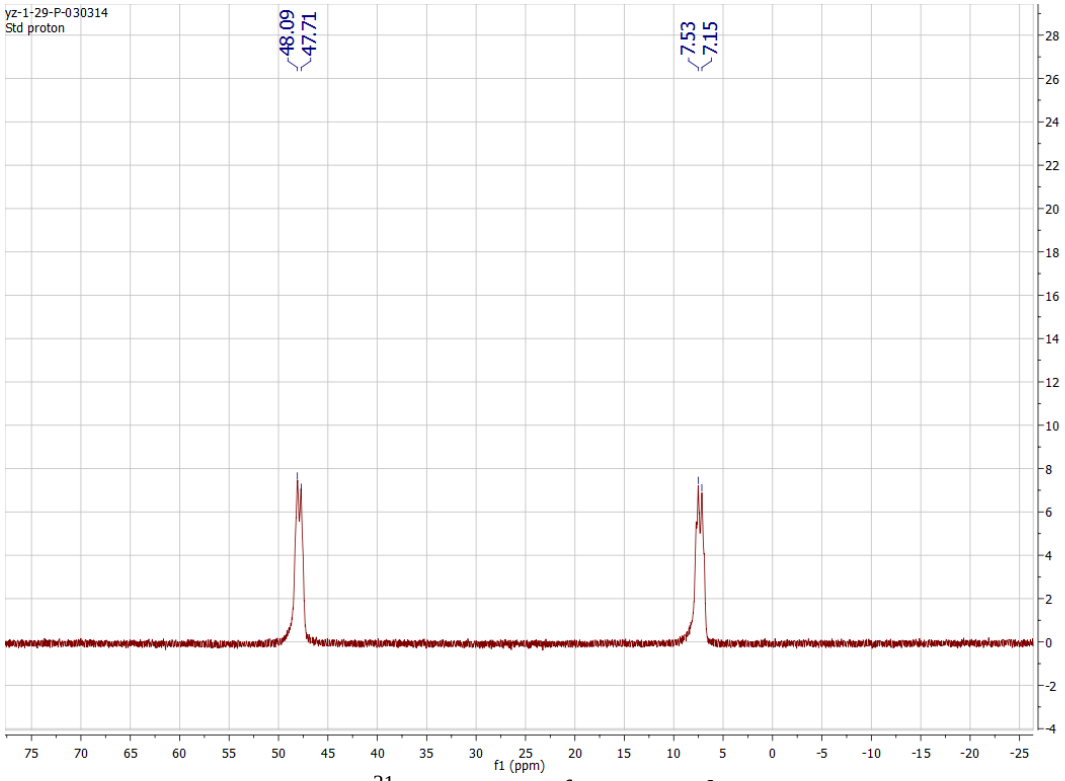
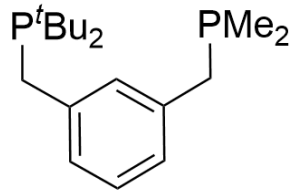
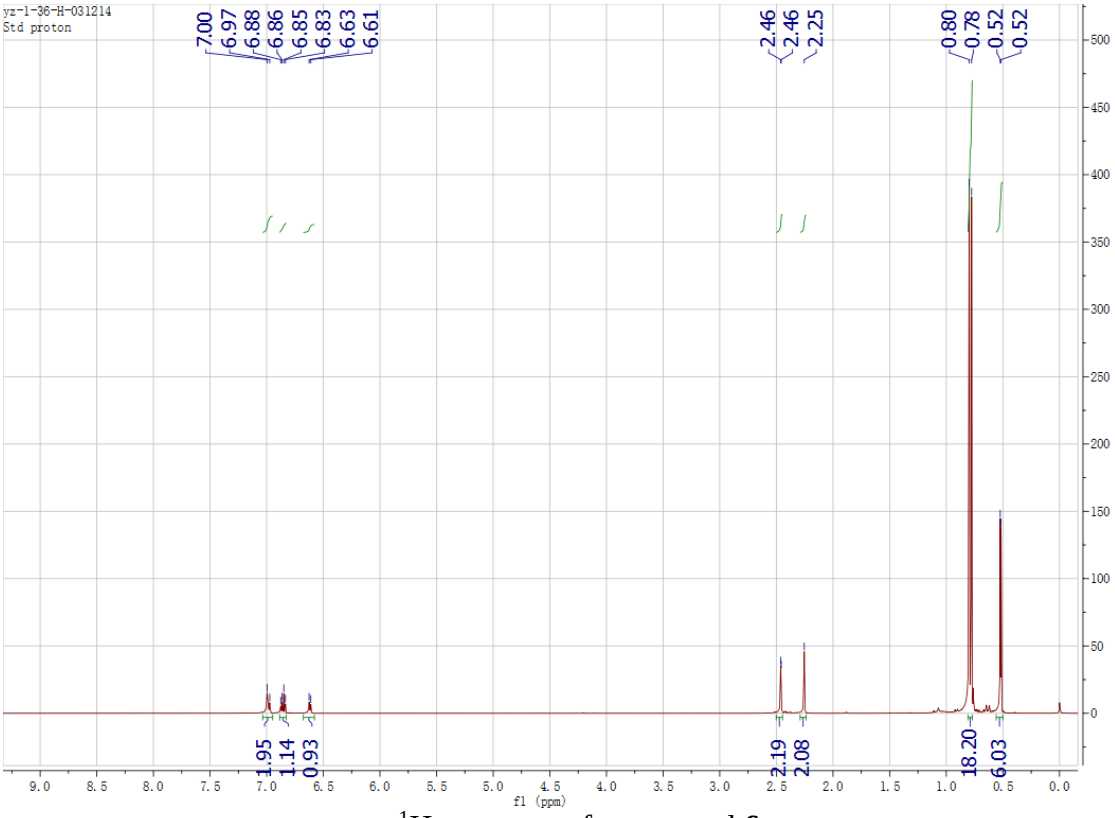


