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# Recent Chemistry Based on the $[Ru\mathit{Cp}(CH_3CN)_3]^+$ Cation: Reappraisal of an Old Precursor

**Christian Slugovc**[1], **Eva Rüba**[1], **Roland Schmid**[1], **Karl Kirchner**[1,*], and **Kurt Mereiter**[2]

[1] Institute of Inorganic Chemistry, Technical University of Vienna, A-1060 Vienna, Austria
[2] Institute of Mineralogy, Crystallography, and Structural Chemistry, Technical University of Vienna, A-1060 Vienna, Austria

**Summary.** This article gives an overview of recent chemistry based on the *tris*-acetonitrile complex $[Ru\mathit{Cp}(CH_3CN)_3]^+$. Due to the labile nature of the $CH_3CN$ ligands, substitution reactions are a dominant feature of this complex. Important derivatives are the highly reactive complexes $[Ru\mathit{Cp}(PR_3)(CH_3CN)_2]^+$ which are a source of the $14e^-$ fragment $[Ru\mathit{Cp}(PR_3)]^+$. These species are catalytically active in the redox isomerization of allyl alcohols to give aldehydes and ketones. Furthermore, the cationic complex $[Ru\mathit{Cp}(\kappa^1(P),\eta^2\text{-}PPh_2CH_2CH_2CH{=}CH_2)(CH_3CN)]PF_6$ derived from the reaction of $[Ru\mathit{Cp}(CH_3CN)_3]^+$ with $PPh_2CH_2CH_2CH{=}CH_2$ is a model compound for studying coupling reactions of olefins and acetylenes. In addition, $[Ru\mathit{Cp}(CH_3CN)_3]^+$ is a valuable precursor for the synthesis of configurationally stable chiral three-legged piano-stool ruthenium complexes. These are currently being intensively investigated as *Lewis* acid catalysts in asymmetric synthesis.

**Keywords.** Ruthenium; Halfsandwich complexes; Catalysis; C–H Activation.

## Introduction

The cationic complex $[Ru\mathit{Cp}(CH_3CN)_3]^+$ (**1**), first prepared by *Gill* and *Mann* in 1982 [1], is a promising versatile synthetic intermediate since the $CH_3CN$ ligands are substitutionally labile [2] and can be replaced by other ligands. Thus, using monodentate $P(OMe)_3$ under various conditions, any mixed complex $[Ru\mathit{Cp}\text{-}(P(OMe)_3)(CH_3CN)_2]^+$, $[Ru\mathit{Cp}(P(OMe)_3)_2(CH_3CN)]^+$, and $[Ru\mathit{Cp}(P(OMe)_3)_3]^+$ is obtainable [1]. Recently, **1** has been converted to the monophosphine compounds $[Ru\mathit{Cp}(\eta^1(P)\text{-}2\text{-}(PPh_2)(C_6H_4CH(O\mathit{R})_2))(CH_3CN)_2]CF_3SO_3$ ($R = Me$, Et) [3]. Due to its high affinity to arene rings, **1** is frequently used as a protecting and/or activating agent for these systems [4, 5] including biologically important molecules

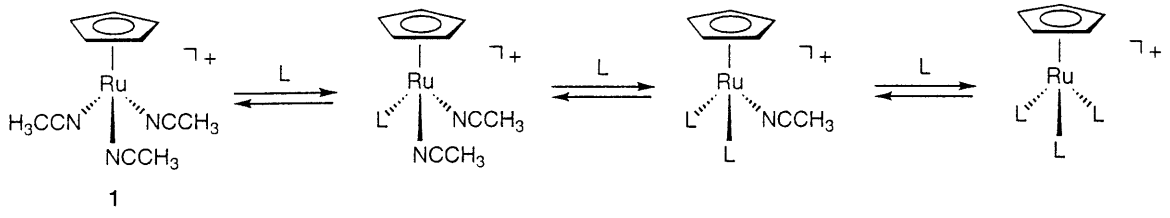
* Corresponding author

such as steroids [6, 7] and amino acids [8–10]. Decomplexation is easily achieved under photochemical conditions unless the arene systems are electron-rich [11]. Furthermore, **1** has found applications in peptide labeling and peptide synthesis leading to intriguing results [12]. Thus, Ru-labeled estradiol has been employed to gain an insight into hormone receptor substrate interactions [13]. Similarly, radiolabeled $[Ru\mathit{Cp}(\text{phenylalanine})]^+$ has been utilized as a pancreatic imaging agent [14]. In peptide synthesis, two cyclic dipeptides (K-13 and OF4949) have been prepared by the ruthenium mediated formation of a biphenylether moiety [15]. Along these lines, even a 17-membered ring became available with 78% isolated yield [16]. Very recently, the related water-soluble $[Ru(\mathit{Cp}CH_2CH_2NH_2)(CH_3CN)_2]^+$ has been synthesized and used in selective arene ring-marking of proteins even in aqueous media [17].

