

Novel Ru-Complex of Methylidiphenylcyclopentadienylide

¹SYEDA ROBINA GILANI* AND ²ZAID MAHMOOD

¹Chemistry Department, University of Engineering & Technology, Lahore, Pakistan.

²Institute of Chemistry, University of Punjab, Lahore, 54590, Pakistan.

(Received on 21st April 2009, accepted in revised form 1st February 2010)

Summary: Ylide CpPMePh₂ was synthesized by the deprotonation of Ylide salt of iodide by using different deprotonating agent like n butyl Li, NaH, (CH₃)₂N Li, isopropyl Li and ((CH₃)₂Si)₂N.Li. Out of all these deprotonating agents only ((CH₃)₂Si)₂N.Li gave pure and better yield. Its complex of Ru was synthesized. A RuCl₂(PPh₃)₃ complex reacted with the freshly synthesized Ylide gave successful required ruthenium complex. The synthesized [Ru(PPh₃)₃(CpPMePh₂)₂]Cl₂ complex was analyzed and verified by ¹H and ³¹P NMR.

Introduction

Ylide is a molecule with positive and a negative charge on adjacent atoms. They appear in organic chemistry as reagents or reactive intermediates and is accompanied by its double bonded resonance structure to some extent.

The most common ylides are phosphonium ylides, [1] used by Ferguson *et. al.*, in Wittig reaction for double bond synthesis from carbonyl groups (C=O). The charge in these Wittig reagents is carried by a phosphorus atom with three phenyl substituent's, commonly alkyl groups. Ylide can be either 'stabilized' or 'non-stabilized'. Ylides react readily with both aldehydes and ketones whereas stabilized ones react only with aldehydes.

According to Raman *et. al.*, [2] Certain nitrogen-based ylides also exist such as azomethine ylide. These compounds can be envisioned as iminium cations placed next to a carbanion. The substitution R¹, R² are electron withdrawing groups. These Ylides can be generated by condensation of an α -amino acid and an aldehyde or by thermal ring opening reaction of certain N-substituted aziridines. Stable carbenes also have a ylide resonance structure *e.g.* Iminophosphoranes (derived from phosphazides), with general structure R₃P⁺-N-R, are intermediate in the Staudinger reduction. The active form of Tebbe's reagent is often considered a titanium Ylide, like Wittig reagent, it is able to replace the oxygen atom on carbonyl groups with a methylene group. As compare to the Wittig reagent, it has more functional group tolerance.

Triphenylphosphonium cyclopentadienylide, (cyclopentadienyldiene triphenylphosphorane) (I) (Fig 1) was first reported in 1956 by Ramirez and Levy [3-5] who also explored its chemistry. They found *inter alia* that I is unusually inert, for instance being un-reactive with ketones, unlike typical ylide. They attributed this unusual stability to the charge delocalization implied by resonance structure Ib, consistent with the relatively high dipole moment of 7.0 D.

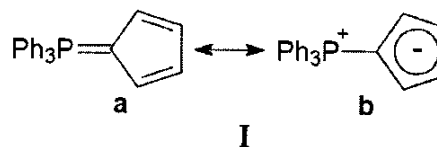


Fig. 1: Resonance structures of cyclopentadienyldiene triphenylphosphorane.

One of the major limitations to the utilization of this class of compounds is the lack of a general synthetic route for C₅H₄PR₃ and other similar ylides. Only a few synthetic methods exist to produce 'Cp' ylides, each with its own drawback. The lack of a general synthetic method means that very few C₅H₄ phosphorus ylides are known and very few metal complexes have been prepared beyond those of C₅H₄PPh₃. The following sections discuss the various synthetic routes for 'Cp' phosphorus Ylides that have been reported.

A similar route had been reported by Mathey *et. al.*, [6] (Fig. 2) in which they used TiCp.

*To whom all correspondence should be addressed.

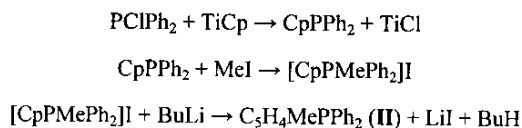
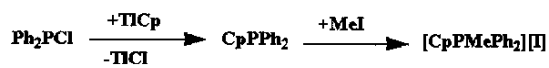
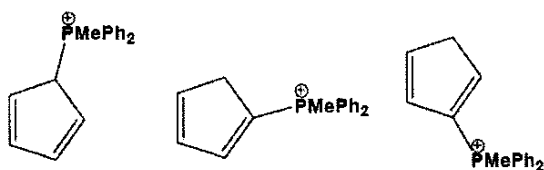


Fig. 2: Synthetic route of Cp' phosphorus Ylide.

The first step of the synthesis involves the exchange of the chloride of the starting chlorophosphine with Cp⁻ in a metathesis using TiCp (Fig. 3). This step generates three isomers of the Cp ring attached to the phosphorus (Fig 4).

Fig. 3: The two-step synthesis of the Ylide salt Ph₂MeP(C₅H₅)I.Fig. 4: The three isomers of the phosphonium salt, [CpPMePh₂][I].

¹H NMR and ³¹P NMR of the crude reaction mixture indicated that we had completed the conversion of the chlorophosphine to the desired product and that the three isomers were present. When CpPPh₂ was synthesized, it had to be used immediately because it decomposes on standing, presumably through Diels-Alder dimerization of the Cp group. In the second step of the synthesis, CpPPh₂ was converted into the phosphonium salt, [(CpPMePh₂)I], by the addition of MeI. Although the phosphonium iodide was impure, it was used successfully in the final step of the synthesis.

A number of metal complexes of cyclopentadienyl Ylide have been reported [7]. John Brownie synthesized and characterized Methyl-diphenylcyclopentadienylide (Fig 5) and its complexes with Group 6 transition metals (Cr, Mo, W) [7].

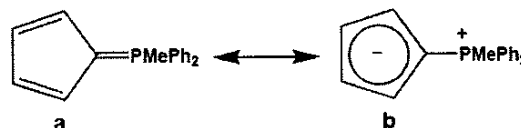


Fig. 5: Methyl-diphenylcyclopentadienylide.

Results and Discussion

Deprotonation of Ylide Salt Using *n*-BuLi

¹H NMR (Scan 1) of the crude sample in CDCl₃ gave very weak signals in the required region. Fresh yellow portion collected, after pumping solvent off was analyzed by ¹H NMR in CDCl₃ (Scan 2) but very weak peak was noticed in the required region.

Using NaH

Deprotonated ylide salt sample by NaH was analyzed by ¹H NMR (Scan 3) in CDCl₃ but no positive results were obtained.