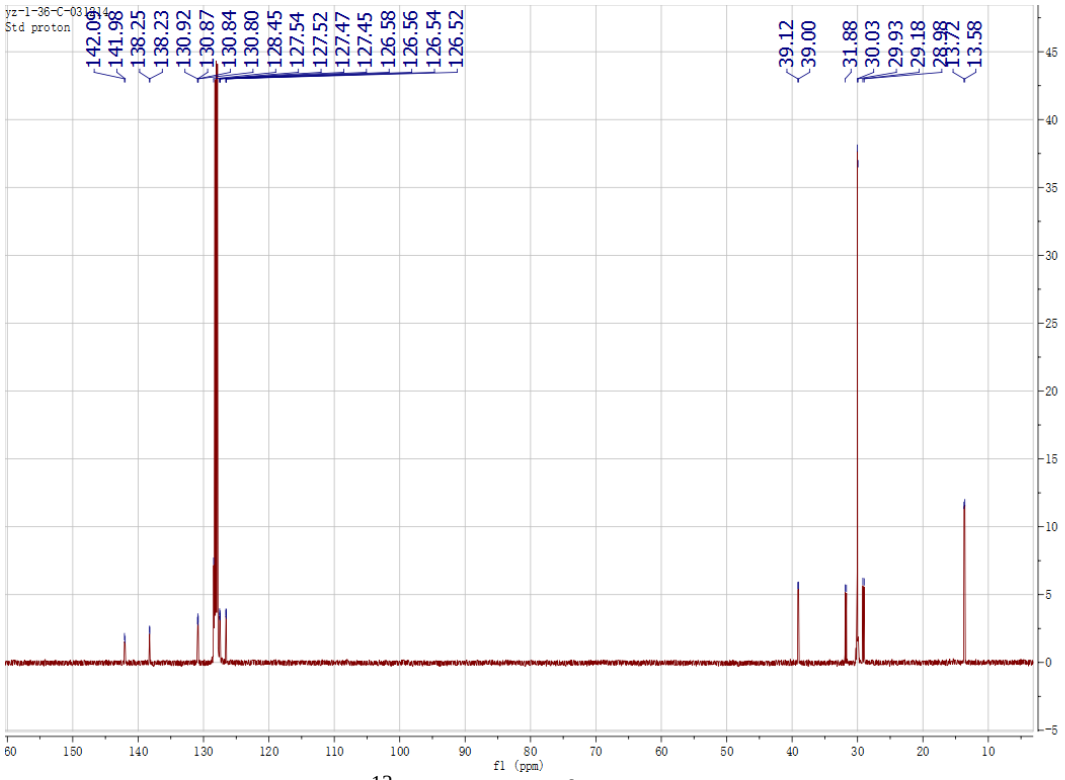
^{31}P spectrum of compound **5**

Compound **6**

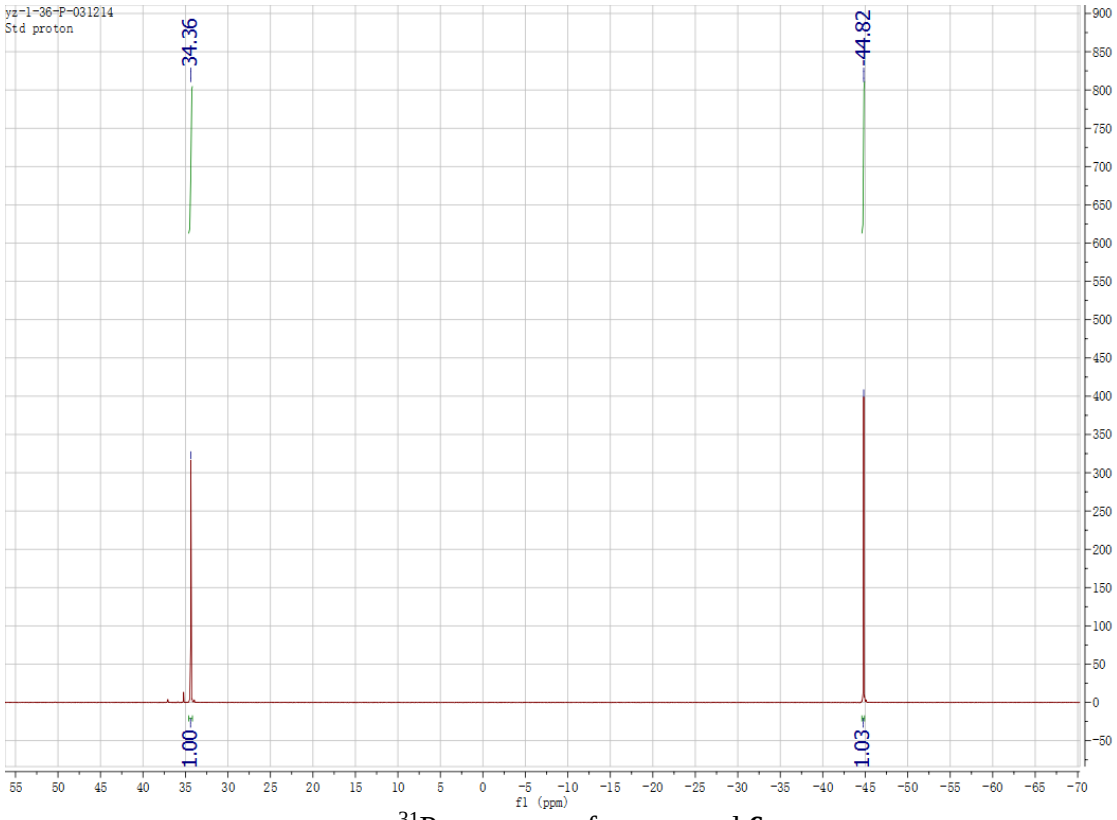




^{1}H spectrum of compound **6**

