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Acid controlled alkyne dimerisation initiated by a Ru–carbene precursor

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Abstract

The Grubb's catalyst $Cl_2(PR_3)_2Ru{=}CHPh$ (**1**) is an excellent precursor for the dimerisation of terminal alkynes. Thermal treatment and addition of two equivalents of phenylacetylene to complex **1** generates a new Ru–vinylidene (**3**). Complex **3** catalyses a selective product formation for *trans*-tail-to-tail enynes. Addition of acetic acid enhances the yield and the reaction rate dramatically and a reversed stereoselectivity for the formation of *Z*-isomers is obtained. The stereoselectivity can be easily tuned by addition of acetic acid. The influence of the acid on the reaction pathway has been revealed. A simple one-pot preparation of tail-to-tail enynes is established.

Keywords: Homogeneous catalysis; Dimerisation; Ruthenium; Carbene ligands; Vinylidene ligands

1. Introduction

Metal vinylidenes (M=C=CHR) have emerged as useful precursors with an unusual reactivity for a variety of organic reactions of industrial importance [1]. The direct simple formation of metal vinylidene intermediates from commercially available terminal alkynes and a metal complex made the transfer from stoichiometric to catalytic reactions possible. Based on the fundamental mechanism metal vinylidenes are involved in catalytic reactions of the type: dimerisation of alkynes, [2+2] cycloaddition, nucleophilic addition to alkynes and radical cycloaromatisation. Direct coupling of 1-alkynes, i.e. dimerisation, represents an easy route to unsaturated dimeric species, in particular 1,3- and 1,4-disubstituted enynes [2]. These are valuable precursors for the synthesis of natural products as well as interesting building blocks for further organic modifications [3–7]. Nucleophilic addition of carboxylic acids to terminal alkynes, also known as vinylation, produces enol esters in a regio- and stereoselective manner. Enol esters are useful intermediates for carbon–carbon and carbon–heteroatom bond formation. They have been used for the selective generation of enolates, acylation of carbonyl compounds and *O*- and *N*-acylation under mild conditions [8–11]. Another important feature is the rearrangement of the vinylidene ligand ([M]=C=CHR) to an alkylidene moiety ([M]=CHR) in the presence of an olefin [12–14]. This enlarges the application field of vinylidenes to valuable, easy accessible precursors for selective cross-metathesis, ring-closing metathesis and ring opening metathesis polymerisation (ROMP). A well-known stable, well-defined metal–alkylidene complex for olefin metathesis is the Grubb's 'first generation' catalyst ($Cl_2(PR_3)_2Ru{=}CHPh$) [15,16]. The wide spread use of the Ru–alkylidene is derived from its activity, stability and functional group tolerance [17–20]. The catalyst remains active in the presence of a variety of functional groups like carbonyls, amides and alkohols. However, the thermolytic decomposition is a major drawback and limits the use in many challenging reactions [21]. The alkylidene decomposition proceeds predominantly via a second order reaction pathway requiring phosphine dissociation. The nature of the inorganic decomposition products still remains uniden-

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tified. Here, we describe the generation of a Ru–vinylidene precursor, from thermal treatment of $Cl_2(PR_3)_2Ru{=}CHPh$ with phenylacetylene, for the dimerisation of terminal alkynes.

2. Results and discussion

2.1. Thermal treatment of $Cl_2(PCy_3)_2Ru{=}CHPh$

The thermal treatment of $Cl_2(PCy_3)_2Ru{=}CHPh$ (complex **1**) at 110 °C in toluene results in a decomposition of the carbene ligand. Grubbs et al. performed similar reactions at 55 °C [21]. They established that the decomposition proceeds via a second order reaction pathway requiring phosphine dissociation. The organic product was determined as stilbene, but the inorganic compound remained unidentified. Our attempts to monitor the thermal decomposition products of complex **1** show the disappearance of the carbene ligand, since ^{1}H- and ^{31}P{H}-NMR analysis show no signal at 20.02 and 36.6 ppm, respectively, after the thermal treatment at 110 °C.

