Chapter-3

Intramolecularly Chelated Ruthenium-based Carbene Complexes
3.1.00 Introduction:

As the world becomes more cost-conscious and environmentally aware, the pursuit of new transition-metal catalysts that are both active and recyclable has become increasingly important to synthetic organic chemists. Recently, the advent of efficient homogeneous ruthenium alkylidene precatalysts\(^1\) have propelled the olefin-metathesis reaction to the forefront of contemporary organic chemistry as a mild and efficient method for C-C bond formation. Given this new-found significance, it is not surprising that the development of reusable catalysts has been the goal of a number of research groups. Various groups have focused on the development of efficient recyclable chiral catalyst for enantioselective synthesis.\(^2\)

Since metathesis reactions are expected to be used in pharmaceutical processes,\(^3\) one has to deal with the most undesirable feature of the catalyst, viz presence of highly colored ruthenium byproducts that are difficult to remove from the organic products.\(^4\) Taken together, recovery of metal impurities and recycling of active catalysts demand that ligand system be suitably designed to serve these purposes. In this context, chelating ligands have been extensively investigated. A metal chelate is often more stable towards competing decomposition reactions, and chelation certainly assists in sequestering metal contaminated minor byproducts.

Various recycling strategies have been shown below:

**Type A:**

The carbene part rather than ancillary ligands on metal acts as an anchor group. The carbene substituent of the initiator is cleaved off during the first turn of the catalytic cycle and metal template is, therefore, released from the polymer and acts as a homogeneous catalyst; it is recaptured by the polymer matrix once the substrate in solution is consumed.\(^5\)
Type B:

A polymer backbone is attached to the donor ligand and it remains with the metal throughout the catalytic cycle. The solubility of initiator and propagating species depend on the solubility of polymer matrix.\(^6\)

![Diagram of Type B](image)

Type C:

The carbene fragment is tethered to the donor ligand. Design of these species is based on the idea that they might be able to regenerate themselves after the productive metathesis is over and the substrate in solution has been quantitatively consumed.\(^7\)

![Diagram of Type C](image)

Several attempts have been made to immobilize a catalyst for metathesis on solid supports.\(^8\) Catalysts *permanently* immobilized on solid supports were found to be less reactive than their homogeneous analogues.\(^9\) Moreover, their recovery and reuse led to significant losses in activity.
3.2.00 Background:

In 1999, Hoveyda and coworkers first introduced the catalyst 1A bearing a chelated ether-functionalized alkylidene moiety (Chart-3.2.01). This Ru-carbene complex offers excellent stability to air and moisture and can be recycled to produce desired products in high yield. Reaction at elevated temperature lead to improved yield of the recovered catalyst. Again, in 2000, Hoveyda reported relatively active, recoverable and recyclable Ru-based NHC complex 1B. The heterocyclic ligand significantly enhance the catalytic activity, and the styrenyl ether allow for easy recovery of the Ru-complex. It promotes ROCM of unstrained cycloalkenes with simple \( \alpha,\beta \)-unsaturated carbonyls under mild conditions. Tri- and tetrasubstituted olefins can be synthesized by RCM under mild condition in a very high yield with >95% recovery of the catalyst.

Chart-3.2.01

Blechert and Wakamatsu have recently shown (Chart-3.2.02) that the replacement of the isopropoxystyrene ligand by BINOL or biphenyl based styrene results in a large improvement in the activity of the catalyst, as complex 2A and 2B are much more active than the previously reported catalysts like "second generation" Grubbs' catalyst. Though the catalyst 2A is chiral, no asymmetric induction was observed. At the same time, it was observed that even a small variation in the isopropoxystyrene can result in a change in the activity of the catalyst. As for modulation of catalytic activity by incorporating an electron-donating or an electron-withdrawing group in the ligand part, it was found that when \( \text{NO}_2 \) group was present in the styrene ligand, an extremely stable and active catalyst 2C was obtained. This catalyst can perform at 0 °C. Activity was found to be in the order of 2A<2B<2C.
According to Furstner, chelation sometimes deters the activity of the catalyst. To prove this, he prepared the catalysts (3A and 3B) and these were significantly less active than their parent compounds (Chart-3.2.03).\textsuperscript{10}

Another example is shown below (Chart-3.2.04) where the chelated catalyst 4A regenerates itself after the reaction is over.\textsuperscript{7a}
Ongoing research not only involves the development of modified recycled efficient catalyst, but it involves the development of chiral recyclable efficient catalyst also. Recently, Hoveyda et al. have developed Ru-based air-stable recyclable chiral catalyst 5A and their reactivity in enantioselective olefin metathesis (Chart-3.2.05). At the same time Schrock and Hoveyda have prepared Mo-based chiral polymer-bound metathesis catalyst 5B (Chart-3.2.05). This polymer supported chiral catalyst possess appreciable reactivity and effects excellent enantioselectivity.

![Chart-3.2.05](chart.png)

3.3.00 Present Work:

In view of the above discussion, we sought to synthesize molecules that would be catalytically active, recoverable at the end of the reaction and recyclable. We were conscious of the fact that ligand modification could either enhance or diminish the reactivity of the metal centre.

