CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL COMPLEXES OF Rh(I), Pd(0), Pt(0) AND Ru(II) WITH N-CARBOETHOXY-4-CHLOROBENZENE AND N-CARBOETHOXY-4-BROMOBENZENE THIOAMIDE LIGANDS

This chapter describes the reactions of [Rh\textsuperscript{I}Cl(EPh\textsubscript{3})\textsubscript{3}], [Pd\textsuperscript{0}(EPh\textsubscript{3})\textsubscript{4}], [Pt\textsuperscript{0}(EPh\textsubscript{3})\textsubscript{4}] (E = P or As), [RuCl\textsubscript{2}(CO)\textsubscript{2}], [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] and [(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}) RuCl(AsPh\textsubscript{3})\textsubscript{2}] with the title ligands Hccet and Hcbt. The Rh(I), Pd(0) and Pt(0) complexes react with the ligands to yield [Rh\textsuperscript{I}Cl(HL)\textsubscript{2} (EPh\textsubscript{3})], [Pd\textsuperscript{0}(HL)\textsubscript{2}(EPh\textsubscript{3})\textsubscript{2}] and [Pt\textsuperscript{0}(HL)\textsubscript{2}(EPh\textsubscript{3})\textsubscript{2}], respectively. [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] gives [RuCl\textsubscript{2}(HL)\textsubscript{2}(PPh\textsubscript{3})]. Similarly the reactions of the ligands with [(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}) RuCl(AsPh\textsubscript{3})\textsubscript{2}] and [RuCl\textsubscript{2}(CO)\textsubscript{2}] led to the formation of the diamagnetic compounds of the type [(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})RuCl(HL)(AsPh\textsubscript{3})] and [RuCl\textsubscript{2}(CO)\textsubscript{2}.(HL)], respectively. These reactions were carried out in dry N\textsubscript{2}
atmosphere. The coordination modes of the ligands have been established on the basis of i.r. spectral data and comparison of reported work.

EXPERIMENTAL

All the chemicals used were either of AnalaR or chemically pure grade. Solvents were dried before use and all the reactions were carried out under dry N₂ atmosphere. The methods of elemental analyses, recording of i.r. and electronic spectra and magnetic measurements have been same as described in previous chapters. Starting compounds [RhCl(EPh₃)₃], [Pd₀(EPh₃)₄], [Pt₀(EPh₃)₄], [RuCl₂(CO)₂], [RuCl₂(PPh₃)₃] and [η⁵-(C₅H₅)RuCl-(AsPh₃)₂] were prepared by literature methods¹-³ and were available from the Research Group of Dr. S.K. Dikshit, I.I.T., Kanpur.

[A] Reactions with N-Carboethoxy-4-chlorobenzene thioamide (Hcct)

(i) Reaction of [RhCl(PPh₃)₃] with Hcct

A solution of [RhCl(PPh₃)₃] (0.46 g, 0.5 mmol) in CH₂Cl₂ (25 ml) was added to a solution of the ligand Hcct (0.16 g, 0.66 mmol) in CH₂Cl₂ (25 ml). The reddish brown solution so obtained was refluxed on a water bath for 15 minutes, and evaporated to dryness. The oily mass thus obtained was dissolved in CH₂Cl₂ (5 ml) and filtered. Petroleum ether (40-60 °C) (20 ml) was added to initiate precipitation and cooled to 0 °C. The yellow complex thus precipitated was separated by centrifugation, washed with petroleum ether and dried \textit{in vacuo}. 
Anal. for [RhCl(Hcct)(PPh₃)]:
Calcd: C, 51.39; H, 3.94; N, 3.16; M, 11.60; S, 7.21;
P, 3.49; Hal, 12.00%.

Found: C, 51.30; H, 3.90; N, 3.05; M, ......; S, 7.20;
P, 3.50; Hal, 12.05%.

(ii) **Reaction of [Pd(PPh₃)₄]** with Hcct

Freshly prepared [Pd(PPh₃)₄] (0.1 g, 0.1 mmol) in CH₂Cl₂ (30 ml) was added to a stirring solution of Hcct (0.073 g, 0.3 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was refluxed for 1-2 hours under dry N₂ atmosphere. The colour of the solution changed from yellow to dark brown, concentrated to ca. half volume under reduced pressure, added petroleum ether (50 ml) (40-60 °C) to give yellow compound, separated by centri-fugation, washed with petroleum ether, and dried in vacuo.

Anal. for [Pd(Hcct)(PPh₃)₂]:
Calcd: C, 60.14; H, 4.47; N, 2.51; M, 9.52; S, 5.73;
P, 5.54; Hal; 6.35%.

Found: C, 60.00; H, 4.50; N, 2.50; M, 9.60; S, 5.80;
P, 5.60; Hal, 6.40%.