^{31}P{H}-NMR shows two types of PCy_3 groups ($\delta =$ 31 and 47 ppm). No evidence is found for a dissociation equilibrium of a phosphine ligand taking place at the metal center since no free PCy_3 is detected. The signal at 31 ppm remains unidentified. Isolation and crystallisation of the inorganic compound was unsuccessful, so the nature of the inorganic complex **2** still remains undetermined.

2.2. Reactivity of complex 1 with PhC≡CH: generation of a Ru–vinylidene

A solution of complex **1** and one equivalent phenylacetylene is treated at reflux of toluene for 60 min. A rapid colour change from purple to red-brown occurs. ^{31}P{H}-NMR reveal a new type of co-ordinated PCy_3 ($\delta = 53$ ppm) and some free phosphine. A Ru–vinylidene complex **3** is formed. Complete formation of complex **3** is not yet achieved, since the signal of complex **2** still remains present. Subsequent addition of another equivalent phenylacetylene at 110 °C results in a quantitative conversion of complex **2** to the Ru=C=CHPh (**3**) after 1 h. ^{13}C{H}-NMR determines the C_α and C_β of the Ru–vinylidene **3** at 341.4 and 118.3 ppm, respectively. Analysing the time evolution of NMR spectra of the reaction between complex **1** and a 10-fold excess of PhC≡CH provided following evidence, (i) All PhC≡CH is consumed in 1 h to produce PhC≡C–CH=CHPh. (ii) Free PCy_3 is detected by ^{31}P{H}-NMR. (iii) No new phosphorus containing species, next to the signals of complex **1** (36.6), **2** (47) and **3** (53 ppm), are detected during the transformation from complex **1** to complex **2** and subsequently to complex **3**. (iv) Extra addition of phenylacetylene results in full conversion to PhC≡C–CH=CHPh. (v) Preferentially tail-to-tail enynes are formed.

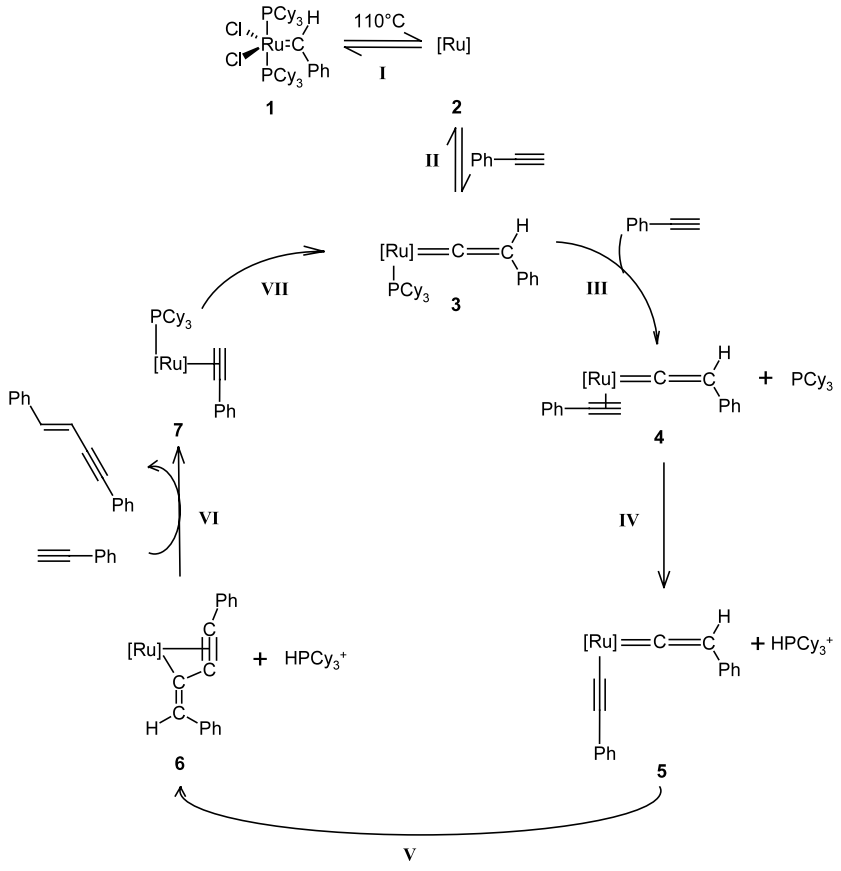
On the basis of this spectroscopic data a mechanistic hypothesis for the Ru-catalysed dimerisation of phenylacetylene is depicted in Scheme 1.

