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Recent Mechanistic and Synthetic Developments in the Chemistry of Transition-Metal Vinylidene Complexes

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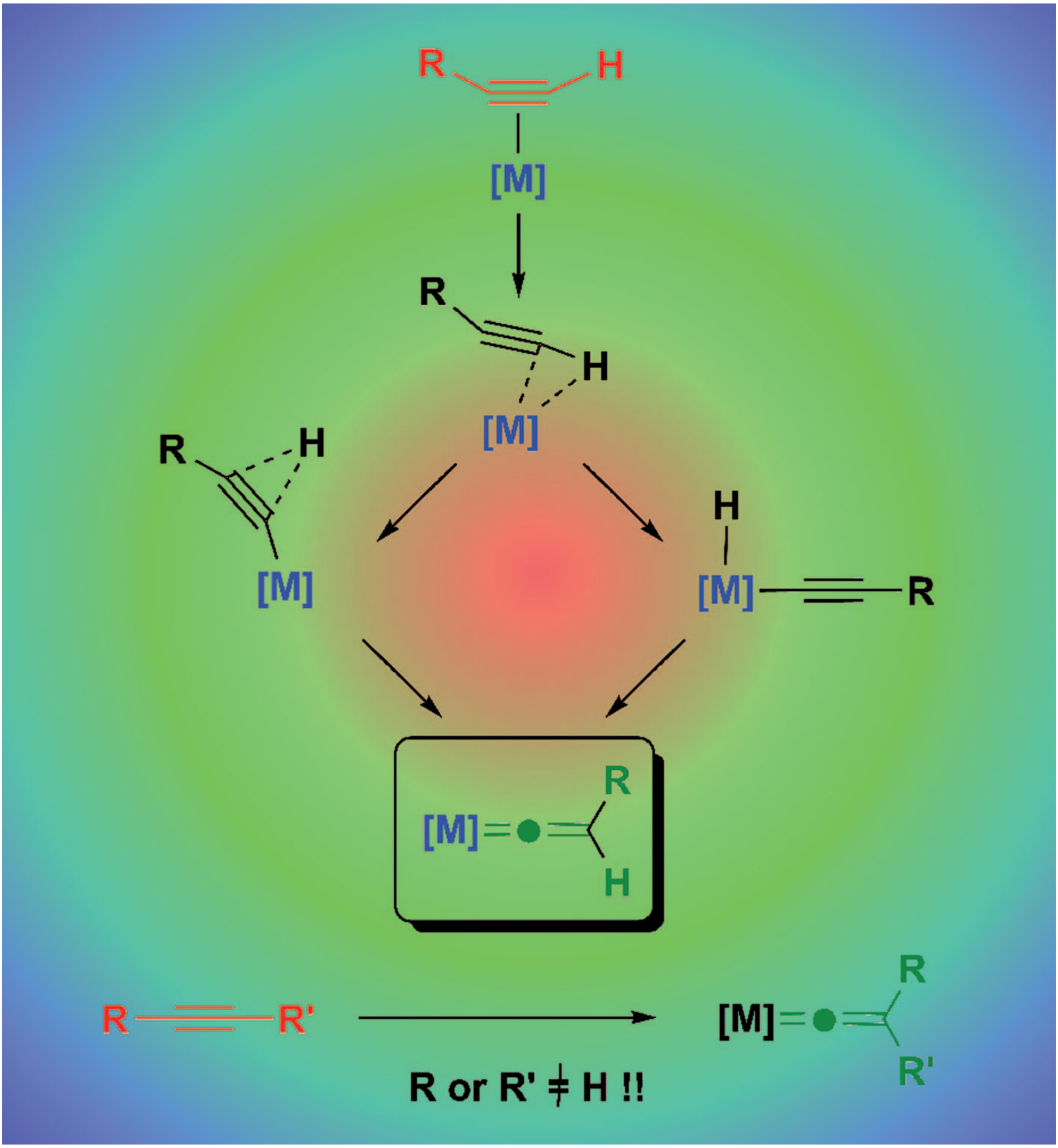


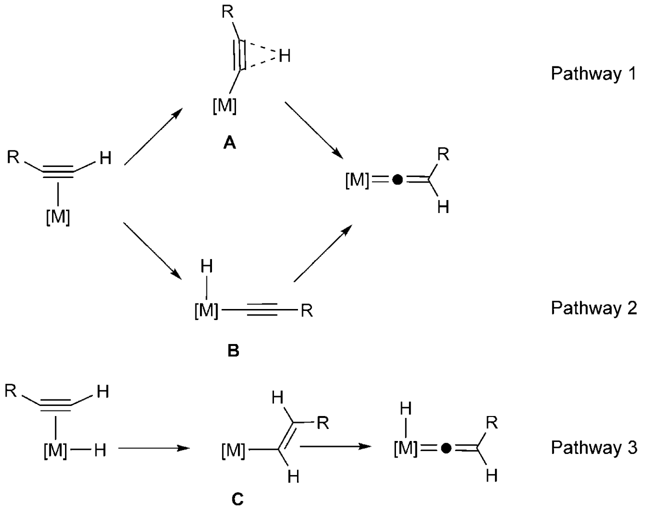
Abstract: Transition-metal vinylidene complexes are intermediates in a number of synthetically important transformations of alkynes. Underpinning these applications is the ability of various electron-rich transition-metal complexes to effectively facilitate the conversion of alkynes into their vinylidene tautomers. Recent experimental and theoretical studies have provided considerable insight into the mechanisms by which this process occurs and they are detailed herein. In particular, it has been demonstrated that different substituents on both the metal and the alkyne may have profound effects on both the kinetic and thermodynamic profiles of the alkyne/vinylidene tautomerisation. An important finding is that internal alkynes may be employed to prepare disubstituted vinylidene complexes under easily accessible conditions. This discovery brings to light a new facet of the potential synthetic applications of transition metal vinylidene complexes.