(iii) **Reaction of [Pt(PPh₃)₄]** with Hcct

Freshly prepared [Pt(PPh₃)₄] (0.12 g, 0.1 mmol) in CH₂Cl₂ (30 ml) was added to a stirring solution of Hcct (0.073 g, 0.3 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was refluxed for 4-5 hours under dry N₂ atmosphere, concentrated to ca. half volume under reduced pressure, added petroleum ether (60-80 °C) to give orange compound, separated by centri-fugation, washed with petroleum ether and dried in vacuo.
Anal. for \([\text{Pt(Hcct)}_2(\text{PPh}_3)_2]\):
Calcd: C, 55.72; H, 4.15; N, 2.32; M, 16.18; S, 5.31;
P, 5.14; Hal, 5.89%.

Found: C, 55.70; H, 4.28; N, 2.29; M, ....; S, 5.40;
P, 5.20; Hal, 5.94%.

(iv) **Reaction of \([\text{RuCl}_2(\text{Hcct})_2(\text{PPh}_3)_3]\) with Hcct**

50 ml of CH$_2$Cl$_2$ solution containing 0.100 g of \([\text{RuCl}_2(\text{PPh}_3)_3]\) (0.1 mmol) and ligand Hcct (0.025 g, 0.1 mmol) was refluxed under dry N$_2$ for three hours. The resulting solution was concentrated up to almost dryness under reduced pressure, the residue was dissolved in minimum quantity of dichloromethane, followed by an addition of petroleum ether with constant stirring. On standing for 1-2 hours, the precipitate settled down. It was centrifuged, washed several times with petroleum ether and dried \textit{in vacuo}.

Anal. for \([\text{RuCl}_2(\text{Hcct})_2(\text{PPh}_3)_3]\):
Calcd: C, 49.51; H, 3.80; N, 3.04; M, 10.97; S, 6.95;
P, 3.36; Hal, 15.42%.

Found: C, 49.55; H, 3.84; N, 3.10; M, ....; S, 6.85;
P, 3.40; Hal, 15.45%.

(v) **Reaction of \([\text{RuCl}_2(\text{CO})_2]\) with Hcct**

50 ml of methanol solution containing 0.114 g of \([\text{RuCl}_2(\text{CO})_2]\) (0.5 mmol) and ligand Hcct (0.12 g, 0.5 mmol) was refluxed for 5-6 hours. The resulting solution was concentrated up to almost dryness under reduced pressure, the residue was dissolved in minimum quantity of CH$_2$Cl$_2$, followed by an addition of excess (150 ml) petroleum ether with constant stirring. On standing for 1-2 hours, the precipitate settled down. It was centrifuged, washed several times with petroleum and dried \textit{in vacuo}.
(vi) Reaction of $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ with Hect

In about 40 ml of methanol solution containing $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ (0.105 g, 0.25 mmol), 25 ml methanol solution of the ligand Hect (0.085 g, 0.35 mmol) was added under dry N$_2$ atmosphere. The resulting mixture was stirred for 2-3 hours. The resulting solution was concentrated upto dryness under reduced pressure, the residue was dissolved in minimum quantity of CH$_2$Cl$_2$ followed by addition of petroleum ether. On scratching the walls of beaker and allowing to stand for 1-2 hours, the precipitate appears. It was centrifuged, washed several times with petroleum ether and dried in vacuo.

Anal. for $[(\eta^5-C_5H_5)RuCl(Hect)(AsPh_3)]$:
Calcd: C, 52.73; H, 3.99; N, 1.86; M, 13.41; S, 4.26;
As, 9.98; Hal, 9.45%.

Found: C, 52.75; H, 4.00; N, 1.90; M, ......; S, 4.30;
As, ......; Hal, 9.50%.

[B] Reactions with N-Carboethoxy-4-bromobenzene thioamide (Hcbt)

(i) Reaction of [RhCl(PPh$_3)_3$] with Hcbt

A solution of [RhCl(PPh$_3)_3$] (0.46 g, 0.5 mmol) in CH$_2$Cl$_2$ (25 ml) was added to a solution of the ligand Hcbt (0.19 g, 0.66 mmol) in CH$_2$Cl$_2$ (25 ml).
The reddish brown solution so obtained was refluxed on a water bath for 15 minutes and evaporated to dryness. The oily mass thus obtained was dissolved in CH₂Cl₂ (5 ml) and filtered. Petroleum ether (40-60 °C) (20 ml) was added to initiate precipitation and cooled to 0 °C. The yellow complex thus precipitated was separated by centrifugation, washed with petroleum ether and dried in vacuo.

Anal. for [RhCl(Hcbt)₂(PPh₃)]:
Calcd:  C, 46.71; H, 3.59; N, 2.87; M, 10.54; S, 6.56; P, 3.17; Hal, 20.01%.

Found: C, 46.75; H, 3.64; N, 3.00; M, ...; S, 6.60; P, 3.20; Hal, 20.10%.

(ii) Reaction of [Pd(PPh₃)₄] with Hcbt

Freshly prepared [Pd(PPh₃)₄] (0.1 g, 0.1 mmol) in CH₂Cl₂ (30 ml) was added to a stirring solution of Hcbt (0.087 g, 0.3 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was refluxed for 1-2 hours under dry nitrogen atmosphere. The colour of the solution changed from yellow to dark brown, concentrated to ca. half volume under reduced pressure, added petroleum ether (50 ml) (40-60 °C) to give yellow compound, separated by centrifugation, washed with petroleum ether, and dried in vacuo.

