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Analysis of the Solid-State Rearrangement of Hydrido-Alkynyl Ruthenium Complexes to their Vinylidene Tautomers

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Summary. The solid-state tautomerization of the hydrido-alkynyl derivatives [*Cp**RuH(C≡C*R*)-(*dippe*)][BPh_4] (*Cp** = C_5Me_5; *R* = $SiMe_3$, Ph, H; *dippe* = 1,2-bis-(diisopropylphosphino)-ethane) to their vinylidene isomers [*Cp**Ru=C=CH*R*(*dippe*)][BPh_4] was studied by IR spectroscopy. Characteristic isothermic α *vs.* t curves for each individual rearrangement process were recorded. Their shape, and hence the isomerization mechanism, depends strongly on the nature of the substituent *R*. The kinetic analysis of the above curves using the *Avrami-Erofeev* provided some mechanistic information about the isomerization process in the solid.

Keywords. Ruthenium; Half-sandwich complexes; Hydrido complexes; Vinylidene complexes; Tautomerization.

Introduction

Theoretical studies [1, 2] have shown that the transition metal promoted isomerization of 1-alkynes to their vinylidene tautomers takes place by a direct 1,2-hydrogen shift in a π-alkyne complex according to Scheme 1.

Alternatively, oxidative addition of the 1-alkyne may occur yielding hydrido-alkynyl species which rearrange to vinylidene *via* a concerted 1,3-hydrogen shift according to Scheme 2.

The latter mechanism it is known to operate in certain Co [3], Rh, and Ir [4] systems in which the electronic configuration of the metal changes from d^8 to d^6 upon oxidative addition. However, this pathway becomes energetically too costly when the electronic configuration of the metal changes from d^6 to d^4 as in the case of Ru(II) to Ru(IV) [1, 2]. Nevertheless our group has recently reported the formation of metastable Ru(IV) hydrido-alkynyl derivatives of the type [*Cp**RuH(C≡C*R*)(*dippe*)][BPh_4] (*R* = COOMe, $SiMe_3$, Ph, H) and their rearrangement to the corresponding vinylidene isomers [*Cp**Ru=C=CH*R*(*dippe*)][BPh_4] [5]. This process occurs in a dissociative, non-concerted fashion. The hydride ligand dissociates from the hydrido-alkynyl as a proton, leaving a neutral alkynyl complex.

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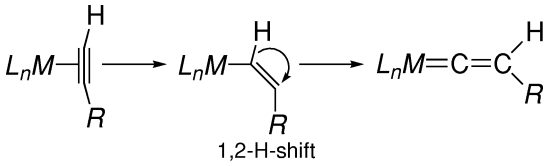
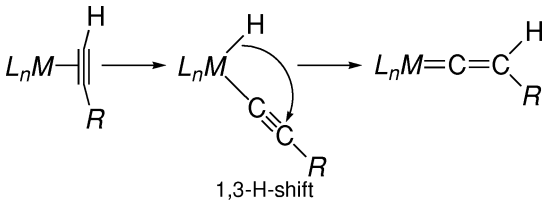
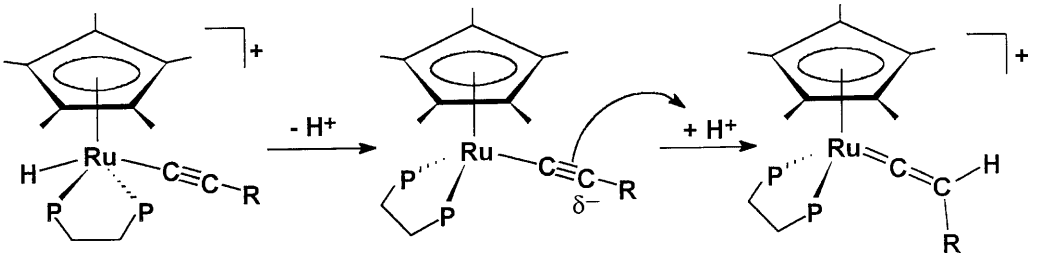


