4.1 STARTING MATERIALS AND LIGANDS

Experimental conditions: All experiments were carried out under absolutely dry conditions in Schlenk tube using a blanket of high purity nitrogen supplied by Indian Oxygen Limited, Pune.

Ruthenium trichloride used was supplied by Johnson Matthey. The purity was checked by chemical analysis before use.

Solvents: Organic solvents such as benzene, n-hexane, chloroform, methylenechloride, acrylonitrile, ether, ethanol, 2-methoxyethanol etc., were of highest purity available in the Indian market. The purity of solvents was checked by gas chromatography and UV spectroscopy.

Reagents and chelating ligands: Formic acid, acetic acid, propionic acid, butyric acid, benzoic acid, p-toluic acid, p-methoxybenzoic acid, acetylacetone (Acac-H), benzoylacetone (Ba-H), 2-hydroxypyridine (PyO-H), 2-hydroxy-6-methylpyridine (MePyO-H), 2-hydroxyacetophenone (Acph-H), 2-hydroxypropiophenone (Prop-H), 2-hydroxybenzophenone (Benz-H), 2-hydroxy-4-methoxy benzophenone (MeBenz-H) were of the best quality available for research purposes and were purified by reported methods wherever necessary.
Gases: Acetylene and nitrogen gases used were supplied by Indian Oxygen Limited, Pune.

Other reagents: Formaldehyde, sodium metal, triphenylphosphine, diphenylacetylene and phenylacetylene etc. were of standard quality (Aldrich, Fluka, E.Merck).
4.2 REACTIONS OF Ru-H BOND OF [RuH₂(CO)(PPh₃)₃] WITH CARBOXYLIC ACIDS

Preparation of dihydridocarbonyltris(triphenylphosphine) ruthenium(II) – [RuH₂(CO)(PPh₃)₃]

The dihydrido carbonyl tris(triphenylphosphine) ruthenium(II) was prepared by the method reported earlier. A solution of 0.52 g (2 mmoles) of hydrated ruthenium trichloride in 20 ml of ethanol, aq. formaldehyde (20 ml 40% w/v solution) and 0.6 g of KOH in 20 ml EtOH were added quickly and successively to a boiling solution of 3.14 g (12 mmoles) of triphenylphosphine in 140 ml of ethanol. The solution was heated under reflux for 15 min. and then cooled. The resultant gray precipitate was separated, washed successively with ethanol, water and hexane and then dried in vacuo. Yield 1.3 g (70% based on RuCl₃.3H₂O).

The crude precipitate was dissolved in minimum volume of warm benzene and the solution was filtered and passed through a 9 x 1" column of activated neutral alumina. The benzene elute was diluted with methanol, concentrated under vacuum and set aside to crystallize at 0°. Crystals of pure RuH₂(CO)(PPh₃)₃ were filtered, washed with hexane and dried in vacuo. White flaky microcrystals of [RuH₂(CO)(PPh₃)₃] melted at 160-162° in air. It is moderately soluble in benzene, chloroform and dichloromethane.

Several new complexes were prepared from [RuH₂(CO)(PPh₃)₃]
by the replacement of hydrido hydrogen as shown in the following reactions.

1. Preparation of \([\text{RuH}((\text{CO})\text{O}_2\text{CCH})\text{PPh}_3]_2\).  

A suspension of \([\text{RuH}_2((\text{CO})\text{PPh}_3)_3]\) (0.91 g, 1 mmol) in (15 ml) 2-methoxyethanol and formic acid (excess, 1.5 ml) was heated under reflux till a clear yellow solution was obtained (2 h). Methanol (10 ml) was added to initiate separation of a white microcrystalline solid which was filtered, washed successively with methanol, water and hexane and dried in vacuo. M.p. 172°. Yield 0.24 g (33%).

2. Preparation of \([\text{RuH}((\text{CO})\text{O}_2\text{CCH}_3)\text{PPh}_3]_2\)^2.  

\([\text{RuH}_2((\text{CO})\text{PPh}_3)_3]\) (0.91 g, 1 mmol) was suspended in 2-methoxyethanol (15 ml) and refluxed. To the boiling suspension was added glacial acetic acid (1.5 ml), and the refluxing was continued for 15 min. during which the mixture became clear and subsequently precipitation commenced. Methanol (20 ml) was then added and after cooling the solution the product separated out was filtered, washed successively with methanol, water and again with methanol and dried in vacuo. The white crystals obtained weighed 0.49 g (70%). M.p. 190°.

3. Preparation of \([\text{RuH}((\text{CO})\text{O}_2\text{CCH}_2\text{CH}_3)\text{PPh}_3]_2\).  

To a boiling suspension of \([\text{RuH}_2((\text{CO})\text{PPh}_3)_3]\) (0.91 g, 1
mmol) in 2-methoxyethanol (15 ml) was added propionic acid (excess, 1.5 ml). The refluxing was continued for a total of 30 min. to get a clear yellow solution. Methanol (20 ml) was added and the mixture was allowed to cool when a white crystalline solid formed which was filtered, washed repeatedly with methanol, water and methanol and finally with hexane and dried in vacuo. M.p. 188°. Yield 0.46 g (64%).

4. Preparation of [RuH(CO)[O₂C(CH₂)₂CH₃](PPh₃)₂].

Butyric acid (excess, 1.5 ml) was added to a boiling suspension of [RuH₂(CO)(PPh₃)₃] (0.91 g, 1 mmol) in 2-methoxyethanol (15 ml). It was refluxed for 45 min. during which a clear orange-yellow solution was obtained. It was cooled and methanol (10 ml) added. The white crystalline product formed was filtered and washed with methanol and finally with hexane and dried in vacuo. M.p. 179°. Yield 0.43 g (62%).

5. Preparation of [RuH(CO)(O₂CC₆H₅)(PPh₃)₂].

A boiling suspension of (0.91 g, 1 mmol) of [RuH₂(CO)(PPh₃)₃] in (15 ml) 2-methoxyethanol was treated with benzoic acid (0.6 g, 5 mmol). After 1 h. refluxing, a clear lemon yellow solution was obtained and subsequently precipitation commenced on addition of methanol (15 ml). On slow cooling of the solution, a white microcrystalline product separated. This was
filtered, repeatedly washed with methanol and dried in vacuo. M.p. 203°. Yield 0.58 g (75%).

6. Preparation of [RuH(CO)(O$_2$C$_6$H$_4$CH$_3$)(PPh$_3$)$_2$].

A suspension of carbonyldihydridotris(triphenylphosphine) ruthenium(II) (0.91 g, 1 mmol) in 2-methoxyethanol (15 ml) and p-toluic acid (0.68 g, 5 mmol) was heated under reflux till a clear yellow solution was obtained (2 h). Methanol (10 ml) was added to initiate the separation of a white microcrystalline solid which was filtered, washed successively with water, methanol and hexane and dried in vacuo. M.p. 217°. Yield 0.56 g (71%).

