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Some acetylene and hydride chemistry of group 8 metal complexes with cyclopentadienyls and their analogous ligands[1]

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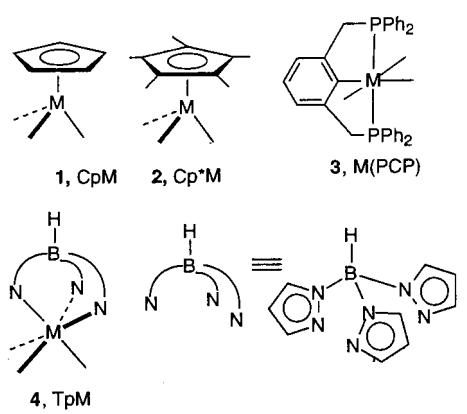
Abstract

The reactivities of several ruthenium complexes with closely related ligands Cp, Cp*, PCP (2,6-$(PPh_2CH_2)_2C_6H_3$) and Tp (hydrotris(pyrazolyl)borate) towards terminal acetylenes are compared. While reactions of terminal acetylenes with ruthenium complexes such as $CpRuCl(PR_3)_2$, $Cp^*RuCl(PR_3)_2$ and $TpRuCl(PR_3)_2$ usually give vinylidene, allenylidene, hydroxyvinylidene or vinylvinylidene complexes, unusual coupling products are produced in the reactions of terminal acetylenes with analogous Ru(PCP) complexes. The structures of group 8 metal hydride complexes of the formula $LRuH_3(L')$ (L = Cp, Cp*, Tp; L′ = PPh_3) and $[LMH_2(L')_2]^+$ (L = Cp, Cp*, Tp; L′ = tertiary phosphine) have also been compared in terms of the relative stability of dihydrogen vs. dihydride forms and *cis* vs. *trans*-dihydride isomers. Although both Cp and Tp are isoelectronic and both facially coordinate to metal centers, they have different abilities to stabilize the dihydrogen ligand. The difference is reflected in the fact that $CpRuH_3(PPh_3)$ and $[CpRuH_2(PPh_3)_2]^+$ are classic metal hydride complexes but $TpRuH(H_2)(PPh_3)$ and $[TpRu(H_2)(PPh_3)_2]^+$ are dihydrogen complexes. Complexes of the formula $[C_5R_5)MH_2(PP)]^+$ (M = Fe, Ru, Os; PP = chelating diphosphine) can adopt either the pure dihydrogen form, or a mixture of dihydrogen and *trans*-dihydride forms, or pure *trans*-dihydride form, or a mixture of *cis*- and *trans*-dihydride forms, depending on metals, C_5R_5 and the chelating ring sizes of diphosphines.

Keywords: Alkyne complexes; Dihydrogen complexes; Hydride complexes; Ruthenium

1. Introduction

Cyclopentadienyl complexes have been intensively studied for their rich chemical and catalytic properties [1]. Parallel to the development of chemistry based on cyclopentadienyl complexes, there have also been interests in the chemistry of complexes with ligands analogous to cyclopentadienyls. The ligands PCP (2,6-$(PPh_2CH_2)_2C_6H_3$) [2–6] and Tp (hydrotris(pyrazolyl)borate) [7] are two examples of such ligands. PCP and Tp are related to Cp and Cp* in that they are all formally five-electron donors on a covalent model and occupy three coordination sites in metal complexes as illustrated by structures **1**–**4**.



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[1] Dedicated to Professor Michael I. Bruce on the occasion of his 60th birthday in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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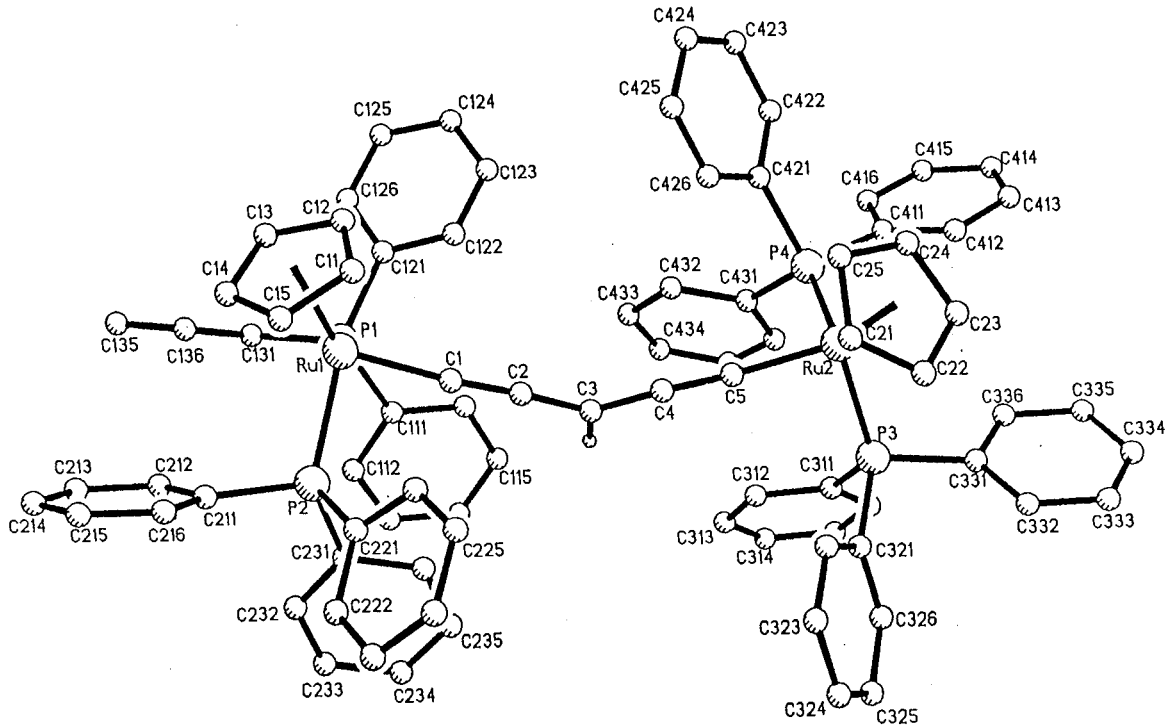


Fig. 1. The molecular structure for $[Cp(PPh_3)_2Ru{=}C{=}C{=}CH{-}C{\equiv}CRu(PPh_3)_2Cp]^+$.

Obviously, these ligands are different in their electronic properties and coordination geometries. As the chemical and catalytic properties of organometallic compounds are dependent on auxiliary ligands and metals, it is of interests to investigate how the reactivity and stability of analogous complexes are changed when the ligands are varied from C_5R_5 to Tp and to PCP.

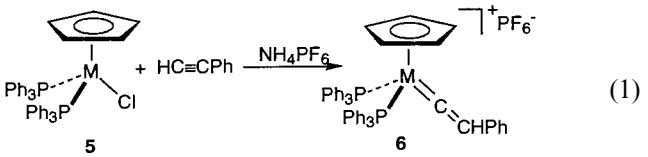
During the past few years, we have employed group 8 metal complexes and especially ruthenium complexes with fragments **1–4** for activation of terminal acetylenes and the dihydrogen ligand. In some cases, significant differences were observed in these systems, especially in their reactivity towards terminal acetylenes and in the ability to stabilize the dihydrogen ligand. This short review intends to discuss the similarities and differences in these systems, mainly based on our own and closely related literature work.