Scheme 1



Scheme 2



Scheme 3

Then, protonation at β-carbon of the alkynyl ligand takes place, furnishing the vinylidene complex as the final thermodynamic product (Scheme 3). Remarkably, the tautomerization process also occurs in the solid state, at a rate strongly dependent on the substituent at the alkynyl ligand. Analogous solid state hydrido-alkynyl to vinylidene rearrangements have been reported for $[CoH(C{\equiv}CR)(PP_3)][BPh_4]$ ($R = SiMe_3$, H, Ph, ^{t}Bu; PP_3 = *tris*-(diphenylphosphinoethyl)-phosphine, $P(CH_2CH_2PPh_2)_3$) [3]. For these, a colour change was observed when a solid sample was heated under N_2, thus indicating conversion to a vinylidene compound. The temperature at which the corresponding colour change was observed was also found to depend strongly on the alkynyl substituent and decreasing in the order $SiMe_3 > Ph \approx H \gg {}^tBu$ [3]. Other thermal and photochemical isomerization reactions are known to occur in the solid state, *e.g.* nitrito to nitro isomerization [6], *cis*- to *trans*- isomerization in metal complexes [7], or the *diag*- to *lat*-isomerization of $[(C_5H_4R)Re(CO)(L)X_2]$ (R = H, Me; L = CO, $P(OPh)_3$; X = Br, I) [8]. Despite of this, the solid state hydrido-alkynyl to vinylidene rearrangement is a more complicated process at the molecular level, which may have important implications, especially in the light of the fact that certain surface-catalyzed reactions involving alkynes have been suggested to proceed *via* vinylidene intermediates [9].

In this work we took advantage of the use of IR spectroscopy as a tool for determining quantitative parameters of the isomerization in the solid state, allowing to obtain α (fraction of transformed solid) *vs.* time curves which provided insight into mechanistic details of the overall process.

Results and Discussion

The solid-state isomerization of the complexes [*Cp**RuH(C≡C*R*)(*dippe*)][BPh_4] (*R* = $SiMe_3$, Ph, H) [5] to their vinylidene tautomers [*Cp**Ru=C=CH*R*(*dippe*)] [BPh_4] was followed by IR spectroscopy. All starting hydrido-alkynyl derivatives display one medium to strong ν(C≡C) vibration at *ca.* 2000 cm^{-1}. When these compounds undergo isomerization to vinylidenes, this ν(C≡C) IR band gradually disappeared, being replaced by a strong absorption at *ca.* 1650 cm^{-1} corresponding to ν(C=C) in the newly formed vinylidene ligand (Fig. 1). Hence, monitoring the disappearance of the ν(C≡C) band as a function of time allowed to evaluate the advance of the solid-state isomerization. The corresponding α (fraction of transformed solid) *vs.* time curves for each compound were derived from sets of the integrated intensity of the ν(C≡C) IR band ($I(t)$) measured at a given instant t. For $R = SiMe_3$ (Fig. 2) and $R = Ph$ (Fig. 3), the isomerization process took place at 25°C, being complete in a few hours. For $R = H$, the isomerization is very slow at room temperature, the amount of untransformed hydrido-alkynyl complex in a solid sample being still high after ten days. For this reason, the isomerization was studied at 50°C (Fig. 4). At this temperature, the process was still slow, but the transformation was completed after a period of 21 h. We also prepared the hydrido-alkynyl derivative [*Cp**RuH(C≡CCOOMe)(*dippe*)][BPh_4], which has been shown to rearrange in solution to its vinylidene isomer [*Cp**Ru=C=CHCOOMe(*dippe*)] [BPh_4] [5]. However, this hydrido-alkynyl complex did not undergo a solid-state