Using (CH₃)₂NLi

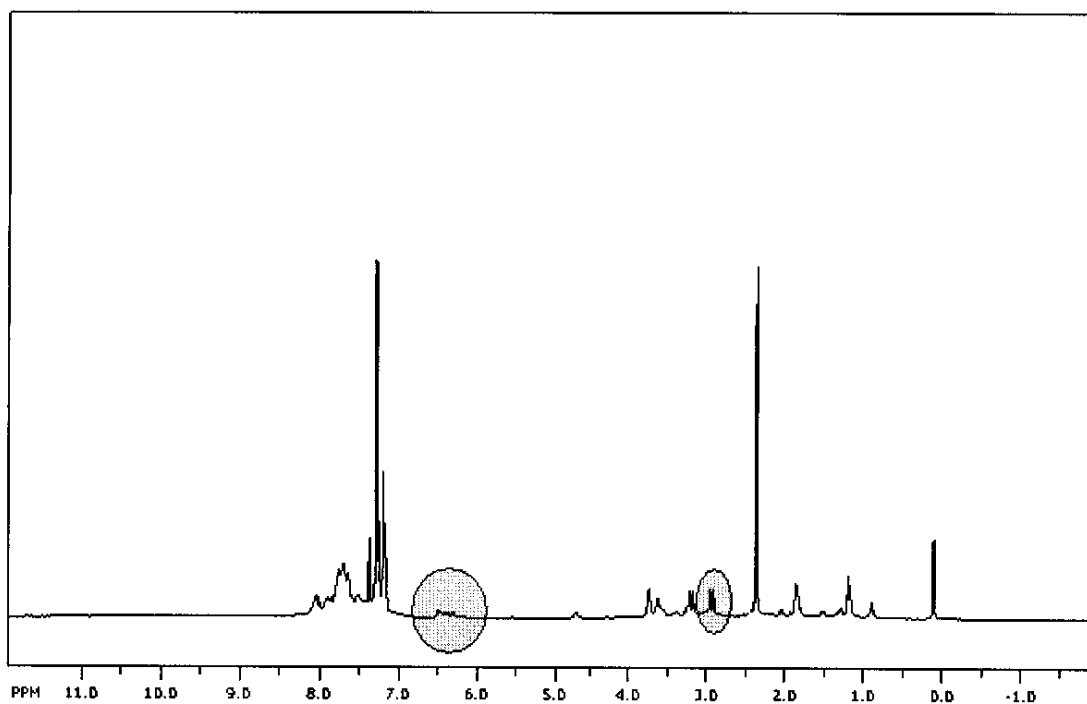
Products obtained from these reactions were mostly oily and brown. Their ¹H NMR was recorded in CDCl₃ (Scan 4), but no fruitful results were noticed. Samples of all above attempts gave very weak peak in ¹H NMR.

Using Isopropyl.Li

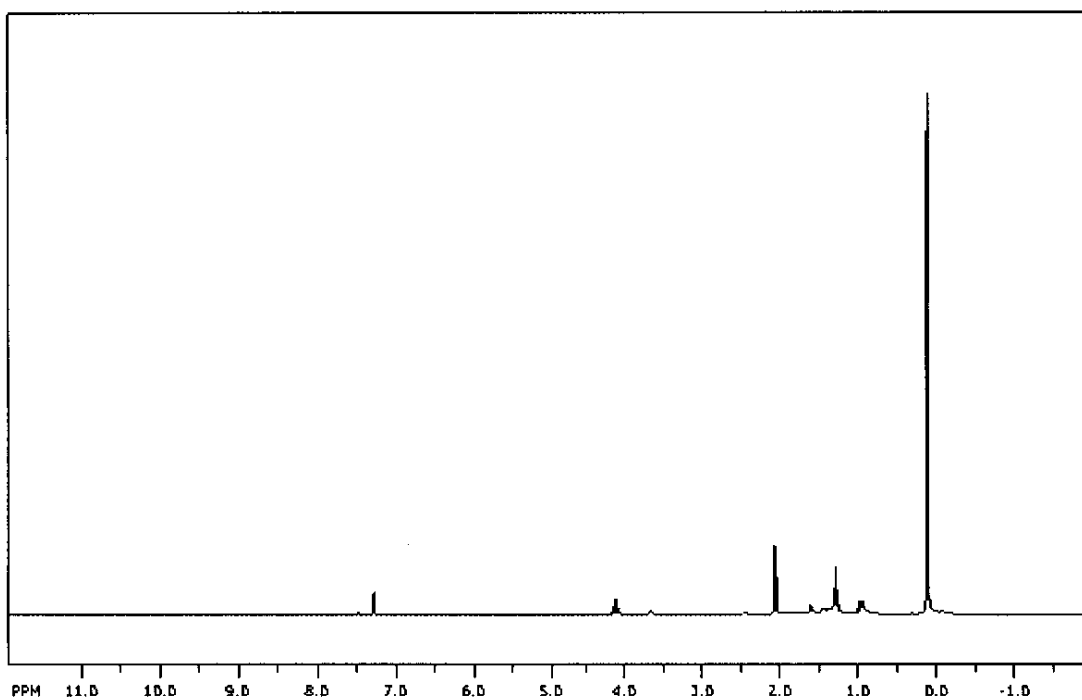
Benzene extracted product obtained by the reaction of Ylide salt and Isopropyl Li showed doublets of -CH₃ (2.3 ppm for methyl) and Cp (6.4 ppm for Cp) in the required regions of ¹H NMR (Scan 5) recorded in CDCl₃, but the peaks were very weak. After several attempts the results were not reproducible.

Using ((CH₃)₃Si)₂N.Li

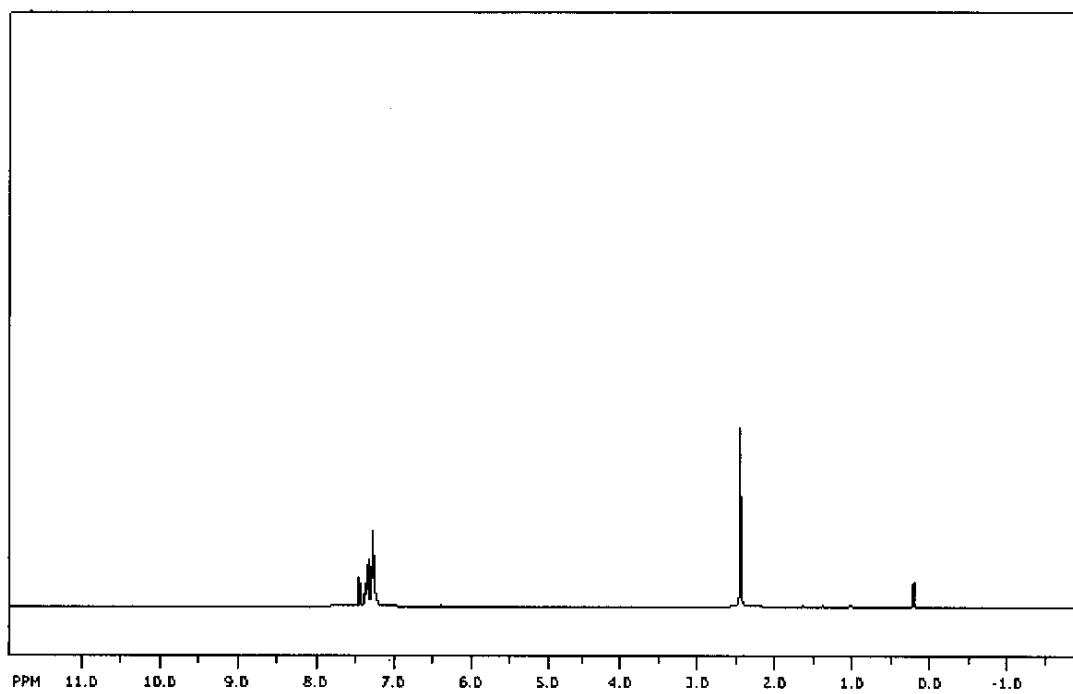
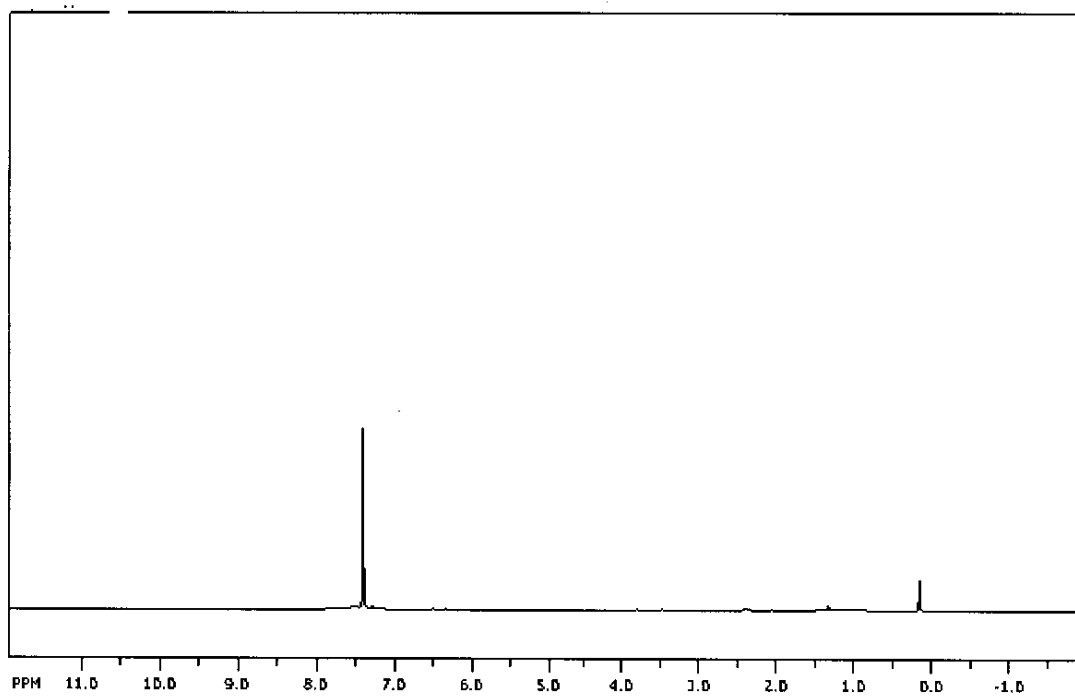
Yellow solid product obtained after 24 h stirring was analyzed by ¹H (Scan 6) and ³¹P (Scan 7) NMR and gave satisfactory doublets for Me and Cp at 2.4 ppm and 6.4 ppm respectively in ¹H NMR and a single peak at 58 ppm in ³¹P NMR. Product obtained was in pure form, unstable in air and yield was 34-40 %.