Keywords: alkynes • half-sandwich complexes • rhodium • ruthenium • vinylidenes

Introduction

Vinylidene, :C=CH$_2$, is the simplest unsaturated carbene and is a high-energy tautomer of acetylene. In a similar vein to many highly reactive transient organic species, vinylidene may be stabilised by coordination to a transition metal.[1–4] Although several different methods are known to generate these ligands, the most convenient is to employ electron-rich metal fragments to facilitate the conversion of terminal alkynes into their isomeric vinylidene forms. Crucially, the vinylidene ligand exhibits marked differences in reactivity when compared to the parent alkyne; notably the α-carbon, which is bound to the metal, is electrophilic, whereas the β-carbon is nucleophilic. This difference in reactivity between alkynes and vinylidenes has been extensively exploited in catalysis. For example, vinylidenes are crucial intermediates in the anti-Markovnikoff addition of various nucleophiles to alkynes.[4–9]

Given this current catalytic interest, it is perhaps unsurprising that attention has also been focused on the precise mechanism by which transition-metal compounds may facilitate the conversion of alkynes into vinylidenes.[10] There are three general pathways by which this transformation may be considered to occur (Scheme 1). A common requirement for all pathways is the initial formation of a complex which contains an alkyne in an η^2-binding mode. Therefore any metal precursor must possess a vacant coordination site that may be generated by dissociation of a labile group or a switch in bonding mode by a ligand such as NO[11,12] or acetate.[13,14] The next stage of the reaction is dependent on the nature of both the ligands and metal complex employed. In the case of pathway 1, the vinylidene ligand is formed by a 1,2-hydrogen atom migration via species such as **A**. In contrast for pathway 2, the formation of the vinylidene ligand occurs via a well-defined intermediate, **B**, in which formal oxidative-addition of the C–H bond has occurred to give an alkynyl hydride complex: a 1,3-hydride migration results in the formation of the vinylidene. In general, pathway 2 is observed in the case of more electron-rich metal complexes. Indeed, by subtle variation of ligands within the coordination sphere of the metal complexes it is possible to switch between the two mechanistic pathways. A final mechanistic process which may afford vinylidene ligands, pathway 3, involves the intermediacy of a metal alkenyl ligand which may be obtained through insertion of an alkyne into a metal hydride bond.[15–17]



Scheme 1. Mechanistic pathways of the conversion of an alkyne ligands into its vinylidene tautomer.

Although this description of the alkyne/vinylidene interconversion is well established, in the last few years a number of recent experimental and theoretical studies have provided important further insight into this process. This Minireview details some of the recent mechanistic findings which focus on the ability of ruthenium and rhodium complexes to perform this reaction. Also discussed within this framework are the recent results which demonstrate that internal alkynes, as opposed to terminal alkynes, may be employed to prepare disubsitituted vinylidene ligands.

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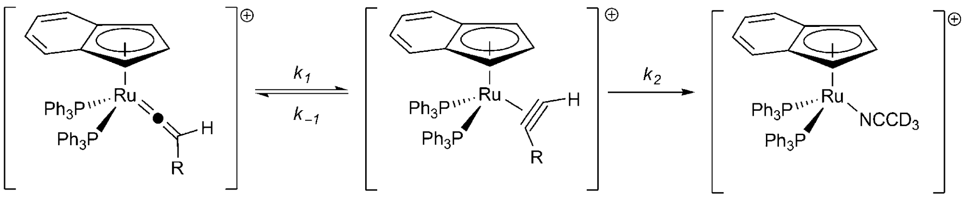
Ruthenium Vinylidene Complexes

Terminal alkynes: Half-sandwich ruthenium complexes have been extensively exploited in the catalytic transformation of alkynes with many of these processes involving the conversion from alkyne to vinylidene ligand.[4] As a library of complexes based on the $[Ru(\eta^5\text{-}L)(L')_2]$ framework (L = 5-electron donor ligand, for example, $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_9H_7$ etc., L′ = 2-electron donor ligand, for example, phosphine, CO etc.) has been prepared, these complexes represent a tuneable steric and electronic framework. The nature of the mechanism of interconversion between the alkyne and vinylidene forms and the relative energies of these species may be tuned by subtle alterations of these ligand sets.



1 2 3

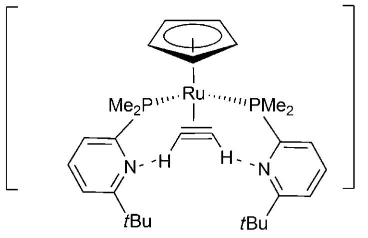
Scheme 2.

In a recent study the effect of the alkyne on this process has provided important insight into the alkyne/vinylidene interconversion.[18] A series of vinylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=CHR)]^+$ (**1**) was prepared with a range of different substituents on the alkyne. In the next stage of the study the complexes were dissolved in CD_3CN and the subsequent conversion into $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(NCCD_3)]^+$ (**3**) and the free alkyne $HC{\equiv}CR$ monitored by NMR spectroscopy (Scheme 2). This allowed for the rate constant, k_1, for the conversion from the vinylidene complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=CHR)]^+$ to the corresponding alkyne species $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(\eta^2\text{-}HC{\equiv}CR)]^+$ (**2**) to be determined. In the case in which R = Ph an Eyring analysis revealed activation parameters of $\Delta H^{\neq} = 24 \pm 1\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\neq} = -3 \pm 2\ \mathrm{cal\,mol^{-1}\,K^{-1}}$: the entropy of activation being consistent with a unimolecular pathway. This kinetic analysis also allowed for the effects of the different substituents on the vinylidene/alkyne transformation to be quantified by a Hammett analysis on a range of aryl-substituted alkynes. A ρ-value of -1.5 was obtained indicating that this transformation is promoted by electron-donating substituents.

The use of isotopically-labelled alkynes also provided important information about this process. For example, reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**4**) with $H^{13}C{\equiv}CPh$ resulted in the formation of $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(={}^{13}C=CHPh)]^+$ ([^{13}C]-**1**), indicating the migratory aptitude of hydrogen is greater than Ph—a similar observation was obtained from the reaction of *cis*-$[RuCl_2(dppm)_2]$ (**5**) with $H^{13}C{\equiv}CPh$ which afforded *trans*-$[RuCl(dppm)_2(={}^{13}C=CHPh)]^+$ ([^{13}C]-**6**).[19] Kinetic isotope effects k_H/k_D of between 1.17 and 1.88 were measured for the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=CHR)]^+$ system—consistent with the proposed 1,2-hydrogen shift.