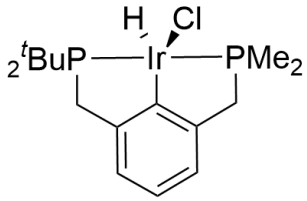


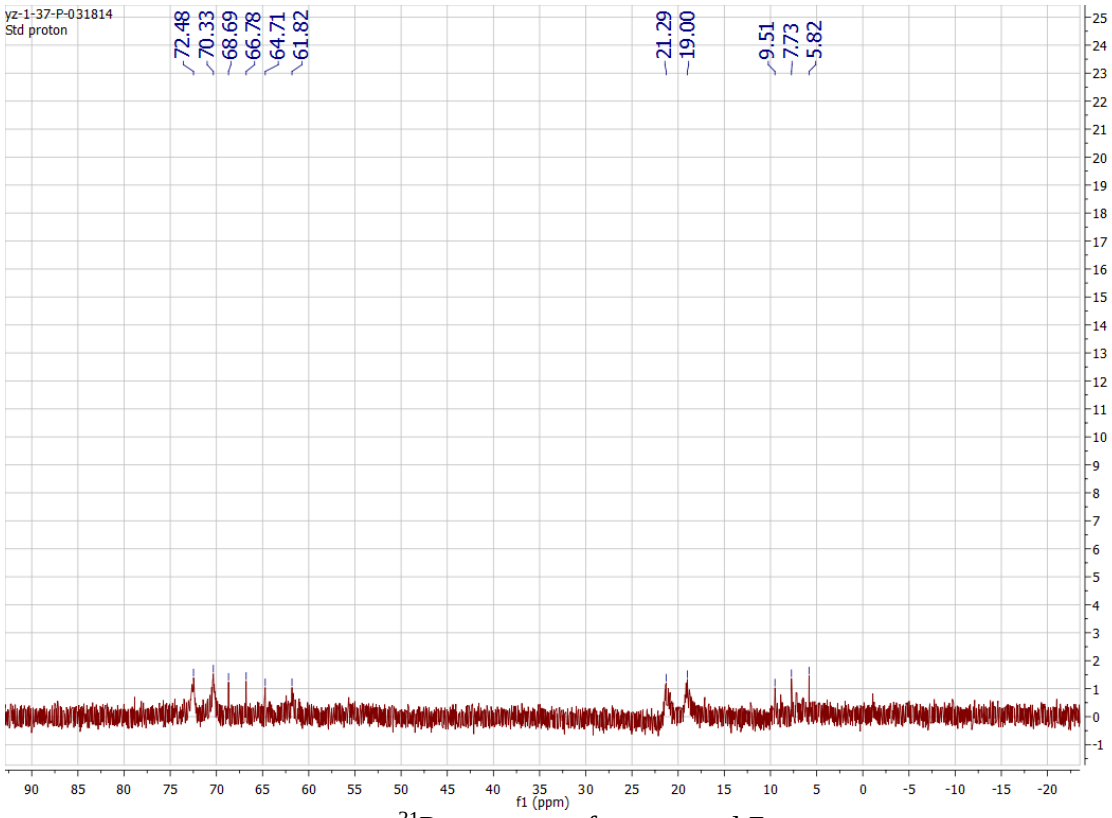
^{13}C spectrum of compound **6**



^{31}P spectrum of compound **6**