2. Reactivity toward terminal acetylenes

*2.1. CpRu, Cp*Ru and TpRu complexes*

One of the most interesting properties of complexes with CpRu or Cp*Ru fragments is that they react with appropriate terminal acetylenes HC≡CR to give vinylidene, hydroxyvinylidene, allenylidene or vinylvinylidene complexes [8,9]. For example, reaction of $CpRuCl(PPh_3)_2$ (**5**) with HC≡CPh in the presence of NH_4PF_6 produced $[CpRu(=C{=}CHPh)(PPh_3)_2]PF_6$ (**6**) (Eq. 1) [10]; reaction of $CpRuCl(PMe_3)_2$ (**7**) with HC≡CC(OH)Ph_2 in the presence of NH_4PF_6 produced $[CpRu(=C{=}C{=}CPh_2)(PMe_3)_2]PF_6$ (**8**) (Eq. 2) [11]; reaction of $Cp^*RuCl(PPh_3)_2$ (**9**) with HC≡CPh produced the neutral vinylidene complex $Cp^*RuCl(=C{=}CHPh)(PPh_3)$ (**10**) (Eq. 3) [12,13]. The electron-rich complex $Cp^*RuCl(PMe_2Ph)_2$ (**11**) reacted with $HC{\equiv}CCH_2OH$ in the presence of NH_4PF_6 to give $[CpRu(=C{=}CHCH_2OH)(PMe_2Ph)_2]PF_6$ (**12**) (Eq. 4) [14]. The chemistry has been applied to catalytic and stiochiometric organic and organometallic synthesis [15]. Using similar tactics, we have recently synthesized interesting C_5H_2- and C_5H-bridged complexes [16,17]. Thus treatment of $[CpRu(PPh_3)_2]BF_4$ (generated in situ from the reaction of complex **5** with $AgBF_4$) with 0.45 equiv. of HC≡CCH(OH)C≡CH led to the formation of the C_5H_2-bridged compound $[Cp(PPh_3)_2Ru{=}C{=}C{=}CH{-}CH{=}C{=}Ru(Cp(PPh_3)_2Cp](BF_4)_2$ (**14**). The reaction likely proceeds via the hydroxyvinylidene complex $[Cp(PPh_3)_2Ru{=}C{=}CHCH(OH){-}CH{=}C{=}Ru(CP(PPh_3)_2CP](BF_4)_2$, which has not been isolated. The C_5H_2-bridged compound **14** reacted with alumina to give the C_5H-bridged compound $[Cp(PPh_3)_2Ru{=}C{=}C{=}CH{-}C{\equiv}CRu(Cp(PPh_3)_2Cp]BF_4$ (**16**). The C_5H-bridged complex **16** has a delocalized structure as indicated by the solution NMR data and has been confirmed by an X-ray diffraction study of $[Cp(PPh_3)_2Ru{=}C{=}C{=}CH{-}C{\equiv}CRu(PPh_3)_2Cp]BPh_4$ (see Fig. 1). Analogous reactions also occurred starting from Cp*RuCl(dppe) (**13**) to afford complexes **15** and **17** (see Scheme 1).

The reactivity of $TpRuClL_2$ complexes towards terminal acetylenes is similar to that of the Cp and Cp* analogs [18,19]. As an example, the vinylidene complex $TpRuCl(C{=}CHPh)(PPh_3)$ (**19**) was formed from the reaction of $PhC{\equiv}CH$ with $TpRuCl(PPh_3)_2$ (**18**) (Eq. 5) [18], which is similar to the reaction of $Cp^*RuCl(PPh_3)_2$ with $PhC{\equiv}CH$ [12,13].



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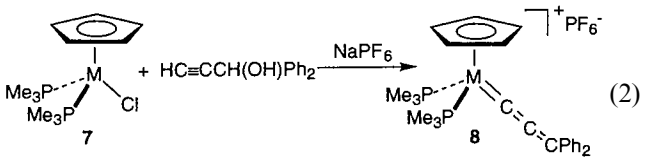

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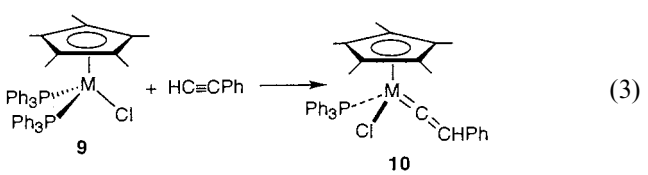

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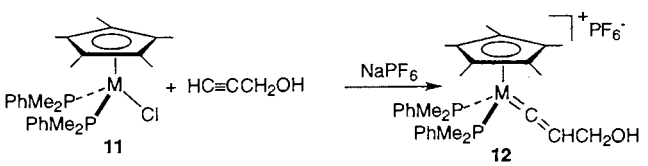

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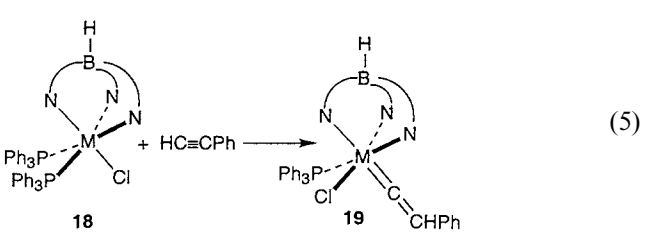

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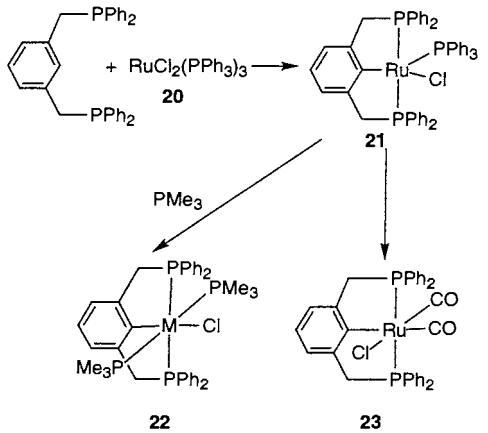
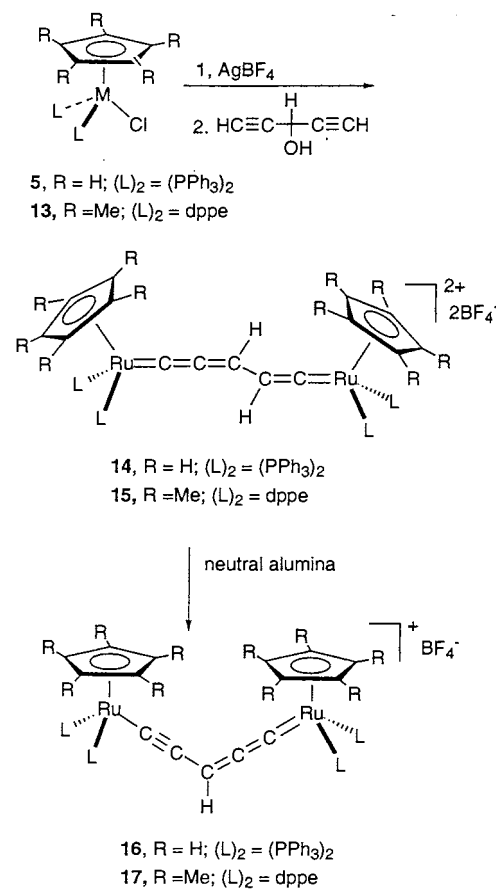
2.2. Ru(PCP) complexes

Easy formation of vinylidene and/or allenylidene complexes from the reactions of terminal acetylenes with complexes containing CpRu, Cp*Ru or TpRu fragments implies that it might be possible to prepare vinylidene and/or allenylidene ruthenium complexes with the PCP ligand. To explore such a possibility, reactions of terminal acetylenes with Ru(PCP) complexes were investigated.