In contrast to the extensive chemistry of **1** in conjunction with arenes, its use towards other ligand systems is relatively undeveloped. A handful of catalytic C-C bond formations mediated by **1**, published by *Trost et al.* [20–22], illustrate the great potential of this type of compounds. Therefore, we wish to report on recent chemistry based on **1** leading to mixed Ru(II) and Ru(IV) halfsandwich complexes and present new reactions derived from these species.

## Reactivity of $[Ru\mathit{Cp}(CH_3CN)_3]^+$ with Non-Aromatic Ligands

As has been shown by *Merbach* and *Ludi*, the $CH_3CN$ ligands in **1** are substitutionally labile with an exchange rate constant of $5.6\,s^{-1}$ at room temperature [2]. Ligand substitution reactions according to Scheme 1 are therefore an important feature. Of course, the distribution of the products formed depends on the nature of the donor molecules used. As an example, treatment of **1** with 1 equivalent of the monodentate compounds $L = PR_3$, $AsR_3$, or $P(OR)_3$ at room temperature affords the cationic complexes $[Ru\mathit{Cp}(L)(CH_3CN)_2]PF_6$ in essentially quantitative yields with no evidence of $[Ru\mathit{Cp}(L)_2(CH_3CN)]PF_6$ being formed (Scheme 2). In the case of $L = CO$, however, the disubstituted compound occurs always as a by-product, even if the exposure to CO is restricted to a few minutes. Furthermore, pyridine, *DMSO* and isocyanides yield only mixtures of mono-, di-, and even small amounts of trisubstituted products. The structure of $[Ru\mathit{Cp}(PPh_3)(CH_3CN)_2]PF_6$, not reported previously [18, 19], is depicted in Fig. 1 with selected bond distances and angles reported in the caption. Structural comparisons to related complexes are presented in Table 1. If the monodendate ligands are used in excess ($\geq$2 equivalents), the disubstituted complexes $[Ru\mathit{Cp}(L)_2(CH_3CN)]^+$ are obtained.

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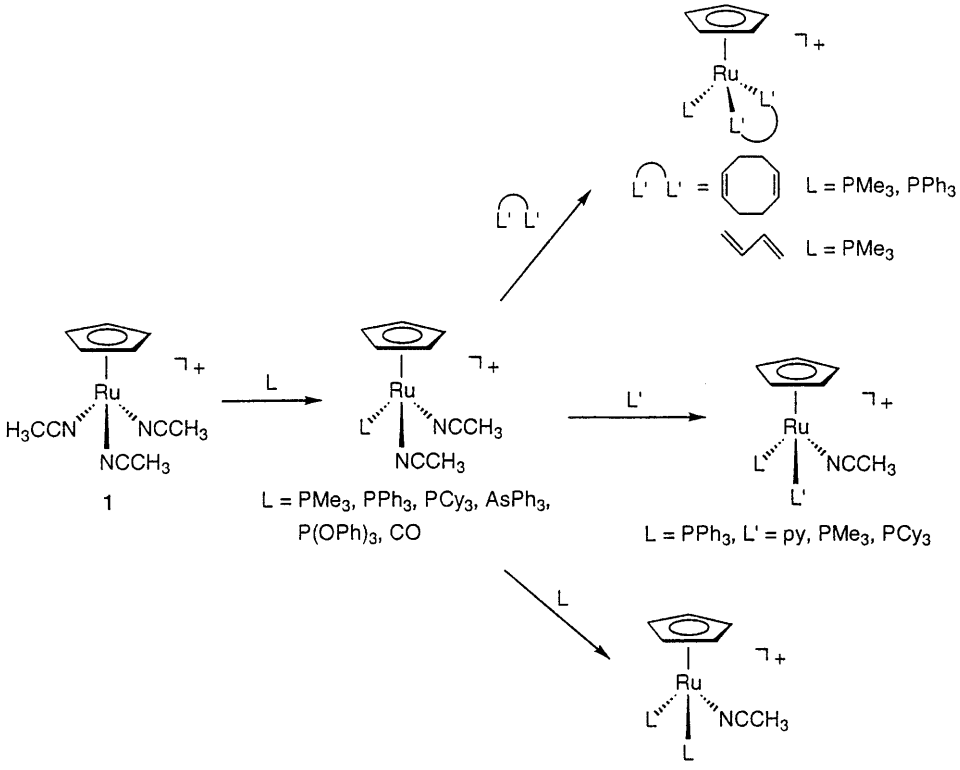
**Scheme 1**