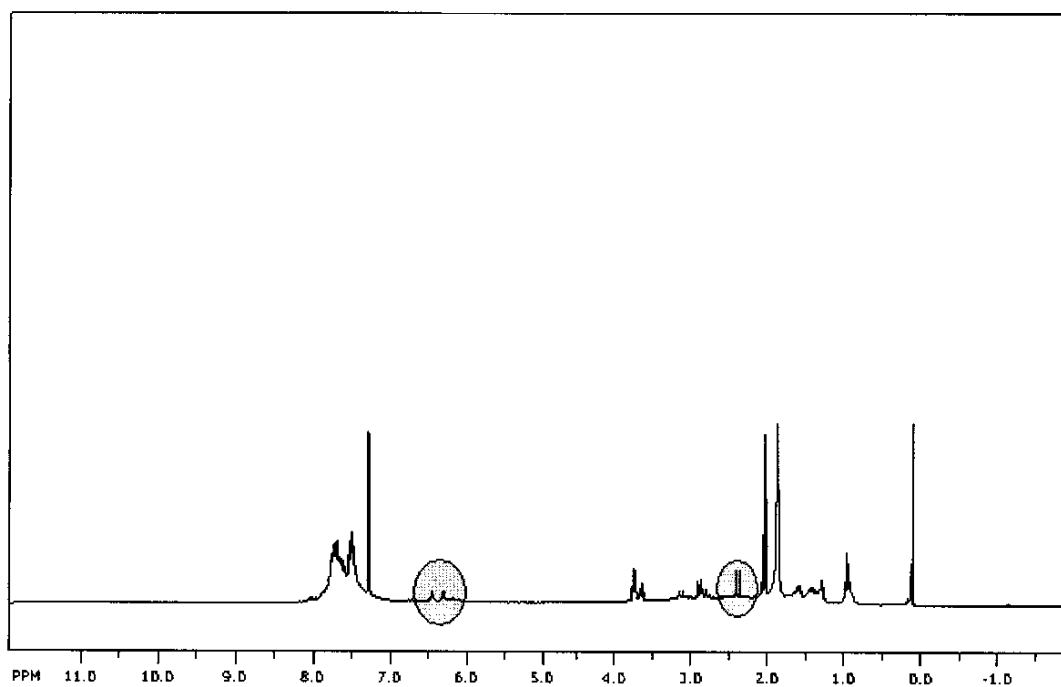


Scan 1: ^1H NMR of the of the crude deprotonated sample Ylide by n butyl Li.
Circles are showing the presence of required signals.

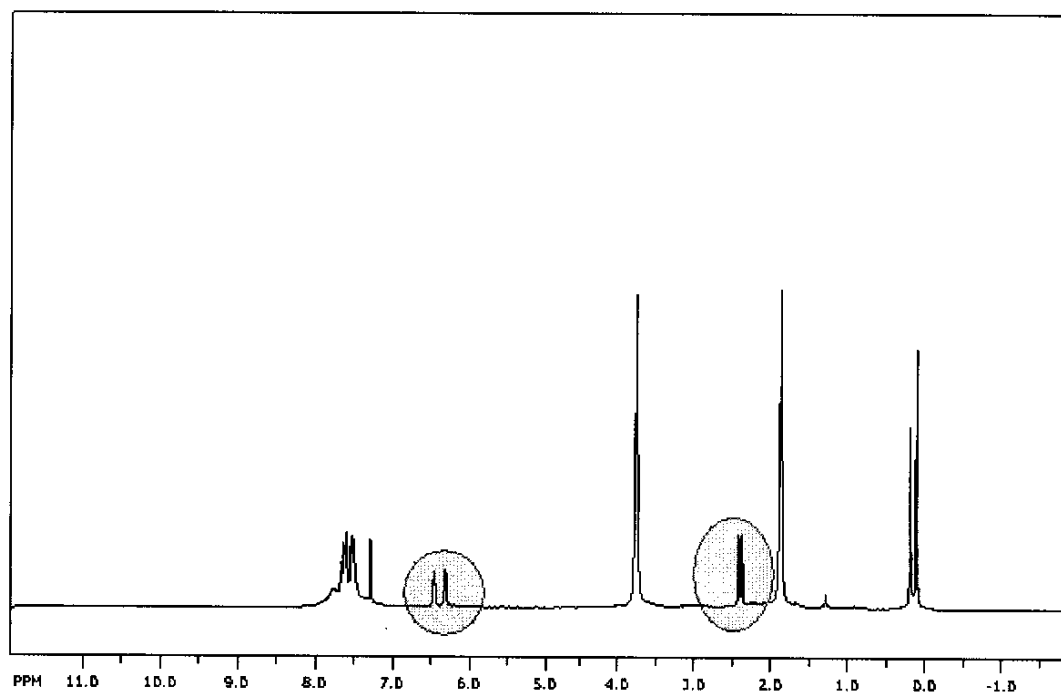


Scan 2: ^1H NMR of the fresh yellow portion obtained by column chromatography of the crude deprotonated sample Ylide by n-butyl Li.