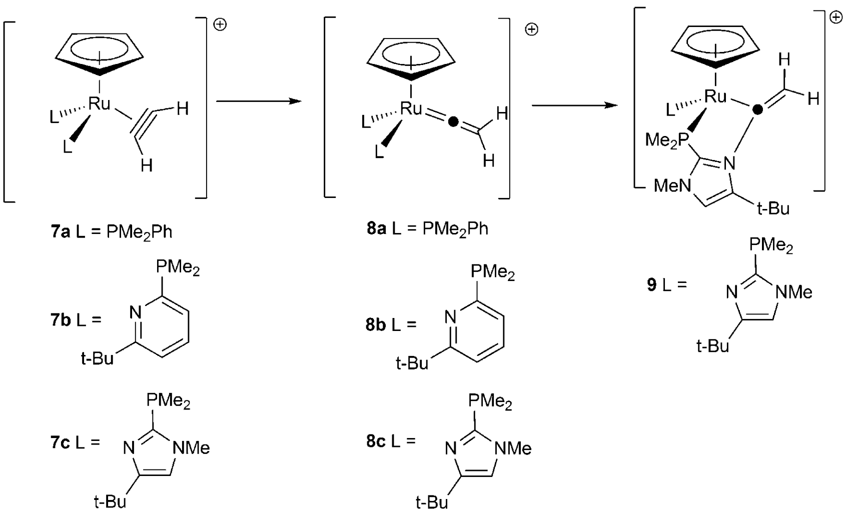
In addition to the effect of the alkyne substituents on the alkyne/vinylidene transformation, a detailed study of how N-heterocycle-substituted phosphine ligands may promote hydrogen transfer has been reported.[20] For example, the conversion of $[Ru(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2(\eta^2\text{-}HC{\equiv}CR)]^+$ (**7a**) into $[Ru(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2(=C=CH_2)]^+$ (**8a**) was shown to occur over the course of 3 h at 50 °C (Scheme 3). In contrast, the corresponding reaction with the pyridyl-substituted phosphine complex **7b** resulted in conversion to **8b** in 3 h at about 0 °C. In the case of the imidazole-containing phosphine ligand neither alkyne complex **7c** nor vinylidene complex, **8c**, could be observed, even at low temperature; the vinyl complex **9** was obtained instead. These data clearly indicate that phosphorus ligands containing pendant base groups significantly enhance the alkyne/vinylidene transformation.

A detailed NMR study of complex **7b** using both ^{15}N-labelled pyridine and ^{13}C-labelled acetylene revealed that the two alkyne CH hydrogen atoms were involved in hydrogen bonding to the nitrogen atom of the pyridine. Calculations using density function theory (B3LYP/(LANL2DZ/6-311+



7b

Jason Lynam obtained both his BSc(Hons) and D.Phil. from the University of York, the latter under the supervision of Dr Roger Mawby. He then undertook a Postdoctoral position at the University of Bath with Professor Michael Green and Dr Andrew Burrows. This research programme was focused on exploring the coordination chemistry of phosphaalkynes and during this period the first example of a phosphaalkyne acting as a four-electron donor to a metal was structurally characterised. In 2000 he was awarded a Ramsay Memorial Fellowship at the University of Bristol, where he established synthetic routes to a series of phosphorus-rich anions and cations. In 2002 he was appointed to a Lectureship in Inorganic Chemistry at the University of York. His current research interests are focused on mechanistic and synthetic aspects of transition metal vinylidene complexes and the use of metal carbonyls as therapeutic carbon monoxide-releasing molecules.

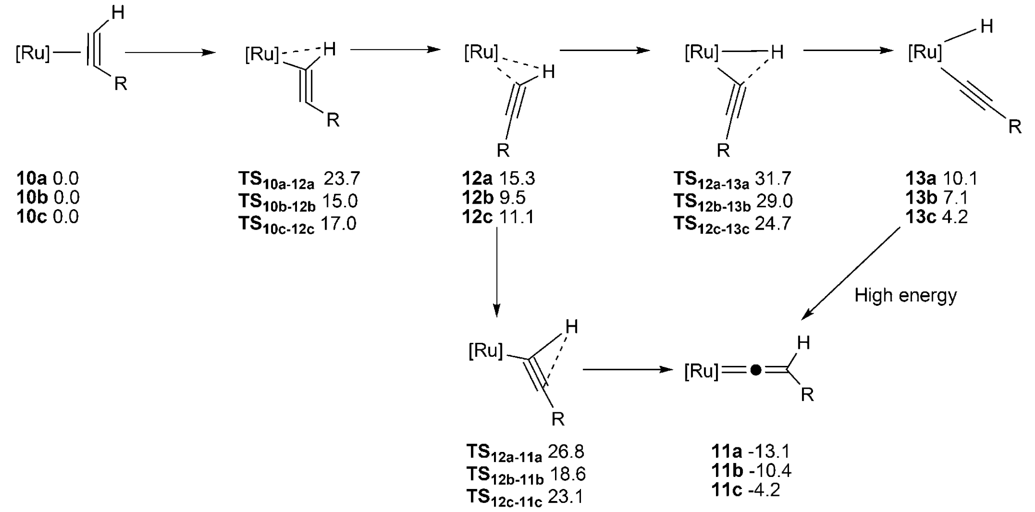


Scheme 3.

G(d,P))) revealed that the difference in energy between **7b** and its vinylidene form **8b** is less ($\Delta G_{(7b-8b)} = -12.7$ kcal mol^{-1}) than in the case in which hydrogen bonding is not possible ($\Delta G_{(7a-8a)} = -17.9$ kcal mol^{-1}). This difference was attributed to a stabilisation of the alkyne complex by the two hydrogen-bonding interactions. Although it is clear that the conversion from the alkyne to the vinylidene complex is considerably more rapid in the case when the phosphine ligand contains an N-heterocycle.

The ability of ruthenium half-sandwich complexes to effect the alkyne/vinylidene transformation has also been studied by density functional theory (BPW91/(LANL2DZ/6-31G**)).[21] Three pathways were considered for the rearrangement of $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2(\eta^2\text{-}HC{\equiv}CR)]^+$ (**10a** R=H; **10b** R=Me) into their vinylidene isomers $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2({=}C{=}CHR)]^+$ (**11a** R=H; **11b** R=Me). Two of the pathways involve the migration of the hydrogen atom without formal addition to the metal whereas the third corresponds to pathway 2 in Scheme 1, in which a formal oxidative-addition pathway is considered to have occurred. The pathways with the lowest barriers are shown in Scheme 4; here the initial hydrogen migration proceeds via $\mathbf{TS_{10-12}}$ to local minimum **12**, which contains the alkyne bound by an η^2(C-H) interaction. Complex **12** is a common intermediate for both the hydrogen migration (pathway 1) and oxidative-addition (pathway 2) routes to the vinylidene complex. In the case of the hydrogen migration pathway, the reaction then proceeds via $\mathbf{TS_{12-11}}$ to afford vinylidene **11**. In the case of the methyl-substituted alkyne, the energies of all the transition states and intermediates en route to **11** are lower than in the hydrogen-substituted case, although the energy of the final product is higher in the case of **11b** than **11a**.