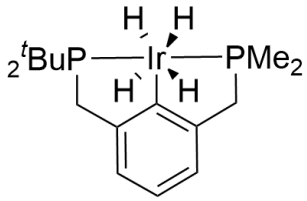
Compound **7**

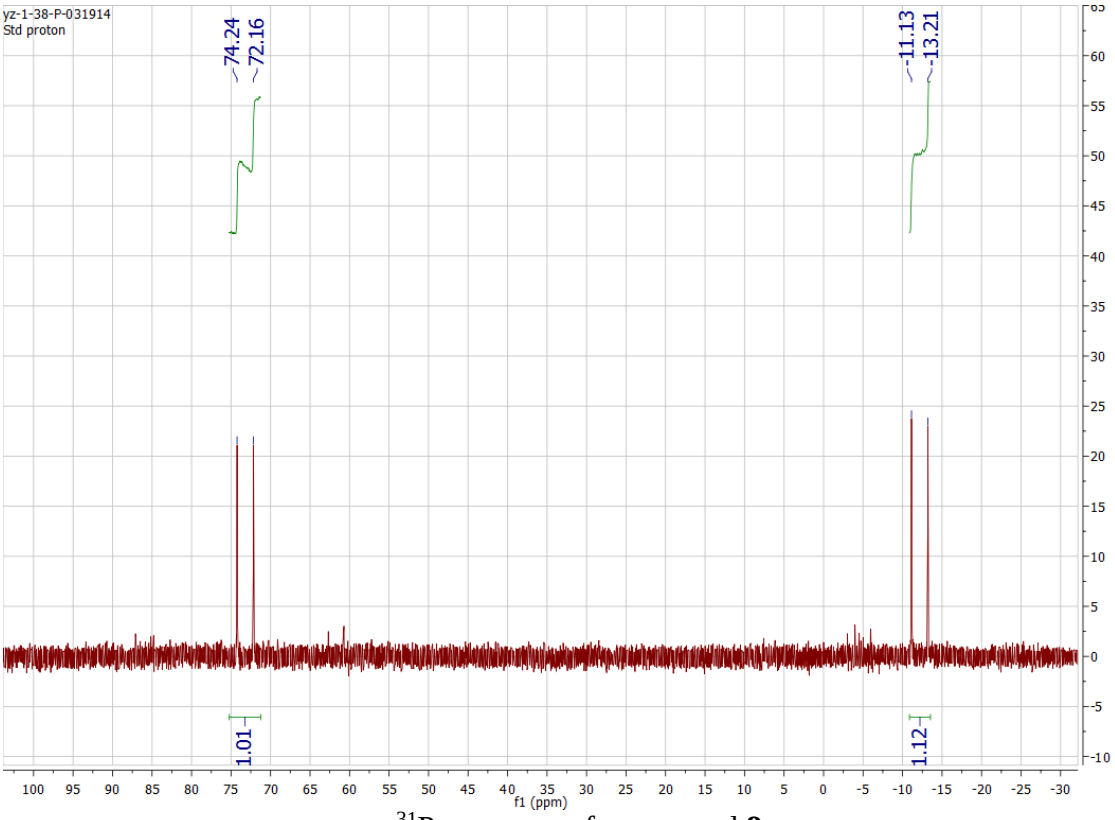




^{31}P spectrum of compound **7**