The key feature of our ligand design was the provision to make the chelating ligand chiral at the backbone. As for the donor group of the ligand, alkoxy, amino and pyrazole were investigated. An aromatic group (Ph or Fc) was used at the backbone so that chirality (planar chirality) could be introduced without disturbing intergroup distances.
A general synthetic route is depicted in Scheme-3.3.01

Scheme-3.3.01

We attempted to synthesize the following six chelated ruthenium-based carbene complexes (6-11) (Chart-3.3.01). Different protocols were employed for the preparation of carbene complexes (6-11). Their preparation and properties have been discussed in this section.

Chart-3.3.01

**Attempted synthesis of pyrazole-based Ru-carbene 6**: Pyrazole-based ligands are easy to prepare and are amenable to diverse structural modifications including chiral variants. Suitably located substituents in the aryl and pyrazolyl rings would permit tuning of donor ability of nitrogen. Also, steric effect and solubility of the ligand can be modulated by incorporating bulky substituents at appropriate positions. Such variations are often crucial for optimizing catalytic activity and solubility in several important reactions. The ligand
was expected to provide an interesting variation to the theme of intramolecularly chelated ligand since pyrazole as a donor is quite different from pyridine, oxazoline or Schiff base. The 3-position of pyrazole is ideally suited for studying steric implications of bulky substituents. Electron density on the pyrazole ring can in principle be tuned by varying substituents at relevant \( p \)-position on aromatic ring.

Complex 6 was expected to provide a simple model for pyrazole donor in ruthenium alkylidene complex. However, reaction of ligand 6a (allylation of 3,5-dimethyl-pyrazole afforded the ligand 6a) with complex (PCy\(_3\))\(_2\)Cl\(_2\)Ru=C(H)Ph, 1a, in dichloromethane produced a new complex in poor yield (Scheme-3.3.02). This compound turned out to be a low melting solid that was obtained as a precipitate from the reaction mixture after addition of methanol. Since the mother liquor did not reveal the presence of starting material 1a, it appears that the methylidene exchange product underwent rapid decomposition after it was formed.

![Scheme-3.3.02](image)

The new product displayed M=C(H) signal in the proton NMR spectrum at 17.74 ppm as doublet (\( J = 8 \) Hz). Instability of the complex did not permit further characterization.

**Synthesis of pyrazole-based Ru-carbene complex 7:** Design of ligand 7a features one aromatic ring joined to a heterocycle that contain the donor atom. 3,5-Dimethyl-1-phenylpyrazole 7c was prepared by reaction of acetylacetone and phenylhydrazine as reported in the literature.\(^2\) We followed an alternative route where substituted pyrazoles are coupled with phenylboronic acid by copper acetate in presence of pyridine.\(^3\) Directed lithiation at 0 °C followed by electrophilic quench with DMF afforded the product 7b. Finally, 7a was obtained from 7b in a very good yield after Wittig reaction. All the compounds are purified by chromatography and characterized by spectroscopic technique. Treatment of 7a (1.5 eq.) with Grubbs’ catalyst, (PCy\(_3\))\(_2\)Cl\(_2\)Ru=C(H)Ph, 1a,
afforded carbene 7 in 98% yield (Scheme-3.3.03). The reaction was performed both at room temperature in dichloromethane or at reflux in benzene, provided far better conversion in lesser time compared to previous one.

**Scheme-3.3.03**

It is a very stable pink solid. In solution, it appears green. Again, after removal of solvent it turns pink. The compound 7 was purified by reprecipitation from dichloromethane-methanol mixture and characterized by spectroscopic technique and elemental analysis. In the proton NMR spectrum, benzylicene proton appears as a doublet at 19.04 ppm (1H, J = 10 Hz), pyrazole proton is at 6.31 ppm as singlet, while two methyl singlets appear at 2.80 and 2.73 ppm. The $^{31}$P absorption for the phosphine is observed at 33.51 ppm. Peak at 1.30-2.45 ppm for proton of PCy$_3$ indicated the presence of one PCy$_3$. Complex 7 is very robust and very stable in air and moisture. It remains stable beyond 220 °C.

**Synthesis of ferrocene-based carbene complex 8**: In keeping with our continuing interest in ferrocene-based ligands we sought to expand the range of ligands used for modification of metathesis catalyst as a basic motif. They are easy to prepare and are amenable to diverse structural modifications including planar-chiral variants. Suitably located substituents in the ferrocene rings would permit tuning of donor ability of the ligand. Design of ligand 8a features one ferrocene ring (aromatic) joined to a overhanging heteroatom (donor atom). $N,N$-Dimethylaminomethylferrocene 8c is made
by treatment of ferrocene with $N,N,N',N'$-tetramethyldiaminomethane and paraformaldehyde in glacial acetic acid under reflux as described in literature.\textsuperscript{14} Directed \textit{ortho}-lithiation of $8c$ at room temperature followed by electrophilic quench with DMF afforded the product $8b$ which provided the ligand $8a$ by Wittig reaction in 87\% yield. Stoichiometric reaction between $8a$ and Grubbs catalyst, $1a$, in dichloromethane afforded catalyst $8$ as a very stable reddish-black solid in 95 \% yield (Scheme-3.3.04).

Complex $8$ was purified by reprecipitation from dichloromethane-methanol mixture and characterized by spectroscopic technique. In the proton NMR spectrum, the metal-carbene (M=CH) peak appears as a doublet at 18.35 ppm (1H, J = 10 Hz). Peak area of proton for cyclohexyl (PCya) group indicated the presence of one PCys only. The $^{31}$P absorption for the phosphine is observed at 38.91 ppm. It is very stable and not sensitive to air or moisture. It decomposes at 180-185 °C.