7. Preparation of [RuH(CO)(O$_2$C$_6$H$_4$OCH$_3$)(PPh$_3$)$_2$].

[RuH$_2$(CO)(PPh$_3$)$_3$] (0.91 g, 1 mmol) was suspended in 2-methoxyethanol (15 ml) and refluxed. To the boiling suspension was added p-methoxybenzoic acid (0.76 g, 5 mmol) and refluxing was continued for 30 min. during which the mixture became clear and subsequently precipitation commenced. Methanol (20 ml) was added and after cooling the solution, the product separated out was filtered, washed successively with methanol, water and methanol, and dried in vacuo. The white microcrystals thus obtained was weighed. M.p. 210°. Yield 0.58 g (73%).
4.3 INSERTION OF ACRYLONITRILE INTO Ru-H BOND OF RUTHENIUM(II) CARBOXYLATES.

1. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CCH}_3)(\text{CH}(\text{CN})\text{CH}_3)(\text{PPh}_3)_2]\).

To a solution of \([\text{RuH}(\text{CO})(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_2]\) (0.356 g, 0.5 mmol) in benzene (50 ml) was added acrylonitrile (1.5 ml). The mixture was stirred at room temperature for 24 h. and the clear yellow solution was then concentrated to one third volume and set aside. The yellow microcrystals separated were washed with hexane and dried in vacuo. M.p. 185°. Yield 0.2 g (52%).

2. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{CH}(\text{CN})\text{CH}_3)(\text{PPh}_3)_2]\).

To a benzene solution (50 ml) of the complex \([\text{RuH}(\text{CO})(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{PPh}_3)_2]\) (0.363 g, 0.5 mmol) an excess of acrylonitrile (1.5 ml) was added with stirring. The mixture was stirred at ambient temperature for 24 h. until the liquid became clear. The solution was evaporated to 2 ml and layered with hexane to get an yellow shining microcrystalline solid. It was filtered, washed with hexane and dried in vacuo. M.p. 222°. Yield 0.19 g (49%).

3. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CH})(\text{CH}(\text{CN})\text{CH}_3)(\text{PPh}_3)_2]\).

A solution of \([\text{RuH}(\text{CO})(\text{O}_2\text{CH})(\text{PPh}_3)_2]\) (0.199 g, 2.5 mmol) in 50 ml benzene was treated with an excess of acrylonitrile (1.5 ml) and stirred for 24 h. at room temperature. The clear light yellow solution was concentrated to a small volume, layered
with hexane and kept aside for crystallization. The pale yellow crystalline solid was filtered, washed with hexane and dried in vacuo. M.p. 184°. Yield 0.06 g (35%).

4. Preparation of $[\text{Ru(CO)}(\text{O}_2\text{C(CH}_2)_2\text{CH}_3)\{\text{CH(CN)CH}_3\}\text{(PPh}_3)_2]$.

An excess of acrylonitrile (1.5 ml) was added to the colorless solution of $[\text{RuH(CO)}(\text{O}_2\text{C(CH}_2)_2\text{CH}_3)(\text{PPh}_3)_2]$ (0.37 g, 0.5 mmol) in benzene (50 ml). It was stirred at ambient temperature for 20 h. until the solution became lemon yellow. The solution was concentrated to 3 ml. Light yellow crystalline product was obtained by slow evaporation of benzene / hexane mixture. Supernatant solution was decanted, solid washed with hexane and dried in vacuo. M.p. 168°. Yield 0.22 g (55%).

5. Preparation of $[\text{Ru(CO)}(\text{O}_2\text{C}_6\text{H}_5)\{\text{CH(CN)CH}_3\}\text{(PPh}_3)_2]$.

A solution of $[\text{RuH(CO)}(\text{O}_2\text{C}_6\text{H}_5)(\text{PPh}_3)_2]$ (0.387 g, 0.5 mmol) in 50 ml benzene was treated with an excess of acrylonitrile and (1.5 ml) stirred for 24 h. at room temperature. The clear light yellow solution was concentrated to 5 ml and diluted with 2 to 3 ml of hexane. After slow cooling, an yellow crystalline complex separated. It was filtered off, washed with hexane and dried in vacuo. M.p. 177°. Yield 0.23 g (57%).
6. Preparation of $[\text{Ru}(\text{CO})(\text{O}_2\text{C}_6\text{H}_4\text{CH}_3)\{\text{CH(\text{CN})CH}_3\}(\text{PPh}_3)_2]$.

To a solution of $[\text{RuH}(\text{CO})(\text{O}_2\text{C}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2]$ (0.387 g, 0.5 mmol) in benzene (50 ml) was added acrylonitrile (1.5 ml). The mixture was stirred at room temperature for 24 h. and the clear yellow solution was then concentrated to one third volume. A few drops of hexane was added and set aside. The yellow microcrystals that separated were washed with hexane and dried in vacuo. M.p. 152°. Yield 0.25 g (59%).

7. Preparation of $[\text{Ru}(\text{CO})(\text{O}_2\text{C}_6\text{H}_4\text{OCH}_3)\{\text{CH(\text{CN})CH}_3\}(\text{PPh}_3)_2]$.

An excess (1.5 ml) of acrylonitrile was added to the colorless solution of $[\text{RuH}(\text{CO})(\text{O}_2\text{C}_6\text{H}_4\text{OCH}_3)(\text{PPh}_3)_2]$ (0.402 g, 0.5 mmol) in benzene (50 ml). It was stirred at ambient temperature for 20 h. until the solution became lemon yellow. The solution was concentrated to 3 ml. Light yellow crystalline product was obtained by slow evaporation of benzene in air. Supernatant solution was decanted and the solid was washed with hexane and dried in vacuo. M.p. 179°. Yield 0.25 g (60%).
4.4 INSERTION OF SYMMETRIC ACETYLENES INTO Ru-H BOND OF HYDRIDORUTHENIUM(II) CARBOXYLATES

1. Preparation of [Ru(CO)(O_2CCH_3)(PPh_3)_2(HC=CH_2)]

Acetylene was bubbled through a benzene (25 ml) solution of [RuH(CO)(O_2CCH_3)(PPh_3)_2] (0.7 g, 1 mmol) at room temperature for 10 min., heated to reflux temperature and the bubbling was continued for a further 30 min. The resulting clear solution was concentrated to a small volume, cooled overnight to give white crystalline solid which was filtered, washed with hexane and dried in vacuo. M.p. 228°. Yield 0.35 g (49%).

2. Preparation of [Ru(CO)(O_2CC_2H_5)(PPh_3)_2(HC=CH_2)]

To a benzene solution of [RuH(CO)(O_2CC_2H_5)(PPh_3)_2] (0.72 g, 1 mmol, in 25 ml) acetylene was bubbled at room temperature for 15 min. Then it was continued for another 30 min. with stirring and mild heating. The resulting clear pale yellow solution was concentrated to ~ 3 ml and cooled to get white crystalline solid which was washed with hexane and dried in vacuo. M.p. 215°. Yield 0.30 g (42%).