**Scheme 2**

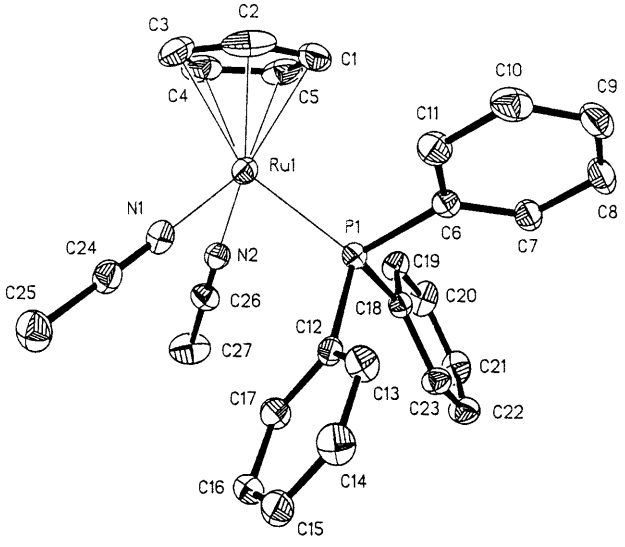



**Fig. 1.** Structural view of $[RuCp(PPh_3)(CH_3CN)_2]PF_6$ showing 20% thermal ellipsoids ($PF_6^-$ omitted for clarity); selected bond lengths and angles: Ru(1)-C(1–5)$_{av}$ = 2.173(5), Ru(1)-P(1) = 2.321(4), Ru(1)-N(1) = 2.057(4), Ru(1)-N(2) = 2.060(4), N(1)-C(24) = 1.130(6), N(2)-C(26) = 1.126(6) Å; C(24)-N(1)-Ru(1) = 175.6(5), C(26)-N(2)-Ru(1) = 177.0(5), N(1)-Ru(1)-N(2) = 85.1(1), N(1)-Ru(1)-P(1) = 91.1(1), N(2)-Ru(1)-P(1) = 88.8(1)°

**Table 1.** Structural comparisons between $[RuCp(CH_3CN)_3]^+$ (**1**), $[RuCp(PPh_3)(CH_3CN)_2]^+$ (**2a**), $[RuCp(PMe_3)(CH_3CN)_2]^+$ (**2b**), and $[RuCp(PCy_3)(CH_3CN)_2]^+$ (**2c**)

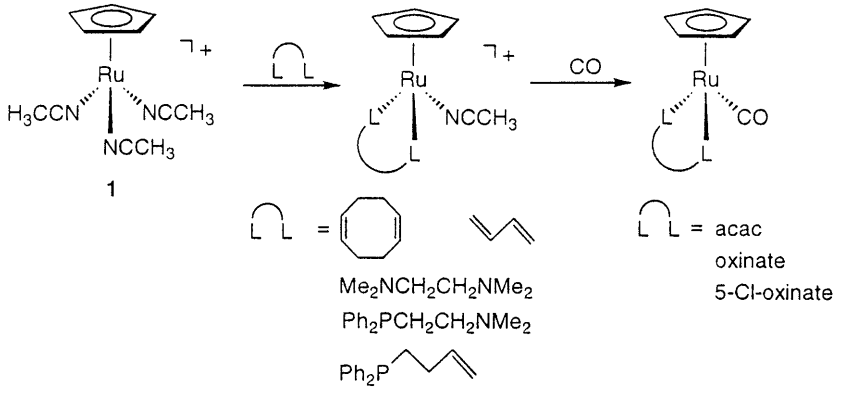
| | **1**[a] | **2a** | **2b**[b] | **2b**[b] |
|---|---|---|---|---|
| Ru-N(av)/Å | 2.083(1) | 2.058(4) | 2.056(3) | 2.053(2) |
| Ru-P/Å | | 2.321(2) | 2.294(1) | 2.359(1) |
| Ru-$C_5$(av)/Å | 2.135(3) | 2.173(5) | 2.177(5) | 2.185(3) |
| C≡N(av)/Å | 1.131(3) | 1.128(6) | 1.136(4) | 1.135(4) |

[a] Ref. [2]; [b] Ref. [18]