When considering the oxidative-addition pathway, it is clear that the barriers to the formation of the alkynyl hydride complexes $[Ru(C{\equiv}CR)(\eta^5\text{-}C_5H_5)(H)(PMe_3)_2]^+$, (**13a** R=H; **13b** R=Me) via $\mathbf{TS_{12-13}}$ are greater than those corresponding to $\mathbf{TS_{12-11}}$. Despite this, transition states $\mathbf{TS_{12-13}}$ are at an accessible energy at room temperature ($\mathbf{TS_{12a-13a}}$ 31.7 kcal mol^{-1}, $\mathbf{TS_{12b-13b}}$ 29.0 kcal mol^{-1}), which, coupled with the fact that the methyl substituted complex **13b**, is only 7.1 kcal mol^{-1} higher in energy than **10b**, indicates that oxidative addition may actually be viable. However, it is the barrier to the subsequent hydride migration onto the β-carbon of the alkynyl ligand (>50 kcal mol^{-1}) which indi-



Scheme 4. $[Ru] = [Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$; relative energies are in kcal mol^{-1}, **a** R=H, **b** R=Me, **c** R=$-C{\equiv}CH$.

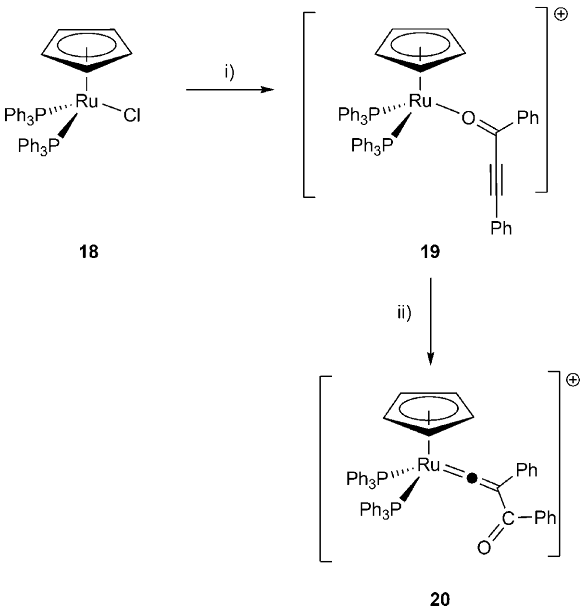
cates that this is probably not a route by which the vinylidene complex is formed. In this context it should be noted that addition of $NaBPh_4$ to $[RuCl(\eta^5\text{-}C_5Me_5)(dippe)]$ (dippe = 1,2-bis(diisopropylphosphino)ethane) followed by certain terminal alkynes gives $[Ru(C{\equiv}CR)(\eta^5\text{-}C_5Me_5)(H)(dippe)]^+$ (**14**).[22] Although complexes **14** ultimately rearrange into their vinylidene isomers, this processes is thought to proceed through a deprotonation/reprotonation mechanism rather than a hydrogen migration.

These data indicate that in this system the formation of the vinylidene complex probably occurs by pathway 1 and although oxidative addition to give **13** may occur, this does not provide a low-energy pathway for the formation of **11**. In the case of the isoelectronic species $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}HC{\equiv}CH)]$ (**15**), the relative energy of the oxidative-addition product $[Mn(C{\equiv}CH)(\eta^5\text{-}C_5H_5)(H)(CO)_2]$ (**16**) is far higher (+19.7 $kcal\,mol^{-1}$) as are the corresponding transition states involved for its formation.[23] This is perhaps as would be expected on replacing the more electron-donating PMe_3 ligands in the ruthenium system for CO.

A theoretical study (B3LYP/LACV3P++**) into the rearrangement of the butadiyne complex $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2(\eta^2\text{-}HC{\equiv}C{-}C{\equiv}CH)]^+$ (**13c**) into the corresponding butatrienylidene $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2({=}C{=}C{=}C{=}CH_2)]^+$ (**17**) has revealed the presence of a similar mechanistic pathway.[24] The calculations indicate that a direct 1,4-hydrogen shift from **13c** to give **17** is unlikely and that a ethynylvinylidene $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2({=}C{=}CH{-}C{\equiv}CH)]^+$ (**11c**) is a plausible intermediate.

The potential energy surface for this transformation is broadly speaking similar to that for complexes **13a** and **13b**. Extensive calculations were performed in order to determine how the formation of **17** from **11c** occurs. By including the effects of THF solvent molecules, it was demonstrated that the lowest energy pathway occurs through a proton migration involving $[H(thf)_2]^+$, reinforcing the protic nature of the vinylidene proton in cationic complexes such as this.

Internal alkynes: The vast majority of stoichiometric and catalytic studies involving metal vinylidene complexes have involved the use of terminal alkynes as precursors. As detailed above, this may be rationalised on the basis of the fact that the migration of a hydrogen atom is crucial to the conversion of the alkyne complex to the subsequent vinylidene and more facile than the migration of an aromatic group, for example. Although examples of the migration of heteroatom groups such $SiMe_3$,[25–30] $SnMe_3$,[31,32] SR[33] and I[34] have been reported, it is not until recently that the migration of a carbon-based group on alkynes has been shown to afford vinylidene complexes. In 2000 Knox demonstrated that a bridging vinylidene ligand could be prepared within the framework of a binuclear ruthenium complex from $MeO_2CC{\equiv}CCO_2Me$.[35] More recently, Shaw and co-workers demonstrated that reaction of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**18**) with PhC≡CCOPh in the presence of suitable halide scavengers results in the ultimate formation of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2({=}C{=}C\{COPh\}Ph)]^+$ (**20**; Scheme 5).[36] Complex **19**, which contains an η^1(O)-bound PhC≡CCOPh ligand, was also observed and shown to convert to **20**.

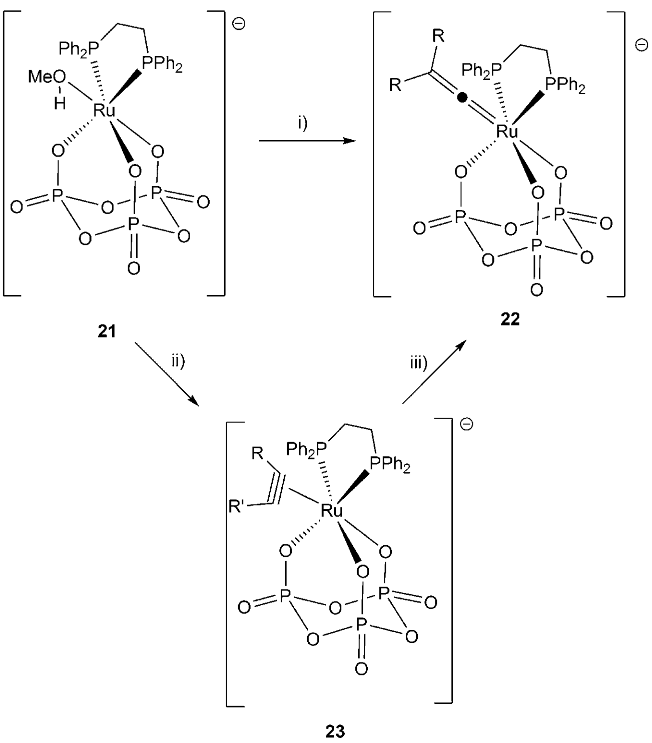


Scheme 5. i) $+AgPF_6$, PhC≡CC(O)Ph, −AgCl; ii) 18 h, 25 °C.