Thermal treatment of the Grubb's catalyst or complex **1** results in an unidentified Ru-compound (complex **2**) (**I**). Addition of two equivalent phenylacetylene is needed to fully transform complex **2** into the vinylidene complex **3** (**II**). The reaction of **3** reacts with further alkyne to form the alkynyl (alkyne) complex **4** (**III**). The formation of complex **4** is consistent with the insertion of PhC≡CH. The mechanism of insertion involves decoordination of a phosphine ligand. This thesis is supported by the following experiment: a 1- to 2-fold excess PCy_3 is added to the reaction mixture. The addition of an increasing amount of phosphine inhibited the reaction completely. Only traces of PhC≡C–CH=CHPh are detected. The decoordination of one phosphine ligand plays a pivotal role in the initiation process. Once complex **4** has rearranged into an alkynyl (vinylidene) complex **5**, the PhC≡C–C=CHPh ligand may be formed via C–C bond formation between the α-carbon of vinylidene and the alkynylligand (**IV**–**V**). The PhC≡C–C=CHPh ligand in **6** will partially dissociate from the Ru-center with generation of a carbanion. This carbanion will then accept hydrogen from the generated $HPCy_3^+$ and will be eliminated as tail-to-tail enynes (**VI**). The free co-ordination places are immediately occupied by a newly incoming alkyne and PCy_3 ligand, with generation of a highly unstable Ru-complex **7**. Subsequent rearrangement of complex **7** regenerates the original alkynyl intermediate **3** (**VII**).

The optimal temperature to promote the reaction process is 110 °C. The reaction is performed at 20, 40, 60, 80 and 110 °C and yielded, respectively, 0, 17, 27, 37 and 92%. It is known from literature that the addition of the second 1-alkyne only proceeds at elevated temperatures [22].

Vinylideneruthenium (II) precursors of the type $RuCl_2(=C=CHR)L_2$ ($R = t$-Bu; $L = PCy_3$, $PiPr_3$) are known to serve as good catalyst precursors for the ROMP of cyclic alkenes and ring closing metathesis (RCM) of α,ω-dienes, α,ω-enynes and dienynes. In the presence of an olefin the Ru–vinylidene is transformed into the active species, i.e. a Ru–alkylidene complex. For this reason, complex **3** was treated with a 10-fold excess of diethyl diallylmalonate (Scheme 2).

After 1 h at 110 °C, a conversion of 51% into the corresponding cyclic alkene is reached. No other reaction products than the ring-closed product were detected. This result also confirms that complex **3** is a Ru–vinylidene.



Scheme 1. Proposed mechanism for the dimerisation of phenylacetylene.

2.3. Catalytic alkyne dimerisation and vinylation

Complex **1** is tested for the dimerisation of phenylacetylene in normal catalytic conditions: alkyne–catalyst = 100/1. After 5 h the reaction yield reaches a plateau. Only 21.4% of the 1-alkyne are converted, with a high regioselectivity for tail-to-tail adducts (92%), with 90% trans substitution.

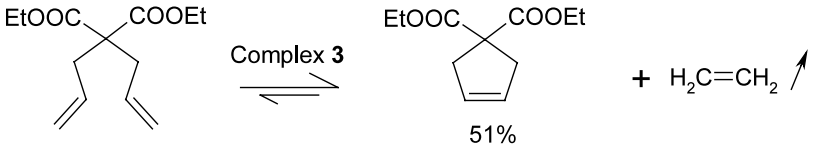
The nucleophilic addition of a carboxylic acid or vinylation proceeds via a similar fundamental mechanism as the dimerisation (Scheme 3).