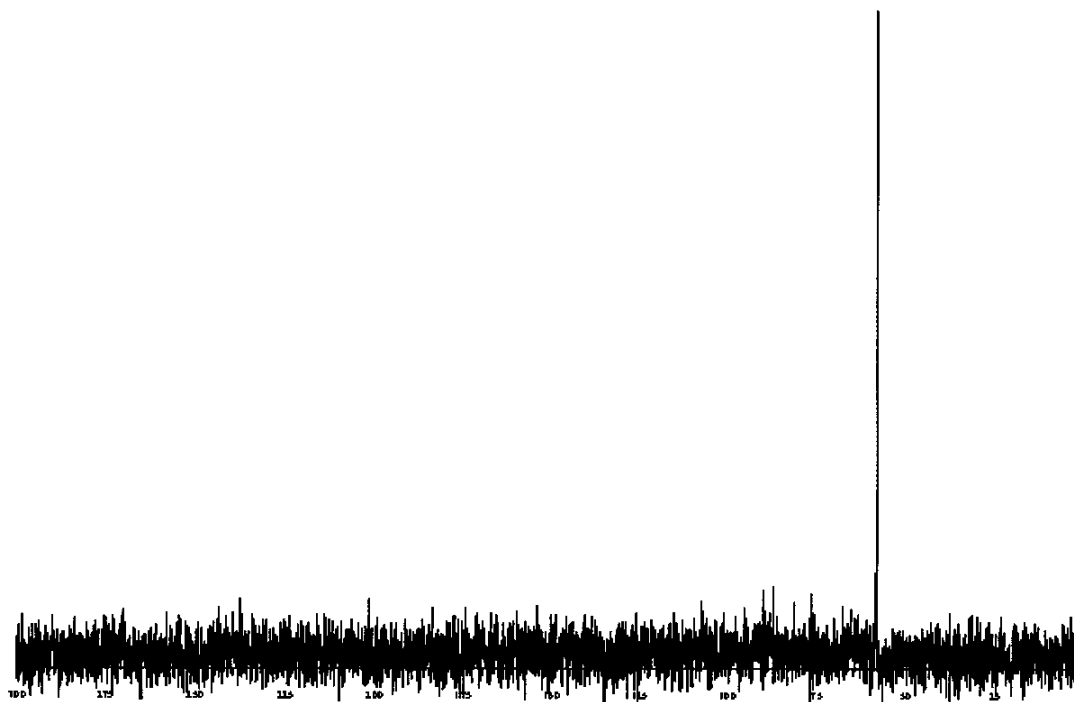
Scan 3: ^1H NMR of the Product deprotonated by NaH.Scan 4: ^1H NMR for the sample obtained by the deprotonation by $(\text{CH}_3)_2\text{N.Li}$



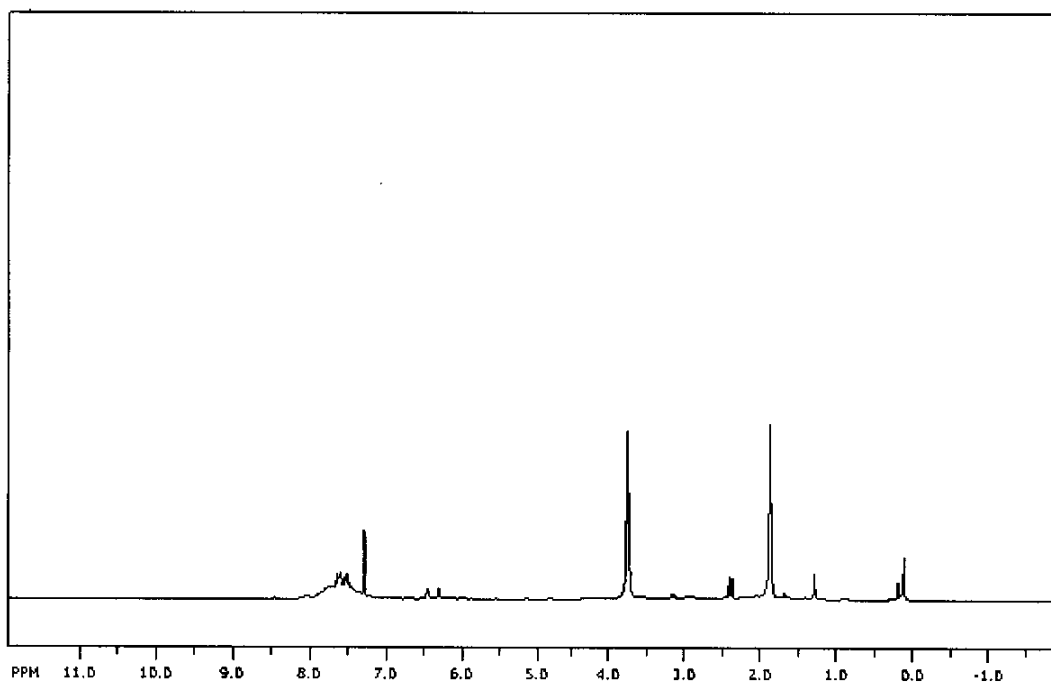
Scan 5: ¹H NMR for the Product with Isopropyl Li
Circles are showing the presence of required signals



Scan 6: ¹H NMR of the sample deprotonated by $(\text{CH}_3)_3\text{Si}_2\text{N}.\text{Li}$ after 24 hrs stirring.
Circles are showing the presence of required signals

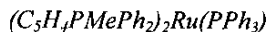


Scan 7: ^{31}P NMR the Ylide sample deprotonated by $((\text{CH}_3)_3\text{Si})_2\text{N.Li}$ after 24 hrs stirring. at 58 ppm.



Scan 8: ^1H NMR after 1 hr Stirring Filtration (as at this stage there were no ppts in the reaction mixture).

Portions of the reaction mixture taken out at different stirring times *i.e.* after 1 h (Scan 8), 2 h (Scan 9) and 3 h stirring were also analyzed by ^1H NMR but no sign of product was observed. Although the % yield of the resulting ylide was relatively low, but the product was easily separated from impurities.



Analysis of the Product of Ylide with $\text{RuCl}_2(\text{PPh}_3)_3$

Green-Brown oily product was obtained and analyzed by ^1H NMR (Scan 10), no required peak was observed in the required region. No fruitful results were observed even by varying temperature or stirring conditions.

Analysis of $\text{Ru}[\text{PPh}_3]_3[\text{N}((\text{CH}_3)_3\text{Si})_2]$

Dark green ppts appeared were filtered dried and analyzed by ^1H NMR (Scan 11) but the required peaks were very weak.

Synthesis of $\text{Ru}[\text{PPh}_3]_3[\text{P}(\text{CH}_3)\text{CpPh}_2]_2$ by the Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with Freshly Synthesized Ylide

^1H (Scan 12) and ^{31}P (Scan 13) NMR (CD_2Cl_2 , 300 MHz) was run giving required peaks in the expected region of ^1H (d Cp-4.3ppm, d CH_3 -2.0 ppm) and ^{31}P (s 37.9 ppm, s 22.8 ppm) NMR. The yield was 24 %. A significant peak shift was observed in both ^1H and ^{31}P NMRs of Ylide before and after coordination with Ru towards high field side.