Some of the Ru(PCP) complexes for testing the reactivity towards terminal acetylenes were prepared according to Scheme 2 [2,3]. Reaction of $RuCl_2(PPh_3)_3$ (**20**) with $1,3\text{-}(Ph_2PCH_2)_2C_6H_4$ produced the coordinatively unsaturated complex $RuCl(PPh_3)(PCP)$ (**21**), which was characterized by X-ray crystallography (see Fig. 2) [2]. The synthetic route to compound **21** is similar to that reported by van Koten and his coworkers [5]. It is interesting to note that Cp or Cp* can form stable complexes $CpRuCl(PPh_3)_2$ [20] or



Scheme 2.



Scheme 1.

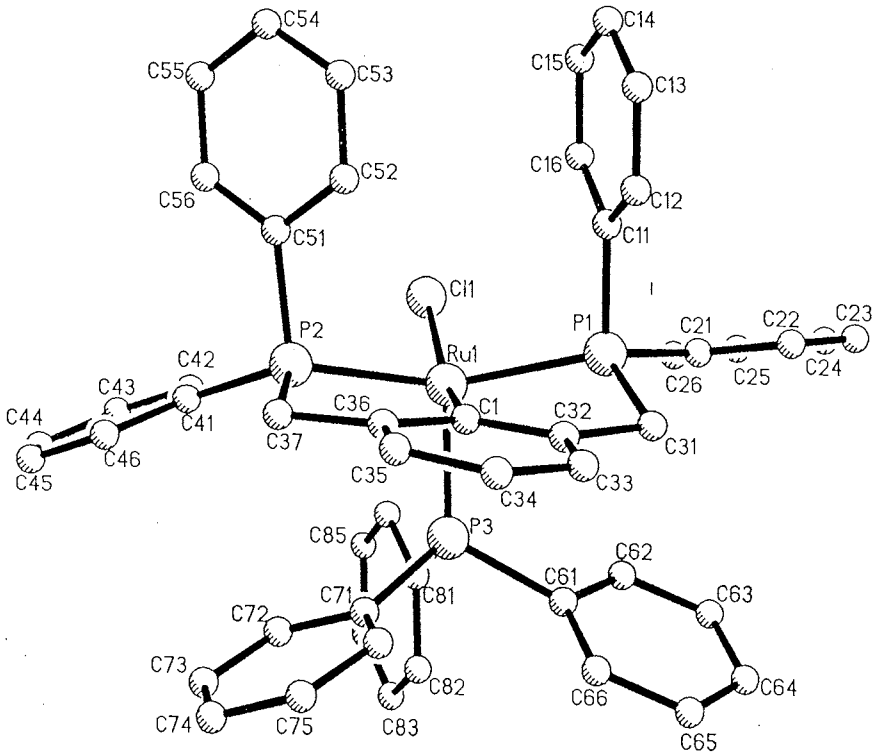


Fig. 2. The molecular structure for $RuCl(PPh_3)(PCP)$.

$Cp^*RuCl(PPh_3)_2$ [21], whereas PCP does not form the analogous 18 electron complexes $RuCl(PPh_3)_2(PCP)$, probably due to the bulkiness of the PCP ligand. Very bulky phosphines such as PCy_3 and $P(i\text{-}Pr)_3$ are known to form stable 16 electron Cp* complexes $Cp^*RuCl(PR_3)$ [22]. The related ligand NCN (2,6-$(Me_2NCH_2)_2C_6H_3$) also forms the similar 16e complex $RuCl(PPh_3)(NCN)$ [23]. Similarities in the chemical and structural properties of Cp* ruthenium complexes and NCN ruthenium complexes have been discussed by van Koten et al. [23].

The bis(trimethylphosphine) compound $RuCl(PMe_3)_2(PCP)$ (**22**) was prepared by treatment of compound **21** with 2 equiv. of PMe_3 at r.t.. A mixture of complexes **21** and **22** were obtained when < 2 equiv. of PMe_3 was used. The easy substitution of PPh_3 ligand in $RuCl(PPh_3)(PCP)$ is in sharp contrast to the more forcing conditions used in the replacement of the PPh_3 ligand in $CpRuCl(PPh_3)_2$ with PR_3 to give $CpRuCl(PPh_3)(PR_3)$ or $CpRuCl(PR_3)_2$ [24].

Reaction of CO with $RuCl(PPh_3)(PCP)$ at r.t. quickly produced the white compound $RuCl(CO)_2(PCP)$ (**23**). The structure of $RuCl(CO)_2(PCP)$ is different from that of $RuCl(PMe_3)_2(PCP)$ in which the two PMe_3 ligands are *trans* to each other. The structural difference between the CO complex **23** and the PMe_3 complex **22** can be attributed to the fact that CO is a very strong π-acceptor and thus the two COs avoid being *trans* to each other and competing for the π-electrons of ruthenium. It is noted that substitution of PPh_3 in $CpRuCl(PPh_3)_2$ or $Cp^*RuCl(PPh_3)_2$ with CO could not be achieved so easily. Thus only one PPh_3 in $CpRuCl(PPh_3)_2$ could be replaced to give $CpRuCl(CO)(PPh_3)$ under forcing conditions (150 atm CO, or 2 atm CO in the presence of sulfur, or via the addition of $Fe_2(CO)_9$ in THF) [25]. A mixture of $Cp^*RuCl(CO)(PPh_3)$ and $Cp^*RuCl(CO)_2$ was obtained from the reaction of 5 atm CO with $Cp^*RuCl(PPh_3)_2$ in refluxing toluene [26]. The easy replacement of PPh_3 in **21** could be attributed to the steric congestion in the PCP complex.

The reactivity of $RuCl(PPh_3)(PCP)$ (**21**) with terminal acetylenes is summarized in Scheme 3 [3,4]. Treatment of **21** with PhC≡CH produced the unexpected coupling product $RuCl(PPh_3)(\eta^4\text{-}PhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (**24**), the structure of which has been confirmed by an X-ray diffraction study (see Fig. 3). Thus one molecule of PhC≡CH is incorporated into the central aromatic ring of the bisphosphine ligand in the form of the vinyl substituent C=CHPh. The X-ray diffraction study shows that the ruthenium center is bound to the vinyl group ($r(Ru–C) = 2.007(8)$ Å) and close to one of the carbon atoms of the central aromatic ring ($r(Ru–C) = 2.437(6)$ Å). Two possible explanations were suggested for the short distance between ruthenium and the *ipso* carbon atom of the central aromatic ring. Due to the special geometry of the chelating ligand, the ruthenium

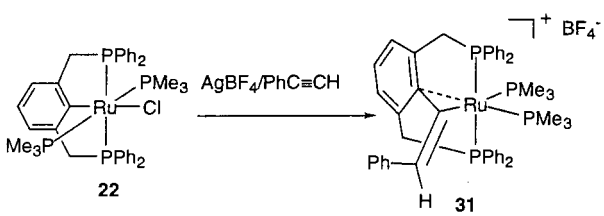
may be forced to a position which is close to the *ipso* carbon of the central aromatic ring. Alternatively, there may be a real bonding interaction between ruthenium and the central aromatic ring. Thus three electrons may formally be donated from the arylvinyl ligand CAr = CHPh to the ruthenium center which then satisfies the 18e rule. One electron comes from the σ-bonded vinyl ligand and the other two from the aromatic ring.