Both catalytic reaction pathways are initiated by a metal–vinylidene intermediate. In both cases Ru-complexes are known as excellent catalysts. This tempted us to test the activity of complex **1** for the vinylation. Complex **1** was treated at 110 °C with 100 equivalent of phenylacetylene and 100 equivalent of acetic acid. The time for completion of the reaction is significantly decreased compared with that of the dimerisation (3.5 vs. 5 h) and the yield increased to 92%. Surprisingly only 5% of the endproducts consists of enol esters. The major adducts are enynes (95%) with a regioselectivity for tail-to-tail adducts and a reversed stereoselectivity for *cis*-substitution.

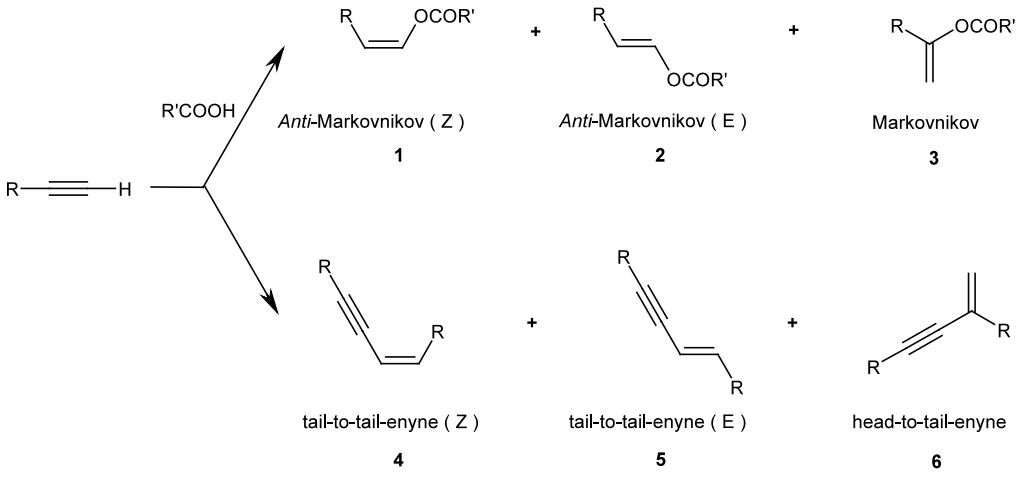
2.4. Influence of acetic acid on the catalytic reaction process

Detailed NMR studies were conducted to determine the role of the acid functionality. The acid has no direct influence on the catalyst, since no covalent or coordinative bond between the acid and the transition metal is detected.

The influence of the carboxylic acid on the terminal alkyne was examined by two different experiments. In the first experiment, the catalytic reaction was performed at different dilution levels of acetic acid. The ratio of catalyst–alkyne–acid was altered from 1/100/1



Scheme 2. RCM of diethyl diallylmalonate catalysed by complex **3**.



Scheme 3. Dimerisation and vinylation of terminal alkynes.

to 1/100/200, only changing the concentration of the acetic acid (Fig. 1).

The optimal ratio for the catalytic reaction is catalyst–phenylacetylene–acetic acid = 1/100/100. At lower concentration of acetic acid, the reaction rate is slower and the obtained yield is decreased. The same observation is made when the molar amount of acid exceeds the amount of phenylacetylene (1/100/200). The acid seems to promote the reaction when the ratio alkyne–acid is equimolar. The acid does not influence the reaction catalytically, but has effect on the reaction on a stoechiometric level.