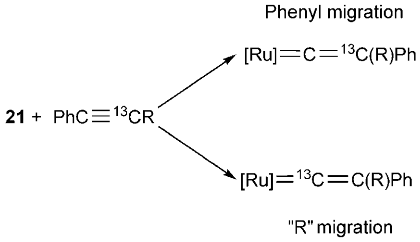
Even more remarkable are the recent reports from Ishii which demonstrate that, under appropriate conditions, it is possible to form vinylidene complexes from unfunctionalised internal alkynes.[37,38] Although the reverse process, the reaction of a disubstituted vinylidene complex to give the corresponding alkyne ligand, has been reported,[39] these recent findings have demonstrated that use of internal alkynes to form vinylidene ligands for which it was not previously thought to be possible.

In the first instance, the reaction between PhC≡CMe and the anion $[Ru(P_3O_9)(dppe)(MeOH)]^-$ (**21**) results in the formation of $[Ru(P_3O_9)(dppe)({=}C{=}C\{Me\}Ph)]^-$ (**22**) in 85 % yield (Scheme 6).[37] The reaction is tolerant to a range of different internal alkynes with reaction times varying from 3 h (in the case of $PhC{\equiv}CC_6H_4\text{-}4\text{-}OMe$) to three days (for example, with $PhC{\equiv}CC_6H_4\text{-}4\text{-}CO_2Et$). In the case of the corresponding reactions with ester-substituted alkynes $RC{\equiv}CR'$ ($R = R'$ CO_2Me; $R = R'$ CO_2Et; R = Me, R' CO_2Et; R = Et, R' CO_2Et) η^2-alkyne complexes $[Ru(P_3O_9)(dppe)(\eta^2\text{-}RC{\equiv}CR')]^-$ (**23**) were obtained after 2 h at 50 °C. These species could be converted to their vinylidene forms by further heating or UV irradiation.

A kinetic study of the conversion of the alkyne complex $[Ru(P_3O_9)(dppe)(\eta^2\text{-}EtC{\equiv}CCO_2Et)]^-$ into $[Ru(P_3O_9)(dppe)({=}C{=}C\{Et\}CO_2Et)]^-$ demonstrated that the reaction obeyed first-order kinetics and is thought not to proceed via an oxidative-addition-type pathway. To gain insight into the mechanism of this a range of alkynes $PhC{\equiv}^{13}CR$ (R = Me, CO_2Et, $C_6H_4\text{-}4\text{-}OMe$, $C_6H_4\text{-}4\text{-}Me$ and $C_6H_4\text{-}4\text{-}CO_2Et$) were employed and, as shown in Scheme 7, the location of the ^{13}C label indicated which organic group has migrated. These data indicate that, within this series, electron-withdrawing



Scheme 6. i) $+RC{\equiv}CR'$; ii) $+RC{\equiv}CR'$; iii) UV light or 70 °C.



Scheme 7. [Ru] = $[Ru(P_3O_9)(dppe)]^-$

groups increase the migratory aptitude in the order $CO_2Et \approx C_6H_4$-4-CO_2Et > Me > Ph > C_6H_4-4-Me > C_6H_4-4-OMe. However, it is important to distinguish this effect from the rate of formation of the vinylidene complexes within this system, which show essentially the opposite trend. Therefore, the rate of formation of the vinylidene complexes is thought to be controlled by the relative stability of the intermediate alkyne complex as opposed to the migratory aptitude of the substituents.

The formation of disubstituted vinylidene complexes from internal alkynes is not, however, limited to this P_3O_9-containing system. Reaction of $[RuCl(\eta^5\text{-}C_5H_5)(dppe)]$ (**24**) with diaryl-substituted alkynes $PhC{\equiv}CAr$ in the presence of $NaBAr^f_4$ ($Ar^f = C_6H_3$-3,5-$(CF_3)_2$) results in the formation of complexes $[Ru(\eta^5\text{-}C_5H_5)(dppe)({=}C{=}C\{Ar\}Ph)]^+$ (**25**).[38] The use of the inert $BAr^f_4{}^-$ ion appears to be crucial as corresponding reaction with $AgPF_6$ or $NaBPh_4$ gave complex mixtures of products. Presumably under the relatively forcing conditions employed in these reactions the robust nature of $BAr^f_4{}^-$ inhibits any side reactions that occur with the more reactive PF_6^- and BPh_4^- ions. This protocol was also successfully applied to half-sandwich compounds based on the $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ and $[Fe(\eta^5\text{-}C_5H_5)(dppe)]^+$ frameworks to give the corresponding vinylidene complexes.

As was the case with the P_3O_9-substituted system, the relative migratory aptitude of the different groups attached to the alkyne was evaluated for the $[Ru(\eta^5\text{-}C_5H_5)(dppe)({=}C{=}C\{Ar\}Ph)]^+$ system with the use of $PhC{\equiv}^{13}CAr$. The same pattern was observed in both cases—the presence of electron-withdrawing group enhancing the migration of the aromatic group relative to phenyl. A Hammett analysis of these data for the migratory aptitude revealed a ρ-value of 2.53. However, the rate of formation of the vinylidene ligand was again most rapid in the case of electron-donating substituents.

In all cases the resulting vinylidene complexes are obtained in good yields (typically between 80–90 %) and, although the conditions required are typically harsher than those involving terminal alkynes, it is evident from these results that access to disubstituted vinylidene complexes from internal alkynes may actually be a general pathway if the appropriate conditions are employed.

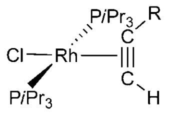
Discussion: The ability of a range of half-sandwich complexes to facilitate the conversion of an internal alkyne into a disubstitued vinylidene is one of the most important findings in this field in recent years. Although the precise mechanism of this process is not yet fully understood, a similar 1,2-shift to that observed in the case of terminal alkynes may be occuring—in this case, however, an η^2-(CC) agostic intermediate related to **12** may be envisaged. One interesting point for discussion is the effect of different functional groups on the rate of formation of both internal and external alkynes. The kinetic studies by Bassetti demonstrated that the rate of formation of **3** from the vinylidene complex **1**, via the alkyne species **2** was more rapid when the substituents on the vinylidene/alkyne were electron-donating. This is consistent with the theoretical calculations on the conversion of **10** into **11**. Changing the substituent on the alkyne from hydrogen to methyl results in the vinylidene-containing species becoming less stable relative to the alkyne, but the transition states and stationary points connecting them are also lower in energy. Therefore, from a kinetic perspective the interconversion between alkyne and vinylidene should become more rapid on the addition of the methyl group, but from a thermodynamic perspective the equilibrium position will move towards the alkyne complex. Consistent with this argument, Ishii and co-workers found, in their studies with internal alkynes, that the rate of formation of the vinylidene complexes was aided when the alkyne was more electron-rich.