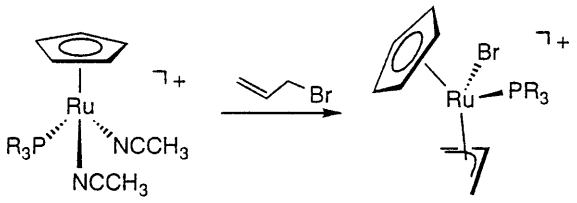
Eventually, $[RuCp(L)(CH_3CN)_2]PF_6$ can be reacted further with another monodendate ($L'$) or bidendate ($L'$-$L'$) ligand to give $[RuCp(L)(L')(CH_3CN)]^+$ and $[RuCp(L)(L'\text{-}L')]^+$. This has been demonstrated in the reaction of $[RuCp(PPh_3)(CH_3CN)_2]PF_6$ with $L' = py$, $PMe_3$, $PCy_3$, and $AsPh_3$ affording the racemic complexes $[RuCp(PPh_3)(L')(CH_3CN)]^+$ in high yields [18]. To quote another example, treatment of $[RuCp(PR_3)(CH_3CN)_2]PF_6$ with *COD* yields the cationic complexes $[RuCp(PR_3)(\eta^2,\eta^2\text{-}COD)]^+$ ($R$ = Ph, Me), whereas with $R$ = *Cy*, presumably for steric reasons, no reaction takes place. Butadiene reacts with $[RuCp(PMe_3)(CH_3CN)_2]PF_6$ to give $[RuCp(PMe_3)(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)]^+$ (Scheme 2).

Of course, **1** also reacts readily with a variety of bidendate ligands such as 1,5-*COD*, 1,3-butadiene, $Me_2NCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2NMe_2$, and $Ph_2PCH_2 \cdot CH_2CH{=}CH_2$ to give the cationic complexes $[RuCp(L\text{-}L)(CH_3CN)]^+$ in good yields (Scheme 3). It is worth noting that in $[RuCp(Me_2NCH_2CH_2NMe_2)(CH_3CN)]^+$ the $CH_3CN$ ligand is extremely labile with an exchange rate of $167\,s^{-1}$ at 25°C (cf. $5.6\,s^{-1}$ in **1**). Thus, $CH_3CN$ is readily replaced by $CD_3CN$ in a solution of $CD_3NO_2$ at room temperature. In the case of $L\text{-}L$ = *acac*, oxinate, or 5-Cl-oxinate, the intermediates $[RuCp(L\text{-}L)(CH_3CN)]$ could not be isolated but were trapped as the stable CO complexes $[RuCp(acac)(CO)]$, $[RuCp(\text{oxinate})(CO)]$, and $[RuCp(\text{5-Cl-oxinate})(CO)]$ (Scheme 3).

Another reactivity pattern of **1** concerns oxidative addition reactions with allyl halides. As an example, allyl bromide affords the Ru(IV) $\eta^3$-allyl com-




**Scheme 3**




**Scheme 4**

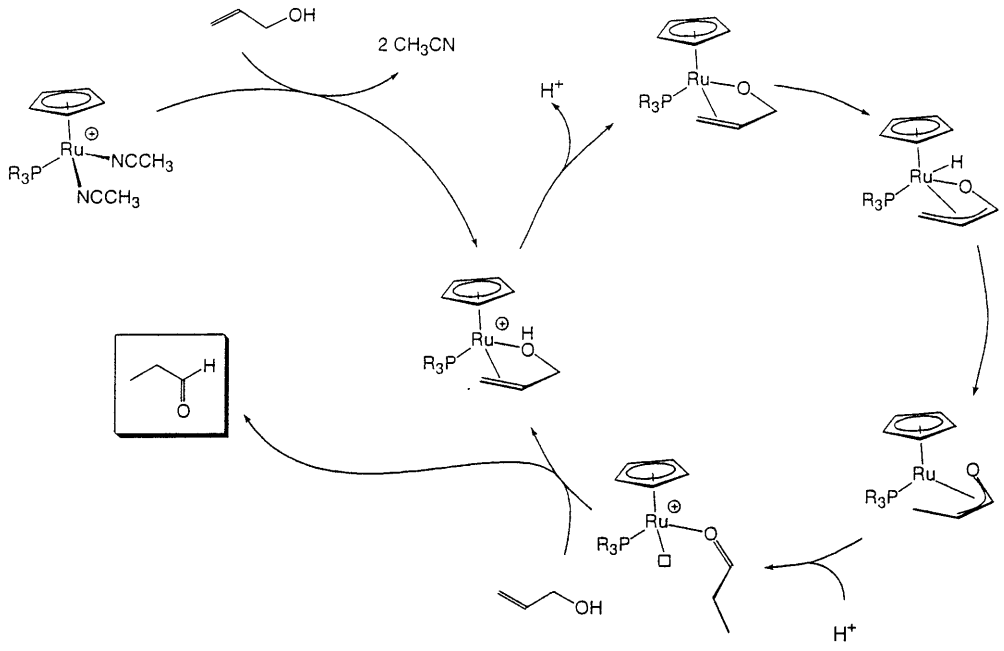
plex $[RuCp(\eta^3\text{-}CH_2CHCH_2)(CH_3CN)Br]PF_6$ in 91% isolated yield. Similarly, $[RuCp(PR_3)(CH_3CN)_2]PF_6$ gives the corresponding Ru(IV) $\eta^3$-allyl complex $[RuCp(\eta^3\text{-}CH_2CHCH_2)(PR_3)Br]PF_6$ also in high isolated yields (Scheme 4).