A mechanism for the formation of complex **24** was suggested in Scheme 4. The coordinatively unsaturated complex **21** reacts with PhC≡CH to give initially the η^2-acetylene intermediate RuCl(PhC≡CH)(PPh_3)(PCP) (**29**) which then rearranges to form the vinylidene complex RuCl(=C=CHPh)(PPh_3)(PCP) (**30**). Migratory insertion of the aryl group of the PCP ligand to the α-carbon atom of the vinylidene ligand would produce the product **24**. The reaction rate for the coupling reaction is so high that the vinylidene intermediate could not be detected during the course of the reaction. The coupling reaction provides a rare example of C–C bond formation between vinylidene and aryl ligands. Precedence for C–C bond formation between vinylidene and aryl ligands was reported by Werner and co-workers, in which RhPh($P(i\text{-}Pr)_3$)$_2$=C=CHR react with CO to give Rh(CO)($P(i\text{-}Pr)_3$)$_2$CPh=CHR (R = Ph, *t*-Bu) [27].

A similar coupling product RuCl(PPh_3)(η^4-$Ph_2C(OH)CH$ = C-2,6-$(Ph_2PCH_2)_2C_6H_3$) (**25**) was obtained from the reaction of RuCl(PPh_3)(PCP) with $HC{\equiv}CC(OH)Ph_2$. The hydroxyvinylidene complex RuCl(PPh_3)(PCP)(=C=CHC(OH)Ph_2) was suggested as the intermediate for the formation of complex **25**. Apparently, dehydration of RuCl(PPh_3)(PCP)(=C=CHC(OH)Ph_2) to give an allenylidene intermediate did not occur before the coupling reaction. It has been shown that spontaneous dehydration of hydroxyvinylidene intermediates to give allenylidene complexes occurs readily on electrophilic ruthenium centers such as $[CpRu(PMe_3)_2]^+$ [11], $[(\eta^5\text{-}C_9H_7)Ru(PR_3)_2]^+$ [28], [RuCl(dppm)2]$^+$ [29], and $[RuCl(N(CH_2CH_2PPh_2)_3)]^+$ [30]. In contrast, stable ruthenium hydroxyvinylidene complexes can be isolated with more electron rich metal centers such as $[Cp^*Ru(PMe_2Ph)_2]^+$ [14], and $RuCl_2((i\text{-}Pr)_2PCH_2CO_2Me)_2$ [31].

When a γ-proton is present in 1-alkynols, dehydrated coupling products could be obtained (see Scheme 3) [3,4]. Thus reactions of 1-ethynylcyclohexanol with RuCl(PPh_3)(PCP) produced the dehydrated coupling product RuCl(PPh_3)(η^4-*cyclo*-C_6H_9–CH=C-2,6-$(PPh_2CH_2)_2C_6H_3$) (**26**) as the predominant metal-containing product, along with oligomeric acetylenes. Pure samples of **26** were obtained by column chromatography on alumina using diethyl ether as the eluting solvent. When HC≡CC(OH)PhMe was used, both the non-dehydrated coupling product RuCl(PPh_3)(η^4-MePhC(OH)CH=C-2,6-$(PPh_2CH_2)_2C_6H_3$) (**27**) and the dehydrated coupling product RuCl(PPh_3)(η^4-CH_2=CPhCH=C-2,6-$(PPh_2CH_2)_2C_6H_3$) (**28**) were produced. The relative amounts of complexes **27** and **28** were found to be dependent on the purity of the solvents used and the reaction time. Water and trace amounts of acids present in the solvents catalyze the conversion of complex **27** to complex **28**. It was suggested that the dehydrated coupling products were produced from the non-dehydrated coupling products.

A coupling reaction also occurred between PhC≡CH and $[Ru(PMe_3)_2(PCP)]^+$ (generated in situ from the reaction of RuCl(PMe_3)$_2$(PCP) (**22**) with $AgBF_4$) to give $[Ru(PMe_3)_2(\eta^4\text{-}PhCH{=}C\text{-}2 \sim 6\text{-}(PPh_2CH_2)_2C_6H_3)]BF_4$ (**31**) (Eq. 6).



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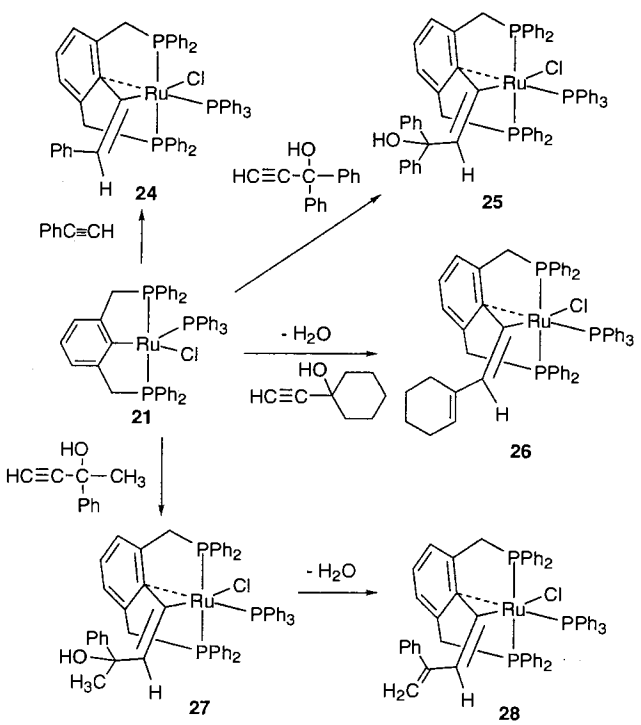


Scheme 3.

2.3. Os(PCP) complexes

In order to see if similar coupling reactions would also occur with analogous osmium system, the reactivity of OsCl(PPh_3)(PCP) towards HC≡CR (R = Ph, $C(OH)Ph_2$) has been investigated. The coordinatively

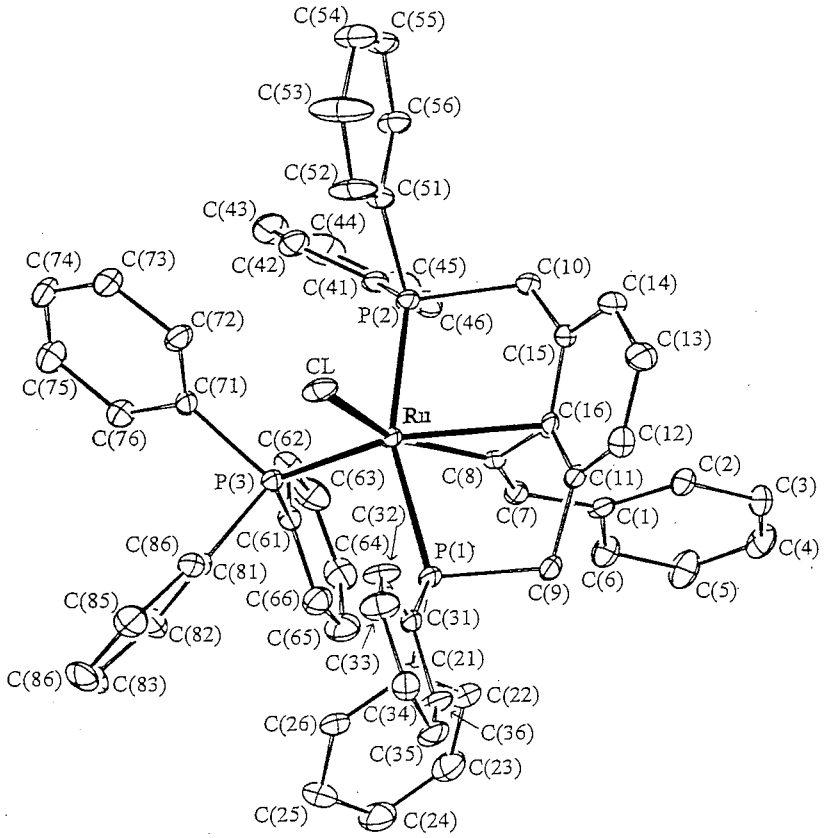
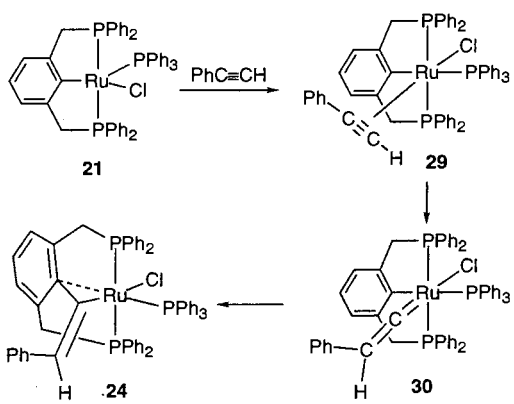