3. Preparation of [Ru(CO)(O_2CC_3H_7)(PPh_3)_2(HC=CH_2)]

[RuH(CO)(O_2CC_3H_7)(PPh_3)_2] (0.74 g, 1 mmol) was dissolved in benzene (25 ml). To that acetylene gas bubbled at room temperature with stirring for 10 min. Then bubbling was continued
for another 45 min. at refluxing temperature. The clear colorless solution was concentrated to a small volume and a few drops of hexane was added. The mixed solution was cooled overnight to yield white microcrystalline product. It was filtered, washed with hexane and dried in vacuo. M.p. 185°. Yield 0.33 g (46%).

4. Preparation of \([\text{Ru(CO)}(\text{O}_2\text{C}_{6}\text{H}_5)(\text{PPh}_3)_2(\text{HC}=\text{CH}_2)]\)

Acetylene was bubbled through a benzene solution (25 ml) of \([\text{RuH(CO)}(\text{O}_2\text{C}_{6}\text{H}_5)(\text{PPh}_3)_2] (0.7 g, 1 \text{ mmol})\) at room temperature for 10 min. and the bubbling was continued for a 30 min. at refluxing temperature. The resulting clear yellow solution was concentrated to a small volume, cooled overnight to get a white crystalline solid, which was washed with hexane and dried in vacuo. M.p. 206°. Yield 0.49 g (67%).

5. Preparation of \([\text{Ru(CO)}(\text{O}_2\text{C}_{6}\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{HC}=\text{CH}_2)]\)

To a benzene (25 ml) solution of \([\text{RuH(CO)}(\text{O}_2\text{C}_{6}\text{H}_4\text{CH}_3)(\text{PPh}_3)_2] (0.7 g, 1 \text{ mmol})\), acetylene was bubbled at room temperature for 15 min. Then it was continued for further 30 min. with stirring and refluxing. The resulting clear pale yellow solution was concentrated to a small volume and cooled to get a white crystalline solid, which was washed with hexane and dried in vacuo. M.p. 214°. Yield 0.39 g (54%).
6. Preparation of \([\text{Ru(CO)(O}_2\text{CC}_6\text{H}_4\text{OCH}_3)(\text{PPh}_3)_2(\text{HC=CH}_2)]\)

\([\text{RuH(CO)(O}_2\text{CC}_6\text{H}_4\text{OCH}_3)(\text{PPh}_3)_2]\) (0.80 g, 1 mmol) was dissolved in benzene (25 ml) and acetylene gas was bubbled at room temperature with stirred for 10 min. Then bubbling was continued for 45 min. at refluxing temperature. Clear colorless solution was concentrated to a small volume and a few drops of hexane was added. The solution was cooled overnight to yield white microcrystalline product. It was filtered, washed with hexane and dried in vacuo. M.p. 216°. Yield 0.42 g (58%).

7. Preparation of \([\text{Ru(CO)(O}_2\text{CC}_3)(\text{PPh}_3)_2(\text{PhC=CHPh})]\)

A mixture of diphenylacetylene (0.89 g, 5 mmol) and \([\text{RuH(CO)(O}_2\text{CC}_3)(\text{PPh}_3)_2]\) (0.71 g, 1 mmol) in freshly distilled benzene (25 ml) was refluxed for 6 h. to give a clear orange-yellow solution. It was concentrated to ~2 ml and layered with hexane under nitrogen to give light yellow crystals which were filtered, washed with diethyl ether and hexane and dried. M.p. 185°. Yield 0.48 g (55%).

8. Preparation of \([\text{Ru(CO)(O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2(\text{PhC=CHPh})]\)

A solution of diphenylacetylene (0.89 g, 5 mmol) and \([\text{RuH(CO)(O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2]\) (0.73 g, 1 mmol) in benzene (25 ml) was heated under reflux for 6 h. After cooling the resultant yellow solution to room temperature, it was filtered to remove any solid impurity formed. The clear yellow filtrate was concentrated to
5 ml under reduced pressure. A few drops of hexane was added and then kept aside for slow crystallization. After about 10 h., a yellow microcrystalline complex separated, which was washed with hexane and dried in vacuo. M.p. 198°. Yield 0.33 g, (38%).

9. Preparation of [Ru(CO)(O₂CC₃H₇)(PPh₃)₂(PhC=CHPh)].

To a solution of [RuH(CO)(O₂CC₃H₇)(PPh₃)₂] (0.74 g, 1 mmol) in dried and distilled benzene (25 ml), phenylacetylene (0.87 g, 5 mmol) was added. The mixture was refluxed for 6 h. to obtain a clear light yellow solution. It was concentrated to about 4 ml under reduced pressure and a few drops of hexane added to initiate the separation of solid. After slow cooling for ~ 6 h. a yellowish microcrystalline solid separated was filtered, washed with hexane and dried under vacuo. M.p. 229°. Yield 0.55 g, (63%).

10. Preparation of [Ru(CO)(O₂CC₆H₅)(PPh₃)₂(PhC=CHPh)]

A mixture of diphenylacetylene (0.89 g, 5 mmol) and [RuH(CO)(O₂CC₆H₅)(PPh₃)₂] (0.77 g, 1 mmol) in freshly distilled benzene (25 ml) was refluxed for 6 h. to give a clear orange-yellow solution. It was concentrated to 2 ml and layered with hexane to yield light yellow crystals which were filtered, washed with hexane and diethyl ether and dried in vacuo. M.p. 247°. Yield 0.33 g (39%).
11. Preparation of [Ru(CO)(O2CC6H4CH3)(PPh3)2(PhC=CHPh)]

A solution of diphenylacetylene (0.89 g, 5 mmol) and [RuH(CO)(O2CC6H4CH3)(PPh3)2] (0.78 g, 1 mmol) in benzene (25 ml) was heated reflux for 10 h. After cooling the resultant clear yellow solution to room temperature and filtering to remove the suspended solid particles, the clear filtrate was concentrated to ~ 1/3 of its original volume. A few drops of hexane was added and then kept aside for slow crystallization. After about 10 h., a yellow microcrystalline solid separated. The supernant solution was decanted and the solid was washed with hexane and dried in vacuo. M.p. 189°. Yield 0.21 g (24%).

12. Preparation of [Ru(CO)(O2CC6H4OCH3)(PPh3)2(PhC=CHPh)]

To a solution of [RuH(CO)(O2CC6H4OCH3)(PPh3)2] (78 g, 1 mmol) in distilled benzene (25 ml) was added diphenylacetylene (0.89 g, 5 mmol) and the resulting reaction mixture was heated for 6 h., to get a clear yellow solution. It was concentrated to a small volume and layered with hexane. After slow cooling at room temperature the yellow microcrystalline solid separated. It was washed several times with hexane and dried in vacuo. M.p. 210°. Yield 0.49 g (57%).
4.5 INSERTION OF PHENYLACETYLENE INTO Ru-H BOND OF [RuH(CO)(O2CR)(PPh3)2]

1. Preparation of [Ru(CO)(O2CC6H5)(PPh3)2(HC=CHPh)]

Phenylacetylene (0.5 ml, excess) was added to a benzene solution of [RuH(CO)(O2CC6H5)(PPh3)2] (0.77 g, 1 mmol) (25 ml) and the mixture was stirred at ambient temperature for 24 h. The resulting clear yellow solution was concentrated and cooled to give bright yellow crystals. M.p. 214°. Yield 0.55 g (71%).