Complex **1** has also been used as a catalyst in C–C coupling reactions reported recently. It has been found to catalyze the intramolecular [5+2] cycloaddition or cycloisomerization of 1,6- and 1,7-enynes [20]. Furthermore, alkylative cycloetherification of $\delta$- or $\varepsilon$-hydroxyallenes with vinylketones [21] and a three-component coupling of alkynes with vinylketones and bromide [22] have been reported to give selectively (*Z*)-vinylbromides. These examples remain the only catalytic reactions involving **1** but clearly demonstrate its potential as a catalyst in selective transformations of organic molecules which may yet to be discovered.

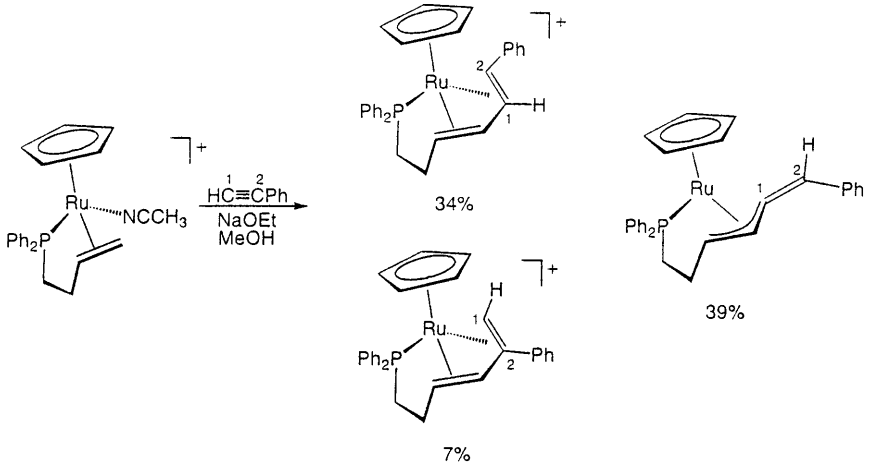
## Utilization of Compounds Derived from $[RuCp(CH_3CN)_3]^+$

Of all the complexes derived from **1**, one of the most reactive is $[RuCp(PR_3)(CH_3CN)_2]^+$ which straightforwardly transforms into the *pseudo*-14e$^-$ fragment $[RuCp(PR_3)]^+$. These species are catalytically active in the redox isomerization of allyl alcohols to give aldehydes and ketones [23]. For instance, neat 2-propenol was reacted with 0.03 mol% of $[RuCp(PPh_3)(CH_3CN)_2]^+$ upon slowly raising the temperature to 80°C bath temperature. A vigorous reaction started at about 68°C (measured in the flask). After 10 min at this temperature, the propanal was collected by distillation (60% yield). The residue consisted of oligo- and polymeric propanal, since the consumption of 2-propenol was complete. The turnover number (*TON*) and turnover frequency (*TOF*) for the generation of propanal were found to be 1800 and 21500 $h^{-1}$, respectively (or 3000 and 36000 $h^{-1}$, if the quantitative consumption of 2-propenol is taken into account). The recently proposed mechanistic rationale for the redox isomerization is in accordance with Scheme 5. For comparison, the hitherto best ruthenium-based catalyst for this particular reaction was $RuCp(PPh_3)_2Cl$ (0.02 mol%)/$NH_4PF_6$ (0.8 mol%) which at 60°C gives only low yields of the two allyl acetals of propanal [24].

