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Reactions of η^5-cyclopentadienylruthenium(II) complexes with γ-hydroxyacetylenes

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Abstract. The complexes $[CpRuL_2Cl]$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$) react with the phenylacetylene, γ-hydroxyacetylenes $HC \equiv CCR_1R_2OH$ ($R_1 = R_2 = H$, Me, and $R_1 = Me$, $R_2 = Et$; CR_1R_2OH = 1-hydroxycyclohexanol) and $NaBF_4$ in methanol, to yield complexes of the type η^1-vinylidenes $[CpL_2Ru^+(=C=CHR)]$, η^1- allenylidene $[CpL_2Ru^+(=C=C=CR_1R_2)]$, and dimeric allenylidene–vinyl and vinylidene–alkylidene complexes. These η^1-vinylidene and η^1-allenylidene complexes are reversibly deprotonated by sodium borohydride in methanol to yield the corresponding η^1-alkynyl complexes $[CpL_2Ru(C \equiv CR)]$.

Keywords. γ-Hydroxyacetylenes; vinylidenes; allenylidenes; cyclopentadiene.

1. Introduction

Although the chemistry of the transition metal–alkylidene (carbene) complexes is now well-explored (Brown 1980; Bruce 1986), it is only in recent years that reliable methods for the syntheses of metal complexes with unsaturated alkylidenes (vinylidene complexes $M=C=CR_2$) (Antonova *et al* 1977; Davidson and Selegue 1978; Bruce and Wallis 1979; Davidson *et al* 1979; Bruce and Swincer 1980, 1983; Davies *et al* 1990; Dixneuf *et al* 1994), and allenylidene ($M=C=C=CR_2$) (Berke 1976, 1980; Fischer *et al* 1976; Selegue 1982; Bruce and Swincer 1983; Selegue *et al* 1991; Gimeno *et al* 1994, 1996) have been developed, Selegue (Selegue 1982, 1983; Selegue *et al* 1991) reported the reaction between $[CpRu(PPh_3)_2Cl]$ and γ-hydroxyacetylenes which yielded allenylidene and dimeric vinylidene complexes. It appears that the formation of alkylidene complexes depends largely upon the nature of the group substituted on the γ-carbon. The reaction between 1-ethynyl-l-cyclohexanol and $[(\eta\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ leads to interesting products where the second molecule of cyclohexanol attacks the vinylidene complex to give an allenylidene complex containing a spirobicylic system (Gimeno *et al* 1994). It is interesting to study the reactions of $[CpRuL_2Cl]$ with various substituted γ-hydroxyacetylenes. We present and discuss here the results of the reactions of $[CpRuL_2Cl]$ with $HC \equiv C\text{–}R$(R=Ph, $-CH_2OH$, $-CMe_2OH$, $-CMeEtOH$, $-C_6H_{10}OH$).

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2. Experimental

Complexes [$CpRuL_2Cl$] (L=PPh_3, $AsPh_3$, $SbPh_3$) were prepared by the literature methods (Bruce and Windsor 1977; Bruce *et al* 1982; Mohan Rao *et al* 1986, 1987). Phenylacetylene and γ-hydroxyacetylenes obtained from Aldrich were used as such. A Bruker W M-400 MHz spectrometer was used for recording the ^{13}C NMR spectra of the complexes at 100 MHz in $CDCl_3$. The physical measurements were described elsewhere (Mohan Rao *et al* 1986).

2.1 *Preparation of monomeric complexes*

2.1a *Syntheses of* [$CpRu(=C=C=CH_2)L_2$]BF_4 *and* [$CpL_2Ru(=C=CHCH_2OH)$]BF_4($L=PPh_3, AsPh_3, SbPh_3$): To a suspension of [$CpRuL_2Cl$] (0·12 mmol) in 20 ml methanol were added propargyl alcohol (0·2 mmol) and $NaBF_4$ (0·05 g, 0·45 mmol). The reaction mixture was refluxed for 30 minutes to yield a deep red solution. The solvent was removed and the crude product was extracted with dichloromethane. Concentration and addition of light petroleum afforded a reddish-tan solid. This precipitate was dissolved in 5 ml of dichloromethane and adsorbed at the top of a short silica gel column and eluted with dichloromethane/acetone (4:1). The first yellow fraction was collected and concentrated on a water bath to about 10 ml. Addition of light petroleum (40–60°) afforded [$CpL_2Ru(C=C=CH_2)$]BF_4 (yellow solid) in 80% yield.