An interesting counterpoint to this discussion is that Ishii demonstrated that electron-deficient groups exhibit a greater migratory aptitude in the formation of the final vinylidene complex when compared to electron-rich analogues. Therefore the migration may be treated as a 1,2-electrophilic shift, which is consistent with the proposal that the migrating hydrogen is considered to be a proton in the case of terminal alkynes. This is also supported by the studies by Grotjahn, which demonstrate that the presence of an internal base assists the alkyne/vinylidene transformation. One interpretation of these data is that the presence of electron-donating substituents lowers barriers across the entire potential-energy surface and, in all cases except that of internal alkynes, these groups are spectators to the final migration process to form the vinylidene complex.

It should, however, be noted that an alternative interpretation of the data has been presented. Bassetti argues that electron-donating groups promote the vinylidene/alkyne conversion they are stabilising a build up of positive charge as the hydrogen migrates as a hydride. Indeed, from this perspective the vinylidene/alkyne transformation may be viewed as a nucleophilic attack by a hydride at the α-carbon of the vinylidene. However, it should be noted that the hydrogen attached to the β-carbon in cationic vinylidene complexes often displays protic character.

Rhodium Vinylidene Complexes

In a series of pioneering studies, Werner established that the $\{RhCl(PiPr_3)_2\}$ fragment could support alkyne, $[RhCl(PiPr_3)_2(\eta^2\text{-}HC{\equiv}CR)]$ (**26**), alkynyl hydride $[RhCl(H)(PiPr_3)_2(C{\equiv}CR)]$ (**27**) and vinylidene $[RhCl(PiPr_3)_2(C{\equiv}CHR)]$ (**28**) ligands. These findings were pivotal in the development of the "oxidative-addition" pathway for the formation of metal vinylidene complexes.[25,40–46] Despite the initial reports in this area being published over 25 years ago, the precise mechanism that connects the three compounds has been the subject of a considerable number of recent experimental and theoretical studies. Much of this work has been focused specifically on the conversion of the alkynyl hydride species to the corresponding vinylidene complexes.



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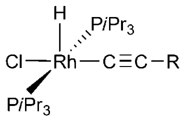

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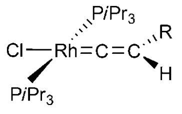

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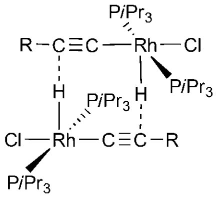

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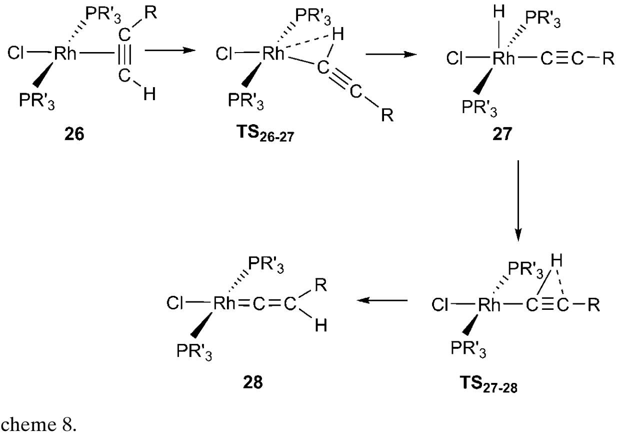
In a series of calculations published in 1997, Wakatsuki and co-workers[47] investigated the conversion from alkyne, alkynyl hydride and vinylidene complexes. One series of calculations from this study appeared to indicate that the alkynyl–hydride–vinylidene conversion may actually proceed in a bimolecular fashion via a species such as **29**. This hypothesis has been tested in a series of elegant labelling experiments by the Grotjahn group.[48–50] In this first instance, the reaction between $[RhCl(PiPr_2Ph)_2]_2$ and a 1:1 mixture of $DC{\equiv}C(CH_2)_3CH_3$ and $HC{\equiv}CCHMe_2$ resulted in a mixture of the vinylidene complexes $[RhCl(=C=CD\{(CH_2)_3CH_3\}(PiPr_2Ph)_2]$ and $[RhCl(=C=CH\{CHMe_2\}(PiPr_2Ph)_2]$: no evidence for H/D exchange was found. In addition, a mixture of $[RhCl(\eta^2\text{-}HC{\equiv}CH)(PiPr_3)_2]$ and $[RhCl(\eta^2\text{-}D^{13}C{\equiv}^{13}CD)(PiPr_3)_2]$ was shown to selectively afford $[RhCl(=C=CH_2)(PiPr_3)_2]$ and $[RhCl(=^{13}C=^{13}CD_2)(PiPr_3)_2]$—again no evidence for isotopic scrambling was observed. These data are consistent with the alkynyl–hydride–vinylidene conversion occurring exclusively by a unimolecular process. In a subsequent kinetic study performed in CH_2Cl_2,[49] Grotjahn also demonstrated that the process appeared to proceed from alkyne complex to alkynyl hydride to vinylidene; however, in this instance it was not possible to observe the alkynyl hydride complex.

In contrast, simply changing the solvent from CH_2Cl_2 to either THF or hexane allowed for all three organometallic complexes to be observed.[51] In these solvents the reaction of the rhodium precursor, $[\{RhCl(PiPr_3)_2\}_2]$, with a terminal alkyne to give **26** was rapid, even at low temperatures—this is not observed in CH_2Cl_2. As the concentration of each of the components of the reaction could be monitored the reaction profile was successfully modelled with a kinetic pathway based on **26**$\rightleftharpoons$**27**$\rightarrow$**28**. Models based on a bimolecular pathway gave very poor fits to the kinetic data. On this basis the balance of experimental evidence points to a mechanism that involves a unimolecular hydride transfer within the alkynyl hydride complex to give the vinylidene product. These experimental findings are supported by a number of theoretical studies. In addition to the studies described earlier by Wakatsuki,[47] calculations by Koga,[52] Grotjahn[49], De Angelis[53], Hall[54] and ourselves[51] have also been reported. This set of studies provides a coherent description of the potential energy surface of the alkyne–vinylidene rearrangement. The results from these studies are collected in Table 1 all energies are given relative to the alkyne complex **26** and a generalised reaction profile is



Scheme 8.