Along these lines, other compounds may be derived from $[RuCp(CH_3CN)_3]^+$ in the future capable of being powerful reagents in homogenous catalysis, supplementing the well established precatalysts $RuCp(PPh_3)_2Cl$ and $RuCp(COD)Cl$ [25]. The advantages of $[RuCp(L)(CH_3CN)_2]^+$ over the others are obvious: first, *L* can easily be modified in a systematic way sterically as well as electronically, the second, no halogen scavenger is required for the creation of a vacant coordination site.

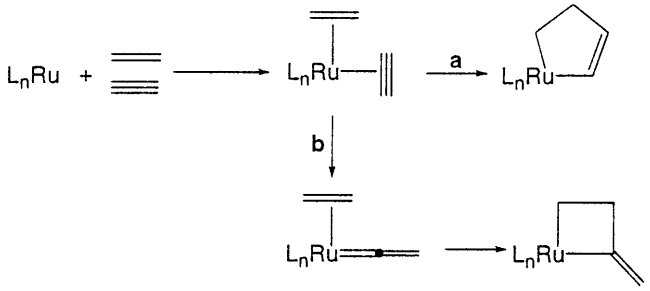


**Scheme 5**



**Scheme 6**

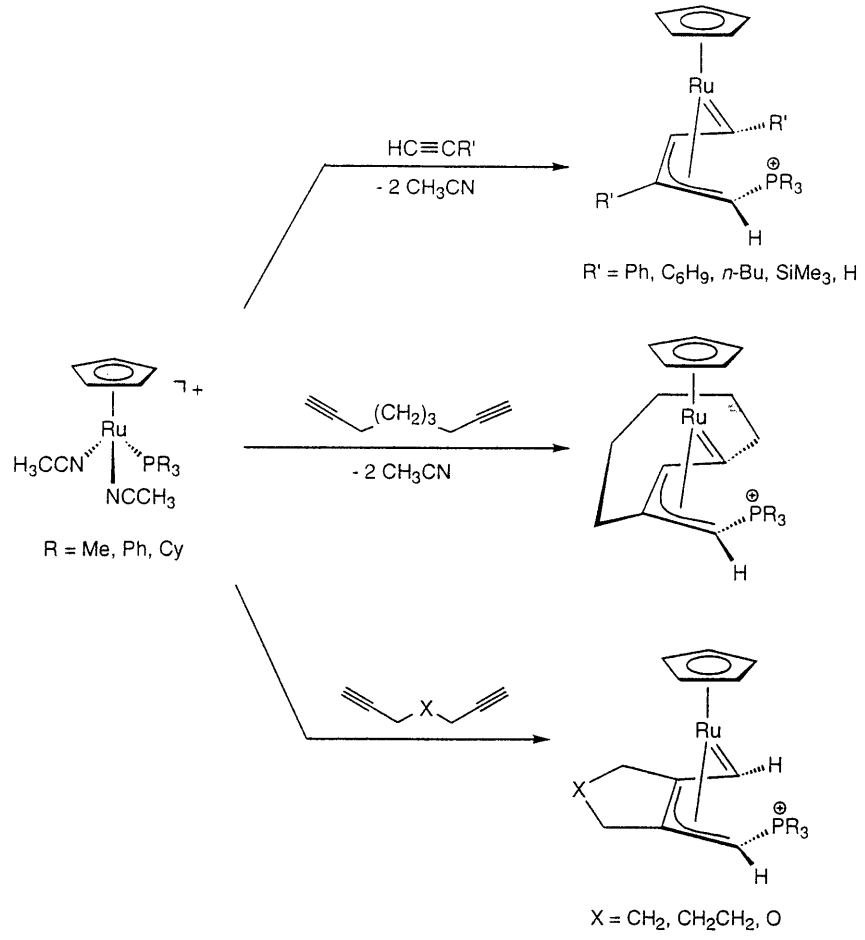
The cationic complex [Ru*Cp*($\kappa^1$(P),$\eta^2$-$PPh_2CH_2CH_2CH{=}CH_2$)($CH_3CN$)]$PF_6$ deserves special comment since it is an interesting model for studying coupling reactions of olefins and acetylenes. Two different competing coupling mechanisms have been identified being operative in the presence of base, but only one in its absence. Treatment of the above complex with HC≡CPh in MeOH in the presence of NaOEt (1 equivalent) at 65°C for 3 h afforded the two isomeric $\eta^4$-butadiene complexes [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CH{=}CHPh$)]$PF_6$ and [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CH_2$)]$PF_6$ as well as the $\eta^3$-butadienyl complex Ru*Cp*($\kappa^1$(P),(3,4,5-$\eta$)-$PPh_2CH_2CH_2CHCHCCHPh$) in 34, 7, and 39% isolated yields, respectively (Scheme 6).