The violet coloured second fraction [$CpL_2Ru(=C=CH-CH_2OH)$]BF_4 was collected on eluting with dichloromethane and acetone (3:2). The eluent was concentrated and the complex was precipitated with diethyl ether in 10% yield.

2.1b *Synthesis of* [$CpL_2Ru(=C=C=\overline{C-(CH_2)_4-CH_2}$]$BF_4$ ($L=PPh_3$, $AsPh_3$, $SbPh_3$): A few drops of 1-ethynyl-1-cyclohexanol were added to a suspension of [$CpRuL_2Cl$] (0·12 mmol) and $NaBF_4$ (0·2 mmol) in methanol (15 ml). The mixture was refluxed for 30 minutes after which the colour of the solution changed to red. The resulting solution was evaporated to near dryness. The residue in 10 ml of dichloromethane was loaded on to a silica gel column (2 cm × 10 cm) and eluted with dichloromethane/acetone (4:1). The major yellow fraction was collected and concentrated, and the compound precipitated using light petroleum. This, on recrystallization with dichloromethane and diethyl ether, afforded a yellow solid [$CpL_2Ru(=C=C=\overline{C-(CH_2)_4-CH_2}$]$BF_4$ (yield 80%).

2.1c *Synthesis of* [$CpL_2Ru(=C=CHPh)$]BF_4($L=AsPh_3$, $SbPh_3$): Addition of phenylacetylene (0·05 g, 0·5 mmol) and sodium tetrafluoroborate (0·03 g, 0·27 mmol) to a suspension of [$CpRuL_2Cl$] (0·2 mmol) in dry methanol (15 ml), followed by refluxing for 30 minutes gave a deep red solution. It was filtered and evaporated to dryness. The residue was extracted with dichloromethane, and the extracts were filtered into light petroleum (excess) to yield a reddish-tan precipitate of [$CpL_2Ru(=C=CHPh)$]BF_4 (yield 80%).

2.1d *Synthesis of* [$CpL_2Ru(-C\equiv C-R)$] ($R=Ph, -CH_2OMe, -\overline{C=CH(CH_2)_3-CH_2}$; $L=PPh_3$, $AsPh_3$, $SbPh_3$): A mixture of [$CpRuL_2Cl$] (0·2 mmol) and a few drops of the corresponding γ-hydroxyacetylene in 15 ml methanol was heated under reflux for 30 minutes. Sodium borohydride was added to the resulting solution whereby a yellowish crystalline compound immediately separated out in quantitative yield. The yellowish crystals were filtered, washed with methanol, diethyl ether and air-dried. The complexes were recrystallized from chloroform/methanol or benzene/methanol.

2.2 *Preparation of dimeric complexes*

2.2a *Synthesis of* $[(Cp)_2L_4Ru_2(\mu\text{-}C_{10}H_{11})]BF_4$ (L=$AsPh_3$, $SbPh_3$): A mixture of $[CpRuL_2Cl]$ (0·7 mmol), sodium tetrafluoroborate (0·5 mmol), and a few drops of $HC \equiv CCMe_2OH$ in 50 ml dry methanol, was refluxed for 30 minutes. The resulting deep blue solution was filtered and evaporated to near dryness. The residue was extracted with dichloromethane (10 ml) and precipitated with light petroleum. The compound was recrystallized from dichloromethane/diethyl ether to give a deep blue complex, $[(Cp)_2Ru_2(\mu\text{–}C_{10}H_{11})L_4]BF_4$ (yield 95%).

2.2b *Synthesis of* $[(Cp)_2L_4Ru_2(\mu\text{-}C_{12}H_{16})]BF_4$ (L=PPh_3, $AsPh_3$, $SbPh_3$): These complexes were synthesized in the same way as above except that $HC \equiv CCMeEtOH$ was used instead. The blue-violet coloured complex $[(Cp)_2Ru_2\ (\mu\text{–}C_{12}H_{16})L_4]BF_4$ was isolated in 95% yield.