**Synthesis of ferrocene-based carbene complex 9:** In this case, the ligand is slightly different from the previous two cases. Here, the donor atom is oxygen (-OMe gr.) which is pendant in the \textit{ortho}-position of vinylferrocene. Our interest was to understand the effect of catalytic activity on the variation of donor atom, therefore, we designed the ligand in such way. Ligand $9a$ was made by alkylation of corresponding alcohol $9b$ which was made by substitution of amine (NMe$_3^+$) of $9c$ by hydroxy (OH). Addition of MeI in solution of $8a$ afforded $9c$. All the compounds were purified by chromatography.
and characterized spectroscopically. Treatment of ligand 9a (excess) with Grubbs’ catalyst in dichloromethane afforded catalyst 9 in 81% yield (Scheme-3.3.05). Complex 9 is comparatively less stable than the N-based catalysts (7, 8 and 11). All the reactions were monitored by TLC. Total disappearance of Grubbs’ catalyst by TLC indicated that the reaction was over.

\[ \text{Scheme-3.3.05} \]

\[
\begin{align*}
&\text{Fe} &\text{Fe} \\
&(\text{Me}_2\text{N})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2 &\text{CHO} \\
&\text{Fe} &\text{Fe} \\
&\text{gla. CH}_2\text{COOH; reflux; 4h} &\text{DMF; 15 min; RT} \\
&\text{BuLi, Et}_2\text{O} &\text{Wittig Rxn.} \\
&\text{9b} &\text{8b} \\
&\text{NaOH(1N)} &\text{Benzene} \\
&\text{reflux} & \\
&\text{Me} &\text{9c} \\
&\text{BuOK} &\text{8a} \\
&\text{Me} &\text{9a} \\
&\text{OMe} &\text{9} \\
&\text{DCM, rt} &
\end{align*}
\]

\[^1\text{H} \text{NMR peak at 18.09 ppm indicated the formation of carbene complex 9, whereas Me peak at 3.76 ppm, and } ^{31}\text{P} \text{ NMR peak at 49.40 ppm indicated that there is chelation between the metal and the “O” atom of the ligand. It decomposes very rapidly in solution.} \]

**Attempted synthesis of ferrocene-based carbene complex 10**: The complex 10 is very similar to complex 9. Ligand 10a was made by alkylation of corresponding alcohol 10b which in turn was prepared by Wittig reaction of ferrocenedicarboxaldehyde, followed by reduction of aldehyde 10c. All the compounds including ligand 10a were purified by chromatography and characterized by spectroscopy. Stoichiometric reaction between 10a and Grubbs’ catalyst in dichloromethane afforded catalyst 10 (Scheme-3.3.06) as reddish
semisolid compound which becomes dark during vacuum drying. It is seemed to be unstable complex. $^1$H NMR of the crude residue indicated the formation of metal-carbene (M=CH, proton peak at 19.02 ppm). Several attempts to completely characterize the complex 10 was unsuccessful.

**Scheme-3.3.06**

![Scheme-3.3.06](image)

**Synthesis of ferrocene-based carbene complex 11**: Ligand 11a is very similar to ligand 8a. Both the ligands can afford the planar-chiral catalyst. In this case, ligand 11a provides one more chiral center excluding planar chiral part. This type of ligand system could offer better selectivity as the chiral center is very closer to the metal-center. Ligand 11a was made from corresponding aldehyde 11b by Witting reaction. Directed ortholithiation of $N,N$-dimethylaminomethylferrocene 11c, which was made by treatment of ferrocenecarboxaldehyde with dimethyl amine and NaCN followed by addition of methyl Grignard,\textsuperscript{15} at room temperature followed by electrophilic quench with DMF afforded the product 11b. All the intermediate compounds were purified by chromatography and characterized by NMR-spectroscopy. Treatment of ligand 11a with Grubbs' catalyst 1a afforded the stable dark-brown solid 12 in 87% yield (Scheme-3.3.07).
Complex 11 was purified by reprecipitation and characterized by spectroscopic technique. In the proton NMR spectrum, the metal-carbene (M=CH) peak appears as a doublet at 18.33 ppm (1H, J = 10 Hz) while peak area of proton for PCy₃ group indicates the presence of one PCy₃ only. The ³¹P absorption for the phosphine is observed at 39.13 ppm. It is very stable and not sensitive to air or moisture. It decomposes at 187 °C.

Reactivity:

All these complexes were tested for RCM. Among these complexes, complex 9 is active for RCM of diethylallylmalonate at room temperature. Others are not even active at elevated temperature (80-90 °C) and in presence of CuCl (2 equiv. of cat).

Complex 7, 8, 9 and 11 were tested for ROMP and it was observed that all the complexes were active for polymerization of DCPD (dicyclopentadiene) at elevated temperature (80-90 °C). Most of them are responsible for the formation of cross-linking polymer (Scheme-3.3.08) which is insoluble in common solvent even under reflux at
>200 °C. Among these complexes, complex 7 and 9 afforded quantitative conversion (91-97%), whereas remaining carbene complexes afforded 50-70% yield. Polymerization of DCPD using Grubbs catalyst 1a, was also performed under solvent-free condition at 60 °C. It also afforded cross-linking polymer in quantitative yield. Checking of catalytic activity of these complexes and characterization of polymers are under way.