2. Preparation of [Ru(CO)(O2CC6H4CH3)(PPh3)2(HC=CHPh)]

To the solution of [RuH(CO)(O2CC6H4CH3)(PPh3)2] (0.78 g, 1 mmol) in freshly distilled benzene (25 ml) was added an excess of phenylacetylene (0.5 ml). The reaction mixture was stirred at ambient temperature for about 24 h. The clear orange-yellow solution resulted was concentrated and kept aside for crystallization. After 5 h. beautiful yellow shining crystals separated were washed with hexane and dried in vacuo. M.p. 210°. Yield 0.28 g (36%).

3. Preparation of [Ru(CO)(O2CC6H4OCH3)(PPh3)2(HC=CHPh)]

An excess of phenylacetylene (0.5 ml) and [RuH(CO)(O2CC6H4OCH3)(PPh3)2] (0.80 g, 1 mmol) in 25 ml freshly distilled benzene were stirred at room temperature for about 22 h. during which the colorless solution changed to orange yellow. The clear solution was concentrated to ~ 1/3 volume and kept
aside for crystallization. Bright yellow crystalline solid separated was washed with hexane and dried in vacuo. M.p. 193°. Yield 0.59 g (75%).

4. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_2\{\text{C}(\text{C}≡\text{CPh})=\text{CHPh}\}]\)

Phenylacetylene (0.5 ml, excess) was added to a benzene (25 ml) solution of \([\text{RuH}(\text{CO})(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_2] (0.71 \text{ g}, 1 \text{ mmol})\) and the mixture was refluxed for 24 h. The resulting clear yellow solution was concentrated to a small volume and diluted with hexane to give a yellow microcrystalline solid. The product was separated and recrystallised from a CH₂Cl₂ / hexane mixture. M.p. 242°. Yield 0.45 g (62%).

5. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2\{\text{C}(\text{C}≡\text{CPh})=\text{CHPh}\}]\)

A mixture of phenylacetylene (0.5 ml, excess) and \([\text{RuH}(\text{CO})(\text{O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2] (0.72 \text{ g}, 1 \text{ mmol})\) in benzene (25 ml) was heated under reflux to yield a deep yellow solution. A yellow precipitate rapidly deposited on cooling. The precipitate was filtered, washed successively with hexane and recrystallised from CH₂Cl₂ / hexane to yield a bright yellow crystalline solid which was filtered and dried in vacuo. M.p. 218°. Yield 0.62 g (69%).

6. Preparation of \([\text{Ru}(\text{CO})(\text{O}_2\text{CC}_3\text{H}_7)(\text{PPh}_3)_2\{\text{C}(\text{C}≡\text{CPh})=\text{CHPh}\}]\)

\([\text{RuH}(\text{CO})(\text{O}_2\text{CC}_3\text{H}_7)(\text{PPh}_3)_2] (0.74 \text{ g}, 1 \text{ mmol})\) was dissolved in
benzene (25 ml) and phenylacetylene (0.5 ml, excess) was added. The mixture was then heated at reflux temperature for about 20 h. Gradually the color changed to orange yellow. The clear solution was concentrated and cooled to obtain bright yellow microcrystalline solid. The solid was filtered washed with four times with 10 ml portions of hexane and dried in vacuum. M.p. 212°. Yield 56 g (63%).

7. Preparation of $[\text{Ru} (\text{CO})(\text{O}_2 \text{C}_6 \text{H}_5)(\text{PPh}_3)_2 \{\text{C}(\text{C} \equiv \text{CPh})=\text{CHPh}]$]

Phenylacetylene (0.5 ml, excess) was added to a benzene (25 ml) solution of $[\text{RuH} (\text{CO})(\text{O}_2 \text{C}_6 \text{H}_5)(\text{PPh}_3)_2]$ (0.77 g, 1 mmol) (25 ml) and the mixture was refluxed for 24 h. The resulting clear yellow solution was concentrated to a small volume and layered with hexane. After slow cooling, yellow shining crystals separated were filtered, washed with hexane and dried in vacuo. M.p. 243°. Yield 0.67 g (76%).

8. Preparation of $[\text{Ru} (\text{CO})(\text{O}_2 \text{C}_6 \text{H}_4 \text{CH}_3)(\text{PPh}_3)_2 \{\text{C}(\text{C} \equiv \text{CPh})=\text{CHPh}]$]

Phenylacetylene (0.5 ml, excess) was added to the solution of $[\text{RuH} (\text{CO})(\text{O}_2 \text{C}_6 \text{H}_4 \text{CH}_3)(\text{PPh}_3)_2]$ (0.78 g, 1 mmol) in benzene (25 ml) and the reaction mixture was refluxed for 24 h. The clear greenish yellow solution was concentrated. On cooling to room temperature, a greenish-yellow crystalline solid separated was washed with hexane and dried in vacuo. M.p. 200°. Yield 0.63 g (72%).
8. Preparation of $[\text{Ru}(\text{CO})(\text{O}_2\text{CC}_6\text{H}_4\text{OCH}_3)(\text{PPh}_3)_2]\{\text{C}(\equiv\text{CPh})=\text{CHPh}\}$

Phenylacetylene (0.5 ml, excess) was reacted with $[\text{RuH}(\text{CO})(\text{O}_2\text{CC}_6\text{H}_4\text{OCH}_3)(\text{PPh}_3)_2]$ (0.80 g, 1 mmol) in refluxing benzene (25 ml) for 24 h. The clear orange yellow solution obtained was concentrated to 1/3 of its original volume and 2-3 drops of hexane was added and cooled to 0°. The yellow crystalline solid obtained was recrystallised from $\text{CH}_2\text{Cl}_2$ / hexane mixture. and dried in vacuo. M.p. 216°. Yield 0.52 g (59%).

4.6 INSERTION OF PHENYLACETYLENE INTO Ru-H BOND OF CHELATED HYDRIDORUTHENIUM(II) COMPLEXES

1. Preparation of $[\text{Ru}(\text{CO})(\text{PyO})(\text{PPh}_3)_2](\text{HC}=\text{CHPh})$]

To a solution of $[\text{RuH}(\text{CO})(\text{PyO})(\text{PPh}_3)_2]^3$ (0.74 g, 1 mmol) in benzene (50 ml) was added a stoichiometric amount of $\text{PhC}≡\text{CH}$ (0.102 g, 1 mmol). The reaction mixture was boiled under reflux for 2h. when the pale yellow solution changed to dark yellow. It was then evaporated to dryness and the yellow solid obtained was dissolved in methylenechloride (3 ml) and layered with hexane to get yellow crystalline solid. M.p. 184°. Yield 0.52 g (62%).