3. Results and discussion

The complexes are formed as a result of the substitution reaction of phenylacetylene or γ-hydroxyacetylenes with $[CpRuL_2Cl]$ complexes. The structural formulae of the complexes are listed in table 1. The spectral data are presented in tables 2 and 3. These

Table 1. Structural formulae of the complexes.
A, B, C and D refer to the general structure for each set of complexes*.

Complex No.	L	R	Complex No.	L	R_1	R_2
Set A			Set C			
1	$AsPh_3$	Ph	6	PPh_3	H	H
2	$SbPh_3$	Ph	7	$AsPh_3$	H	H
3	PPh_3	CH_2OH	8	$SbPh_3$	H	H
4	$AsPh_3$	CH_2OH	9	PPh_3	$=C(CH_2)_4CH_2$	
5	$SbPh_3$	CH_2OH	10	$AsPh_3$	$=C(CH_2)_4CH_2$	
			11	$SbPh_3$	$=C(CH_2)_4CH_2$	
Set B			Set D			
12	$AsPh_3$	Ph	20	$AsPh_3$	H	Me
13	$SbPh_3$	Ph	21	$SbPh_3$	H	Me
14	PPh_3	CH_2OMe	22	PPh_3	Me	Et
15	$AsPh_3$	CH_2OMe	23	$AsPh_3$	Me	Et
16	$SbPh_3$	CH_2OMe	24	$SbPh_3$	Me	Et
17	PPh_3	$C=C(CH_2)_3CH_2$				
18	$AsPh_3$	$C=C(CH_2)_3CH_2$				
19	$SbPh_3$	$C=C(CH_2)_3CH_2$				

*A: $[CpL_2Ru{=}C{=}CHR]^+$; B: $[CpL_2Ru{-}C \equiv C{-}R]$; C: $[CpL_2Ru{=}C{=}C{=}CR_1R_2]^+$; D:

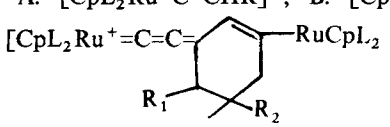


Table 2. Spectral data for η^1-vinylidene, η^1-allenylidene and η^1-alkynyl complexes.

Compd. No.	IR[a] (cm^{-1})	1H NMR (ppm)[b]				^{13}C NMR (ppm)[b]					
		Cp	CH_2	=CH	OH	Cp	Ph	M=C	C=C	=CR	Others
1	1640	5·35		5·6*t*		90·76	127–134·2			94·78	88·72
2	1645	4·95		5·2*t*							
3	1610	5·04	3·2[d]	5·21	2·02	90·74	127–134·2	306		94·7	
4	1615	4·93	3·2[d]	5·16	2·02						
5	1615	5·2	3·3[d]	5·2	2·02						
6	1960	5·0	3·5			90·79	127·2–134·8		202·87	94·6	93·67, 91·74, 91·36
7	1960	5·1	3·55								
8	1965	5·2	3·4								
9	1970	5·0	1·5[b]			93·09	127·32–134·0		191·22		17·55–51·73
10	1970	5·1	1·5[b]								
11	1960	5·2	1·5[b]								
12	2085	4·2									
13	2085	4·2									
14	2090	4·0	4·3		3·2(δOCH_3)	81·27	127·133·7		138·02–138·72		
15	2090	4·1	4·3								
16	2090	4·2	4·35								
17	2090	4·2	1·6[d]		5·46[e]						
18	2080	4·2	1·5[d]								
19	2080	4·2	1·5[d]								

[a] $\nu_{(C=C)}$ (*asym*) or $\nu_{(C-C=C)}$ (*asym*); KBr pellets; [b] Solvent $CDCl_3$. Aromatic protons of other coligands appear in the region δ 7·0–8·0 as broad multiplets; [c] Centre of a broad unresolved multiplet, *t* = triplet, *m* = multiplet; [d] broad multiplet; [e] broad peak

Table 3. Spectral data for dimeric complexes.