Fig. 3. The molecular structure for $RuCl(PPh_3)(\eta^4$-PhCH=C-2,6$(PPh_2CH_2)_2C_6H_3)$.

unsaturated complex $OsCl(PPh_3)$(PCP) was prepared from the reaction of $OsCl_2(PPh_3)_3$ with 1,3-$(Ph_2PCH_2)_2C_6H_4$ in isopropanol. Reactions of Os-$Cl(PPh_3)$(PCP) with PhC≡CH and $Ph_2(OH)CC{\equiv}CH$ gave the vinylidene complexes $OsCl(=C{=}CHPh)(PPh_3)$(PCP) and $OsCl(=C{=}CHC(OH)Ph_2)(PPh_3)$(PCP), respectively. Interestingly, the osmium vinylidene complexes are stable in both solid state and solution in an inert atmosphere at room temperature and could not be converted to the expected coupling products [32]. In contrast, the ruthenium vinylidene complexes Ru(C=CHR)(PPh_3)(PCP), which were proposed to be the key intermediates in the coupling reactions, appear to be too reactive to be observed. The difference between the ruthenium and osmium systems could be attributed to the more stronger Os=C bond.



Scheme 4.

3. Group 8 metal hydride complexes containing Cp, Cp*, Tp and PCP

3.1. Relative stability of dihydrogen and dihydride tautomers of $[(\eta^5$-$C_5R_5)MH_2L_2]^+$ (M = Fe, Ru, Os)

Dihydrogen complexes are an unique class of hydride complexes in which the H–H bond is retained. In the past decade a large amount of work has been carried out on the synthesis and characterization of this interesting class of compounds [33]. Dihydrogen complexes can be regarded as the intermediates in the oxidative addition of H_2 molecule to metal complexes. In this regard, it is of interest to study the relative stability of the dihydride and dihydrogen forms. Complexes of the formula $[(\eta^5$-$C_5R_5)MH_2L_2]^+$ (M = Fe, Ru, Os; L = two electron donors) represent one of the most well studied series of hydride complexes. These complexes exist in pure dihydrogen form, or a mixture of dihydrogen and *trans*-dihydride form, or pure *trans*-dihydride form, or

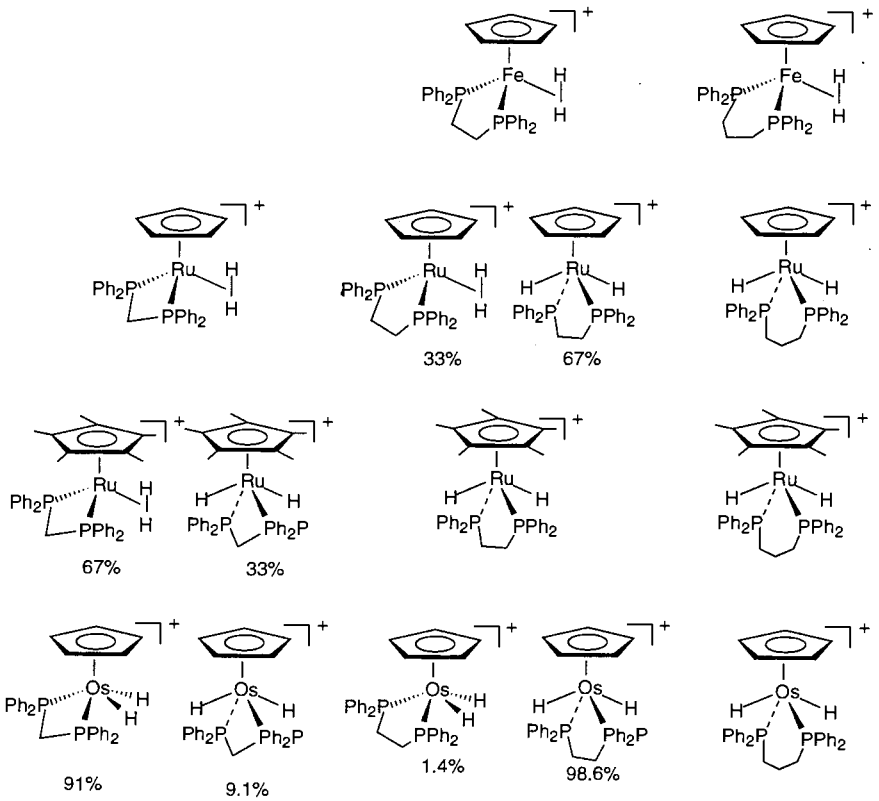


Chart 1.

a mixture of *cis*- and *trans*-dihydride forms [34–52]. Some of these reported complexes are listed in Table 1, along with the ^1J(HD) coupling constants for the corresponding isotopomers.

Complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2L_2]^+$ (M = Fe, Ru, Os; L = two electron donors) could be easily prepared by protonation of $(\eta^5\text{-}C_5R_5)MHL_2$. For example, we have recently prepared $[CpMH_2(PP)]BF_4$ by protonation of CpMH(PP) (M = Fe, PP = dppe, dppp; M = Os, PP = dppm, dppe, dppp) with $HBF_4 \cdot OEt_2$ [34]. The protonation reaction performed at low temperature could produce unstable dihydrogen intermediates which may isomerize to stable dihydride complexes on warming. Alternatively, reactions of $[(\eta^5\text{-}C_5R_5)ML_2]^+$ with hydrogen may also produce $[(\eta^5\text{-}C_5R_5)MH_2L_2]^+$.

As shown in Table 1, the thermodynamically stable structures of $[(\eta^5\text{-}C_5R_5)MH_2L_2]^+$ at r.t. are dependent on metals, C_5R_5, the electronic properties of L and even the sizes of the chelating rings if L_2 are chelating diphosphines. To illustrate these effects, the thermodynamically stable forms of complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(PP)]^+$ at r.t. are presented in Chart 1.