Another Route of Synthesizing $\text{Ru}(\text{PPh}_3)_3(\text{C}_5\text{H}_4\text{PMePh}_2)(\text{PF}_6)_2$

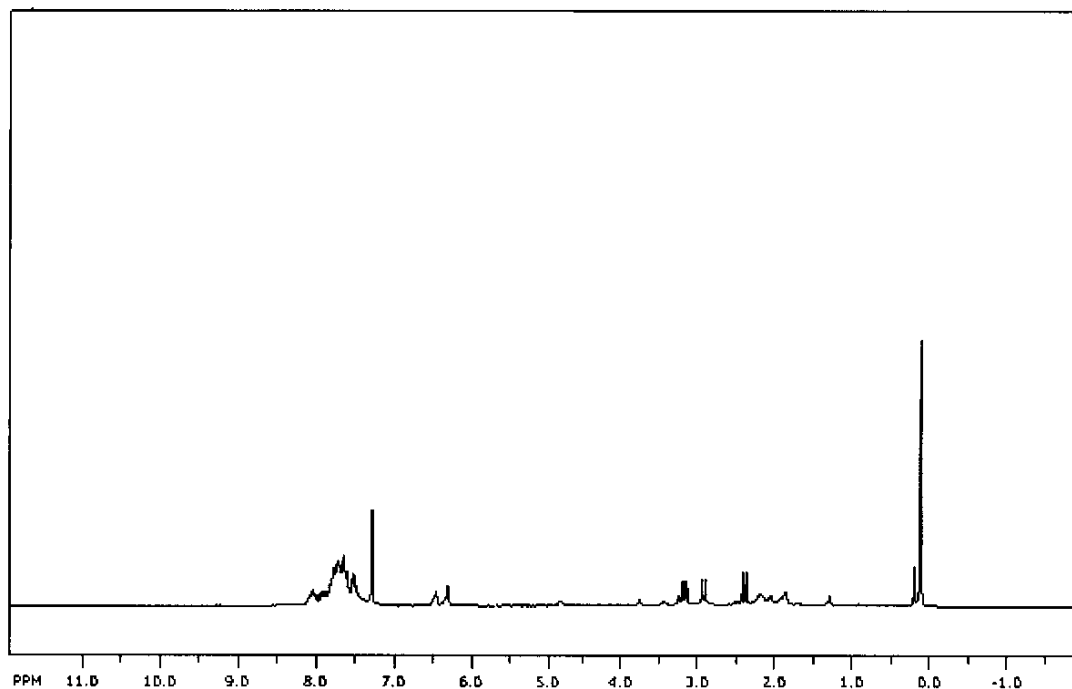
Synthesized complex with indenyl ylide the green brown solid was analyzed by ^1H NMR but very weak peak was observed.

Alternate Method used with this Ylide for Complex Synthesis

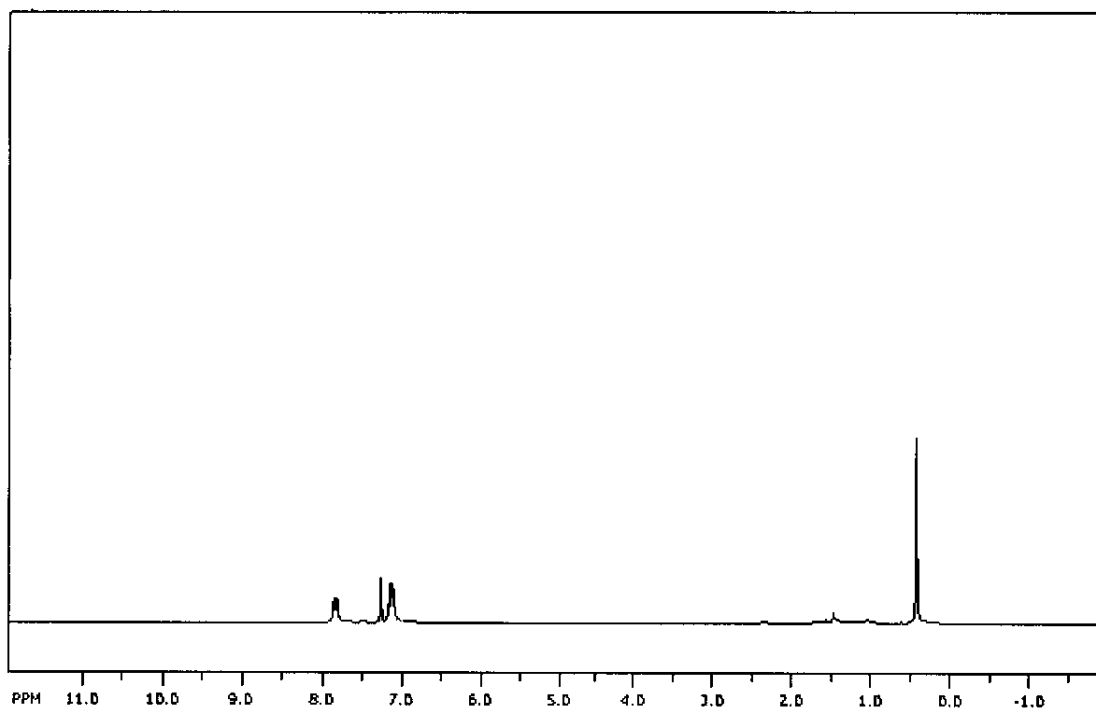
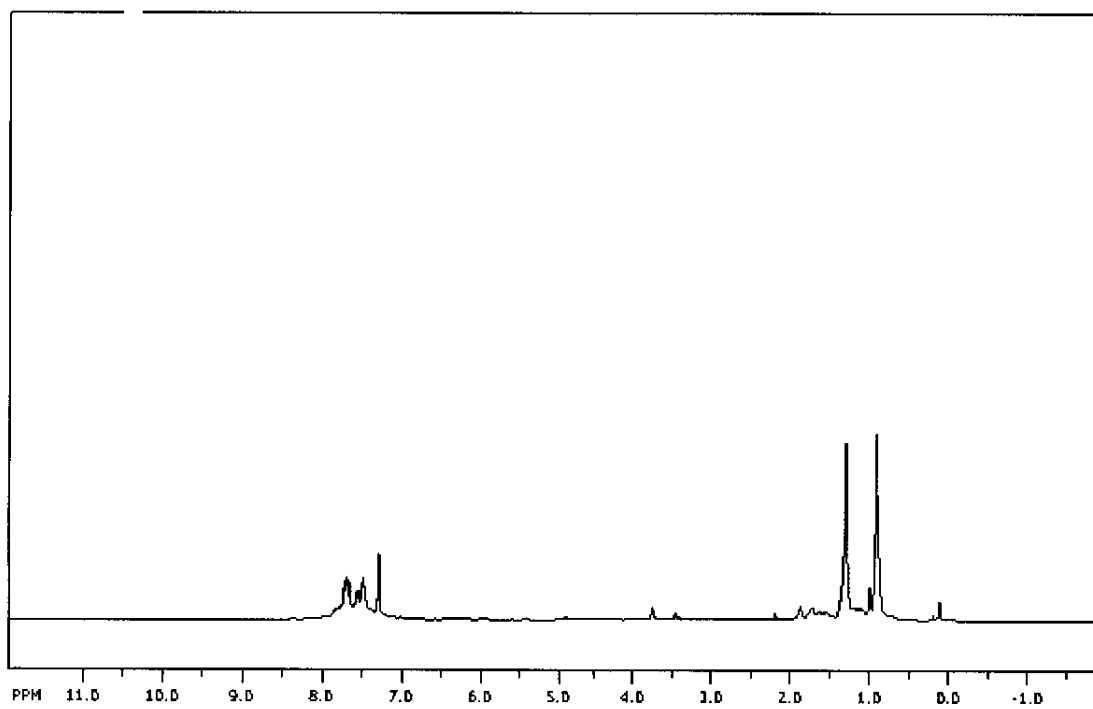
The dark green brown product was filtered dried and analyzed by ^1H NMR (Scan 14), but no promising results were observed.