Scheme-3.3.08
3.4.00 Conclusion:

We devised a convenient synthesis and characterized intramolecularly chelated metal-carbenes. Most of the metal-carbenes are very stable and catalytically active. Particularly, N-ligand-based catalysts are very robust. Ferrocene and pyrazole are good template to introduce chirality in the catalyst. These new complexes could provide the starting point of designing air-stable, recyclable chiral-catalyst. Preliminary studies of catalytic activity are not satisfactory, but it perhaps can be tuned by ligand variation. Moreover, it is observed that the N-ligand based catalysts are much more stable compared to O-ligand-based catalysts. In conclusion, our strategy of making modified catalyst is very unique and could be useful one.
Experimental

All reactions were performed under inert atmosphere of argon, using freshly distilled, degassed solvents. Diethyl ether and THF were freshly distilled over sodium benzophenone ketyl. Dichloromethane was freshly distilled over P₂O₅ followed by calcium hydride. "BuLi, 'BuLi and Grubb's catalyst were prepared by us according to literature procedure. All other solvents were dried according to established procedure; all the starting materials and complexes were prepared following the reported procedure; ferrocene and few chemicals were used as purchased from Aldrich, Lancaster and SD Fine Chemicals, India. NMR spectra were recorded on a Bruker AC200, MSL300 or DRX500 spectrometer. The ¹H NMR, ¹³C NMR and ³¹P nuclei were studied at 200 or 500, 50.32 and 125.76, 81.02 and 202.46 MHz respectively. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were performed on a Carlo-Erba 1100 automatic analyzer at NCL microanalysis facility. DSC was recorded on a PERKIN ELMER DSC-7 (calibrated with Indium) under nitrogen atmosphere. Heating range was 50-300 °C (10 °C/min).

Preparation of N-phenyl-3,5-dimethylpyrazole 7c:

Procedure 1. It was prepared according to the reported procedure¹² from acetylacetone (10 g, 98.90 mmol) and phenylhydrazine (10.81 g, 100 mmol). Yield: (15 g, 81%).

Procedure 2. Distilled pyridine (6.7 ml, 41.66 mmol) was added to a mixture of 3,5-dimethylpyrazole (2 g, 20.83 mmol), phenylboronic acid (5.07 g, 41.66 mmol) and copper acetate (6.23 g, 31.24 mmol) in dichloromethane (20 ml). Activated, powdered molecular sieve (4 Å) was also added. After stirring for 2 days under dry air, the reaction mixture was filtered through celite and the filtrate was concentrated. The product was purified by flash chromatography.

Compound 7c:
Yield : 2.86 g, 80%
\[ ^1H \text{NMR (CDCl}_3\] : \[ \delta 7.41-7.43 (5H, m), 6.00 (1H, s), 2.28 (3H, s), 2.30 (3H, s). \]

\[ ^13C \text{NMR (CDCl}_3\] : \[ \delta 147.8, 139.3, 138.3, 128.1, 126.1, 123.6, 106.3, 12.7, 11.4. \]

**Preparation of 7b**: To a solution of N-phenyl-3,5-dimethylpyrazole (3.44 g, 20 mmol) in 100 ml dry THF, \(^6\)BuLi (15 ml 1.41M, 21.15 mol) was added dropwise at 0°C and yellow color of the solution changed successively to blue, yellow, and brown. The reaction mixture was stirred for 4 h followed by addition of DMF (1.6 ml, 21 mmol) at 0°C. Stirring was continued for additional 3 h and quenched with water and extracted with ethyl acetate (40 ml \(\times\) 3). Combined organic phase was dried over \(\text{Na}_2\text{SO}_4\) and concentrated. The crude semi-solid product was purified by flash chromatography to obtain 7b as a semi-solid.

**Compound 7b**

**Yield** : 3.12 g, 78%

**IR (CHCl\(_3\))** : 1693, 1600, 1556, 1498, 1460, 1419, 1398, 1365, 1259 cm\(^{-1}\)

\[ ^1H \text{NMR (CDCl}_3\] : \[ \delta 9.64 (1H, s), 7.39-8.06 (4H, m), 6.07 (1H, s), 2.31 (3H, s), 2.20 (3H, s). \]

\[ ^13C \text{NMR (CDCl}_3\] : \[ \delta 189.8, 149.8, 141.5, 134.2, 132.7, 128.9, 128.3, 127.7, 106.9, 13.4, 11.7. \]

**Preparation of 7a**: A solution of compound 7b (200 mg, 1 mmol) in dry THF (7 ml) was stirred at -40°C. A freshly prepared solution of ylide [prepared from methyltriphenylphosphonium iodide salt (800 mg, 2 mmol) and \(^6\)BuLi (1 ml of 1.54 M, 1.5 mmol) in THF (20 ml)] was added. Stirring was continued at room temperature for 5 h. THF was evaporated and ethyl acetate (25 ml) was added followed by quenching with water (10 ml). Organic layer was washed with brine solution. Solvent was removed under reduced pressure and the residue was purified by flash chromatography. The product was a colorless liquid.