**Scheme 7**

When the reaction of **1** with HC≡CPh (3 equivalents) is run in the absence of base, one obtains [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH$=CH–CH=CHPh)]$PF_6$ and [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*)-$PPh_2CH_2CH_2CH$=CH–CPh=$CH_2$)]$PF_6$ in 56 and 15% isolated yield. As indicated by NMR monitoring, the consumption of **1** is complete after 1 h, giving the above complexes in a 3.3:1.0 ratio in addition to small amounts of polymeric materials but with no evidence of formation of the $\eta^3$-butadienyl complex [26]. Actually, this coupling mode is not restricted to terminal alkynes. In a similar fashion, [Ru*Cp*($\kappa^1$(P),$\eta^2$-$PPh_2CH_2CH_2CH$=$CH_2$)($CH_3CN$)]$PF_6$ was found to react with 1.5 equivalents of internal alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2 =$ Ph, Et; $R^1 =$ Ph, $R^2 =$ Et) to give the $\eta^4$-butadiene complexes [Ru*Cp*($\kappa^1$(P), $\eta^4$-(3*Z*,5*Z*)-$PPh_2CH_2CH_2CH$=CH–CPh=CHPh)]$PF_6$, and [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH$=CH–CEt=CHEt)]$PF_6$ as well as the two regioisomers [Ru*Cp*($\kappa^1$(P),$\eta^4$-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH$=CH–CEt=CHPh)]$PF_6$ and [Ru*Cp*($\kappa^1$(P), $\eta^4$-(3*Z*,5*Z*)-$PPh_2CH_2CH_2CH$=CH–CPh=CHEt)]$PF_6$. These observations are summarized in Scheme 7. Accordingly, oxidative coupling (path *a*) and [2+2] cycloaddition to a vinylidene intermediate (path *b*), followed by deprotonation to give a $\eta^3$-butadienyl complex, can occur simultaneously and competitively [27].

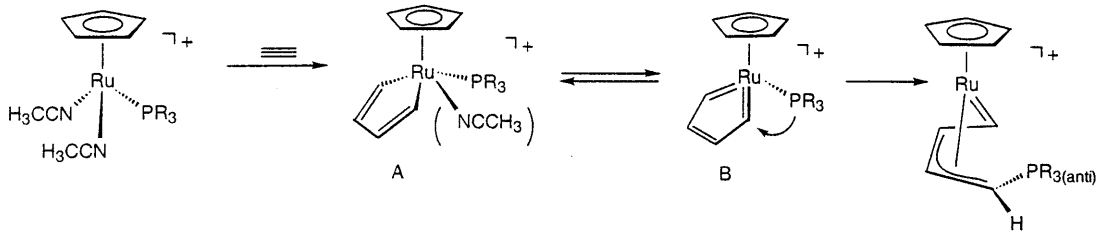
Transition metal complexes having a vacant coordination site or bearing weekly coordinating ligands are known to generate a rich chemistry with alkynes to give, for instance, vinylidene complexes [28], metallacyclopentadienes [29], and in some cases metallacyclopentatrienes [30]. All of these species are particularly interesting in view of being reactive intermediates in organic and organometallic synthesis as well as in catalytic processes, *e.g.* the polymerization and cyclization or alkynes. Since the labile complexes [Ru*Cp*($PR_3$)($CH_3CN$)$_2$]$PF_6$ essentially are synthetic equivalents to the 14-electron fragment [Ru*Cp*($PR_3$)]$^+$, they react readily with 1,6-heptadiyne and HC≡C*R*′ (*R*′ = Ph, $C_6H_9$, *n-Bu*, H) to yield ruthenium allyl carbene complexes rather than ruthenacyclopentadiene or ruthenacylcopentatriene complexes. For instance, treatment of [Ru*Cp*($PR_3$)($CH_3CN$)$_2$]$PF_6$ with 1 equivalent of 1,6-heptadiyne results in the formation of the dark red allyl carbene complex [*Cp*Ru(=CH-$\eta^3$-$C(CH_2)_3CCHPR_3$)]$PF_6$. Other diynes react analogously. Thus, with 1,7-octadiyne and dipropargyl ether the allyl carbenes [*Cp*Ru(=CH-$\eta^3$-$C(CH_2)_4CCHPR_3$)]$PF_6$ and [*Cp*Ru(=CH-$\eta^3$-$C(CH_2OCH_2)CCHPR_3$)]$PF_6$ are obtained. Furthermore, [Ru*Cp*($PR_3$)($CH_3CN$)$_2$]$PF_6$ reacts with HC≡C*R*′ (*R*′ = Ph, $C_6H_9$, *n-Bu*, H) and 1,8-nonadiyne to give the allyl carbene complexes [*Cp*Ru(=C(*R*′)-($\eta^3$-CHC(*R*′)CHP$Me_3$)]$PF_6$ in high yields with the substituents exclusively in