Compd. No	IR ($\nu_{C=C=C}$) (asym)[a] (cm^{-1})	Proton NMR[b] (δ ppm)						^{13}C NMR[b] (δ ppm)		
		Cp1	Cp2	CH_3	CH_2	CH_2^1	=CH	Cp1	Cp2	Ru=C
20	1970	4·7	4·45	0·8	3·0	1·3	5·0 *m*			
21	1970	4·7	4·45	0·8	3·0	1·3	5·0 *m*			
22	1970	4·55	4·43	0·5		1·6	5·0 *m*	90·76	90·59	277·56
23	1970	4·6	4·45	0·5		1·6				
24	1970	4·54	4·42	0·5		1·6				

[a]KBr pellets; [b] In $CDCl_3$, *m* = multiplets

are air-stable and highly soluble in solvents like methanol, dichloromethane and tetrahydrofuran, but are insoluble in light petroleum and diethyl ether.

3.1 *Reactions of phenylacetylene*

$[CpL_2RuCl]$ complexes react with phenylacetylene in the presence of sodium tetrafluoroborate in methanol and gave the reddish vinylidene complexes $[CpL_2Ru{=}C{=}CHPh]$ 1 (L = $AsPh_3$) and 2 (L=$SbPh_3$). The IR spectra of these complexes show a strong band at 1640 cm^{-1} due to ($\nu_{C=C}$) (Bruce and Swincer 1983; Bruce 1991), besides the characteristic bands of ligand triphenylarsine and triphenylstibine at 1622 cm^{-1} (Silverstein *et al* 1974) and BF_4^- at 1050 cm^{-1} (Bruce 1986). Proton NMR spectra of these complexes exhibited a sharp singlet due to cyclopentadienyl protons at 5·0 ppm and broad multiplets in the aromatic region 7·0–8·0 ppm assigned to phenyl and EPh_3 (E=As, Sb) groups. In addition, a single sharp peak at 5·43 ppm is assigned to the proton on β-carbon. Deprotonation of these cationic complexes 1 and 2 by sodium borohydride gave enynyl complexes $[CpL_2Ru{-}C{\equiv}CPh]$ (12, L=$AsPh_3$; 13, $SbPh_3$) in quantitative yield. These complexes were characterized by their IR absorption band at 2080 cm^{-1} due to $\nu_{C\equiv C}$ and proton NMR data.

3.2 *Activation of propargyl alcohol and 1-ethynyl-1-cyclohexanol by complexes* $[CpRuL_2Cl]$

Propargylic alcohol derivatives are easily available terminal alkynes and their activation by ruthenium(II) complexes has been shown to generate, via spontaneous dehydration, either stable allenylidene complexes such as $[CpRu(=C=C=CPh_2)L_2]PF_6$ [L=PMe_3; $P(OMe)_3$] (Selegue 1982; Selegue *et al* 1991), $[(C_6Me_6)Ru(C{=}C{=}C(Ph)(C_5H_4FeCp)Cl(PMe_3)]PF_6$ (Dixneuf *et al* 1990, 1992) and $[Ru(C{=}C{=}CR_2)(dppe)_2Cl]PF_6$ (Dixneuf *et al* 1991, 1994) or reactive intermediates that give deprotonated and dimerized products (Selegue 1983; Gimeno *et al* 1994). Complexes such as $[Ru{=}C(OR)CH{=}CR_2(Cl)(PMe_3)(C_6Me_6]PF_6$ (Dixneuf *et al* 1990, 1992) are known to be formed on addition of alcohol to the electrophilic alkenylcarbene intermediate.

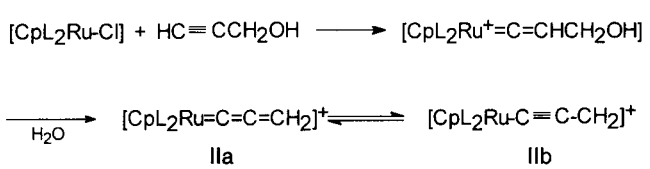
Prop-2-yn-1-ol reacts with $[CpRuL_2Cl]$ in methanol in presence of sodium tetrafluoroborate to give violet coloured 3-hydroxyvinylidene complexes in low yields. Under the same reaction conditions, hydroxy vinylidenes spontaneously dehydrate to give allenylidene complexes, which are stabilized due to their mesomeric forms IIa and