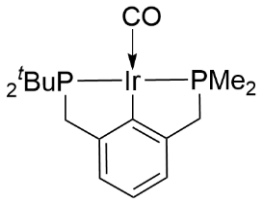
Compound **8**

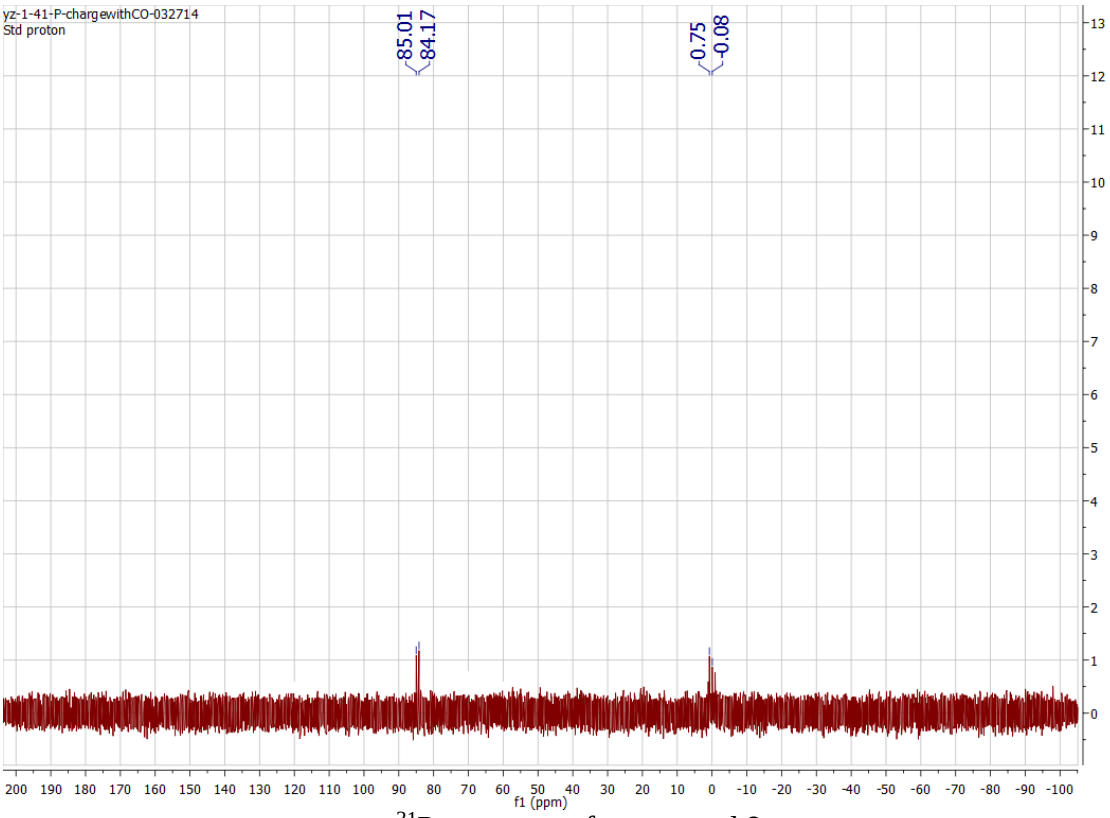




^{31}P spectrum of compound **8**