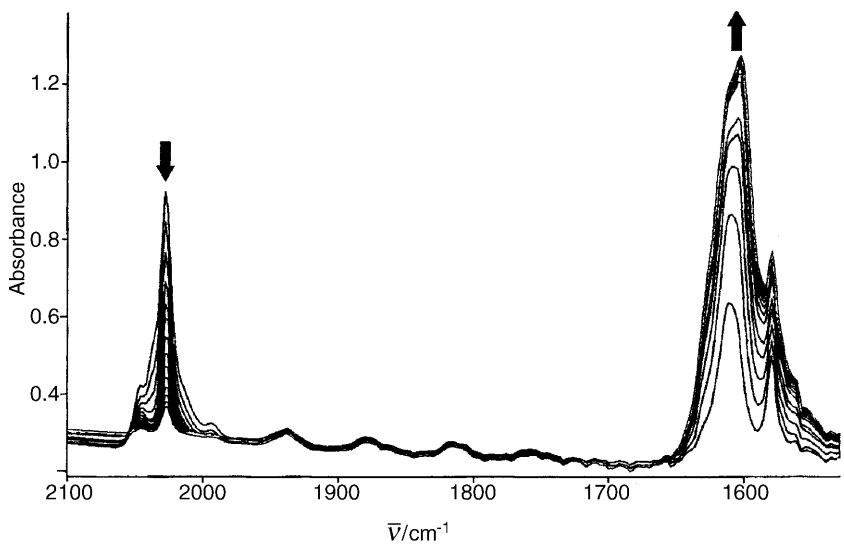


Fig. 1. IR spectra of [(C_5Me_5)RuH(C≡C$SiMe_3$)(*dippe*)][BPh_4] as a function of time (regular intervals of 20 min), showing the decrease in the intensity of the ν(C≡C) band and the increase of the ν(C=C) band corresponding to the vinylidene tautomer [(C_5Me_5)Ru=C=CH$SiMe_3$(*dippe*)][BPh_4]

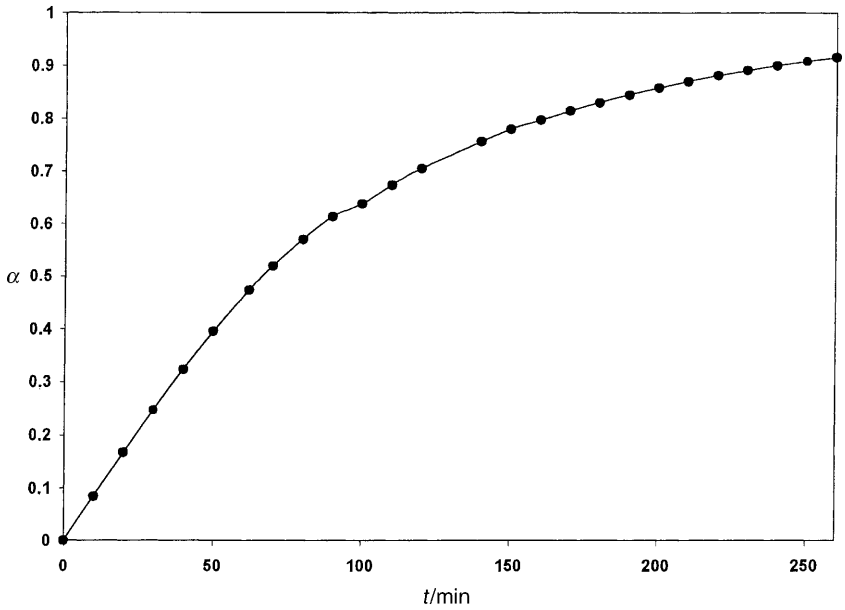


Fig. 2. α *vs.* t plot for the rearrangement $[(C_5Me_5)RuH(C{\equiv}CSiMe_3)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CHSiMe_3(dippe)][BPh_4]$