Anal. for [Pd(Hcbt)₂(PPh₃)₂]:
Calcd:  C, 55.71; H, 4.15; N, 2.32; M, 8.82; S, 5.31; P, 5.14; Hal, 13.25%.

Found: C, 55.75; H, 4.20; N, 2.40; M, 8.92; S, 5.40; P, 5.20; Hal, 13.35%.
(iii) **Reaction of \([\text{Pt}(\text{PPh}_3)_4]\) with Hcbt**

Freshly prepared \([\text{Pt}(\text{PPh}_3)_4]\) (0.12 g, 0.1 mmol) in CH$_2$Cl$_2$ (30 ml) was added to a stirring solution of Hcbt (0.087 g, 0.3 mmol) in CH$_2$Cl$_2$ (10 ml). The reaction mixture was refluxed for 4-5 hours under dry nitrogen atmosphere, concentrated to ca. half volume under reduced pressure, added petroleum ether (60-80 °C) to give orange compound, separated by centrifugation, washed with petroleum ether and dried *in vacuo*.

Anal. for \([\text{Pt}(\text{Hcbt})_2\text{PPh}_3)_2]\):

Calcd: C, 51.90; H, 3.86; N, 2.16; M, 15.07; S, 4.94;
P, 4.78; Hal, 12.34%.

Found: C, 52.00; H, 3.90; N, 2.15; M, ......; S, 5.00;
P, 4.82; Hal, 12.40%.

(iv) **Reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) with Hcbt**

50 ml of CH$_2$Cl$_2$ solution containing 0.100 g of RuCl$_2$(PPh$_3$)$_3$ (0.1 mmol) and the ligand Hcbt (0.029 g, 0.1 mmol) was refluxed under dry N$_2$ atmosphere for three hours. The resulting solution was concentrated upto almost dryness under reduced pressure, the residue was dissolved in minimum quantity of dichloromethane, followed by an addition of petroleum ether with constant stirring. On standing for 1-2 hours, the precipitate settled down. It was centrifuged, washed several times with petroleum ether and dried *in vacuo*.

Anal. for \([\text{RuCl}_2(\text{Hcbt})_2(\text{PPh}_3)]\):

Calcd: C, 45.16; H, 3.47, N, 2.77; M, 10.01; S, 6.34;
P, 3.07; Hal, 22.86%.

Found: C, 45.20; H, 3.50; N, 2.75; M, ......; S, 6.35;
P, 3.09; Hal, 22.90%.
(v) **Reaction of [RuCl₂(CO)₂]** with Hcbt

0.114 g of [RuCl(CO)₂] (0.5 mmol) and the ligand Hcbt (0.14 g, 0.5 mmol) in 50 ml of methanol solution was refluxed for 5-6 hours. Under reduced pressure, the resulting solution was concentrated up to almost dryness and the residue was dissolved in minimum quantity of CH₂Cl₂, followed by an addition of excess (150 ml) petroleum ether with constant stirring. On standing the solution mixture for 1-2 hours, the precipitate settled down. It was centrifuged, washed several times with petroleum ether and dried in vacuo.

Anal. for [RuCl₂(CO)₂(Hcbt)]:
Calcd: C, 31.86; H, 2.21; N, 3.10; M, 22.36; S, 7.08; Hal, 33.39%.

Found: C, 31.90; H, 2.28; N, 3.15; M, ......; S, 7.10; Hal, 33.40%.

(vi) **Reaction of [(η⁵-C₅H₅)RuCl(AsPh₃)₂]** with Hcbt

In about 40 ml of methanol solution containing [(η⁵-C₅H₅)-RuCl(AsPh₃)₂] (0.105 g, 0.25 mmol) 25 ml methanol solution of the ligand Hcbt (0.10 g, 0.35 mmol) was added under dry N₂ atmosphere. The resulting mixture was stirred for 2-3 hours. The resulting solution was concentrated up to dryness under reduced pressure, the residue was dissolved in minimum quantity of CH₂Cl₂ followed by addition of petroleum ether. On scratching the walls of beaker and allowing to stand for 1-2 hours, the precipitate appears. It was centrifuged, washed several times with petroleum ether and dried in vacuo.
Anal. for \([\eta^5-C_5H_5]RuCl(Hcct)(AsPh_3)\):

- Calculated: C, 49.79; H, 3.77; N, 1.76; M, 12.71; S, 4.02; As, 9.42; Hal, 14.51%.
- Found: C, 49.81; H, 3.78; N, 1.80; M, ....; S, 4.05; As, ....; Hal, 14.60%.