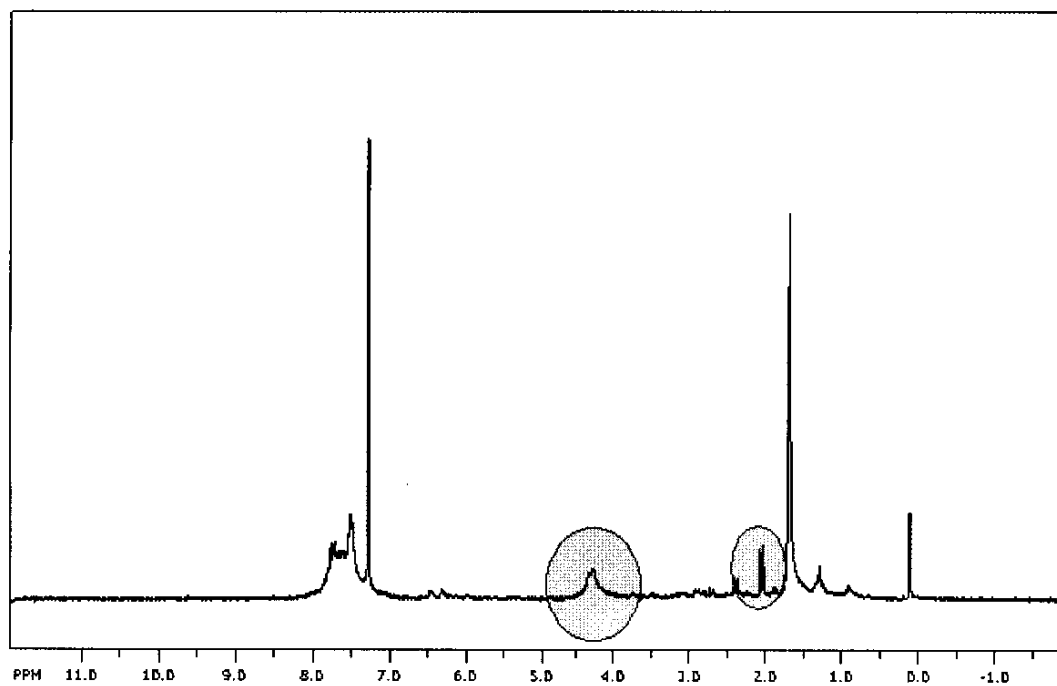
Discussion

Synthesis of ylide salt is direct and gave 80 % yield. The problem faced was the deprotonation of



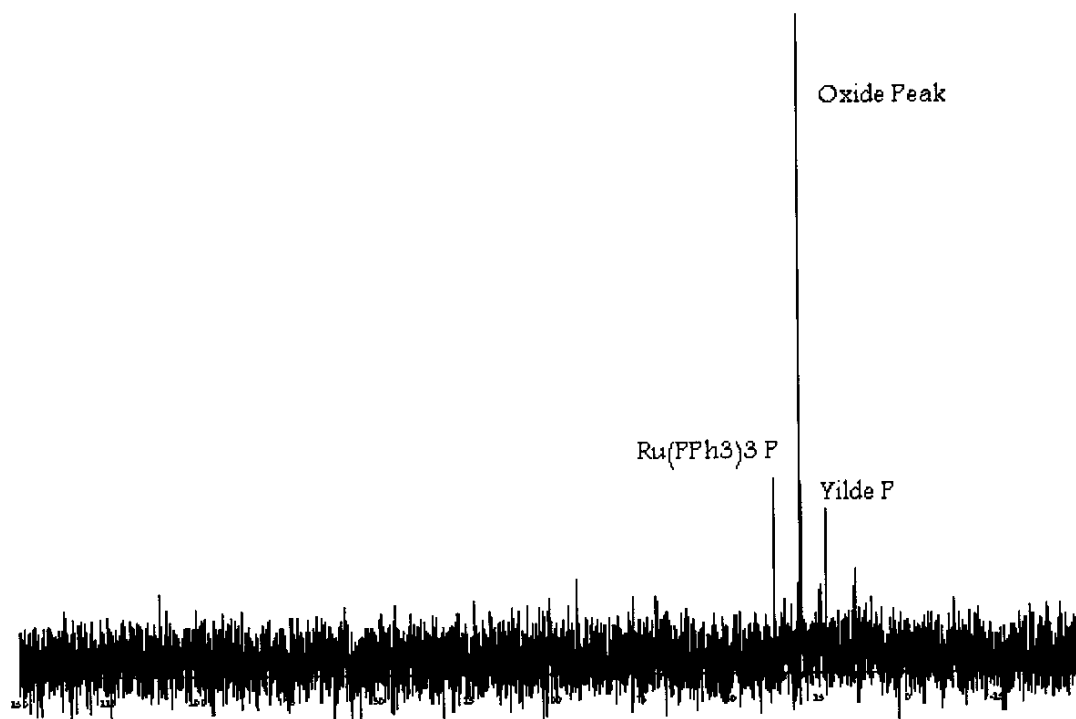
Scan 9: ^1H NMR after 2 hrs stirring without filtration.

Scan 10: ¹H NMR of the Product obtained by the reaction of Ylide with RuCl₂(PPh₃)₃.Scan 11: ¹H NMR of the above synthesized product.

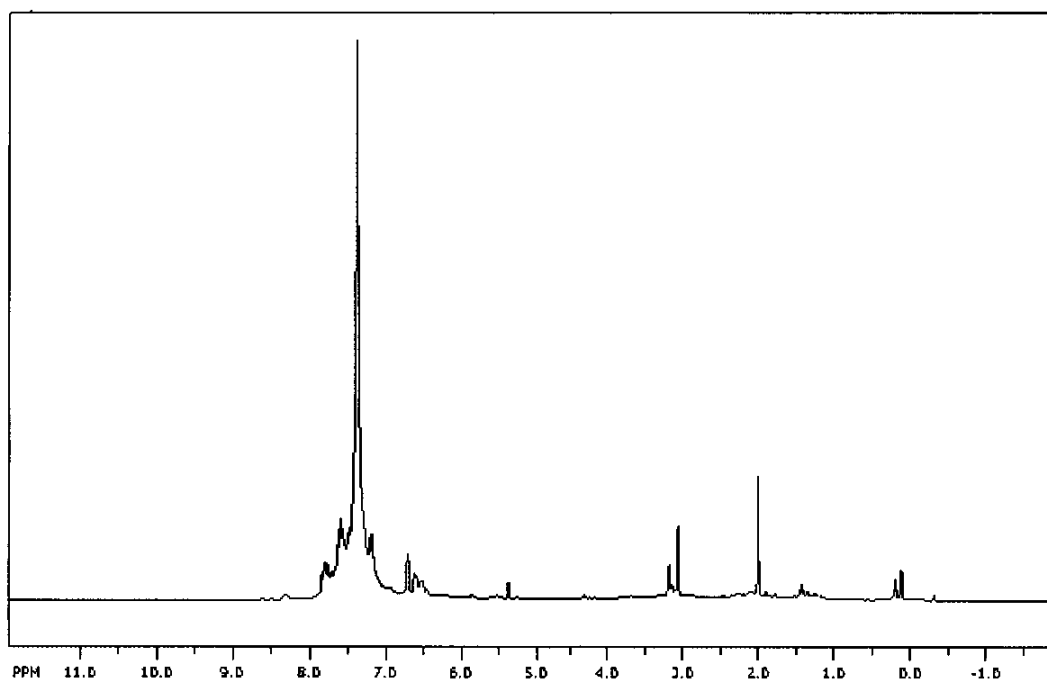


Scan 12: ^1H NMR of Ru-Yilde complex directly synthesized by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with freshly synthesized Ylide.

Circles are Showing the Presence of Required Signals



Scan 13: ^{31}P NMR of $[\text{Ru}(\text{PPh}_3)_3(\text{CpP}(\text{CH}_3)\text{Ph}_2)_2]\text{Cl}_2$.

Scan 14: ^1H NMR of $\text{Ru}(\text{PPh}_3)_3(\text{Ylide})_2(\text{PF}_6)_2$.

the ylide salt to convert $-\text{C}_5\text{H}_5$ to $-\text{C}_5\text{H}_4$. For this deprotonation first *n*-butyl Li was used following Brownie's method which was found to be very successful giving crude brown oil but even can't be purified by alumina column. Other deprotonating agents tried were NaH, $(\text{CH}_3)_2\text{NLi}$, and Isopropyl Li but all gave unsatisfactory results. Though in case of Isopropyl.Li weak doublets for $-\text{C}_5\text{H}_4$ and $-\text{CH}_3$ were observed but yield was very low in crude product.