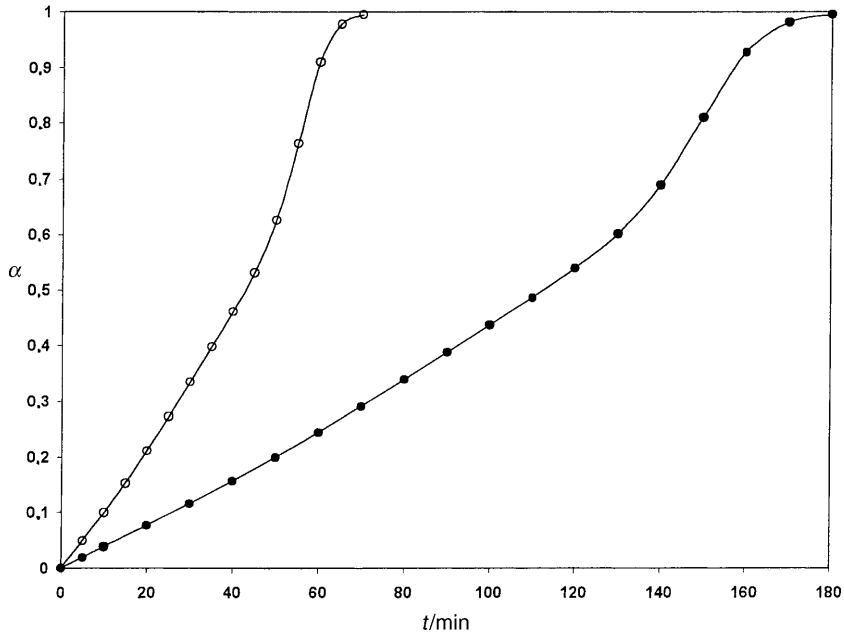


Fig. 3. α *vs.* t plots for the rearrangements a) $[(C_5Me_5)RuH(C{\equiv}CPh)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CHPh(dippe)][BPh_4]$ (O) and b) $[(C_5Me_5)RuD(C{\equiv}CPh)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CDPh(dippe)][BPh_4]$ (●)

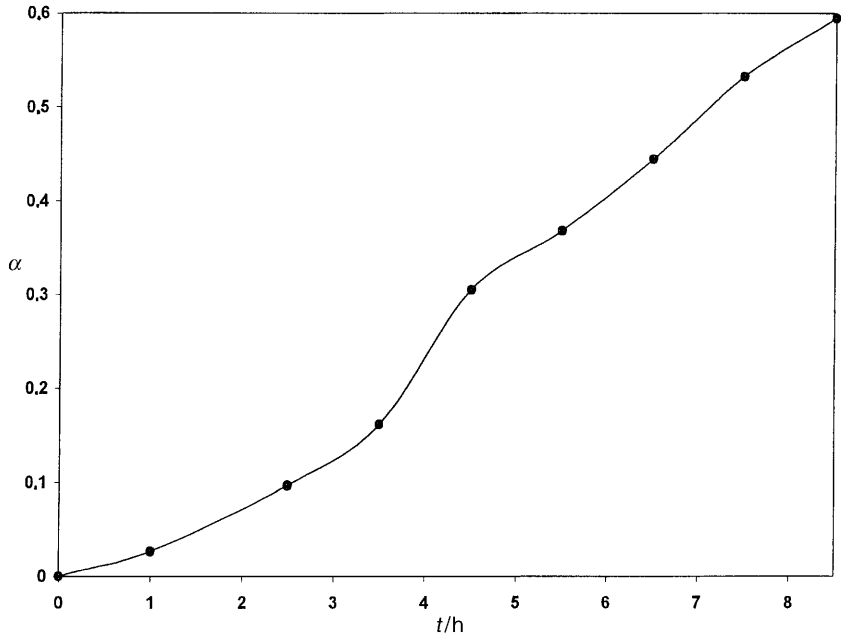


Fig. 4. α *vs.* t plot for the rearrangement $[(C_5Me_5)RuH(C{\equiv}CH)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CH_2(dippe)][BPh_4]$ at 50°C

Table 1. Comparison between the observed half-lives for the isomerization $[Cp^*RuH(C{\equiv}CR)(dippe)][BPh_4] \rightarrow [Cp^*Ru{=}C{=}CHR(dippe)][BPh_4]$ in acetone solution and in the solid state, both at 25°C unless otherwise stated

R	$t_{1/2}$/min (solution)	$t_{1/2}$/min (solid state)
COOMe	4.6[a]	no isomerization
$SiMe_3$	2.4	66
Ph	0.5	43
Ph[b]	0.5	115
H[c]	1.7	420

[a] At 0°C; [b] half-lives for the deuterated derivative $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$; [c] at 50°C

isomerization at room temperature, and, apparently, decomposition occurred prior to isomerization when the sample was heated. This stability towards solid-state isomerization allowed to determine the crystal structure of $[Cp^*RuH(C{\equiv}CCOOMe)(dippe)][BPh_4]$ by single crystal X-ray diffraction [5], but no α *vs.* t curve was obtained in this particular case.