**RESULTS AND DISCUSSION**

The triphenylphosphine complexes of Rh(I), Pd(0), Pt(0) and Ru(II) react with the ligands, Hcct and Hcbt in dichloromethane and undergo substitution reactions. Two molecules of triphenylphosphine are replaced by two molecules of Hcct or Hcbt. Thus,

\[
\text{RhCl}(\text{PPh}_3)_3 + 2 \text{HL} \rightarrow [\text{RhCl}_2(\text{HL})_2(\text{PPh}_3)] + 2(\text{PPh}_3)
\]

\[
[M(\text{PPh}_3)_4] + 2 \text{HL} \rightarrow [M(\text{HL})_2(\text{PPh}_3)_2] + 2(\text{PPh}_3)
\]

\[
[\text{RuCl}_2(\text{PPh}_3)_3] + 2 \text{HL} \rightarrow [\text{RuCl}_2(\text{HL})_2(\text{PPh}_3)] + 2(\text{PPh}_3)
\]

\((M = \text{Pd or Pt}; \text{HL} = \text{Hcct or Hcbt})\)

In case of \([\eta^5-C_5H_5]RuCl(\text{AsPh}_3)_2\), one molecule of triphenylarsine is substituted by one molecule of ligand when the reaction is carried out in methanol solution.

\[
[(\eta^5-C_5H_5)\text{RuCl}(\text{AsPh}_3)_2] + \text{HL} \rightarrow [(\eta^5-C_5H_5)\text{RuCl}(\text{HL})(\text{AsPh}_3)] + (\text{AsPh}_3).
\]

The ligands react with \([\text{RuCl}_2(\text{CO})_2]\) in methanol solution in 1:1 molar ratio and addition reaction takes place:

\[
[\text{RuCl}_2(\text{CO})_2] + \text{HL} \rightarrow [\text{RuCl}_2(\text{CO})_2(\text{HL})]
\]
Analytical data are consistent with the stoichiometry proposed for the complexes (Table 9). The compounds are, in general, air stable and soluble in organic solvents.

**IR Spectra**

The major i.r. bands comparison of i.r. spectra of complexes (Figs. 57-68) with ligands are given in Table 10. The mode of bonding of ligands were decided on the basis of shifts in the positions of \(\nu_{(NH)}\), \(\nu_{(C=O)}\), \(\nu_{(C=S)}\) and four thioamide bands after complexation.

**[RhCl\((HL)_2(PPh_3)\]**

The thioamide band I \((\delta_{NH} + \nu_{CN})\) which appears in ligands around at 1540 cm\(^{-1}\) is shifted to higher wave number (ca. 40 cm\(^{-1}\)) in case of complexes. The band due to \(\nu_{C=O}\) (~1765 cm\(^{-1}\)) shifts to lower wave numbers (ca. 35 cm\(^{-1}\)) while the band due to \(\nu_{C=S}\) (~1130 cm\(^{-1}\)) remains unchanged after complexation. The shifts indicate the involvement of carbonyl oxygen in bond formation. Two bands appears at 370 cm\(^{-1}\) and 330 cm\(^{-1}\) in case of complexes may due to \(\nu_{(Rh-O)}\) and \(\nu_{(Rh-Cl)}\), respectively.\(^5,6\)

**[Pd\((HL)_2(PPh_3)\]**

A band around 3300 cm\(^{-1}\) due to \(\nu_{NH}\) is present in these complexes. The band due to \(\nu_{C=O}\) appears at a higher wave number (ca. 15 cm\(^{-1}\)) while thioamide band IV and the band due to \(\nu_{C=S}\) shift to lower wave numbers (ca.
20 cm\(^{-1}\) and 10 cm\(^{-1}\)). Above recorded shifts in various i.r. bands are indicative of the bonding through sulphur in the complexes.

**[Pt(HL)\(_2\)(PPh\(_3\))]**

The band due to \(v_{\text{NH}}\) (~3220 cm\(^{-1}\)) present in ligands disappears in the i.r. spectra of these complexes. The band due to \(v_{\text{C}=\text{O}}\) (~1765 cm\(^{-1}\)) goes up by 35 cm\(^{-1}\) while thioamide band IV and the band due to \(v_{\text{C}=\text{s}}\) go down by 30 cm\(^{-1}\) and 10 cm\(^{-1}\), respectively. These shifts in major i.r. bands indicate the bonding through thiocarbonyl sulphur.

**[RuCl\(_2\)(HL)\(_2\)(PPh\(_3\))]**

The band due to \(v_{\text{C}=\text{O}}\) of the ligand shift to lower wave number by 10-15 cm\(^{-1}\) in complexes with either broadening or splitting into two bands. This indicates that both ligand molecules are in \(cis\)-position in the complexes. The thioamide band IV and \(v_{\text{C}=\text{s}}\) band shift to higher wave number (10-25 cm\(^{-1}\)), thus ruling out the possibility of coordination through sulphur. The thioamide band I goes higher by (15-30 cm\(^{-1}\)) indicating non-involvement of nitrogen in co-ordination. There are unsystematic shifts in the position of thioamide bands II and III for drawing any significant inferences.

The characteristic peaks of triphenylphosphine appears in the spectra of the above complexes.