Finally *bis* trimethylsilyl amide lithium was used for deprotonation which proved very successful in deprotonating the ylide salt giving the ylide in quite pure form giving clear doublets for Cp and Me in the expected regions.

Experimental

Synthesis of $[\text{C}_5\text{H}_5\text{PMePh}_2][\text{I}]$

A suspension of 20.0 g of TiCp (0.074 mol) in 200 mL of ether was treated drop wise with 13.3 mL of Ph_2PCl (0.073 mol). As the reaction proceeded (Fig 6), the flask warmed and the solution turned slightly yellow. After stirring for 1 h, the reaction

was filtered to remove TiCl, and the phosphine, $\text{P}(\text{C}_5\text{H}_5)\text{Ph}_2$, was immediately treated *in situ* with 4.5 mL of MeI (0.072 mol). As the alkylation reaction proceeded, a colorless product is precipitated. The reaction mixture was stirred for 3 h and 22.9 g of the colorless phosphonium salt ($[\text{PMe}(\text{C}_5\text{H}_5)\text{Ph}_2][\text{I}]$) was collected by filtration (81% yield). After purification the salt was therefore used as obtained in the next step.

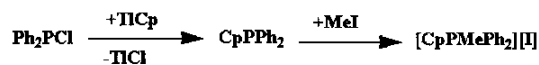


Fig. 6: The two-step synthesis of the Ylide salt $\text{Ph}_2\text{MeP}(\text{C}_5\text{H}_5)\text{I}$.

Deprotonation of Ylide Salt

Using *n*-butyl Li

To prepare ylide, *n*-BuLi was used for deprotonation of ylide salt (Fig 7) $(\text{C}_5\text{H}_5\text{PMePh}_2)\text{I}$ following John Brownie's procedure [7]. According to which a suspension of 10.1 g of $[\text{PMe}(\text{C}_5\text{H}_5)\text{Ph}_2][\text{I}]$ (0.026 mol) in 150 mL of THF was cooled in an ice

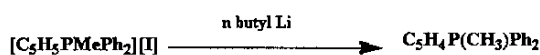


Fig. 7: Deprotonation of Yilde salt using n-butyl Li.

bath and treated drop wise with 17.7 mL of 1.6 M *n*-BuLi in hexanes (0.028 mol). As the *n*-BuLi was added, the solution warmed up and the solid disappeared, generating a deep orange-red solution. The reaction was stirred until no solid remained, at which point the reaction was hydrolyzed by the addition of 20 mL of H₂O. This caused the formation of a colourless solid, while the solution turned yellow. The organic layer was decanted and the aqueous layer was washed with 3×75 mL of toluene. The organic layers were combined and the solvent was removed *in vacuo* to yield an orange solid which was extracted with 200 mL of ethyl acetate and passed through a silica column using ethyl acetate as the elutant.

In the above method the yield was very low. The same procedure was repeated using various deprotonating agents. Other agents used were NaH, isopropyl lithium and Lithium Diethyl Amide, but all of these attempts for deprotonation were gave very low yield. In all of these reactions brown oily product was obtained which was extracted by benzene and was purified by 1:1 benzene/*n*-hexane mixture. The product obtained by column chromatography was analyzed through proton NMR but clear signals were not observed.

A suspension of ylide salt in THF was added slowly to a solution of *n*-butyl Li immersed in dry ice/acetone bath with temperature ranging between -0 to -70 °C and stirred for 24 h but there was not success in reproducing the required product. The product was in crude oily form. ¹H NMR of the crude sample in CDCl₃ was recorded. Crude oily sample was then purified by running through Alumina column using 50% benzene/*n*-hexane mixture. Fresh yellow portion was collected, after pumping solvent off sample was analyzed by ¹H NMR in CDCl₃.

Using NaH

After unsuccessful attempts with *n*-butyl Li, NaH was used for the deprotonation of ylide salt by varying the conditions of temperature (ranging from room temp. to approx -70 °C) and stirring times

(ranging from 1 h to 24 h), and its ¹H NMR was recorded, (Fig. 8).

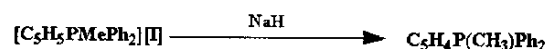
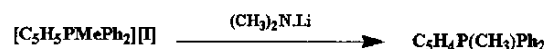


Fig. 8: Deprotonation of Yilde salt using NaH.

Using (CH₃)₂N.Li

(CH₃)₂N.Li was also tried for the deprotonation of Ylide salt by varying the conditions of temperature and stirring as with NaH, Products obtained from these reactions were mostly oily and brown (Fig. 9).

Fig. 9: Deprotonation of Yilde salt using (CH₃)₂N Li.

Using Isopropyl.Li

Isopropyl Li was also tried for the deprotonation of ylide salt at very low temperature and stirred overnight. The sample was again crude brown sticky oil. Sample was extracted with benzene, which was then pumped off, resulting product was yellow sticky oil, (Fig. 10) which was later analyzed by ¹H NMR in CDCl₃.

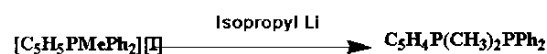


Fig. 10: Deprotonation of Yilde salt using Isopropyl Li.

Using ((CH₃)₃Si)₂NLi

Finally Lithium *bis* trimethyl silyl amide was used for deprotonation, (Fig. 11). A suspension of 10.1 g of [PMe(C₅H₅)Ph₂][I] (0.026 mol) in 150 mL of dry THF was cooled in dry ice bath temperature maintained at approx -70 °C and added drop wise in (Me₃Si)₂N.Li in dry THF cooled in dry ice/acetone bath at approx -70 °C. As the Ylide salt suspension was added in (Me₃Si)₂N.Li, the solid disappeared, generating a deep yellow solution. The reaction was stirred for six hours at low temperature and 24 hours

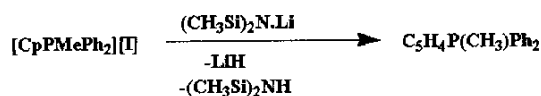


Fig. 11: The one-step deprotonation of the Ylide salt $\text{Ph}_2\text{MeP}(\text{C}_5\text{H}_5)\text{I}$. to give $\text{Ph}_2\text{MeP}(\text{C}_5\text{H}_4)$.

at room temp, a colorless solid was appeared, while the solution turned yellow. After stirring, the ppts were filtered out and the solvent was pumped off leaving yellow sticky solid which later was washed by ether giving the required product which was obtained in quite pure yellow solid form. Sample was analyzed by ^1H -NMR and ^{31}P -NMR (CDCl_3 , 300 MHz).

Small portions of the reaction mixture were taken out at different stirring times *i.e.* after 1 h, 2 h and 3 h stirring were also analyzed by ^1H -NMR.

Synthesis of $(\text{C}_5\text{H}_4\text{PMePh}_2)_2\text{Ru}(\text{PPh}_3)$

Different synthetic routes were adapted to synthesis $(\text{C}_5\text{H}_4\text{PMePh}_2)_2\text{Ru}(\text{PPh}_3)$.

Synthesis of Ruthenium Precursor [8]

Ruthenium Precursor was synthesized using Itoh *et al.*, (Terry) method. 6.014 g of Zinc dust (92.0 mmol) was placed in a Schlink tube filled with Ar gas and 12.5 mL of 1,5-cyclooctadiene (101.3 mmol) and 5 mL of methanol was added. This solution flask was then fitted with a condenser and placed in a heated ultrasonic bath. 0.533 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (2.04 mmol) was then dissolved in 12 mL of methanol and this red solution was added in very small instalments through a septum placed at the top of the condenser. The ultrasonic bath was kept at a temperature of about -60 to -70 °C for approx 4 h. The resulting dark brown solution was then extracted from the excess settled zinc into a clean flask and a vacuum was applied to dry the product. ^1H NMR analysis of the resulting reddish brown, oily solid in C_6D_6 was then used to verify the desired product present in the solution.