Both the rates of isomerization and the shapes of the α *vs.* t curves were found to be strongly dependent of the alkynyl substituents. For comparison, the half-lives ($t_{1/2}$) for each of the isomerization reactions both in solution and in the solid state are listed in Table 1. In the case of $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$, a remarkable isotopic effect was observed. The half-life for the transformation of $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$ to $[Cp^*Ru{=}C{=}CHPh(dippe)][BPh_4]$ was 43 min, whereas for the deuterated derivatives $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$ a value of 115 min

was found. This contrasted sharply with the lack of an observed isotopic effect for the same rearrangement process in solution. The α *vs.* t curves for the isomerization of both [Cp^*RuH(C≡CPh)(*dippe*)][BPh_4] and [Cp^*RuD(C≡CPh)(*dippe*)][BPh_4] showed the same sigmoidal shape. These observations were consistent with the fact that the movements of hydrogen atoms, possibly in the form of protons, are the controlling step in the rearrangement process which is most likely intermolecular, as it happens in solution. Furthermore, the movement of protons among transition metal cationic complexes in lattices has been well documented [10]. The isomerization of [Cp^*RuH(C≡CH)(*dippe*)][BPh_4] to the primary vinylidene complex [Cp^*Ru=C=CH_2(*dippe*)][BPh_4] is a special case. When obtained by reaction of [Cp^*RuCl(*dippe*)] [11] with $NaBPh_4$ and acetylene in MeOH, the solid samples containing [Cp^*RuH(C≡CH)(*dippe*)][BPh_4] are always mixed with similar amounts of the π-alkyne complex [Cp^*Ru(η^2-HC≡CH)(*dippe*)][BPh_4], which also rearranges to the primary vinylidene compound [Cp^*Ru=C=CH_2(*dippe*)][BPh_4], both in solution and in the solid state [5]. Whereas, due to an equilibrium between the hydrido-alkynyl and π-alkyne isomers, in solution the isomerization of both [Cp^*RuH(C≡CH)(*dippe*)][BPh_4] and [Cp^*Ru(η^2-HC≡CH)(*dippe*)][BPh_4] to [Cp^*Ru=C=CH_2(*dippe*)][BPh_4] occur at the same rate, in the solid state the rearrangement of the latter is much faster. It takes place even at room temperature, and, from the mechanistic point of view, *via* a 1,2-hydrogen shift. In the solid state, this process involves just an alkyne slippage, not very different from the slippage proposed for the nitrito to nitro isomerization [6]. It is not clear whether the cations [Cp^*Ru(η^2-HC≡CH)(*dippe*)]$^+$ and [Cp^*RuH(C≡CH)(*dippe*)]$^+$ are both present within the same crystal lattice, or whether the solid sample consists of separate microcrystals of [Cp^*Ru(η^2-HC≡CH)(*dippe*)][BPh_4] and [Cp^*RuH(C≡CH)(*dippe*)][BPh_4]. In any case, the transformation of [Cp^*RuH(C≡CH)(*dippe*)][BPh_4] into [Cp^*Ru=C=CH_2(*dippe*)][BPh_4] is slower and more complex than those of the derivatives with $R = SiMe_3$ or Ph, as inferred from its α *vs.* t curve (Fig. 4). The acceleration observed at *ca.* 4 h seems to be associated with changes in the lattice due to the complete conversion of the π-alkyne isomer into vinylidene.

The *Avrami-Erofeev* equation (Eq. (1)) [12] has been widely used for the kinetic analysis of α *vs.* t curves of processes such as thermal decomposition of solids, phase transformations, and solid-solid reactions.

$$\alpha = 1 - \exp(-(kt)^n) \tag{1}$$

The exponent n relates to the operating mechanism for the solid transformation and contains information about the number of steps in nuclei formation and the dimension of the nuclei growth within the crystal. The constant k is a rate constant, and as such a quantitative measure of the speed at which the transformation occurs. The values of n and k can be determined taking logarithms twice in Eq. (1), thus leading to Eq. (2):

$$\log\left(\log\left(\frac{1}{1-\alpha}\right)\right) = n\,\log k + n\,\log t + \log\log e \tag{2}$$

Therefore, plotting $\log(\log(1/(1-\alpha)))$ against $\log t$ yields a straight line of slope n. From the intercept, the value of k can be calculated. We applied this model to the α *vs.* t curves for the isomerization reactions of [Cp^*RuH(C≡C$SiMe_3$)(*dippe*)]