**[RuCl\(_2\)(CO)\(_2\)(HL)]**

The band at 1765 cm\(^{-1}\) \((v_{\text{C}=\text{O}})\) shifts to 1770 cm\(^{-1}\). Thus, the possibility of carbonyl oxygen as donor site is excluded. Bands at around 1130 cm\(^{-1}\) \((v_{\text{C}=\text{s}})\) and around 850 cm\(^{-1}\) (thioamide band IV) in the i.r. spectra of ligands
appears at ~1115 and ~840 cm\(^{-1}\) in the complexes with reduced intensity. This observation supports the bonding through thiocarbonyl sulphur. The thioamide band I appearing at ~1540 cm\(^{-1}\) in case of ligands shifts to lower wave number (~1500 cm\(^{-1}\)). This indicates metal-nitrogen bond formation. It has been shown\(^8\) that thioamide band I (\(\delta_{\text{N-H}} + \nu_{\text{C=O}}\)) will undergo red shift in case of bonding through nitrogen whereas it will show blue shift because of bonding through sulphur. Thus, decrease in the position of 1540 cm\(^{-1}\) band indicates relatively stronger interaction of nitrogen with metal. Thioamide band II (\(\nu_{\text{C=O}} + \delta_{\text{NH}} + \delta_{\text{Cl}}\)) (~1360 cm\(^{-1}\)) and thioamide band III (\(\nu_{\text{C=S}} + \nu_{\text{C-N}}\)) (1075 cm\(^{-1}\)) as expected\(^9\) shift to lower wave numbers ~1320 cm\(^{-1}\) and ~1040 cm\(^{-1}\), respectively.

Two C\(=\)O stretching frequencies in [RuCl\(_2\)(CO)\(_2\)] are at 2060 and 2000 cm\(^{-1}\) which shift to higher frequencies (ca. 40 cm\(^{-1}\)). This shows that the title ligands are weak \(\pi\)-acid ligands. The medium intensity bands appear in the region 330-450 cm\(^{-1}\) may be due to coupled vibrations of terminal \(\nu_{\text{(Ru-Cl)}}\), \(\nu_{\text{(Ru-S)}}\) and \(\nu_{\text{(Ru-N)}}\).\(^{10}\)

\([\eta^5-(C_5H_5)RuCl(HL)(AsPh_3)]\)

The band due to \(\nu_{\text{C=O}}\) of the ligands goes down by 15 cm\(^{-1}\). Band at 1585 cm\(^{-1}\) (\(\nu_{\text{C=N}}\)) shifts to higher value (1600 cm\(^{-1}\)). This indicates that there is a coordination through carbonyl oxygen in these complexes. All the characteristic bands of AsPh\(_3\)\(^{10}\) and \(\eta^5-C_5H_5\) (820-850 cm\(^{-1}\))\(^{11}\) appear in the spectra of the complexes. The new bands of medium intensity in the region of 350-480 cm\(^{-1}\) may be attributed to coupled vibrations of \(\nu_{\text{(Ru-Cl)}}\), \(\nu_{\text{(Ru-O)}}\) or \(\nu_{\text{(Ru-N)}}\).
Electronic Spectra

The electronic spectra of the ligand Hcct and complexes were taken in dichloromethane (Figs. 69-74), the band positions and their assignments are given in Table 11.

The spectra of the complexes showed continuous absorption in the visible region, therefore, some of d-d transitions were probably masked by this continuous absorption or by charge transfer (CT) or intraligand (IL) bands. Some of the intraligand (IL) bands were present in complexes with small shifts. The intense bands at 230-245 nm and 270-285 nm are assigned to charge transfer transitions.

Magnetic Properties

All complexes are diamagnetic at room temperature.

Structural Aspects of Complexes

On the basis of analytical, spectral and magnetic measurement data, the complexes [RhCl(HL)₂(PPh₃)] may be assigned to possess a square planar (trans) geometry with bonding through carbonyl oxygen of the ligands.
Similarly, a tetrahedral geometry is proposed for \([\text{Pd(HL)}_2(\text{PPh}_3)_2]\) and \([\text{Pt(HL)}_2(\text{PPh}_3)_2]\) complexes where the ligands have been shown to ligate through thiocarbonyl sulphur.

![Chemical structure](image)

\((M = \text{Pd, Pt}; \text{R} = 4-\text{ClC}_6\text{H}_4, 4-\text{BrC}_6\text{H}_4)\)