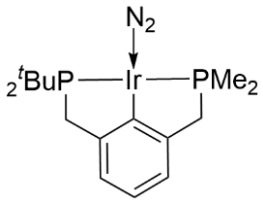
Compound **9**

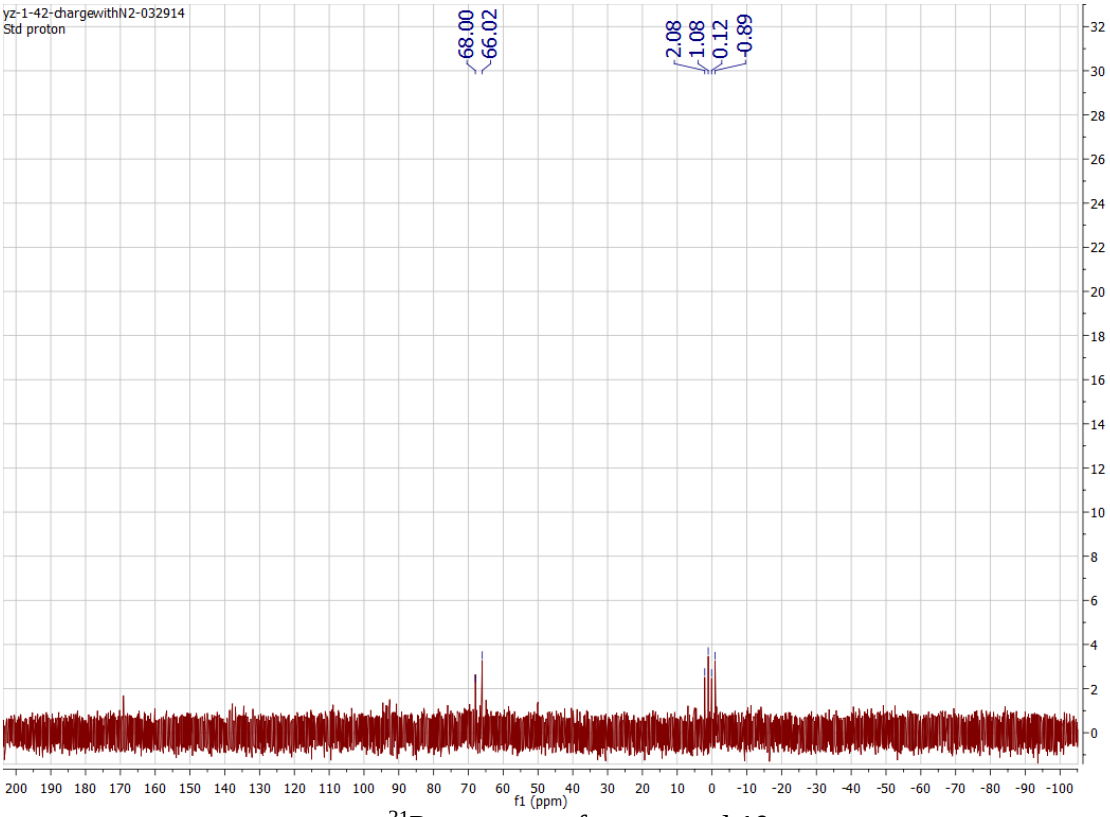




^{31}P spectrum of compound **9**

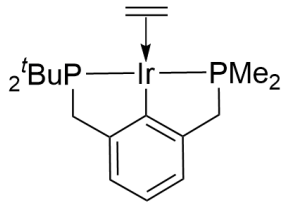