2. Preparation of $[\text{Ru}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2](\text{HC}=\text{CHPh})$

$[\text{RuH}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2]$ (0.76 g, 1 mmol) was dissolved in benzene (50 ml), mixed with phenylacetylene (0.102 g, 1 mmol) and refluxed for 3 h. during which the color of the solution turned
orange. The contents were concentrated to about 4 ml and kept for crystallization at ambient temperature for 12 h. The pale yellow crystals separated were collected, washed with hexane and dried in vacuo. M.p. 182°. Yield 0.50 g (59%).

3. Preparation of \([\text{Ru}(\text{CO})(\text{Acac})(\text{PPh}_3)_2(\text{HC}=\text{CHPh})]\)

\([\text{RuH}(\text{CO})(\text{Acac})(\text{PPh}_3)_2]_4\) (0.75 g, 1 mmol) and phenylacetylene (0.102 g, 1 mmol) were mixed in benzene (50 ml). The mixture was refluxed for 4 to 5 h. The clear pale yellow solution obtained was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$. To the CH$_2$Cl$_2$ solution a few drops of hexane were added and the mixture was kept for crystallization at ambient temperature. The pale yellow microcrystalline solid separated was filtered, washed with hexane and dried in vacuo. M.p. 175°. Yield 0.54 g (63%).

4. Preparation of \([\text{Ru}(\text{CO})(\text{Ba})(\text{PPh}_3)_2(\text{HC}=\text{CHPh})]\)

A mixture of \([\text{RuH}(\text{CO})(\text{Ba})(\text{PPh}_3)_2]\) (0.81 g, 1 mmol) and phenylacetylene (0.102 g, 1 mmol) in benzene (50 ml) were refluxed for 4 h. The resulting orange colored solution was filtered and concentrated to ~ 1/3 of its original volume. A few drops of hexane were added and upon cooling at room temperature, a yellow crystalline solid separated. It was filtered, washed with hexane and dried in vacuo. M.p. 154°. Yield 0.50 g (55%).
5. Preparation of \([\text{Ru(CO)}(\text{Acph})(\text{PPh}_3)_2(\text{HC} = \text{CHPh})] \)

Phenylacetylene (0.102 g, 1 mmol) was added to the solution of \([\text{RuH(CO)}(\text{Acph})(\text{PPh}_3)_2]^5 \) (0.78 g, 1 mmol) in benzene (50 ml). The reaction mixture was refluxed for 3 h., during which color turned to orange yellow. It was concentrated to about 4 ml and layered with hexane. The yellow solid which settled on cooling was filtered, washed thoroughly with hexane and dried in vacuo. M.p. 152°. Yield 0.45 g (51%).

6. Preparation of \([\text{Ru(CO)}(\text{Prop})(\text{PPh}_3)_2(\text{HC} = \text{CHPh})] \)

To a solution of \([\text{RuH(CO)}(\text{Prop})(\text{PPh}_3)_2] \) (0.80 g, 1 mmol) in benzene (50 ml) was added a stoichiometric amount of PhC=CH (0.102 g, 1 mmol). The reaction mixture was boiled under reflux for 6h. when the pale yellow solution changed to dark yellow. It was evaporated to dryness and the yellow solid obtained was dissolved in methylenechloride (3 ml) and layered with hexane to get yellow crystalline solid. M.p. 157°. Yield 0.38 g (43%).

7. Preparation of \([\text{Ru(CO)}(\text{Benz})(\text{PPh}_3)_2(\text{HC} = \text{CHPh})] \)

\([\text{RuH(CO)}(\text{Benz})(\text{PPh}_3)_2] \) (0.851 g, 1 mmol) was dissolved in benzene (50 ml), mixed with phenylacetylene (0.102 g, 1 mmol) and refluxed for 3 h., during which the color turned orange yellow. The contents were concentrated to about 4 ml and kept for crystallization at ambient temperature for 12 h. The pale yellow crystals separated were collected, washed with hexane and dried.
in vacuo. M.p. 176°. Yield 0.46 g (48%).

8. Preparation of $[\text{Ru(CO)}(\text{MeBenz})(\text{PPh}_3)_2(\text{HC=CHPh})]$ 

$[\text{RuH(CO)}(\text{MeBenz})(\text{PPh}_3)_2]$ (0.88 g, 1 mmol) and phenylacetylene (0.102 g, 1 mmol) were mixed in benzene (50 ml). The mixture was refluxed for 4 to 5 h. The clear pale yellow solution was evaporated to dryness and extracted with CH$_2$Cl$_2$, a few drops of hexane were added and the mixture was kept for crystallization at ambient temperature. The yellowish microcrystalline solid separated was filtered out, washed with hexane and dried in vacuo. M.p. 180°. Yield 0.49 g (50%).

9. Preparation of $[\text{Ru(CO)}(\text{PyO})(\text{PPh}_3)_2\{\text{C(=CPh)(=CHPh)}\}]$

Phenylacetylene (0.5 ml, excess) was added to a benzene (50 ml) solution of $[\text{RuH(CO)}(\text{PyO})(\text{PPh}_3)_2]$ (0.74 g, 1 mmol) and the mixture was refluxed for 24 h. The resulting clear yellow solution was concentrated to a small volume and diluted with hexane to give a precipitate of yellow microcrystals. The product was recrystallised from a CH$_2$Cl$_2$ / hexane mixture. M.p. 194°. Yield 0.304 g (32%).

10. Preparation of $[\text{Ru(CO)}(\text{MePyO})(\text{PPh}_3)_2\{\text{C(=CPh)(=CHPh)}\}]$

Phenylacetylene (0.5 ml, excess) was reacted with $[\text{RuH(CO)}(\text{MePyO})(\text{PPh}_3)_2]$ (0.762 g, 1 mmol) in refluxing benzene
(50 ml) for 20 h. The clear yellow solution was concentrated to ~1/3 volume and to it 2/3 drops of hexane was added and cooled to 0°. The yellow crystalline solid formed was filtered, washed with hexane and dried in vacuo and weighed. M.p. 124°. Yield 0.47 g (49%).

11. Preparation of [Ru(CO)(Acac)(PPh3)2{C(C=CHPh)=CHPh}]

To a solution of [RuH(CO)(Acac)(PPh3)2] (0.753 g, 1 mmol) in freshly distilled benzene (50 ml), phenylacetylene (0.5 ml, excess) was added. The reaction mixture was refluxed for 20 h. The pale yellow solution was concentrated to 3 ml and kept for crystallization. The greenish yellow microcrystalline solid separated, was filtered, washed with hexane and dried in vacuo. M.p. 184°. Yield 0.41 g (43%).

12. Preparation of [Ru(CO)(Ba)(PPh3)2{C(=CPh)=CHPh}]

Phenylacetylene (0.5 ml, excess) and [RuH(CO)(Ba)(PPh3)2] (0.81 g, 1 mmol) were refluxed together in benzene (50 ml) for 24 h. to obtain a clear orange yellow solution. Excess of benzene was removed in vacuo and the contents were cooled to obtain an orange yellow microcrystalline product which was washed with hexane and dried. M.p. 113°. Yield 0.37 g (36%).