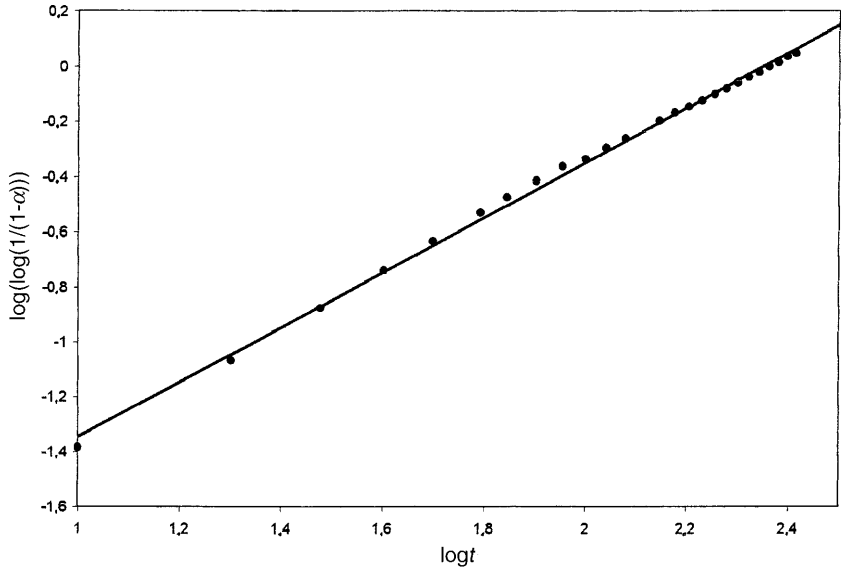


Fig. 5. Plot of $\log(\log(1/(1-\alpha)))$ against $\log t$ for the rearrangement $[(C_5Me_5)RuH(C{\equiv}CSiMe_3)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CHSiMe_3(dippe)][BPh_4]$

$[BPh_4]$, $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$, and $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$. In the case of $[Cp^*RuH(C{\equiv}CSiMe_3)(dippe)][BPh_4]$, the best least squares fit yielded the values $n = 1$ and $k = (1.05 \pm 0.05) \cdot 10^{-2}\,\mathrm{min}^{-1}$ (Fig. 5) for $0 < \alpha < 0.9$. This means that, as it happens in solution, the operating rate law in this case is of first order, which is consistent with a random nucleation in which each of the cations in the solid has equal probability towards isomerization by intermolecular migration. In this case, the rate was directly proportional to the amount of non-transformed material $(1 - \alpha)$.

For the isomerization of $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$, and also in the case of $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$, the overall process could be separated into two steps upon application of the *Avrami-Erofeev* equation. In the interval $0 < \alpha < 0.6$, for $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$ $n = 1.23 \pm 0.03$ and $k = (1.6 \pm 0.1) \cdot 10^{-2}$, and for $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$ $n = 1.16 \pm 0.03$ and $k = (6.0 \pm 0.1) \cdot 10^{-3}$ (Fig. 6a). In the upper interval $(0.6 < \alpha < 1)$ there was a change in the magnitude of n and k, resulting in the values $n = 4.6 \pm 0.5$ and $k = (2.1 \pm 0.5) \cdot 10^{-2}$ for $[Cp^*RuH(C{\equiv}CPh)(dippe)][BPh_4]$ and $n = 5 \pm 0.4$ and $k = (8 \pm 3) \cdot 10^{-3}$ for $[Cp^*RuD(C{\equiv}CPh)(dippe)][BPh_4]$ (Fig. 6b). In these two cases, and for the first part of the process, n-values close to 1.2 suggest a reaction controlled by the advance of the interphase generated as the cations undergo rearrangement to vinylidene with concomitant hydrogen (proton) migration across the lattice. At a certain moment, when $\alpha \approx 0.6$, there is a change in the controlling step, which becomes then the nucleation in the untransformed material as indicated by the values of n between 4 and 5. However, the last part of this process must be taken with due caution, since the validity of kinetic analyses using α *vs.* t data is usually restricted to the interval $0.05 < \alpha < 0.65$. However, it must also be noted that the distinctive sigmoid shape of the two curves for these isomerizations, *e.g.*