The metals have strong influences on the relative stability of the dihydrogen and dihydride forms of complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(PP)]^+$. For analogous complexes, the relative stability of dihydrogen form decreases when the metal is replaced by a heavier element. For example, protonation of CpMH(dppe) (M = Fe, Ru, and Os) at r.t. produced the dihydrogen complex $[CpFe(H_2)(dppe)]^+$ [34], a mixture of dihydrogen complex $[CpRu(H_2)(dppe)]^+$ and dihydride complex *trans*-$[CpRuH_2(dppe)]^+$ [38], and the dihydride complex $[CpOsH_2(dppe)]^+$ [34], respectively. Such a trend in the relative stability of dihydrogen and dihydride forms is consistent with the fact that the relative energy of d electrons involved in backdonation to the σ^* orbital of the dihydrogen ligand increases down a group.

Electronic properties of ligands L also affect the relative stability of the dihydrogen and dihydride forms. Presence of π-acid ligands increases the stability of the dihydrogen form. For example, while $[CpRuH_2(PPh_3)_2]^+$ is a classic hydride complex [43], $[CpRu(H_2)(CO)(PPh_3)]^+$ is a dihydrogen complex [40]; while $[CpOsH_2(PPh_3)_2]^+$ [50] and $[CpOsH_2(CO)(P(i\text{-}Pr)_3)]^+$ [51] are hydride complexes, the analogous dicarbonyl complexes exist as a mixture of the dihydride complex $[Cp^*OsH_2(CO)_2]^+$ and the dihydrogen complex $[Cp^*Os(H_2)(CO)_2]^+$ [52].

Replacement of Cp with Cp* could decrease the relative stability of the dihydrogen form. Thus $[CpFe(H_2)(dppe)]^+$ is stable at r.t. [34], but $[Cp^*Fe(H_2)(dppe)]BF_4$ is only stable at low temperature and isomerizes to *trans*-$[Cp^*FeH_2(dppe)]BF_4$ on warming [37]. While only the dihydrogen form is observed

Table 1
Dihydrogen and dihydride complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(L)_2]^+$ and the J(HD) values for the corresponding isotopomers[a]

Complexes	J(HD), Hz	References
$[CpFe(H_2)(dppe)]BF_4$	30.7	[34]
trans-$[CpFeH_2(dippe)]BPh_4$		[35]
$[CpFe(H_2)(dppp)]BF_4$	29.0	[34]
$[CpFe(H_2)(CO)(PPh_3)_2]BAr_4$	31.7	[36]
$[CpFe(H_2)(CO)(PEt_3)_2]BAr_4$	31.6	[36]
$[Cp^*Fe(H_2)(dppe)]BF_4$[b]	27	[37]
trans-$[Cp^*FeH_2(dppe)]BF_4$		[37]
trans-$[(Cp^*FeH_2(dippe)]BPh_4$		[35]
$[CpRu(H_2)(dppm)]PF_6$	21.9	[38]
$[CpRu(H_2)(dppe)]PF_6$[c]	24.9	[38]
trans-$[CpRu(H_2)(dppe)]PF_6$		[38]
trans-$[CpRuH_2(dppp)]PF_6$		[38]
$[CpRu(H_2)(dmpe)]BF_4$[d]	22.1	[39,40]
trans-$[CpRuH_2(dmpe)]BF_4$		[39,40]
$[CpRu(H_2)(dmdppe)]BF_4$[e]	23.8	[40]
trans-$[CpRuH_2(dmdppe)]BF_4$		[40]
$[CpRu(H_2)(prophos))]BF_4$		[40]
trans-$[CpRuH_2(prophos)]BF_4$		[40]
$[CpRu(H_2)(dippe)]BF_4$[b]	20.5	[41]
trans-$[CpRuH_2(dippe)]BF_4$		[41]
$[CpRu(H_2)(dape)]BF_4$[f]	24.3	[42]
trans-$[CpRuH_2(dape)]BF_4$		[42]
$[CpRu(H_2)(dtfpe)]BF_4$[g]	25.3	[42]
trans-$[CpRuH_2(dtfpe)]BF_4$		[42]
$[CpRu(H_2)(PPh_3)_2]BF_4$[b]	26.5	[40]
trans-$[CpRuH_2(PPh_3)_2]BF_4$		[43]
trans-$[CpRuH_2(PMe_3)_2]BF_4$		[44]
$[CpRu(H_2)(CO)(PPh_3)]BF_4$		[39,40]
$[CpRu(H_2)(CO)(PMe_2Ph)]BF_4$		[39,40]
$[CpRu(H_2)(CO)(PMe_3)]BF_4$	28.5	[39,40]
$[CpRu(H_2)(CO)(PCy_3)]BF_4$[h]	28.5	[39,40]
trans-$[CpRuH_2(CO)(PCy3_)]BF_4$		[39,40]
trans-$[CpRu(H_2)(PPh_3)(CN\text{-}t\text{-}Bu)]PF_6$	28.6	[45]
$[Cp^*Ru(H_2)(dppm)]BF_4$[i]	20.9	[42,46,47]
trans-$[Cp^*RuH_2(dppm)]BF_4$		[42,46]
trans-$[Cp^*RuH_2(dppe)]BF_4$		[48]
$[Cp^*Ru(H_2)(dppp)]BF_4$[b]	23.3	[46]
trans-$[Cp^*RuH_2(dppp)]BF_4$		[46]
trans-$[Cp^*Ru(H_2)(dippe)]BF_4$[b]	21	[41]
trans-$[Cp^*RuH_2(dippe)]BF_4$		[41]
$[Cp^*Ru(H_2)PPh_3)_2]BF_4$[b]	24.0	[40]
trans-$[Cp^*RuH_2(PR_3)_2]BF_4$ ($PR_3 = PPh_3$, $PMePh_2$)		[42,46]
trans-$[Cp^*RuH_2(PR_3)_2]BPh_4$ ($PR_3 = PMe_2Ph$, PMe_3)		[46]
$[Cp^*Ru(H_2)(CO)(PCy_3)]BF_4$	29.2	[40]
$[Cp^*Ru(H_2)(CO)_2]BF_4$	32	[49]
cis-$[CpOsH_2(dppm)]BF_4$[j]	3.0	[34]
trans-$[CpOsH_2(dppm)]BF_4$		[34]
cis-$[CpOsH2(dppe)]BF_4$[k]		[34]
trans-$[CpOsH_2(dppe)lBF_4$		[34]
cis-$[CpOsH_2(dppp)]BF_4$[b]		[34]
trans-$[CpOsH_2(dppp)]BF_4$		[34]
trans-$[CpOsH_2(PR_3)_2]CF_3SO_3$ ($(PR_3)_2 = PPh_3$, Ph_2PhMe, $(PPh_3)(P(OEt)_3)$),		[50]
trans-$[CpOsH_2(CO)(P(i\text{-}Pr)_3)]BF_4$		[51]
$[Cp^*Os(H_2)(CO)_2]OTf$[l]		[52]
trans-$[Cp^*OsH_2(CO)_2]OTf$		[52]

[a] Abbreviations: dape, $(MeO\text{-}p\text{-}C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}OMe)_2$; dippe, $P(i\text{-}Pr)_2CH_2CH_2P(i\text{-}Pr)_2$; dmdppe, $PMe_2CH_2CH_2PPh_2$; dmpe, $PMe_2CH_2CH_2PMe_2$; dppe, $PPh_2CH_2CH_2PPh_2$; dppm, $PPh_2CH_2PPh_2$; dppp, $PPh_2CH_2CH_2CH_2PPh_2$; dtfpe, $(CF_3\text{-}p\text{-}C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}CF_3)_2$; prophos, $PPh_2CH(Me)CH_2PPh_2$; Ar, $3,5(CF_3)_2C_6H_3$.