**Compound 7a**

**Yield** : 170 mg, 86%
IR (CHCl₃) : 1629, 1602, 1554, 1494, 1461, 1421, 1377, 1365 cm⁻¹
¹H NMR (CDCl₃, 500 MHz) : δ 7.66-7.70 (1H, m), 7.27-7.46 (3H, m), 6.24-6.29 (1H, m), 6.00 (1H, s), 5.66-5.69 (1H, d, J = 15 Hz), 5.24-5.26 (1H, d, J = 10 Hz), 2.34 (3H, s), 2.05 (3H, s).
¹³C NMR (CDCl₃, 125.76 MHz) : δ 148.6, 141.3, 137.1, 135.6, 131.7, 129.1, 128.3, 125.9, 116.5, 105.4, 13.4, 11.2.

Preparation of Complex 7: Compound 7a (119 mg, 0.6 mmol) in 2 ml of dry benzene was added to a solution of Ru-benzyldene complex 1a (410 mg, 0.5 mmol) in benzene (5 ml). The reaction mixture was stirred under reflux for 30-40 min. The solution turned purple to green. Solvent was removed followed by addition of dry methanol at 0 °C, which afforded 7 as a pale pink solid.

Compound 7 : Yield : 312 mg, 98%
IR (CHCl₃) : 1554, 1489, 1462, 1377 cm⁻¹
¹H NMR (CDCl₃, 500 MHz) : δ 19.04 (1H, d, J = 10 Hz), 7.34-7.74 (4H, m), 6.31 (1H, s), 2.80 (3H, s), 2.73 (3H, s), 1.30-2.45 (33H, m).
¹³C NMR (CDCl₃, 125.76 MHz) : δ 290.2, 152.3, 144.1, 141.3, 131.9, 128.1, 127.3, 124.7, 122.8, 112.4, 34.5, 30.1, 27.87, 26.5, 16.3, 15.2.
³¹P NMR (CDCl₃, 202.46 MHz) : δ 33.51.
MP : >200 °C
Analysis : Calcd : C: 56.60, H: 7.07, N: 4.40
Found : C: 56.58, H: 6.99, N: 4.38

N,N,N,N-tetramethyldiaminomethane and N,N-dimethylaminomethylferrocene 8c were prepared according to literature procedure.

Preparation of N,N-dimethylaminomethylferrocene 8c : A mixture of 2.55 g (25 mmol) of N,N,N,N-tetramethyldiaminomethane, 0.79 g (25 mmol) of paraformaldehyde and 20 g (33 mmol) of glacial acetic acid was heated for a few minutes until solution occurred, and 9.3 g (50 mmol) of ferrocene was then added
with stirring. The mixture was refluxed for 5 h. The solution was cooled and 30 ml of water was added with stirring. The resulting mixture was filtered and the solid was washed with dilute acetic acid followed by water. The clear filtrate was chilled in an ice bath and made strongly alkaline with 50% of NaOH solution. The resulting mixture was extracted 3-4 times with ether and the combined extract was washed with brine. The ethereal solution was dried over Na$_2$SO$_4$. After removing ether the residue was passed through the silica gel column [elution with pet-ether/Et$_2$O/Et$_3$N (20:70:10), then with MeOH/Et$_2$O/Et$_3$N (5:90:5)] to obtain the pure product.

**Compound 8c**

**Yield**

571 g, 47%

$^1$H NMR (CDCl$_3$, 200 MHz)

δ 3.99-4.10 (9H, m), 3.16 (2H, bs), 2.05 (6H, bs).

### Preparation of $\cdot$-tetramethyldiaminomethane

To an ice-cold, stirred solution of 162 mg (2 mmol) of 37% aqueous formaldehyde, was added 722 mg (4 mmol) of 25% aqueous dimethylamine solution maintaining the temperature below 15 C. After stirring for 0.5 h, solid KOH was added until two layers separated. The upper layer was removed and dried over solid KOH. After filtering, product was distilled to give volatile, colorless liquid (bp: 83 °C).

**Yield**

178 mg, 87%

$^1$H NMR (CDCl$_3$, 200 MHz)

δ 2.66 (2H, s), 2.18 (12H, s).

### Preparation of Compound 8b

To a solution of 8c (62 mg, 0.255 mmol) in 3 ml dry diethyl ether, 'BuLi (0.35 ml of 1.1M, 0.344 mmol) was added very slowly at room temperature. The reaction mixture was stirred for 15 min followed by addition of DMF (0.2 ml, 0.256mmol). Stirring was continued for additional 15 min. Then it was quenched with moist ether and brine. The product was extracted with ether (10 ml x 3). Combined organic phase was dried over Na$_2$SO$_4$ and concentrated. The crude yellowish red semi-solid product was purified by flash chromatography [elution with pet-ether/Et$_2$O /Et$_3$N (20:70:10), then with MeOH/Et$_2$O/Et$_3$N (5:90:5)] to obtain 8b.
Compound 8b:

Yield: 65 mg, 94%

$^1$H NMR (CDCl$_3$, 500 MHz):
δ 10.07 (1H, s), 4.75 (1H, s), 4.59 (1H, s), 4.53 (1H, s), 4.20 (5H, s), 3.82 (1H, d, J = 10 Hz), 3.33 (1H, d, J = 10 Hz), 2.19 (6H, s).