13. Preparation of [Ru(CO)(Acph)(PPh3)2{C(=CPh)=CHPh}]

[RuH(CO)(Acph)(PPh3)2] (0.789 g, 1 mmol) and phenylacetylene
(0.5 ml, excess) were refluxed in freshly distilled benzene (50 ml). The contents were concentrated at reduced pressure to obtain a fine yellow crystalline powder. It was recrystallised from CH₂Cl₂ / hexane 1:1 mixture. The bright yellow solid was washed with hexane and dried in vacuo at room temperature. M.p. 112°. Yield 0.39 g (39%).

14. Preparation of [Ru(CO)(Prop)(PPh₃)₂{(C≡CPh)=CHPh}]

Phenylacetylene (0.5 ml, excess) was added to a benzene solution of [RuH(CO)(Prop)(PPh₃)₂] (0.80 g, 1 mmol) in 50 ml and the mixture was refluxed for 24 h. The resulting clear yellow solution was concentrated to a small volume and diluted with hexane to give a precipitate of yellow microcrystals. The product was recrystallised from a CH₂Cl₂ / hexane mixture. M.p. 179°. Yield 0.43 g (43%).

15. Preparation of [Ru(CO)(Benz)(PPh₃)₂{(C≡CPh)=CHPh}]

[RuH(CO)(Benz)(PPh₃)₂] (0.851 g, 1 mmol) and phenylacetylene (0.5 ml, excess) were refluxed in freshly distilled benzene (50 ml). The contents were concentrated at reduced pressure to obtain a yellow fine crystalline powder. It was recrystallised from CH₂Cl₂ / hexane 1:1 mixture. The bright yellow solid was washed with hexane and dried in vacuo at room temperature. M.p. 238°. Yield 0.43 g (41%).
16. Preparation of \([\text{Ru}(\text{CO})(\text{MeBenz})(\text{PPh}_3)_2\{\text{C}(\text{C}=\text{CPh})=\text{CHPh}\}]\)

Phenylacetylene (0.5 ml, excess) was reacted with \([\text{RuH}(\text{CO})(\text{MeBenz})(\text{PPh}_3)_2]\) (0.88 g, 1 mmol) in refluxing benzene (50 ml) for 20 h. The clear yellow solution was concentrated to ~1/3 volume and to it a few drops of hexane were added and cooled to 0°. The yellow crystalline solid formed was filtered, washed with hexane and dried in vacuo and weighed. M.p. 205°. Yield 0.32 g (30%).

4.7 SUBSTITUTED TRIAZOLES AND THIADIAZOLES USED FOR THE STUDIES

1. 3,4-Substituted 1,2,4-triazole-5-thione

a. 3,4-Dimethyl-1,2,4-triazole-5-thione \(\text{H}[\text{MMTT}]\)

This ligand was prepared by adopting the procedure reported earlier. To a solution of acetyl hydrazide (7.4 g, 0.1 mol), dissolved in absolute alcohol (70 ml), methylisothiocyanate (7.3 g, 0.1 mol) was added and refluxed on a waterbath for 8 h. At the end of the reflux period the alcohol was evaporated under vacuum to obtain a yellow viscous liquid. A 10% \(\text{Na}_2\text{CO}_3\) solution was added to render it alkaline and again refluxed for 7 h. to complete cyclization. Conc. HCl was added slowly to make the reaction mixture acidic and the fluffy solid separated was filtered, washed with water and was recrystallised from alcohol. The pale yellow solid was soluble in most of the organic solvents except n-hexane. M.p. 210°. Yield 5.80 g (45%).
b. 3-Methyl-4-phenyl-1,2,4-triazole-5-thione \( \text{H[MMM]} \)

A solution of acetyl hydrazide (7.4 g, 0.1 mol) in absolute ethanol (80 ml) was added to a solution of phenylisothiocyanate (13.5 g, 0.1 mol) in ethanol (50 ml). The mixture was heated on a waterbath for 7 h. and the alcohol was removed under vacuum. The substituted thiosemicarbazide formed was refluxed with a 10% \( \text{Na}_2\text{CO}_3 \) solution for 7 h. and then acidified with conc. \( \text{HCl} \) to obtain the cyclized product. The crude yellow solid separated was filtered and recrystallised from absolute alcohol to yield a white crystalline solid, which was filtered, washed and dried in vacuo. M.p. 221°. Yield 10.5 g (55%).

c. 3-Formyl-4-phenyl-1,2,4-triazole-5-thione \( \text{H[HPP]} \)

This new triazole was prepared by refluxing formyl hydrazide (3.0 g, 0.05 mol) with phenylisothiocyanate (6.7 g, 0.05 mol) in absolute alcohol (80 ml) for 7 h. The alcohol was removed in vacuum and the yellow viscous liquid was made alkaline with a 10% \( \text{Na}_2\text{CO}_3 \) solution and again refluxed for 6 h. to complete cyclization. Conc. \( \text{HCl} \) was added slowly to make it acidic upon which white solid separated, which was filtered, dried and recrystallised from absolute alcohol. The product was separated and dried in vacuo. M.p. 166°. Yield 3.01 g (34%).

d. 3-Phenyl-4-methyl-1,2,4-triazole-5-thione \( \text{H[PMM]} \)

Benzoyl hydrazide (6.8 g, 0.05 mol) was dissolved in
absolute alcohol (100 ml) and to it methylisothiocyanate (3.65 g, 0.05 mol) was added and refluxed on waterbath for 7-8 h. The ethanol was removed under reduced pressure and a 10% Na₂CO₃ solution was added to the yellow viscous liquid till alkaline. It was further refluxed for 7 h. On cooling, conc. HCl was added cautiously till acidic. The yellow crude solid separated was filtered, dried and then recrystallised from absolute alcohol. The product was dried in vacuo at 60°. M.p. 167°. Yield 5.4 g (57%).

2. 5-Alkylthio-1,3,4-thiadiazoline-2-thione

a. 5-Methylthio-1,3,4-thiadiazoline-2-thione H[MTD]

This was prepared by a slight modification of the general procedure described in the literature. 2,5-Dimercapto-1,3,4-thiadiazole (6.0 g, 0.04 mol) was dissolved in 70 ml hot alcohol and to it potassium hydroxide (2.24 g, 0.04 mol) in 50 ml alcohol was added. The mixture was heated on waterbath for 10 minutes and cooled to room temperature. Methyl iodide (5.68 g, 0.04 mol) was added to it and the mixture was again gently refluxed on waterbath for 5 h. The deep colored solution formed was cooled to room temperature and the precipitated KI was filtered off. The solution was evaporated to dryness and the crude brown product was recrystallised from benzene. M.p. 135°. Yield 4.0 g (50%).
b. 5-Isopropylthio-1,3,4-thiadiazole-2-thione  H[IsoprTD]