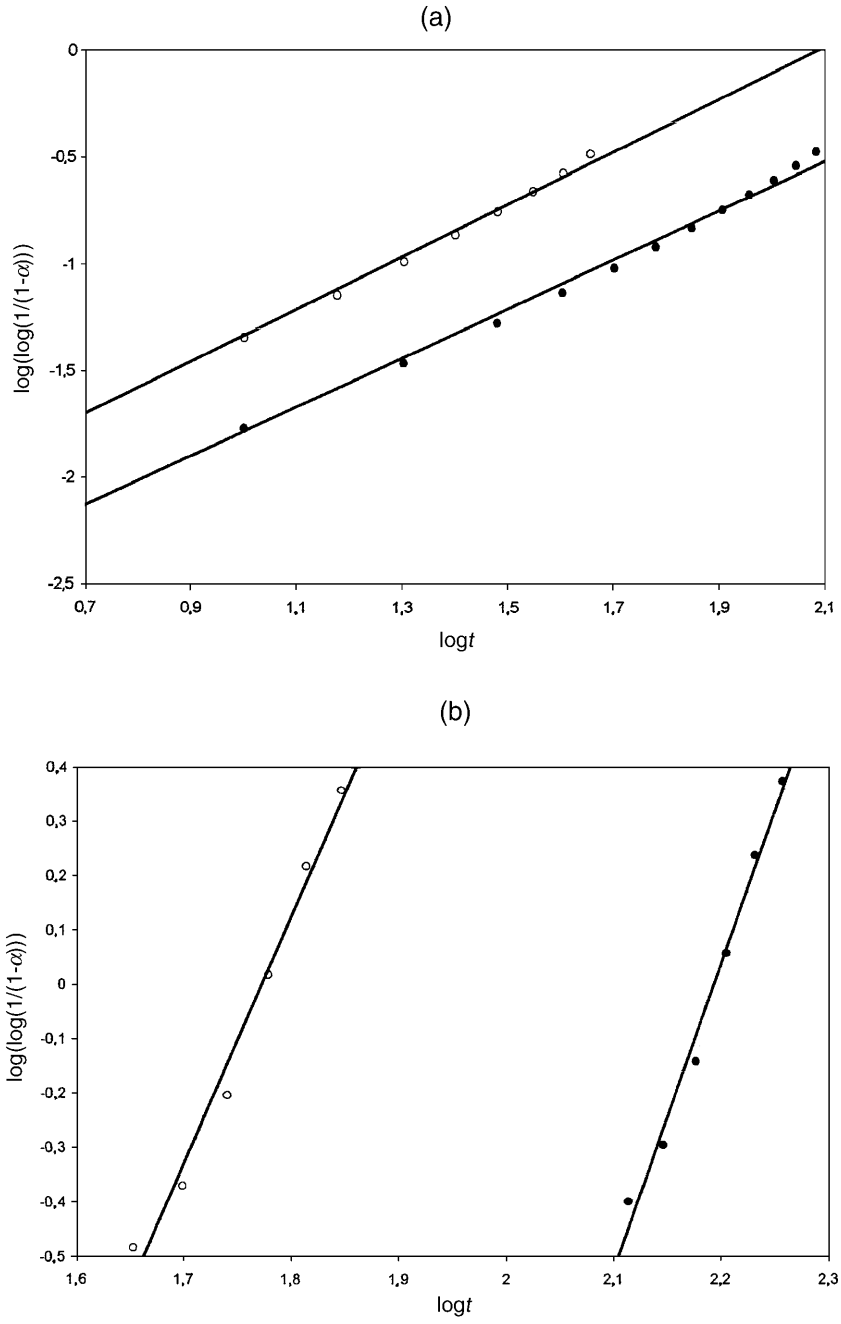


Fig. 6. Plots of $\log(\log(1/(1-\alpha)))$ against $\log t$ for the rearrangements $[(C_5Me_5)RuH(C{\equiv}CPh)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CHPh(dippe)][BPh_4]$ (O) and $[(C_5Me_5)RuD(C{\equiv}CPh)(dippe)][BPh_4] \rightarrow [(C_5Me_5)Ru{=}C{=}CDPh(dippe)][BPh_4]$ (•); a) $0 < \alpha < 0.6$, b) $0.6 < \alpha < 1$

compared to that of the $SiMe_3$ derivative, suggests that a real alteration in the rate controlling step takes place at this point.