Preparation of 8a: A solution of compound 8b (70 mg, 0.258 mmol) in dry THF (4 ml) was stirred at -40 °C. A freshly prepared solution of ylide [prepared from methyltriphenylphosphonium iodide salt (210 mg, 0.5 mmol) and $^t$BuLi (0.35 ml of 1.1 M, 0.387 mmol) in THF (10 ml)] was added. Stirring was continued at room temperature for 5 h. THF was evaporated and ethyl acetate (20 ml) was added followed by quenching with water (1 ml). Organic layer was washed with brine solution. Solvent was removed under reduced pressure and the residue was purified by flash chromatography [elution with pet-ether/Et$_2$O/Et$_3$N (20:70:10), then with MeOH/Et$_2$O/Et$_3$N (5:90:5)]. The product was a yellowish red semi-solid.

Compound 8a:

Yield: 61 mg, 87%

IR (CHCl$_3$):
3085, 2935, 2854, 2813, 2765, 1626, 1466, 1454, 1352, 1253, 1105, 1011 cm$^{-1}$

$^1$H NMR (CDCl$_3$, 500 MHz):
δ 6.55-6.61 (1H, m), 5.41 (1H, d, J = 15 Hz), 5.08 (1H, d, J = 15 Hz), 4.47 (1H, s), 4.26 (1H, s), 4.19 (1H, s), 4.04 (5H, s), 3.51 (1H, d, J = 10 Hz), 3.28 (1H, d, J = 10 Hz), 2.18 (6H, s).

$^{13}$C NMR (CDCl$_3$, 125.76 MHz):
δ 132.9, 111.8, 83.5, 82.4, 71.4, 70.7, 69.7, 67.5, 65.2, 57.1, 44.8.

Preparation of Complex 8: Compound 8a (41 mg, 0.15 mmol) in 1 ml of dry dichloromethane was added to a solution of Ru-benzylidene complex 1a (82 mg, 0.1 mmol) in dichloromethane (2 ml). The reaction mixture was stirred at room temperature for 45 min. When the solution turned purple to dark red, volume of the solvent was reduced followed by addition of dry methanol at 0 °C, which afforded 8 as dark brown solid powder.
Compound 8
Yield: 65 mg, 92%
IR (CHCl₃): 2931, 2852, 1670, 1448, 1352, 1296, 1143, 1107 cm⁻¹
¹H NMR (CDCl₃, 500 MHz): δ 18.35 (1H, d, J = 10 Hz), 4.61 (1H, s), 4.44 (2H, s), 4.32 (5H, s), 3.07 (IH, s), 3.17 (1H, s), 1.26-2.81 (39H, m).
¹³C NMR (CDCl₃, 125.76 MHz): 34.9, 34.8, 30.3, 27.9, 26.4.
³¹P NMR (CDCl₃, 202.46 MHz): δ 38.91
MP: 182 °C dec.
Analysis:
Calcd: C: 54.31, H: 7.07, N: 1.98
Found: C: 54.29, H: 7.00, N: 1.89

Preparation of Compound 9c: To a ice-cold solution of 8a (1 mmol) in dry benzene (3 ml), Mel (2 mmol) was added dropwise. The solution was stirred at room temperature for 1 h during which precipitate was formed. The resulting yellow precipitate was collected in quantitative yield by filtration.

Preparation of Compound 9b: To a 10 ml of NaOH (1N) solution, compound 9c (1 mmol) was added and the reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was extracted 2-3 times in ether. The combined ether extract was dried over MgSO₄ and then passed through silica gel column. After removal of ether yellow semi-solid 9b was obtained in 77% yield.

Preparation of Compound 9a: To a solution of 9b (100 mg, 0.408 mmol) in 3 ml Mel, 'BuOK (69 mg, 0.619 mmol) was added at room temperature. The reaction mixture was stirred for 2 h. Then the reaction was filtered and passed through silica gel column to obtain pure product as yellow semi-solid.

Compound 9a
Yield: 103 mg, 97%
IR (CHCl₃): 1658, 1460, 1448, 1377, 1278, 1105, 1085 cm⁻¹
¹H NMR (CDCl₃, 500 MHz): δ 6.54-6.60 (1H, m), 5.41-5.45 (1H, d, J = 20 Hz), 5.12-5.14 (1H, d, J = 10 Hz), 4.48 (2H, s), 4.31 (1H, s), 4.22 (2H, s), 4.08 (5H, s), 3.33 (3H, s).
Preparation of Complex 9: Compound 9a (25 mg, 0.098 mmol) in 1 ml of dry dichloromethane was added to a solution of Ru-benzylidene complex 1a (40 mg, 0.049 mmol) in dichloromethane (2 ml). The reaction mixture was stirred at room temperature for 45 min. When the solution turned purple to dark red, volume of the solvent was reduced followed by addition of dry methanol at 0 °C, which afforded 9 as dark brown solid powder.

Compound 9:

Yield: 27 mg, 81%

IR (CHCl₃): 1940, 1681, 1629, 1446, 1382, 1348, 1236, 1176, 1089 cm⁻¹

¹H NMR (CDCl₃, 500 MHz): δ 18.10 (1H, d, J = 10 Hz), 4.07-4.49 (10H, m), 3.75 (3H, s), 1.27-2.19 (33H, m).

¹³C NMR (CDCl₃, 125.76 MHz): δ 132.7, 112.5, 83.6, 81.6, 71.1, 69.6, 69.1, 67.9, 66.5, 57.6, 29.6.