Synthesis of $\text{RuCl}_2(\text{PPh}_3)_3$ [9]

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol was refluxed for 5 min After cooling the solution was treated with an excess of freshly recrystallized PPh_3 , (Fig 12) and

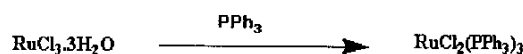


Fig. 12: Synthetic route of $\text{RuCl}_2(\text{PPh}_3)_3$.

PPh_3 refluxed for 3 h. Product was filtered washed and dried as shiny black crystals.

Reaction of Ylide with $\text{RuCl}_2(\text{PPh}_3)_3$

$\text{RuCl}_2(\text{PPh}_3)_3$ solution in THF was added in the suspension of Synthesized Ylide $[\text{C}_5\text{H}_4\text{PMePh}_2]$ in THF in 1: 2 molar ratio, and stirred for 24 hrs at room temperature green-brown oily product was obtained (Fig. 13) and ^1H NMR was run. The same procedure was repeated by changing the temperature condition from room temperature to 50 °C. The reaction was refluxed at 50 °C for 4 to 5 h and then kept on stirring for 24 h at room temperature and again analyzed by ^1H NMR.

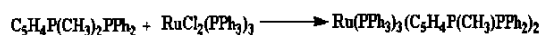


Fig. 13: Reaction of Ylide with $\text{RuCl}_2(\text{PPh}_3)_3$.

Expected Reaction

Synthesis of $\text{Ru}[\text{PPh}_3]_3[\text{N}((\text{CH}_3)_3\text{Si})]_2$

$\text{RuCl}_2(\text{PPh}_3)_3$ was reacted with $[(\text{CH}_3)_3\text{Si}]_2\text{N.Li}$ in 1:2 molar ratio at very low temp. approx -70 °C in a dry ice bath and stirred for 24 h (Fig. 14), and the product was reacted with Ylide Salt (Fig. 15) in 1:2 Molar Ratio w.r.t Ru complex dark green ppts appeared were filtered dried and analyzed by ^1H NMR.

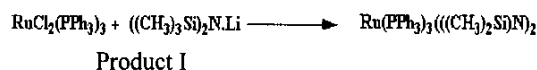


Fig. 14: Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $[(\text{CH}_3)_3\text{Si}]_2\text{N.Li}$ to give $\text{Ru}[\text{PPh}_3]_3[\text{N}((\text{CH}_3)_3\text{Si})]_2$.

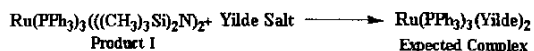


Fig. 15: Reaction of $\text{Ru}[\text{PPh}_3]_3[\text{N}((\text{CH}_3)_3\text{Si})]_2$ with Yilde.

Synthesis of Ru[PPh₃]₃[P(CH₃)CpPh₂]₂ by the Reaction of RuCl₂(PPh₃)₃ with Freshly Synthesized Ylide

Ylide Salt was reacted with ((CH₃)₃Si)₂N.Li in dry ice/Acetone bath at approx. -60 -70 °C for 4 h and then at room temp for 24 h. Colorless ppts were filtered and in the filtrate solution of RuCl₂(PPh₃)₃ in THF was added and the reaction mixture was stirred for 24 h at room temp. Colorless ppts appeared were filtered, during stirring the solution developed a black-green color. Solvent was pumped off from the black-green filtrate and the dark green solid residue was washed with 3×10 ml. of ether. The solid was dried and analyzed by ¹H and ³¹P NMR (CD₂Cl₂, 300 MHz).

Another Route of Synthesizing Ru(PPh₃)₃(C₅H₄PMePh₂)(PF₆)₂

Synthesis of Ru(PPh₃)₃(Yilde)₂PF₆

The above complex synthesized with indenyl ylide using AgPF₆, first reacted RuCl₂(PPh₃)₃ with AgPF₆ in dry CH₃CN, (Fig. 16). The reaction mixture was stirred for 24 h at room temperature.

The product I (Fig. 16) was then reacted with Indenyl ylide to obtain the required complex (Fig. 17) at room temperature stirred for 24 h.

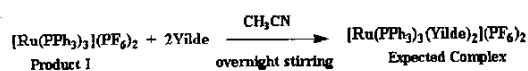


Fig. 17: Reaction of Ru(PPh₃)₃(Yilde)₂PF₆ with Yilde to yield expected complex [Ru(PPh₃)₃(Yilde)₂](PF₆)₂.

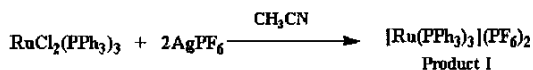


Fig. 16: Synthetic route of Ru(PPh₃)₃(Yilde)₂PF₆.

Alternate Method used with this Ylide for Complex Synthesis

Another route of synthesis was adopted, ruthenium material RuCl₂(PPh₃)₃ was dissolved in dry CH₃CN, silver hexafluorophosphate dissolved in

CH₃CN was added in 1:2 molar ratio. The solution stirred under argon overnight, then it was filtered to remove AgCl, to get product I (Fig. 18). Product I was then reacted with freshly synthesized ylide [CpP(CH₃)Ph₂]. To the filtrate of product I ylide solution in dry CH₃CN under argon was added drop wise in 1:2 molar ratio with respect to RuCl₂(PPh₃)₃ and stirred for a day, (Fig. 19). The dark green brown product was filtered dried and analyzed by ¹H NMR.

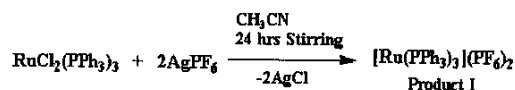


Fig. 18: Reaction of RuCl₂(PPh₃)₃ with silver hexafluorophosphate to give [Ru(PPh₃)₃](PF₆)₂.

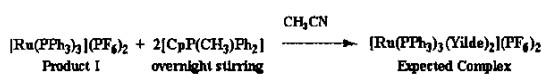


Fig. 19: Reaction of [Ru(PPh₃)₃](PF₆)₂ with [CpP(CH₃)Ph₂]. To yield [Ru(PPh₃)₃(Yilde)₂](PF₆)₂.

References

1. Ferguson, Marcelle L; Senecal, Too D, Groendyke, Todd M, Anna K. *Journal of American Chemical Society*, **128**, 4576 (2006).
2. M. Raman Patel and P. Narsshintha Argadc, *Journal of Organic Chemistry*, **72**, 4900 (2007).
3. F. Ramirez and S. Dershowitz, *Journal of Organic Chemistry*, **22**, 41 (1957).
4. F. Ramirez and S. Levy, *Journal of American Chemical Society*, **79**, 6167 (1957).
5. F. Ramirez and S. Levy, *Journal of Organic Chemistry*, **23**, 2035 (1958).
6. F. Mathey and J.-P. Lampin, *Tetrahedron*, **31**, 2685 (1975).
7. J. Brown, PhD thesis (Department of Chemistry, Queen University, Kingston Ontario, Canada) (2007).
8. K. Itoh, H. Nagashima, T. Ohshima, N. Oshima and H. Nishiyama, *Journal of Organic Chemistry*, **272**, 179 (1984).
9. Synthesis of Organometallic Compounds—A Practical Guide, Edited By Sanshiro Komiya, John Wiley & Sons (1997).