IIb (scheme 1) Fischer *et al* 1976). IR spectra of the allenylidene complexes exhibited characteristic bands at 1970 cm^{-1} ($\nu_{C=C=C}$) (Bruce and Swincer 1983) and at 1640 cm^{-1} ($\nu_{C=C}$) due to 3-hydroxyvinylidenes. Proton NMR spectra of the propadienylidene complexes show a sharp peak at 3·3 ppm for CH_2 group besides a sharp peak at 5·0 ppm due to the cyclopentadienyl ligand. The ^{13}C NMR spectra show a low intensity peak at 306 ppm due to metal-bonded carbene carbon (α-carbon) and a peak at 120 ppm due to β-carbons. The spectra also show a signal due to cyclopentadienyl carbons at 90 ppm.

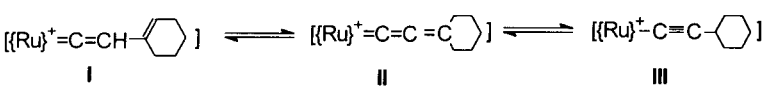
Selegue *et al* (1991) have reported that reaction of 1-ethynyl-1-cyclohexanol and $[CpRu(PPh_3)_2Cl]$ does not give an isolable complex. We however were able to isolate pure enynyl complexes (17–19) and allenylidene complexes (9–11) along with some vinylidene isomers (Gimeno *et al* 1996). Proton NMR spectra of 1-ethynyl-1-cyclohexanol allenylidene complexes show two sharp singlets for cyclopentadienyl protons at 5·0 and 5·05 ppm, and a weak and broad band at 1565 cm^{-1} due to the vinyl group and a strong band at 1970 cm^{-1} due to allenylidene group are also observed in their IR spectra. Carbon 13 NMR spectra of these complexes exhibited a number of signals in the upfield region due to the cyclohexane carbons. One can explain the appearance of these peaks on the assumption that an equilibrium (scheme 2) exists between three mesomeric forms similar to that proposed in the structural analyses of $[(CO)_5Cr(\eta^1\text{-}C{=}C{=}C(Ph)(NMe_2)]$ (Fischer *et al* 1976) and $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]$ (Selegue 1982).

This equilibrium has been established by Hoffmann and coworkers (Schilling *et al* 1977) in order to maximise π-orbital overlap in the model compound $[(CO)_2CpFe(\eta'\text{-}C{=}C{=}CH_2)]^+$. There is a substantial contribution from the two different mesomeric forms I and II where the cationic charge is stabilized by both the metal centre and the cyclohexane allenylidene (carbenium) moiety. This is evident from their IR and NMR spectra by the presence of a large number of peaks due to both the mesomeric forms I and II.

Though Selegue has reported (Selegue and Young 1985) the formation of the isomer I (scheme 2) by the reaction of $[CpRu(PMe_3)_2Cl]$ with ethynyl cyclohexanol, there exists an equal possibility of the formation of isomer II. The IR spectra of these complexes exhibit a very weak band at 1565 cm^{-1} due to the presence of the isomer of type I as a trace which we were not able to isolate. However the reaction of these complexes with base $NaBH_4$ yielded neutral complexes $[Ru{-}C{\equiv}C{-}\overline{C{=}CH(CH_2)_3{-}CH_2}]$ exclusively.