Preparation of Compound 10c: A solution of ferrovecenedicarboxaldehyde 10d (200 mg, 0.826 mmol) in dry THF (7 ml) was stirred at -40 °C. A freshly prepared solution of ylide [prepared from methyltriphenylphosphonium iodide salt (500 mg, 1.24 mmol) and tBuLi (0.54 ml of 1.54 M, 0.830 mmol) in THF (15 ml)] was added. Stirring was continued at room temperature for 3 h. THF was evaporated and ethyl acetate (25 ml) was added followed by quenching with water (10 ml). Organic layer was washed with brine solution. Solvent was removed under reduced pressure and the residue was purified by flash chromatography. The product was yellow solid in 62% yield (123 mg).
Compound 10c:
\(^1^H\) NMR (CDCl\(_3\), 500 MHz): \(\delta 9.89\) (1H, s), 6.35 (1H, bs), 5.40 (1H, bs), 5.14 (1H, bs), 4.17-4.72 (8H, 4bs).

Preparation of Compound 10b: To a ice-cold stirred solution of 10c (100 mg, 0.042 mmol) in 10 ml of MeOH, 20 mg of NaBH\(_4\) was added portion wise. The stirring was continued for 15 min. Then MeOH was removed and 20 ml diethyl ether was added followed by addition of dilute aqueous NH\(_3\) solution. After washing the ether layer with brine, it was dried over Na\(_2\)SO\(_4\). Removal of ether and purification the residue by column chromatography afforded the semi-solid yellow product 10b in 89% yield (90 mg).

Compound 10b:
\(^1^H\) NMR (CDCl\(_3\), 200 MHz): \(\delta 6.40-6.54\) (1H, m), 5.43-5.43 (1H, d, J = 18 Hz), 5.07-5.12 (1H, d, 14 Hz), 4.15-4.39 (10H, m), 1.71 (1H, bs).

Preparation of Compound 10a: To a solution of 10b (100 mg, 0.408 mmol) in 3 ml MeI, tBuOK (69 mg, 0.619 mmol) was added at room temperature. The reaction mixture was stirred for 2 h. Then it was filtered and passed through silica gel column to obtain pure product as yellow semi-solid.

Compound 10a:
Yield: 103 mg, 97%
IR (CHCl\(_3\)): 1733, 1629, 1465, 1448, 1382, 1236, 1188, 1176, 1089 cm\(^{-1}\)
\(^1^H\) NMR (CDCl\(_3\), 500 MHz): \(\delta 6.39-6.44\) (1H, m), 5.33-5.36 (1H, d, J = 15 Hz), 5.06-5.08 (1H, d, J = 10 Hz), 4.33 (2H, s), 4.12-4.33 (8H, 4s), 3.32 (3H, s).
\(^1^3^C\) NMR (CDCl\(_3\), 125.76 MHz): \(\delta 134.1, 111.3, 83.9, 83.4, 70.5, 70.4, 69.4, 69.1, 67.1, 57.5\).

Attempted synthesis of Complex 10: Compound 10a (25 mg, 0.098 mmol) in 1 ml of dry dichloromethane was added to a solution of Ru-benzylidene complex 1a (40 mg, 0.049 mmol) in dichloromethane (2 ml). The reaction mixture was stirred at room temperature for 45 min. After reaction was over (confirmed by TLC), volume of the
solution was reduced followed by addition of dry methanol at 0 °C, which afforded 10 as a dark brown solid powder. The compound was kept for vacuum drying, during which it became black. $^1$H NMR of the residue indicated the formation of metal-carbene (M=CH, proton peak at 19.02 ppm). Instability of the complex 10 did not allow further characterization.

**Aminonitrile11d** and corresponding **tertiary amine 11c** were prepared according to literature procedure.

**Preparation of aminonitrile 11d**: To a stirred solution of 52 mg (0.5 mmol) of sodium bisulfite in 1 ml of water, 100 mg (0.5 mmol) of crude ferrocenecarboxaldehyde in 1.5 ml of methanol was added. After 5 min, 30 mg (0.7 mmol) of dimethylamine (0.1 ml of 50% aqueous solution) was added. The mixture was cooled in an ice bath, and a solution of 24.5 mg (0.5 mmol) of sodium cyanide in 0.5 ml of water was added dropwise with stirring. The color changed from red to orange. Ether (10 ml) was added and the reaction mixture was stirred at room temperature for 4 h, then extracted three times with ether. The combined ethereal extract was dried over magnesium sulfate, and the solvent was removed. The residual oil crystallized on adding petroleum ether to obtain light brown plates of aminonitrile 11d.

**Compound 11d**:  
**Yield**: 120 mg, 92%  
**MP**: 86°C  
$^1$H NMR (CDCl$_3$, 500 MHz)  
δ 4.64 (1H, s), 4.43 (1H, s), 4.30 (1H, s), 4.25 (7H, s), 2.29 (6H, s).