[b] Only stable at low temperatures, will isomerize to *trans*-dihydride complexes at room temperature.

[c] In equilibrium with *trans*-$[CpRuH_2(dppe)]PF_6$ in a ratio of 1:2.

[d] In equilibrium with *trans*-$[CpRuH_2(dmpe)]PF_6$ in a ratio of 86:14.

[e] In equilibrium with *trans*-$[CpRu(H_2)(dmdppe)]PF_6$ in a ratio of 34:66.

[f] In equilibrium with *trans*-$[CpRuH_2(dape)]PF_6$ in a ratio of 1:2.6.

[g] In equilibrium with *trans*-$[CpRuH_2(dtfpe)]PF_6$ in a ratio of 1:1.6.

[h] Co-exist with 2–3% *trans*$[CpRuH_2(CO)(PCy_3)]BF_4$.

[i] In equilibrium with *trans*-$[Cp^*RuH_2(dppm)]PF_6$ in a ratio of 2:1.

[j] In equilibrium with *trans*-$[CpOsH_2(dppm)]BF_4$ in a ratio of 10:1.

[k] In equilibrium with *trans*-$[CpRuH_2(dppe)]BF_4$ in a ratio of 1:70.

[l] In equilibrium with *trans*$[Cp^*OsH_2(CO)_2]OTf$ in a ratio of 13:87.

for $[CpRu(H_2)(dppm)]BF_4$ [38], the corresponding Cp* complex exists as a mixture of the dihydrogen form $[Cp^*Ru(H_2)(dppm)]BF_4$ and the dihydride form $[Cp^*RuH_2(dppm)]BF_4$ in a ratio of 2:1 [42]. Similarly, $[Cp^*RuH_2(dppe)]BF_4$ only exists in the dihydride form [48], the corresponding Cp complex exists as a mixture of the dihydrogen form $[CpRu(H_2)(dppe)]BF_4$ and the dihydride form $[CpRuH_2(dppe)]BF_4$ in a ratio of 1:2 [38]. The decreased stability of the dihydrogen form for the corresponding Cp* complexes can be attributed to the more electron donating ability of the Cp* ligand.

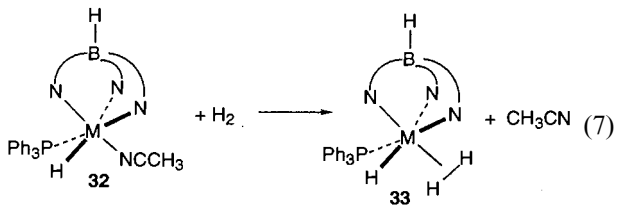
Interestingly, the chelating ring sizes could also have drastic effect on the relative stability of the dihydrogen and dihydride forms, as shown in Chart 1. Chelating ligands with smaller bite angles favor the dihydrogen form. For example, Simpson et al. reported that protonation of CpRuH(dppm), CpRuH(dppe) and CpRuH(dppp) produced $[CpRu(H_2)(dppm)]^+$, $[CpRu(H_2)(dppe)]^+/[CpRuH_2(dppe)]^+$ (in a ratio of 1:2) and $[CpRuH_2(dppp)]^+$, respectively [38]. It is also interesting to note that although Cp*RuH(dppm) and CpRuH(dmpe) ($dmpe = Me_2PCH_2CH_2PMe_2$) are more electron rich than $CpRuH(PPh_3)_2$, the protonated products of these monohydride complexes are $[Cp^*Ru(H_2)(dppm)]^+/[Cp^*RuH_2(dppm)]^+$ (2:1 ratio) [42], $[CpRu(H_2)(dmpe)]^+/[CpRuH_2(dmpe)]^+$ (6:1 ratio) [39], and $[CpRuH_2(PPh_3)_2]^+$ [42], respectively.

Dihydride complexes of the type $[(\eta^5\text{-}C_5R_5)MH_2(PR_3)_2]^+$ ($M = Ru$, Os) usually adopt *trans* geometry. However, we have recently shown that $[CpOsH_2(PP)]^+$ can also adopt *cis* geometry, when PP are the diphosphine ligands dppm and dppe [34]. At r.t. in dichloromethane solution, $[CpOsH_2(dppm)]BF_4$ and

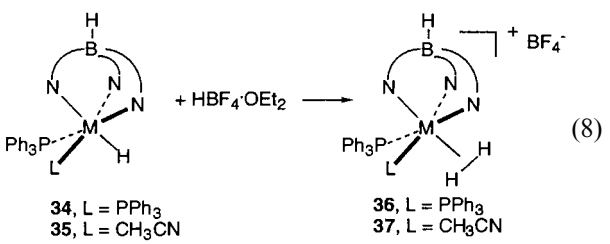
$[CpOsH_2(dppe)]BF_4$ exist as a mixture of *cis* and *trans* isomers in a ratio of 10:1 and 1:70, respectively. The dppp complex $[CpOsH_2(dppp)]BF_4$ behaves like $[CpOsH_2(PPh_3)_2]^+$ and just adopts the *trans* geometry. The relatively large size of osmium and small bite angles of dppm and dppe are the most likely factors contributing to the stability of *cis*-$[CpOsH_2(PP)]^+$.

3.2. Dihydrogen complexes with TpRu fragment

During the course of investigating chemical and catalytic properties of TpRu complexes, we have recently prepared and characterized TpRu dihydrogen complexes $TpRuH(H_2)(PPh_3)$ (**33**) [53] and $[TpRu(H_2)(PPh_3)(L)]BF_4$ ($L = PPh_3$, **36**; $L = CH_3CN$, **37**) [54]. These complexes were prepared by the reactions shown in Eqs. 7 and 8, respectively.



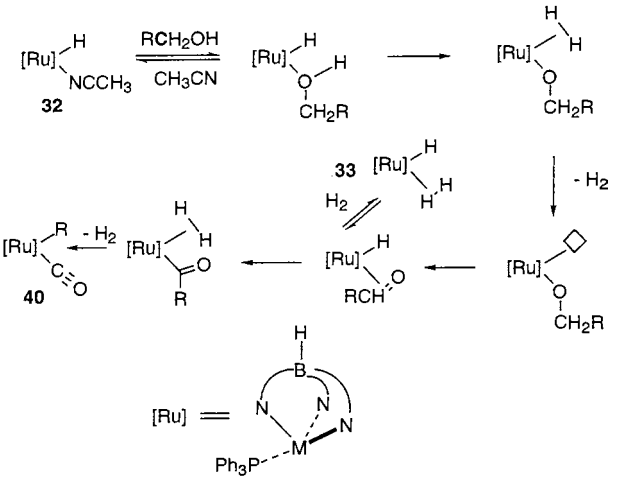
(7)



(8)

Chaudret et al. have also reported several ruthenium dihydrogen complexes with hydrotris(pyrazolyl)borate and related ligands including $TpRuH(H_2)_2$ and $TpRuH(H_2)(PCy_3)$ [55].