Scheme 1



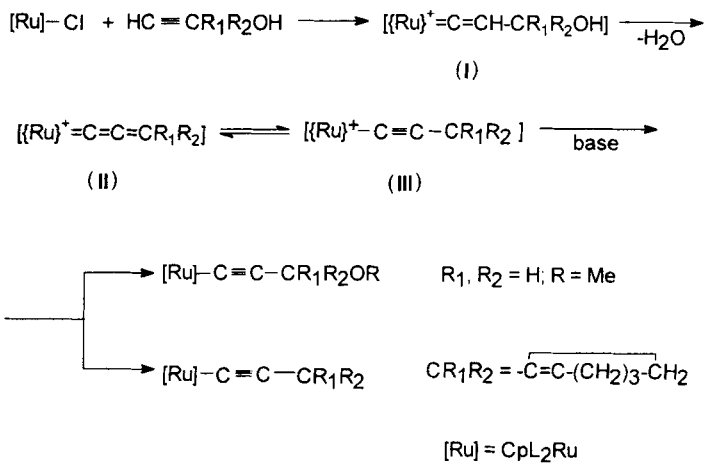
Scheme 2

Moreover, this observation is further supported by the fact that the formation of η^1-allenylidene and η^1-vinylidene complexes of the isomer II and isomer I were not formed by dehydrobromination in the reaction of $HC \equiv C-C_6H_{10}Br$ with $[CpRuL_2Cl]$ even after refluxing for a few hours. Formation of 1-vinylidene complex $[Ru^+=C=CH-C_6H_{10}Br]$ was also not observed, indicating that dehydration is necessary for these reactions. The low field signal due to α-carbon in the ^{13}C NMR spectra of the $[Ru=C=C=\overline{C-(CH_2)_4-CH_2}]$ complexes was not observed, due to the high relaxation period. The β-carbon showed a resonance at 191 ppm and the Cp carbons at 90 ppm. Besides these, a number of peaks were observed in the 0–60 ppm region due to the cyclohexene group.

All the vinylidene and allenylidene complexes were converted to neutral complexes on treatment with sodium borohydride. These complexes were readily characterised by a strong absorption for $\nu_{C\equiv C}$ in their IR spectra at 2080 cm^{-1} and a single sharp peak at 4·1 ppm in their proton NMR spectra due to Cp protons. The proton NMR spectra of several $[CpL_2Ru]^+$ derivatives in literature suggest a direct relationship between the chemical shift of the Cp group and the degree of 'electron richness' at the metal site (Treichel and Komar 1980; Treichel *et al* 1984). The high chemical shift (4·1 ppm) of the Cp protons in neutral complexes as compared to that of the cationic complexes of η^1-vinylidene or η^1-allenylidene (5·0 ppm) suggests high electron density (Treichel and Komar 1980; Treichel *et al* 1984) at the metal site in the neutral complexes. This is due to the ethynyl ligand which is a weak π-acid compared to the vinylidene or allenylidene ligands (π-acid η^1-C=C–R or π-acid η^1–C=C=CR_2) bonded to the metal centre (Treichel and Komar 1980). ^{13}C NMR spectra of the complexes (9, 10, 11) exhibited several resonances in the region of the cyclohexane carbons whereas only four signals were observed for cyclohexene in the corresponding alkynyl complexes (17, 18 and 19).

Addition of an OMe^- group regioselectively takes place at the γ-carbon in alkynyl complexes of propargyl alcohol (14, 15, 16). Reports are available in literature where the attack of the base can also take place at the α-carbon. The choice of the site of attack depends upon the hard or soft nature (Berke *et al* 1981) of the base. Thus, Berke reported that in the manganese complexes, the OMe^- group attacks the α-carbon, and bases like PPh_3 attack the γ-carbon. In the present case, the presence of a 2080 cm^{-1} band and the absence of any band due to $\nu_{C=C}$ or $\nu_{C=C=C}$ in their IR spectra suggest the formation of a C ≡ C bond which is possible only when the OMe^- group attacks the γ-carbon. One of the many possible explanations for the latter behaviour is the relatively lower steric hindrance at the γ-carbon compared to that at the α-carbon. These complexes show a sharp singlet at 3·2 ppm due to the OMe protons.

In the case of complexes containing 1-ethynyl-1-cyclohexanol, dehydration involves the ring proton with the formation of a double bond in the ring. $Ru-C \equiv C-\overline{C=CH(CH_2)_3-CH_2}$ (Selegue 1991). In these complexes, dehydration can take place by two possible routes: (1) Formation of η^1-allenylidene (II, scheme 2) or (2) formation of η^1-vinylidene (I, scheme 2). In the presence of $NaBH_4$, we were able to isolate η^1-alkynyl complexes having double bonds in the cyclohexane ring. Similar conclusions were drawn in the reaction of $[CpRu(PMe_3)_2Cl]$ with 1-ethynyl-1-cyclohexanol in the presence of base (Selegue *et al* 1991). We, therefore, propose that the formation of all the neutral (η^1-alkynyl) complexes takes place in accordance with scheme 3 which was proposed earlier (Selegue *et al* 1991). Although a number of bases like NEt_3, NaOMe have been used in the literature