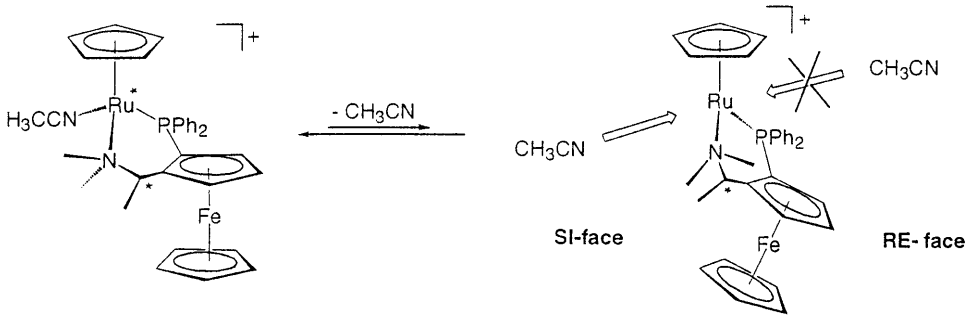

**Scheme 8**

positions 1 and 3 (Scheme 8) [31]. All these reactions are essentially quantitative; unfortunately, no intermediates could be detected.

A possible reaction mechanism that accounts for the formation of allyl carbene complexes is presented in Scheme 9. At first, a metallacylopentatriene intermediate may be formed with subsequent migration of the tertiary phosphine to one of the two electrophilic carbene carbon atoms. It should be mentioned that analogous




**Scheme 9**




**Scheme 10**

ruthenacyclopentatriene complexes are stable species provided that potential nucleophilic ligands are absent.

Finally, complex **1** turned out to be a valuable precursor for the synthesis of configurationally stable chiral three-legged piano-stool ruthenium complexes. These type of compounds are currently being intensively investigated as *Lewis* acid catalysts in asymmetric C-C bond-forming procedures such as *Diels-Alder* and related reactions. Compounds utilized so far are halfsandwich Ru(arene) [32] and Ru*Cp* and Ru*Cp*$^*$ complexes containing tethered functional groups of $C_2$ symmetric bisphosphines as chiral auxiliaries [33]. Whereas for the Ru(arene) systems a broad variety of co-ligands can be employed, for related Ru*Cp* compounds no easy and general synthetic approach is known. This situation may be remedied by employing **1** in conjunction with, for instance, chiral phosphinoamineferrocenes.

Treatment of **1** with ligands of the type $PN^x$ ($PN^1 = (R_c,S_{pl})$-2-(1-N,N-dimethylaminoethyl)-1-diphenylphosphinoferrocene, $PN^2 = (S_{pl})$-2-(N,N-dimethylaminomethyl)-1-diphenylphosphinoferrocene, and $PN^3 = (R_c,S_{pl})$-2-(1-N,N-diethylaminoethyl)-1-diphenylphosphinoferrocene)) affords [$S_{Ru}$-Ru*Cp*($PN^x$)(CH$_3$CN)]$^+$ in essentially quantitative yield, with a diastereomeric excess of above 98%. This high *de* is of thermodynamic origin. The acetonitrile ligand is again labile (with a first order rate constant of $9.2 \cdot 10^{-2}\,s^{-1}$), shifting the equilibrium to the thermodynamically favoured diastereomer (Scheme 10) [34].

Subsequent substitution of CH$_3$CN by HC≡CPh and CO provides access to chiral (at the metal) vinylidene and CO complexes [Ru*Cp*($PN^x$)(=C=CHPh)]$^+$ and [Ru*Cp*($PN^x$)(CO)]$^+$, respectively. Particularly in the latter, the CO ligand is no longer labile so that a (kinetically controlled) *de* of 28–87% (depending on $PN^x$) has been obtained. However, the *de* can be raised to above 98% under photochemical conditions where the CO-ligand is labilized, or, in the case of $PN^3$, by heating taking advantage of the hemilability of the NEt$_2$ group. Thus, configurationally stable chiral (at ruthenium) *pseudo*-tetrahedral three-legged piano-stool complexes [Ru*Cp*($PN^x$)*L*]$^+$ can be obtained. In the case of $L$ = CH$_3$CN and CO, these are able to provide a vacant coordination site.

## Acknowledgements

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