From the structural point of view, the hydrido-alkynyl to vinylidene rearrangement involves a series of important stereochemical changes in the cation,

whereas the anion should not be affected. These changes can be summarized as *a*) modification of the angle C-C-*R* in the alkynyl ligand from *ca*. 180° to *ca*. 120° in the vinilydene moiety C=CH*R* and *b*) change in the dihedral angle formed by the plane defined by the C_5 ring of the *Cp** ligand and the plane defined by the Ru and the two P atoms. This dihedral angle has a value of 79° in the structurally characterized complex [*Cp**RuH(C≡CCOOMe)(*dippe*)][BPh_4] [5], whereas in the vinylidene isomer [*Cp**Ru=C=CHCOOMe)(*dippe*)][BPh_4] it is close to 60° which means a considerable dislocation for the phosphorus atoms and their alkyl substituents. It is evident that in these structural changes there is a direct involvement of the *R* groups of the alkynyl ligand, and this explains the strong rate dependence observed. Still, the hydrogen atom bound to Ru must travel a considerable distance during isomerization, this being a controlling step in the rearrangement process, at least for [*Cp**RuH(C≡CPh)(*dippe*)][BPh_4] as inferred from the important isotopic effect measured. Nevertheless, hydrogen migration is likely to be one of the most importants rate-limiting factors in all cases.

Compatibility between the crystal structures of the starting and final products also affects to the overall rate of transformations in solids. If the structural differences between the initial and final products are very small, nucleation is very easy and the process occurs fast. However, if there are no structural similarities between the two products, nucleation is difficult or even impossible. The so-called topotactic transitions constitute an intermediate case in which a structural relationship exists between the initial and final product, but still structural reorganization is necessary [13]. This may well be the case for our system, as indicated by preliminary studies by powder X-ray diffraction for the isomerization of [*Cp**RuH(C≡CH)(*dippe*)][BPh_4]. The powder diffractograms showed that the final vinylidene product [*Cp**Ru=C=CH_2(*dippe*)][BPh_4] is crystalline, and hence the crystal lattice is not destroyed upon isomerization. Further studies by this and other techniques, such as scanning electron microscopy and differential scanning calorimetry, will prove useful in gathering information concerning structural changes during the solid state isomerization process.

Experimental

All synthetic operations were performed under a dry N_2 or Ar atmosphere following conventional *Schlenk* or dry-box techniques. The hydrido-alkynyl derivatives [(C_5Me_5)RuH(C≡C*R*)(*dippe*)][BPh_4] ($R = SiMe_3$, Ph, H) were prepared according to reported procedures [5], starting from [*Cp**RuCl(*dippe*)] [11]. IR spectra were recorded as Nujol mulls on a Perkin Elmer FTIR Spectrum 1000 spectrophotometer at 25°C. The α (fraction of transformed solid) *vs*. time curves were obtained by monitoring the decrease of the integrated intensity of the ν(C≡C) IR band for each compound as a function of time. The value of α at a given *t* instant was calculated from Eq. (3).

$$\alpha(t) = (I(t=0) - I(t))/I(t=0) \tag{3}$$

In the case of [(C_5Me_5)RuH(C≡CH)(*dippe*)][BPh_4], which does not rearrange at an appreciable rate at 25°C, the sample was kept in an oven at 50±3°C. At regular time intervals, the sample was taken out, and its IR spectrum was recorded at room temperature. After recording each spectrum, the sample was returned back to the oven, and the cycle was repeated over a period of 10 h. After 21 h at 50±3°C, conversion to [(C_5Me_5)RuH(C≡CH)(*dippe*)][BPh_4] was found to be complete. Rate constants (*k*) and the values of *n* were derived from least-squares fits of $\log(\log(1/(1-\alpha)))$ *vs*. $\log t$

plots (*Avrami-Erofeev* equation). The uncertainty in the value of n and in the isomerization rate constant represents one standard deviation ($\pm\sigma$) derived from the slope and the intercept of the best fit lines.

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