The complexes \([\text{RuCl}_2(\text{HL})_2(\text{PPh}_3)_2]\) seem to retain the structural characteristics of the parent compound, \([\text{RuCl}_2(\text{PPh}_3)_3]\) which is an unusual example of 5-coordinate Ru(II). It has been shown\(^1\) by X-ray crystal structure analysis that this complex is penta-coordinated having distorted square based pyramidal geometry. The two chlorine atoms and the two molecules of triphenylphosphine in the basal plane are trans to each other whereas the third triphenylphosphine is the apical one. The next closest approach to the ruthenium, in the position trans to the apical phosphorus atom, is made by hydrogen atom on a \(\beta\)-carbon of a phenyl ring; the metal hydrogen distance is approximately 2.59 \(\text{Å}\), but there is no evidence for a metal-hydrogen interaction. Thus, the compound is a true pentacoordinated specie, and that its stability arises from intramolecular blocking of the unused octahedral site by the phenyl ring. The ligands behave as mono-dentate through carbonyl oxygen. The \(\beta\)-hydrogen of third triphenyl-phosphine trans to carbonyl oxygen of the ligand is responsible for stability of the complexes due to blocking of the sixth position resulting in a quasi-octahedral structure, as shown below:
The ligands react with [RuCl₂(CO)₂] to give the complexes of the type [RuCl₂(CO)₂(HL)] and on the basis of spectral shifts it has been unequivocally established that the ligands are NS donor. Thus, the following tentative geometry may be assigned to these complexes:

![Distorted octahedral structure](image)

In case of complexes, [(η⁵-C₅H₅)RuCl(ligand)(AsPh₃)] four thioamide bands and νC=S of ligands are not discernible, it has been concluded from the shifts in other bands of i.r. spectra that there is coordination through carbonyl oxygen in these complexes.

The ground state of ruthenium(II) in octahedral complexes is ^1A_{1g} and the excited states are ^3T₁g, ^3T₂g, ^1T₁g and ^1T₂g. Therefore, four transition bands due to transition from ^1A_{1g} to ^3T₁g, ^3T₂g, ^1T₁g and ^1T₂g are possible, but as transitions ^1A_{1g}→^3T₁g and ^3T₂g are spin forbidden (singlet→triplet), they are too weak to be observed and only two spin-spin allowed transitions, ^1A_{1g}→^1T₁g or ^1T₂g are expected. In our case the electronic spectra of the complexes showed continuous absorption in the visible region, therefore,
some of d-d transitions were probably masked by this continuous absorption or by charge transfer (CT) or interligand (IL) band.

The diamagnetism of Ru(II), d⁶ systems indicate the spin pairing, hence distorted octahedral structure,¹³ assuming that η²-C₅H₅ group occupies three coordination sites, is preferred over tetrahedral or distorted tetrahedral as spin pairing is not possible in later cases. Thus, on the basis of analytical, spectral and magnetic moment data the following structure is proposed for these complexes.

![Distorted octahedral structure](image)

(Distorted octahedral)
### TABLE 9: Analytical Data of Rh(I), Pd(0), Pt(0) and Ru(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P.* (°C)</th>
<th>Yield (%)</th>
<th>% Found (Calculated)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>X</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(RhCl(Hcct)₂(PPh₃)]</td>
<td>Yellow</td>
<td>125</td>
<td>60</td>
<td></td>
<td>51.30</td>
<td>3.90</td>
<td>3.05</td>
<td>7.20</td>
<td>12.05</td>
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<td></td>
<td>(51.39)</td>
<td>(3.94)</td>
<td>(3.16)</td>
<td>(7.21)</td>
<td>(12.00)</td>
<td>(3.49)</td>
</tr>
<tr>
<td>[(Pd(Hcct)₂(PPh₃)]</td>
<td>Yellow</td>
<td>195d</td>
<td>52</td>
<td></td>
<td>60.00</td>
<td>4.50</td>
<td>2.50</td>
<td>5.80</td>
<td>6.40</td>
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<td>(60.14)</td>
<td>(4.47)</td>
<td>(2.51)</td>
<td>(5.73)</td>
<td>(6.35)</td>
<td>(5.54)</td>
</tr>
<tr>
<td>[(Pt(Hcct)₂(PPh₃)]</td>
<td>Orange</td>
<td>193</td>
<td>55</td>
<td></td>
<td>55.70</td>
<td>4.28</td>
<td>2.29</td>
<td>5.40</td>
<td>5.94</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(55.72)</td>
<td>(4.15)</td>
<td>(2.32)</td>
<td>(5.31)</td>
<td>(5.89)</td>
<td>(5.14)</td>
</tr>
<tr>
<td>[(RuCl₂(Hcct)₂(PPh₃)]</td>
<td>Maroon</td>
<td>135</td>
<td>70</td>
<td></td>
<td>49.55</td>
<td>3.84</td>
<td>3.10</td>
<td>6.85</td>
<td>15.45</td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(49.51)</td>
<td>(3.80)</td>
<td>(3.04)</td>
<td>(6.95)</td>
<td>(15.42)</td>
<td>(3.36)</td>
</tr>
<tr>
<td>[(RuCl₂(CO)₂(Hcct)]</td>
<td>Y.B.</td>
<td>&gt;200</td>
<td>30</td>
<td></td>
<td>30.44</td>
<td>2.20</td>
<td>3.00</td>
<td>6.80</td>
<td>22.60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(30.54)</td>
<td>(2.12)</td>
<td>(2.97)</td>
<td>(6.79)</td>
<td>(22.58)</td>
<td>-</td>
</tr>
<tr>
<td>[(η⁵-C₅H₅)RuCl-(Hcct)(AsPh₃)]</td>
<td>Y.B.</td>
<td>110</td>
<td>25</td>
<td></td>
<td>52.75</td>
<td>4.00</td>
<td>1.90</td>
<td>4.30</td>
<td>9.50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(52.73)</td>
<td>(3.99)</td>
<td>(1.86)</td>
<td>(4.26)</td>
<td>(9.45)</td>
<td>-</td>
</tr>
<tr>
<td>[(RhCl(Hcbt)₂(PPh₃)]</td>
<td>Yellow</td>
<td>122</td>
<td>60</td>
<td></td>
<td>46.75</td>
<td>3.64</td>
<td>3.00</td>
<td>6.60</td>
<td>20.10</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(46.71)</td>
<td>(3.59)</td>
<td>(2.87)</td>
<td>(6.56)</td>
<td>(20.01)</td>
<td>(3.17)</td>
</tr>
<tr>
<td>[(Pd(Hcbt)₂(PPh₃)]</td>
<td>Yellow</td>
<td>190d</td>
<td>50</td>
<td></td>
<td>55.75</td>
<td>4.20</td>
<td>2.40</td>
<td>5.40</td>
<td>13.35</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(55.71)</td>
<td>(4.15)</td>
<td>(2.32)</td>
<td>(5.31)</td>
<td>(13.25)</td>
<td>(5.14)</td>
</tr>
<tr>
<td>[(Pt(Hcbt)₂(PPh₃)]</td>
<td>Orange</td>
<td>190</td>
<td>55</td>
<td></td>
<td>52.00</td>
<td>3.90</td>
<td>2.15</td>
<td>5.00</td>
<td>12.40</td>
<td>4.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(51.90)</td>
<td>(3.86)</td>
<td>(2.16)</td>
<td>(4.94)</td>
<td>(12.34)</td>
<td>(4.78)</td>
</tr>
</tbody>
</table>