To a hot solution of 2,5-dimercapto-1,3,4-thiadiazole (4.5 g, 0.03 mol) in 60 ml alcohol, a hot solution of potassium hydroxide (1.68 g, 0.03 mol) in 40 ml alcohol was added. The reaction mixture was refluxed on a waterbath for 15 min. and cooled to room temperature. Isopropyl bromide (3.69 g, 0.03 mol) was added to it and the reaction mixture was again heated gently for 5 h. The dark colored solution formed was cooled to room temperature and the white solid separated was filtered off. The dark filtrate was evaporated completely and the crude product was recrystallised from benzene to get yellowish fluffy solid. M.p. 100°. Yield 2.65 g (46%).

c. 5-Butylthio-1,3,4-thiadiazole-2-thione  H[BuTD]

2,5-Dimercapto-1,3,4-thiadiazole (4.5 g, 0.03 mol) was dissolved in 60 ml hot absolute alcohol. Potassium hydroxide (1.68 g, 0.03 mol) dissolved in 40 ml alcohol was added and the mixture was heated on a waterbath for 10 min. and cooled to room temperature. Butyl iodide (5.52 g, 0.03 mol) was added to it and the mixture was further refluxed gently for 5 h. on water bath. The deep colored solution formed was cooled to room temperature and the KI formed was filtered off. The solution was evaporated to dryness and the crude product was recrystallised from benzene to yield a light colored solid. M.p. 85°. Yield 3.34 g (54%).
4.8 REACTIONS OF FIVE COORDINATED RUTHENIUM(II) COMPLEXES WITH DISUBSTITUTED TRIAZOLES AND THIADIAZOCES

Preparation of five coordinate 16 electron unsaturated ruthenium(II) complexes.

\[ [\text{RuCl(CO)(PPh}_3]^2(\text{HC=CHPh})]^{9}. \]

An excess of phenylacetylene (0.5 ml) was added to a solution of \([\text{RuHCl(CO)(PPh}_3]^3 \) (0.3 g, 0.315 mmol) in \(\text{CH}_2\text{Cl}_2\) (10 ml) when the solution became red. After half an hour stirring, the solution was concentrated and the red solid precipitated by the addition of diethyl ether. It was filtered and recrystallised from a \(\text{CH}_2\text{Cl}_2 / \text{diethyl ether}\) mixture. Yield 0.178 g (70%).

\[ [\text{RuCl(CO)(PPh}_3]^2(\text{PhC=CHPh})]^{9}. \]

An excess of solid PhC=CHPh (0.3 g, 1.5 mmol) was added to a solution of \([\text{RuHCl(CO)(PPh}_3]^3 \) (0.3 g, 0.315 mmol) in \(\text{CH}_2\text{Cl}_2\) (10 ml) until the solution became red and the mixture was refluxed with stirring. After half an hour the solution was concentrated and chromatographed on a Florosil column and eluted with \(\text{CH}_2\text{Cl}_2\). The red-orange solid was isolated by adding hexane to it. The green residue which remained on the column was further eluted with \(\text{CH}_2\text{Cl}_2\), but the solution could not yield solid in sufficient amount for characterization. Recrystallisation of the red solid from \(\text{CH}_2\text{Cl}_2 / \text{diethylether}\) gave crystals suitable for X-ray crystallographic study. Yield 0.205 g (75%).
1. Preparation of [Ru(CO)(MMTT)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}]

To an orange solution of [RuCl(CO)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}] (0.395 g, 0.5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 ml) was added a 5 ml methanolic solution of the sodio derivative of the ligand H[MMTT] (0.076 g, 0.6 mmol). The reaction mixture was stirred for 2 h. at ambient temperature and the resulting yellow solution was concentrated to 2 ml, a few drops of hexane was added to precipitate the product as yellow crystalline solid. M.p. 223°. Yield 0.22 g (52%).

2. Preparation of [Ru(CO)(MPTT)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}]

To a 10 ml CH\textsubscript{2}Cl\textsubscript{2} solution containing [RuCl(CO)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}] (0.395 g, 0.5 mmol) was added a methanolic solution of excess of sodio derivative of H[MPTT] (0.114 g, 0.6 mmol) and stirred. The solution rapidly turned yellow. Stirring was continued for 2 h., solution was then concentrated to 3 ml. and a few drops of hexane was added and kept aside for crystallization. The yellow shining needle shaped crystals separated were filtered and dried in vacuo. M.p. 249°. Yield 0.32 g (67%).

3. Preparation of Ru(CO)(HPTT)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}

To a dichloromethane solution (10 ml) of the complex [RuCl(CO)(HC=CHPh)(PPh\textsubscript{3})\textsubscript{2}] (0.395 g, 0.5 mmol), a slight excess of sodium salt of H[HPTT] (0.106 g, 0.6 mmol), dissolved in
methanol (5 ml), was added with stirring. The solution immediately turned yellow. The stirring was continued for 2 h. The solution was filtered to remove fine suspended particles and the clear yellow solution was evaporated to dryness. The solid product obtained was recrystallised from CH₂Cl₂ / MeOH mixture and dried in vacuo. M.p. 234°. Yield 0.191 g (41%).

4. Preparation of [Ru(CO)(PMTT)(HC=CHPh)(PPh₃)₂]

To a slight excess of sodio derivative of H[PMTT] (0.114 g, 0.6 mmol) in 5 ml methanol, a solution of [RuCl(CO)(HC=CHPh)(PPh₃)₂] (0.395 g, 0.5 mmol) in 10 ml methylene chloride was added with stirring. Immediately the color of the solution changed to yellow. Stirring was continued for 3 h. and the reaction mixture was filtered. The clear yellow solution was concentrated to ~ 3 ml and a few drops of methanol were added. The shining yellow needle shaped crystals separated were filtered and dried in vacuo. M.p. 213°. Yield 0.33 g (70%).

5. Preparation of [Ru(CO)(MTD)(HC=CHPh)(PPh₃)₂]

The sodium salt of H[MTD] (0.092 g, 0.6 mmol) dissolved in 5 ml of methanol was added with stirring to a solution of [RuCl(CO)(HC=CHPh)(PPh₃)₂] (0.395 g, 0.5 mmol) in CH₂Cl₂ (10 ml). The solution turned greenish yellow and stirring was continued until the color changed to yellow (2 h.). The solution was then concentrated until a yellow precipitate appeared and then to
bring about complete precipitation hexane was added slowly. The solid was filtered and dissolved in CH₂Cl₂. The solution was concentrated and hexane was added to precipitate the pure product. The solid was filtered and dried in vacuo. M.p. 209°. Yield 0.22 g (49%).

6. Preparation of [Ru(CO)(IsoprTD)(HC=CHPh)(PPh₃)₂]

To a dichloromethane solution (10 ml) of the complex [RuCl(CO)(HC=CHPh)(PPh₃)₂] (0.395 g, 0.5 mmol), a slight excess of sodio derivative of H[IsoprTD] (0.115 g, 0.6 mmol) dissolved in methanol (5 ml) was added with stirring. The solution turned greenish yellow and the stirring was continued until the liquid became yellow in color (2 h.). The solution was evaporated in vacuo and residue dissolved in CH₂Cl₂. The fine suspended particles were filtered off and a yellow solid was precipitated by adding hexane to the filtrate. The crystalline complex obtained was further crystallized from CH₂Cl₂/MeOH mixture. M.p. 226°. Yield 0.223 g (48%).