**Preparation of compound 11c**: A solution of 260 mg (1 mmol) of aminonitrile 11d in 2 ml. of dry ether was added dropwise to a stirred solution of methylmagnesium iodide (MeMgI) prepared from 2 mmol each of methyl iodide and magnesium (50 mg) in 10 ml. of dry ether. After stirring for one hour and standing overnight, the reaction mixture was cooled and decomposed with ammonium chloride solution. The compound was extracted in ether. After removal of ether, product was purified by silica gel column. Recrystallization from 95% ethanol afforded red plates.
**Compound 11c**

Yield : 222 mg, 89%

MP : 137°C

**H NMR (CDCl₃, 500 MHz)**

δ 4.10-4.14 (9H, m), 3.58-3.63 (IH, 4s), 2.09 (6H, s), 1.45-1.46 (3H, d, J = 5 Hz).

**Preparation of Compound 11b**: To a solution of 11c (150 mg, 0.602 mmol) in 10 ml dry diethyl ether, 'BuLi (0.8 ml of 1.1M, 0.9 mmol) was added very slowly at room temperature. The reaction mixture was stirred for 15 min followed by addition of DMF (0.6 ml, 0.768 mmol). Stirring was continued for additional 15 min. The reaction was quenched with moist ether and brine. The product was extracted with ether (10 ml × 3). Combined organic phase was dried over Na₂SO₄ and concentrated. The crude yellowish red semi-solid product was purified by flash chromatography [elution with pet-ether/Et₂O/Et₃N (20:70:10), then with MeOH/Et₂O/Et₃N (5:90:5)].

**Compound 11b**

Yield : 127 mg, 76%

**H NMR (CDCl₃, 200 MHz)**

δ 10.08 (1H, s), 4.11-4.79 (9H, m), 2.05 (6H, s), 1.44-147

**C NMR (CDCl₃, 50.32 MHz)**

δ 193.2, 128.4, 91.1, 72.4, 71.2, 70.2, 69.4, 55.4, 40.2, 14.7.

**Preparation of Compound 11a**: A solution of compound 11b (170 mg, 0.614 mmol) in dry THF (7 ml) was stirred at −40 °C. A freshly prepared solution of ylide [prepared from methyltriphenylphosphonium iodide salt (500 mg, 1.23 mmol) and 'BuLi (0.84 ml of 1.1 M, 0.921mmol) in THF (20 ml)] was added. Stirring was continued at room temperature for 5 h. THF was evaporated and ethyl acetate (30 ml) was added followed by quenching with water (1 ml). Organic layer was washed with brine solution. Solvent was removed under reduced pressure and the residue was purified by flash chromatography [elution with pet-ether/Et₂O/Et₃N (20:70:10), then with MeOH/Et₂O/Et₃N (5:90:5)]. The product was a yellowish red semi-solid.

**Compound 11a**

Yield : 138 mg, 82%
IR (CHCl₃) : 2936, 2766, 1626, 1454, 1352, 1254 cm⁻¹
¹H NMR (CDCl₃, 500 MHz) : δ 6.54-6.68 (1H, m), 5.32-5.41 (1H, d, J = 16 Hz), 5.02-5.08 (1H, d, J = 12 Hz), 4.51 (1H, m), 4.19-4.23 (2H, m), 4.04 (5H, s), 3.73-3.83 (1H, q, J = 6 Hz), 2.08 (6H, s), 1.52 (3H, d, J = 6 Hz).
¹³C NMR (CDCl₃, 125.76 MHz) : δ 133.5, 111.0, 87.1, 82.7, 69.9, 68.0, 67.1, 64.5, 56.0, 40.7, 15.5.

Preparation of Complex 11: Ligand 11a (41 mg, 0.15 mmol) in 1 ml of dry dichloromethane was added to a solution of Ru-benzylidene complex 1a (82 mg, 0.1 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 45 min. After that, volume of the solvent was reduced followed by addition of dry methanol at 0 °C, afforded 11 as a dark brown solid powder.

Compound 11 : Yield : 63 mg, 87%
IR (CHCl₃) : 2927, 2852, 1930, 1733, 1625, 1448, 1290, 1274 cm⁻¹
¹H NMR (CDCl₃, 500 MHz) : δ 18.32-18.34 (1H, d, J = 10 Hz), 4.26-4.70 (9H, m), 2.63 (3H, s), 1.26-2.07 (42H, m).
¹³C NMR (CDCl₃, 125.76 MHz) : δ 293.1, 95.7, 89.1, 71.3, 70.3, 69.5, 69.2, 67.2, 57.4, 44.1, 37.7, 34.9, 30.4, 30.3, 28.0, 26.50, 8.8.
³¹P NMR (CDCl₃, 202.46 MHz) : δ 39.13
MP : 187 °C dec.
Analysis : Calcd : C: 54.92, H: 7.21, N: 1.94
Found : C: 54.88, H: 7.19, N: 1.91

Typical procedure for ROMP of DCPD: A freshly prepared solution of complex 7 in DCPD ([DCPD]/[catalyst] = 100:1) was poured into a preheated (85 °C) glass chamber. After 5 min, it was cooled to collect a fine sheet of polymer in quantitative yield. Differential Scanning calorimetry (DSC) experiment indicated that the polymer is amorphous (Tg : 87 °C).
References


2. See the references 5-9 in Chapter 2.


5. a) See the references 45 and 46 (Scheme-2.2.04) in Chapter 2.

6. a) See the example A, B, C and D of Chart-2.2.24 in Chapter 2.


9. See the references 46, 47 in Chapter 2.


11. See ref. 6 in chapter 2.


16. See ref. 31 in Chapter 2.