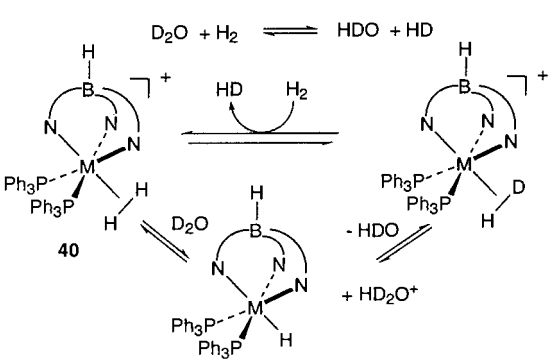
Dihydrogen complex **33** can be regarded as the analog of the classic trihydride complex $CpRuH_3(PPh_3)$ (**38**) [56]. Dihydrogen complex **36** can be regarded as the analog of the classic dihydride complex $[CpRuH_2(PPh_3)_2]^+$ (**39**). Thus, although both Tp and Cp are isoelectronic and both facially coordinate to ruthenium, they have different ability to stabilize the dihydrogen ligand. The Tp ligand has a higher tendency than Cp to stabilize dihydrogen ligand. The same phenomenon has also been noted by others [57–59], as exemplified by the structures of $[Cp^*IrH_3(PMe_3)]^+$ and



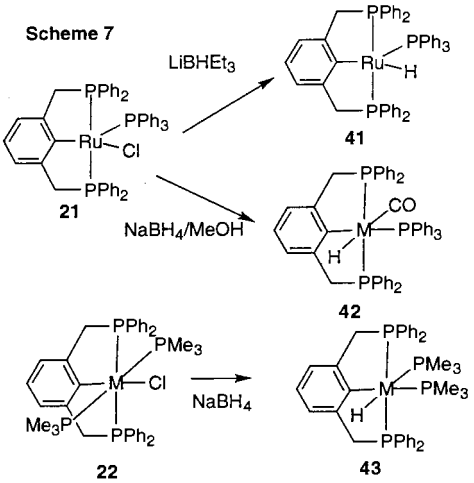
Scheme 5.

$[TpIrH(H_2)(PMe_3)]^+$ [58], and the structures of $[CpOsH_2(P(i\text{-}Pr)_3)(CO)]^+$ [51] and $[TpOsH_2(P(i\text{-}Pr)_3)(CO)]^+$ [59]. The difference could be related to the electronic properties of Tp and Cp. It has been suggested that TpM fragment has strongly directional frontier orbitals to bind three additional ligands to form octahedral complexes while cyclopentadienyl ligands are rather ineffective in promoting strongly directional frontier orbitals due to the symmetry and diffuse electron clouds [60]. Thus CpRu can form seven coordinated complexes easily, but TpRu has a low tendency to do so in order to achieve strong σ-bonding interaction with the other three ligands. These arguments could explain why $CpRuH_3(PPh_3)$ and $[CpRuH_2(PPh_3)_2]^+$ are classic hydride complexes but $TpRuH(H_2)(PPh_3)$ and $[TpRu(H_2)(PPh_3)_2]^+$ are dihydrogen complexes, because the latter complexes would be seven coordinated if they were dihydride complexes.

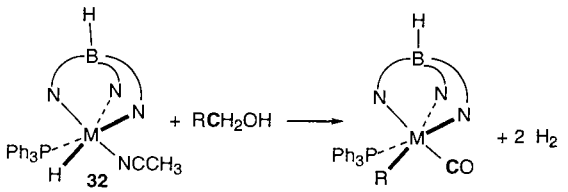
The dihydrogen complex **33** was observed in the early stage of the reactions of $TpRuH(CH_3CN)(PPh_3)$ (**32**) with RCH_2OH to give the CO-containing products $TpRuR(CO)(PPh_3)$ (**40**, Eq. 9) [53].



Scheme 6.



Scheme 7.



40, R = H, CH_3, C_2H_5, n-C_3H_5, C_6H_5, C_6H_4Cl-4, $C_6H_4CH_3$-4 (9)

Scheme 5 is a suggested mechanism for the formation complexes **40**. The easy formation of H_2 intermediates and subsequently easy loss of the H_2 ligand accounts for the facile formation of the final decarbonylated products **40**. It is noted that $Cp^*RuH_3(PR_3)$ could be prepared from the reaction of $Cp^*RuCl_2(PR_3)$ with $NaBH_4$ in ethanol [56]. In principle, a similar decarbonylation could also occur here. However, such a decarbonylation reaction was not noted in the reaction. The difference could be related to the fact that dibydrogen complexes could be formed on the TpRu system, but not on the Cp*Ru system.

The dihydrogen complex $[TpRu(H_2)(PPh_3)_2]^+$ (**36**) was found to be an active catalyst for H/D exchange between H_2 and D_2O by the mechanism shown in Scheme 6 [54]. We also reported that the TpRu dihydrogen complexes **36** and **37** are involved in catalytic hydrogenation reactions [54].

3.3. Hydride complexes with Ru(PCP) fragments

In view of the different structural properties of $CpRuH_3(PPh_3)$ vs. $TpRuH(H_2)(PPh_3)$ and $[CpRuH_2(PPh_3)_2]^+$ vs. $[TpRu(H_2)(PPh_3)_2]^+$, we became interested in the structural properties of analogous Ru(PCP) complexes such as $RuH(H_2)(PPh_3)(PCP)$ (or $RuH_3(PPh_3)(PCP)$) and $[Ru(H_2)(L)_2(PCP)]^+$ (or $[RuH_2(L)_2(PCP)]^+$). To this end, several precursors to the targeted complexes were prepared as shown in Scheme 7 [2]. It was anticipated that reaction of complex **41** with H_2 could give $RuH(H_2)(PPh_3)(PCP)$ or $RuH_3(PPh_3)(PCP)$. Unfortunately, the affinity of H_2 to $RuH(PPh_3)(PCP)$ appears to be too low and no reaction was observed under 1 atm H_2. Protonation of complex **42** or **43** with $HBF_4 \cdot OEt_2$ also failed to generate the expected dihydrogen (or dihydride) complexes. It is likely that the expected dihydrogen complexes were produced in theseprotonation reactions. However the dihydrogen ligand is too labile to isolate the dihydrogen complexes. One might expect that a H_2 ligand on the TpRu fragments is less labile than that on the Ru(PCP) fragments, because the H_2 ligand is trans to a nitrogen donor in TpRu complexes, but *trans* to a stronger *trans* influence ligand (phosphorus or carbon donor) in the Ru(PCP) cases.

4. Conclusion

Although the ligands Cp, Cp*, PCP and Tp are closely related in that they are all formally five-electron donors on a covalent model and occupy three coordination sites in a metal complex, their complexes can have significantly different properties. While reactions of terminal acetylenes with ruthenium complexes such as $CpRuCl(PR_3)_2$, $Cp^*RuCl(PR_3)_2$ and $TpRuCl(PR_3)_2$ usually give vinylidene, allenylidene, hydroxyvinylidene or vinylvinylidene complexes, unusual coupling products are produced in the cases of the analogous Ru(PCP) complexes. Hydride complexes of Cp, Cp*, PCP, and Tp can have different structural properties and stability. For example, $TpRuH(H_2)(PPh_3)$ and $[TpRu(H_2)(PPh_3)_2]^+$ are dihydrogen complexes; $CpRuH_3(PPh_3)$ and $[CpRuH_2(PPh_3)_2]^+$ are classic hydride complexes; and the analogous Ru(PCP) complexes could not be characterized so far. Complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2L_2]^+$ (M = Fe, Ru, Os; PP = chelating diphiosphine) can adopt pure dihydrogen form, or a mixture of dihydrogen and *trans*-dihydride form, or pure *trans*-dihydride form, or a mixture of *cis*- and *trans*-dihydride forms, depending on metals, C_5R_5 and ligand L. Smaller chelating ring sizes increase the stability of dihydrogen or *cis*-dihydride forms.

Acknowledgements

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