Table 1. Relative free energies [kcal mol^{-1}] of $\mathbf{TS_{26-27}}$, **27**, $\mathbf{TS_{27-28}}$ and **28** relative to the corresponding alkyne complexes **26**.

Entry	Complex	TS_{26-27}	27	TS_{27-28}	28	Theoretical method	Ref.
1	$[RhCl(PiPr_3)(=C=CH_2)]$	6.8	−0.8	26.1	−14.7	B3LYP/(LANL2DZ/6-31+G**)	[53]
2	$[RhCl(PiPr_3)(=C=CHPh)]$	3.0	−5.2	19.5	−9.6	B3LYP/(LANL2mDZ/cc-pVDZ/D95)	[54]
3	$[RhCl(PH_3)(=C=CH_2)]$	20.2	10.0	28.7	−7.3	B3LYP/(LANL2DZ/6-31++G**)	[52]
4	$[RhCl(PH_3)(=C=CHMe)]$	16.3	9.7	26.0	−1.9	B3LYP/(LANL2DZ/6-31++G**)	[52]
5	$[RhCl(PH_3)(=C=CHSiMe_3)]$	18.5	7.9	26.0	−4.1	B3LYP/(LANL2DZ/6-31++G**)	[52]
6	$[RhCl(PH_3)(=C=CHMe)]$[a]	42.2	21.7	47.4	−1.9	B3LYP/(LANL2DZ/6-31++G**)	[52]
7	$[RhCl(PH_3)(=C=CHSiMe_3)]$[b]	19.6	6.4	19.7	−4.1	B3LYP/(LANL2DZ/6-31++G**)	[52]
8	$[RhCl(PiPr_3)(=C=CH_2)]$	16.1	3.4	25.5	−17.5	ONIUM (BLYP/DQZ :UFF)[c]	[49]
9	$[RhCl(PiPr_2Im)(=C=CH_2)]$	18.5	7.8	26.2	−14.4	ONIUM (BLYP/DQZ :UFF)[c]	[49]
10	$[RhCl(PiPr_2Ph)(=C=CH_2)]$	18.0	5.9	26.4	−15.1	ONIUM (BLYP/DQZ :UFF)[c]	[49]
11	$[RhCl(PiPr_2\{o\text{-tol}\})(=C=CH_2)]$	19.0	7.8	26.4	−14.9	ONIUM (BLYP/DQZ :UFF)[c]	[49]
12	$[RhCl(PH_3)(=C=CH_2)]$	23.5	7.4	27.1	−7.7	(RI-)PBE0/TZVP//(RI-)BP86/SV(P)	[51]
13	$[RhCl(PMe_3)(=C=CH_2)]$	26.6	3.4	31.0	−6.0	(RI-)PBE0/TZVP//(RI-)BP86/SV(P)	[51]
14	$[RhCl(PMe_3)(=C=CHPh)]$	25.4	4.3	29.5	−0.2	(RI-)PBE0/TZVP//(RI-)BP86/SV(P)	[51]
15	$[RhCl(PMe_3)(=C=CHMe)]$	23.3	4.1	28.8	−0.7	(RI-)PBE0/TZVP//(RI-)BP86/SV(P)	[51]
16	$[RhCl(PiPr_3)(=C=CHPh)]$	22.3	-0.4	22.2	–	experimental	[51]
17	$[RhCl(PiPr_3)(=C=CHPh)]$	22.7	0.0	22.9	–	experimental	[51]
18	$[RhCl(PiPr_3)(=C=CHnBu)]$	20.8	-0.2	23.0	–	experimental	[51]

[a] Methyl migration pathway. [b] Silyl migration pathway. [c] Free-energy corrections using B3LYP/LANL2DZ.

shown in Scheme 8. All of the calculations show a similar set of features; for example, the alkyne, alkynyl hydride and vinylidene complexes are all stationary points: the vinylidene complexes are the global minima and in every instance the alkynyl hydride and alkyne complex are within 10 kcal mol^{-1} in energy. The actual C−H activation pathway proceeds in each case by a η^2-CH agostic-type complex ($\mathbf{TS_{26\text{-}27}}$, Scheme 8), which is, of course, similar to the initial activation processes predicted in the ruthenium case for both the hydrogen migration and oxidative-addition processes. It should be noted that in the calculations reported by Koga[52] and Grotjahn[49] the η^2-CH complex is a stationary point, whereas in the those performed by De Angelis[53] and Hall[54] this complex corresponds to a transition state connecting alkyne and alkynyl hydride complexes. In all cases, the rate-limiting step (i.e., highest energy transition state) involves the conversion of the alkynyl hydride to the vinylidene via $\mathbf{TS_{27\text{-}28}}$. All of these studies indicate that a unimolecular pathway is in operation, consistent with the experimental data.

In light of the results from the ruthenium system in which internal alkynes have been employed to prepare vinylidene ligands,[37,38] it is interesting to note that Koga also calculated the pathway from $[RhCl(\eta^2\text{-}HC{\equiv}CMe)(PH_3)_2]$ to $[RhCl(=C=CHMe)(PH_3)_2]$ via $[RhCl(C{\equiv}CH)(Me)(PH_3)_2]$; that is, a methyl migration mechanism (Table 1, entry 5).[52] Unsurprisingly, the activation of the C−Me bond has a far higher activation energy (42.2 kcal mol^{-1}) and the resulting methyl complex $[RhCl(C{\equiv}CH)(Me)(PiPr_3)_2]$ is considerably higher in energy (21.7 kcal mol^{-1}) than the corresponding alkynyl hydride complex $[RhCl(C{\equiv}CMe)(H)(PiPr_3)_2]$ (16.3 kcal mol^{-1}). These data are consistent with the fact that hydride migration is probably the dominant pathway in the formation of vinylidene complexes from terminal alkynes. However, it is worth noting that the corresponding silyl-migration pathway from $[RhCl(\eta^2\text{-}HC{\equiv}CSiMe_3)(PH_3)_2]$ (Table 1, entry 6) is almost isoenergetic with the hydride migration pathway. As stated previously, the formation of vinylidene complexes through silyl migration is relatively well established.[25–30]

The available experimental data[51] (Table 1, entries 15–17) for each step within this process are also in broad agreement with these calculations. Notably, the data indicate that the alkyne complex and alkynyl hydride species are typically at very similar energy, although the difference in energies between the barriers for C−H activation and hydride migration are smaller. In addition, the effects of the alkyne substituents observed in the experimental system are essentially reproduced by the calculations. For example, the exchange of the phenyl group $[RhCl(\eta^2\text{-}HC{\equiv}CPh)(PiPr_3)_2]$ by an alkyl chain $[RhCl(\eta^2\text{-}HC{\equiv}CnBu)(PiPr_3)_2]$ results in a lowering of the activation barrier for alkyne/alkynyl hydride interconversion—the barrier to the ultimate formation of the vinylidene complex remained very similar. This observation was reproduced on calculations with $[RhCl(\eta^2\text{-}HC{\equiv}CPh)(PMe_3)_2]$ and $[RhCl(\eta^2\text{-}HC{\equiv}CMe)(PMe_3)_2]$ and this reflects the findings from the ruthenium system discussed previously where electron-donating groups facilitate the alkyne/vinylidene transformation.