Table 9 (contd.)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P. *</th>
<th>Yield</th>
<th>% Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>[RuCl₂(Hcbt)₂-</td>
<td>Maroon</td>
<td>130</td>
<td>72</td>
<td>45.20</td>
</tr>
<tr>
<td>(PPh₃)]</td>
<td></td>
<td></td>
<td></td>
<td>(45.16)</td>
</tr>
<tr>
<td>[RuCl₂(CO)₂(Hcbt)]</td>
<td>Reddish brown</td>
<td>&gt;200d</td>
<td>36</td>
<td>31.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(31.86)</td>
</tr>
<tr>
<td>[(η⁵-C₅H₅)RuCl(Hcbt)-</td>
<td>Reddish brown</td>
<td>105</td>
<td>30</td>
<td>49.81</td>
</tr>
<tr>
<td>(AsPh₃)]</td>
<td></td>
<td></td>
<td></td>
<td>(49.79)</td>
</tr>
</tbody>
</table>

*Melting points are uncorrected; d = decomposes; Y.B. = yellowish brown.
TABLE 10: Major i.r. Bands (cm\(^{-1}\)) of Rh(I), Pd(0), Pt(0) and Ru(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{(\text{NH})})</th>
<th>(v_{(\text{C}=\text{O})})</th>
<th>(v_{(\text{C}=\text{S})})</th>
<th>Thioamide bands</th>
<th>Possible coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ligand(Hcct)]</td>
<td>3225m</td>
<td>1765s</td>
<td>1130m</td>
<td>I: 1540s 1360s 1075s 850s</td>
<td>-</td>
</tr>
<tr>
<td>[RhCl(Hcct)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1730s</td>
<td>1140m</td>
<td>II: 1580s 1370s 1070s 870s</td>
<td>O</td>
</tr>
<tr>
<td>[Pd(Hcct)(_2)(PPh(_3))]</td>
<td>3300m</td>
<td>1780s</td>
<td>1120s</td>
<td>III: 1550s 1370s 1075s 830s</td>
<td>S</td>
</tr>
<tr>
<td>[Pt(Hcct)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1800s</td>
<td>1120s</td>
<td>IV: 1560s 1375s 1070s 820s</td>
<td>S</td>
</tr>
<tr>
<td>[RuCl(_2)(Hcct)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1725br</td>
<td>1145m</td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>[RuCl(_2)(CO)(_2)(Hcct)]*</td>
<td>-</td>
<td>1770s</td>
<td>1115m</td>
<td></td>
<td>N and S</td>
</tr>
<tr>
<td>[(((\eta^5)-C(_5)H(_5))RuCl(Hcct)-(AsPh(_3)))]#</td>
<td>-</td>
<td>1750s</td>
<td>1135m</td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>[Ligand(Hcbt)]</td>
<td>3220m</td>
<td>1765s</td>
<td>1130m</td>
<td>I: 1540s 1360s 1080s 850s</td>
<td>-</td>
</tr>
<tr>
<td>[RhCl(Hcbt)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1735s</td>
<td>1140m</td>
<td>II: 1580s 1370s 1070s 870s</td>
<td>O</td>
</tr>
<tr>
<td>[Pd(Hcbt)(_2)(PPh(_3))]</td>
<td>3300m</td>
<td>1780s</td>
<td>1120s</td>
<td>III: 1550s 1375s 1075s 825s</td>
<td>S</td>
</tr>
<tr>
<td>[Pt(Hcbt)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1790s</td>
<td>1120s</td>
<td>IV: 1555s 1370s 1065s 820s</td>
<td>S</td>
</tr>
<tr>
<td>[RuCl(_2)(Hcbt)(_2)(PPh(_3))]</td>
<td>-</td>
<td>1725br</td>
<td>1145m</td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>[RuCl(_2)(CO)(_2)(Hcbt)]*</td>
<td>-</td>
<td>1765s</td>
<td>1110m</td>
<td></td>
<td>N and S</td>
</tr>
<tr>
<td>[(((\eta^5)-C(_5)H(_5))RuCl(Hcbt)-(AsPh(_3)))]#</td>
<td>-</td>
<td>1745s</td>
<td>1135m</td>
<td></td>
<td>O</td>
</tr>
</tbody>
</table>