7. Preparation of [Ru(CO)(BuTD)(HC=CHPh)(PPh₃)₂]

To an orange solution of [RuCl(CO)(HC=CHPh)(PPh₃)₂] (0.395 g, 0.5 mmol) in CH₂Cl₂ (10 ml) was added the sodio derivative of the ligand H[BuTD] (0.123 g, 0.6 mmol) in methanol (2 ml). The reaction mixture was stirred for 12 h. at ambient temperature.
The resulting solution was concentrated to 2 ml and a few drops of hexane was added to obtain the product as an yellow crystalline solid. M.p. 211°. Yield 0.185 g (39%).

8. Preparation of [Ru(CO)(MMTT)(PhC=CHPh)(PPh₃)₂]

To a 10 ml of a CH₂Cl₂ solution containing 0.434 g. of [RuCl(CO)(PhC=CHPh)(PPh₃)₂] (0.5 mmol) was added with stirring a small excess of sodio derivative of H[MMTT] (0.076 g, 0.6 mmol) in 5 ml methanol. The solution turned rapidly yellow. Stirring was continued for 2 h., the solution then concentrated to 3 ml and a few drops of hexane were added and kept aside for crystallization. The yellow crystalline solid separated was filtered and dried in vacuo. M.p. 244°. Yield 0.22 g (46%).

9. Preparation of [Ru(CO)(MPTT)(PhC=CHPh)(PPh₃)₂]

To a dichloromethane solution (10 ml) of the complex [RuCl(CO)(PhC=CHPh)(PPh₃)₂] (0.434 g, 0.5 mmol) a slight excess of sodium salt of H[MPTT] (0.114 g, 0.6 mmol), dissolved in methanol (5 ml) was added with stirring. The solution immediately turned yellow. The stirring was continued for 2 h. It was filtered to remove fine suspended particles and the clear solution was evaporated to dryness. The residue was dissolved in CH₂Cl₂ / MeOH mixture, and crystallized product was dried in vacuo. M.p. 216°. Yield 0.22 g (43%).
10. Preparation of $[\text{Ru} (\text{CO})(\text{HPTT})(\text{Ph} = \text{CHPh})(\text{PPh}_3)_2]$ 

A slight excess of sodium salt of H[HPTT] (0.106 g, 0.6 mmol) dissolved in 5 ml of methanol was added with stirring to a solution of $[\text{RuCl} (\text{CO})(\text{Ph} = \text{CHPh})(\text{PPh}_3)_2]$ (0.434 g, 0.5 mmol) in CH$_2$Cl$_2$ (10 ml). The solution turned greenish yellow and the stirring was continued until it became yellow (2 h.) The solution was then concentrated until a yellow precipitate appeared and to bring about complete precipitation, hexane was added slowly. The precipitate filtered off and dissolved in CH$_2$Cl$_2$. The solution was filtered, concentrated and hexane added to complete precipitation of the pure product which was filtered and dried in vacuo. M.p. > 250°. Yield 0.19 g (38%).

11. Preparation of $[\text{Ru} (\text{CO})(\text{PMTT})(\text{Ph} = \text{CHPh})(\text{PPh}_3)_2]$ 

To a slight excess of sodio derivative of H[PMTT] (0.114 g, 0.6 mmol) in 5 ml MeOH, a dark orange solution of $[\text{RuCl} (\text{CO})(\text{Ph} = \text{CHPh})(\text{PPh}_3)_2]$ (0.434 g, 0.5 mmol) in 10 ml methylene chloride was added with stirring. Immediately the color changed to yellow. Stirring was continued for 3 h. and the reaction mixture was filtered. The clear yellow solution was concentrated to ~ 3 ml and a few drops of methanol were added. The shining microcrystalline solid separated was dried in vacuo. M.p. 202°. Yield 0.24 g (47%).
12. Preparation of [Ru(CO)(MTD)(PhC=CHPh)(PPh₃)₂]

An orange solution of [RuCl(CO)(PhC=CHPh)(PPh₃)₂] (0.434 g, 0.5 mmol) in methylene chloride (10 ml) was added to the sodio derivative of the ligand H[MTD] (0.098 g, 0.6 mmol) in methanol (5 ml). The reaction mixture was stirred for 2 h. at ambient temperature. The resulting yellow solution was concentrated to ~3 ml and to that a few drops of hexane were added to obtain the yellow microcrystalline product. M.p. 194°. Yield 0.22 g (45%).

13. Preparation of [Ru(CO)(IsoprTD)(PhC=CHPh)(PPh₃)₂]

To a well stirred 10 ml methylene chloride solution containing 0.434 g (0.5 mmol) of [RuCl(CO)(PhC=CHPh)(PPh₃)₂] was added, an excess of sodio derivative of H[IsoprTD] (0.115 g, 0.6 mmol) in 5 ml methanol. The solution turned rapidly yellow in color. Stirring was continued for 2 h. and solution was then concentrated to 3 ml, a few drops of hexane were added and kept aside for crystallization. The yellow microcrystalline solid separated was filtered and dried in vacuo. M.p. 183°. Yield 0.22 g (43%).

14. Preparation of [Ru(CO)(BuTD)(PhC=CHPh)(PPh₃)₂]

A slight excess of sodio derivative of H[BuTD] (0.123 g, 0.6 mmol) dissolved in 5 ml of methanol was added with stirring to a solution of [RuCl(CO)(PhC=CHPh)(PPh₃)₂] (0.434 g, 0.5 mmol) in methylene chloride (10 ml). The solution turned greenish yellow
and the stirring was continued until it became yellow (2 h.). The solution was then concentrated until a yellow precipitate appeared and to bring out complete precipitation, hexane was added slowly. The precipitate was filtered off and dissolved in methylene chloride. The solution was filtered, concentrated and hexane was added to precipitate the pure product. Dried in vacuo. M.p.198°. Yield 0.22 g (42%).
IR spectra of the compounds were recorded on a Perkin-Elmer 1620 FT-IR spectrophotometer provided with KBr optics.

UV spectra were run on a Shimadzu UV 2101-PC UV / VIS scanning spectrophotometer.

$^1$H NMR spectra were recorded as CDCl$_3$ solutions on a Bruker WH-90 FT spectrophotometer at 90 MHz. $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker MSL-200 or -300 FT spectrophotometer operating at 200 and 300 MHz.

The purity of solvents and liquid ligands was tested on a Shimadzu GC-17 A gas chromatograph (with microprocessor) using suitable columns. Elemental analyses were carried out in the Micro-analysis section of this laboratory.

Molecular weights were determined using Knauer Vapor Pressure Osmometer.

The mass spectra of the ligands were recorded on Finnigan Mat 1020B mass spectrometer.
4.10 REFERENCES