Although, on the whole, the calculations and experimental data provide a coherent picture of this transformation, it is worth noting that the predicted barrier for the interconversion of the alkyne **26** and alkynyl hydride **27** complexes shows the most significant deviation of all the calculated barriers. In the case of the calculations performed by De Angelis and Hall this barrier was predicted to be small (6.8 and 3.0 kcal mol^{-1} respectively). However, the results from the experimental studies and other calculations place a far higher barrier on this process.

One final point to note is the effect played by the phosphine ligand in this transformation. The kinetic study performed by Grotjahn and co-workers demonstrated that the rate of hydrogen shift is 9.6 times greater in this rhodium-containing system when the phosphine used in the reaction was P*i*Pr$_2$Im (Im = imidazole) with a pendant nitrogen atom, rather than P*i*Pr$_2$Ph. The most significant rate enhancements were observed in the step involving the conversion of alkynyl hydride **27** to vinylidene **28**. In studies on a related system, Hall[54] has systematically examined the effects of different phosphine ligands on the conversion between alkyne, alkynyl hydride and vinylidene ligands supported by the $\{Rh(C{\equiv}CPh)(PR_3)_2\}$ group. The result of these calculations indicated that both the alkynyl hydride and vinylidene complex are significantly stabilised relative to the alkyne complex in the presence of electron-donating phosphine ligands. A similar observation was made by De Angelis.[53] Clearly, electron-donating ligands will stabilise the higher oxidation state alkynyl hydride complex, whereas the stabilisation of the vinylidene probably results from a combination of steric factors and the fact that it is a better π acceptor than the η^2-coordinated alkyne.

Summary and Outlook

It is clear that the mechanism for the alkyne/vinylidene tautomerisation process contains a number of common features in all cases studied. Coordination of the alkyne to the metal is a pre-requisite to this process and the next stage in all pathways is the formation of a species in which the alkyne has slipped to give an η^2-(CH) agostic complex (**12**, Scheme 4; $\mathbf{TS_{26-27}}$, Scheme 8). Although the exact nature of this η^2-(CH) agostic complex as either a transition state or intermediate appears to be system-dependant, it does appear to be a common structural motif that facilitates the C−H bond cleavage step, either by 1,2-hydrogen migration (pathway 1) or oxidative-addition (pathway 2) route. In this context it is worth noting that the latter pathway is favoured in electron-rich systems, whereas in less electron-rich systems it is the former. In both cases, DFT calculations indicate that an intial oxidative-addition process is viable, but in less electron-rich systems the subsequent hydrogen migration process from the alkynyl hydride is at too high an energy to be considered a possible pathway. Therefore in this case hydrogen migration occurs directly from the η^2-(CH) species to give the final product.

It is also evident that the ligands in the metal coordination sphere may substantially affect the reaction pathway. It is established that electron-rich phosphine ligands, for example, aid the oxidative-addition pathway in the case of half-sandwich ruthenium complexes. One important general trend that is apparent in both the ruthenium and rhodium chemistry described above is that the presence of uncoordinated nitrogen atoms as part of an N-heterocycle in the phosphine ligand significantly enhances the rate of formation of the vinylidene complexes. Very recent results from the Carmona group have illustrated that the uncoordinated nitrogen atom may act as an intramolecular base assisting the deprotonation of an iridium η^2-alkyne complex with subsequent protonation of an alkynyl ligand.[58]

In addition, the results from these studies demonstrate that the substituents on the alkyne may also affect the potential-energy surface of the reaction. The general trend observed in both the ruthenium- and rhodium-based systems is that electron-donating substituents on alkynes enhance the rate of the alkyne–vinylidene transformation. This is supported by DFT calculations, which indicate electron-donating groups on the alkyne lower the transition states connecting the alkyne and vinylidene complexes, but destabilise the vinylidene complex relative to the alkyne. Given the subtleties of this reaction pathway, it is evident that in order to accurately reproduce the experimental situation, DFT calculations should be performed as far as possible on experimentally relevant models.

Arguably the most significant recent finding in this field is that internal unfunctionalised alkynes may be used as precursors to di-substituted vinylidene complexes using common organometallic reagents. This appears to be a hitherto unexplored facet of the chemistry of metal vinylidene complexes and a detailed mechanistic understanding of this process is clearly required. The conversion of an internal alkyne into its vinylidene tautomer represents one of the most facile examples of sp–sp^2/sp–sp^3 carbon–carbon bond cleavage by a transition-metal complex. In this context it is interesting to note that the photochemical activation of the C−C bond in complexes $[PtL_2(\eta^2\text{-}PhC{\equiv}CPh)]$ (L_2 = chelating P–P or P–N ligand) has been demonstrated to afford the oxidative-addition products $[PtL_2(C{\equiv}CPh)(Ph)]$.[55,56] This reaction may even be performed in the solid state.[57] However, in these platinum-containing examples, the activated product is thermodynamically unstable with respect to the starting complex, in marked contrast to the vinylidene complexes formed by C−C bond activation.

The conversion of internal alkynes into their corresponding vinylidene ligands is also important from a catalytic perspective. Not only should this process be considered as a plausible step in existing catalytic cycles, but these studies should also prompt new investigations into how disubstituted vinylidene ligands may be exploited in synthetic chemistry.

Note Added in Proof

Since this manuscript was submitted a number of publications concerning the synthesis of vinylidene ligands have been published. For example, in work related to that described above undertaken by Shaw,[36] the ability of ruthenium complexes containing trispyrazoylborate ligands to facilitate the isomerisation of internal alkynones $PhC{\equiv}CCOR$ into their vinylidene tautomers $[Ru{=}C{=}C(COR)Ph]$ has been reported.[59] In this case it was possible to observe η^1(O)-bound species related to **19** and, in addition, a complex in which the alkynone is bound as a π complex. Indeed, it is thought that the vinylidene complex is formed by a 1,2-acyl migration from this π complex. Also, it has also been shown that both allenes[60] and alkylidenecyclopropanes[61] may be employed to prepare ruthenium and osmium vinylidene complexes respectively. In the latter case, the metal deconstructs the cyclopropane to from both the vinylidene ligand and ethene.

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