s = strong; m = medium; br = broad

* Two strong bands at 2100 cm\(^{-1}\) and 2040 cm\(^{-1}\) also appear due to \(v_{(\text{C}=\text{O})}\).

# Band due to \(v_{(\text{C}=\text{N})}\) which appear in ligands at 1585-1580 cm\(^{-1}\) shifts to 1600 cm\(^{-1}\).
### TABLE 11: Electronic Spectra of Rh(I), Pd(0), Pt(0) and Ru(II) Complexes of Ligand [Hcct]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Band position $\lambda_{\text{max}}$ (nm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand [Hcct]</td>
<td>445</td>
<td>$n\rightarrow\pi^*$</td>
</tr>
<tr>
<td></td>
<td>305</td>
<td>$\pi\rightarrow\pi^*$</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td>ILCT</td>
</tr>
<tr>
<td>[RhCl(Hcct)$_2$(PPh$_3$)]</td>
<td>310</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>230 (sh)</td>
<td>CT</td>
</tr>
<tr>
<td>[Pd(Hcct)$_2$(PPh$_3$)$_2$]</td>
<td>280</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>CT</td>
</tr>
<tr>
<td>[Pt(Hcct)$_2$(PPh$_3$)$_2$]</td>
<td>285</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>CT</td>
</tr>
<tr>
<td>[RuCl$_2$(Hcct)$_2$(PPh$_3$)]</td>
<td>500</td>
<td>$^1A_{1g}\rightarrow^1T_{1g}$</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>236</td>
<td>CT</td>
</tr>
<tr>
<td>[RuCl$_2$(CO)$_2$(Hcct)]</td>
<td>350</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>CT</td>
</tr>
<tr>
<td>[($\eta^5$-C$_5$H$_5$)RuCl(Hcct) - (AsPh$_3$)]</td>
<td>376 (br, sh)</td>
<td>IL</td>
</tr>
<tr>
<td></td>
<td>238</td>
<td>CT</td>
</tr>
</tbody>
</table>
Figure 57. IR Spectra of \([\text{RhCl(Hcct)}_2(\text{PPh}_3)]\)
Figure 58. IR Spectra of \([\text{Pd}(\text{Hcct})_2(\text{PPh}_3)_2]\)
Figure 59. IR Spectra of $[\text{Pt(Hcct)}_2(\text{PPh}_3)_2]$
Figure 60. IR Spectra of $\text{RuCl}_2(\text{Hect})_2(\text{PPh}_3)$
Figure 61. IR Spectra of [RuCl₂(CO)₂(Hcct)]
Figure 62. IR Spectra of \([\eta^5C_5H_5]RuCl(\text{Hect})(\text{AsPh}_3)\]
Figure 63. IR Spectra of [RhCl(Hcbt)_2(PPh_3)]
Figure 64. IR Spectra of $[\text{Pd(Hcbt)}_2(\text{PPh}_3)_2]$
Figure 65. IR Spectra of [Pt(Hcbt)₂(PPh₃)₂]
Figure 66. IR Spectra of [RuCl$_2$(Hcbt)$_2$(PPh$_3$)$_2$]
Figure 67. IR Spectra of [RuCl$_2$(CO)$_2$(Hcbt)]
Figure 68. IR Spectra of \([\eta^5-\text{C}_5\text{H}_5\text{RuCl(Hcbt)(AsPh}_3\text{)}]\)
Figure 69. Electronic Spectra of [RhCl(Hect)$_2$(PPh$_3$)]
Figure 70. Electronic Spectra of $[\text{Pd}(\text{Hcct})_2(\text{PPh}_3)_2]$
Figure 71. Electronic Spectra of [Pt(Hcct)$_2$(PPh$_3$)$_2$]
Figure 72. Electronic Spectra of \([\text{RuCl}_2(\text{Hect})_2(\text{PPh}_3)]\)
Figure 73. Electronic Spectra of [RuCl$_2$(CO)$_2$(Hcct)]
Figure 74. Electronic Spectra of $[\eta^5-C_5H_5]RuCl(Hcct)(AsPh_3)$
REFERENCES