Compound **10**

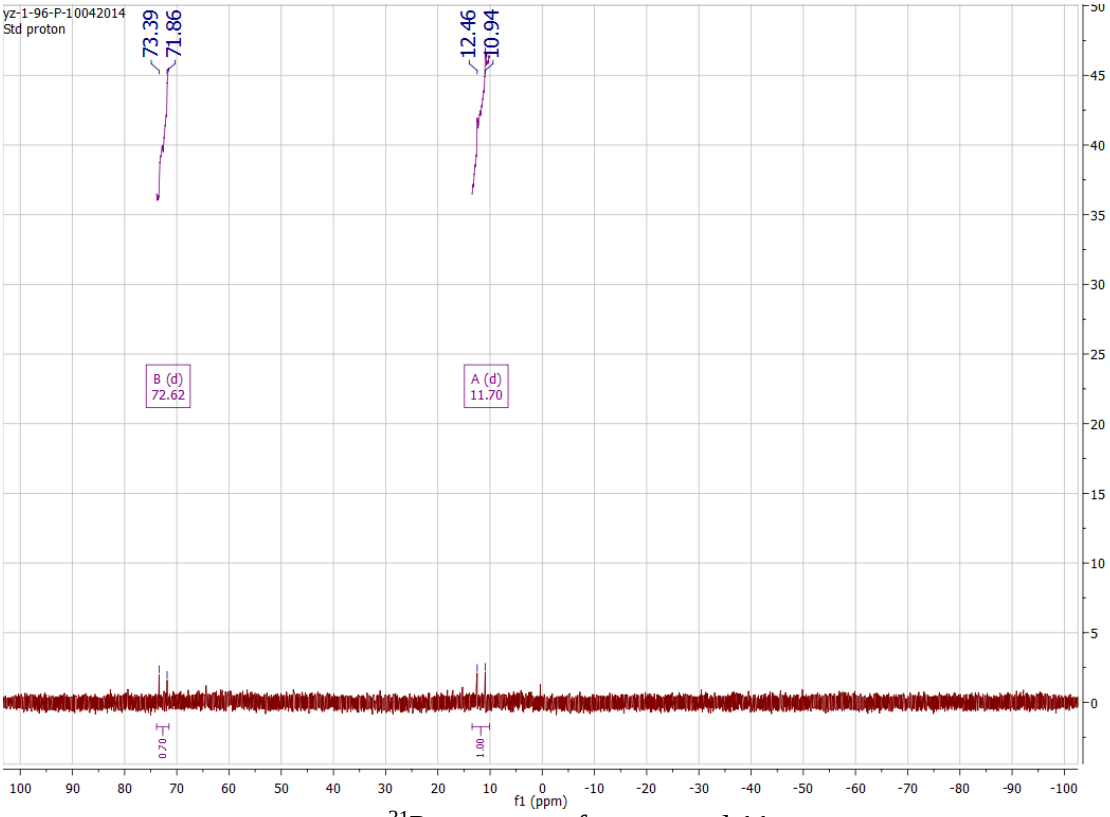




^{31}P spectrum of compound **10**

Compound **11**





^{31}P spectrum of compound **11**