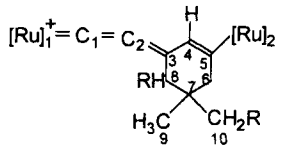
Scheme 3

to isolate neutral complexes from the cationic ones, we were able to isolate neutral complexes only in the presence of $NaBH_4$, whereas hydrido (Ru–H) complexes were isolated in the presence of other bases (Bruce *et al* 1984).

3.3 *Activation of 3-methyl-3-hydroxybuta-1-yne and 3-methyl-3-hydroxy penta-1-yne*

The deep-blue allenylidene-vinyl complexes (20 to 24) were synthesized by refluxing $[CpRuL_2Cl]$ with substituted propargyl alcohols, viz. 3-methyl-3-hydroxybuta-1-yne and 3-methyl-3-hydroxypenta-1-yne in methanol. Though Selegue (1983) first reported the formation of the vinylidene–alkynyl complex by stirring $(CpRu(PPh_3)_2Cl]$ with $HC \equiv C–CMe_2OH$ in methanol for 21 hours, we were able to isolated them within 30 minutes by refluxing in methanol. Table 3 lists the IR, NMR data of these complexes. These complexes were found to be similar in their chemical behaviour to those reported and therefore are assumed to be dimers of the expected dialkyl-allenylidene complexes [Ru=C=C=C(Me)R] (R=Me, Et). The central portion of the cation is illustrated in figure 1. Two typical $[CpRuL_2]$ moieties are bonded to a bridging C_nH_m ($n = 10$ or 12; $m = 12$ or 16) ligand that results in the formation of two carbon–carbon bonds (C_4–C_5 and C_7–C_8) between two C=C=CMeR (R=Me, Et) moieties with simultaneous migration of two protons. The Ru_1–C_1–C_2–C_3 group comprises an allenylidene linkage as suggested by the IR spectra that exhibit a band at 1970 cm^{-1} (Bruce and Swincer 1983) due to asymmetric $\nu_{C=C=C}$) and the second ruthenium atom is bonded to the cyclohexene ring by a vinylidene carbon bond between Ru_2 and C_5 similar to the one described by Selegue (1983).

Carbon 13 NMR spectrum of the complex (22) clearly indicates the presence of an unsaturated alkylidene group {δC 277·2 (C_1), 198·39 (C_2); 142·43 (C_3), 140·36(C_4), 151·55 (C_5), and 27 to 68 for cyclohexene ring carbons}. The shift of the Cp carbons upfield is in accord with the highfield shift of the Cp protons in proton NMR spectra because of the high 'electron richness' at the metal centres due to high conjugation of the [Ru=C=C=C–C=C–Ru] system (Treichel and Komar 1980). The increased conjugation in the blue complexes is further demonstrated by the shift in the position of



[Ru] = [CpL$_2$Ru] R = H or Me

Figure 1. The proposed structure of the dimeric complexes.

λ_{max} in their electronic spectra towards the low energy regions (575 or 500 nm) as compared to that in the tan coloured complexes (λ_{max} = 375–425 nm).

The deep-blue solutions of allenylidene-vinyl complexes show λ_{max} at 575 nm in organic solvents, and are stable for several days. They become deep red-purple (λ_{max}: 500 nm) dicationic complexes in presence of strong acids like $HClO_4$ and trifluoroacetic acid. The red-purple solutions are highly sensitive towards atmospheric moisture, the presence of which leads to the parent blue solutions. The dicationic species can be produced by protonating the β-carbons (C_2) of the monomeric complexes which can be readily deprotonated using any base like NH_4OH.

The formation of all these complexes with γ-hydroxycetylenes suggests that these reactions undoubtedly proceed via the dehydration of a hydroxy vinylidene intermediate. Dimerization of [CpL$_2$Ru(C=C=CRMe)] proceeds via the vinylidene intermediate to give allenylidene-vinyl or vinylidene-alkynyl complexes.

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