In the second experiment, 100 equivalents of labelled acetic acid (CH_3COOD) were added to a catalyst–phenylacetylene solution (1/100). The reaction is performed at 110 °C in a sealed NMR tube. At several time intervals, ^{1}H-NMR analysis is conducted. After 3 h of reaction 97% of the phenylacetylene is converted into the dimeric products (PhC≡C–CH=CDPh) and a signal due to CH_3COOH at 12.4 ppm appears. This is confirmed by GC–MS analysis, which shows a defragmentation pattern characteristic to PhC≡C–CH=CDPh. The same results are obtained with a phenylacetylene–CH_3COOD–catalyst ratio equal to 10/10/1. These data confirm that the acid influences the reaction stoechiometrically.

The combined two experiments clearly prove a direct influence of acetic acid on the reaction pathway. Acetic

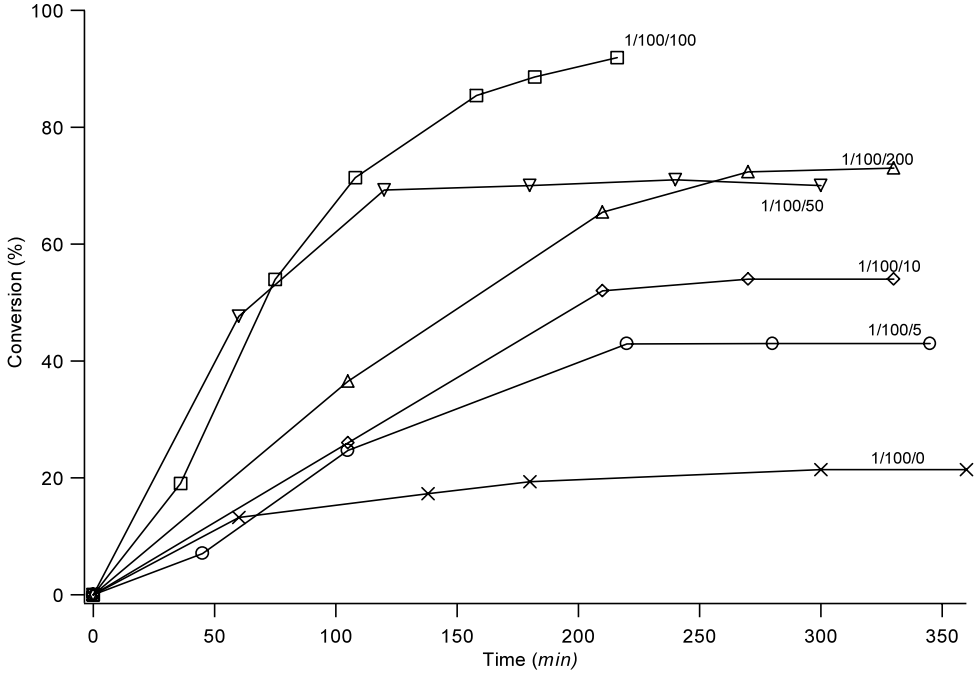
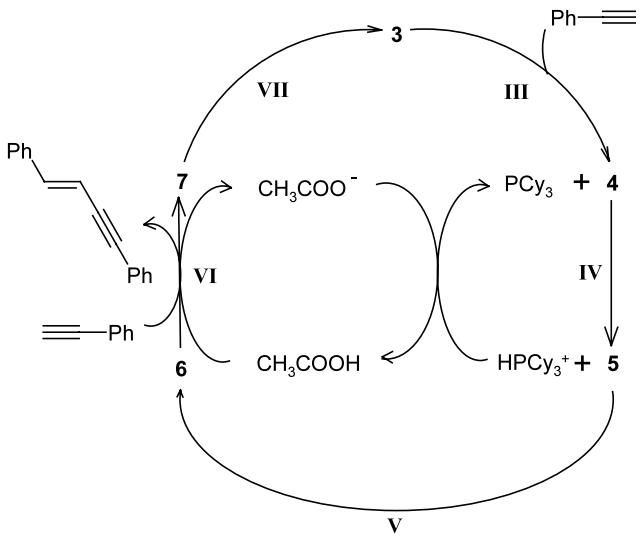


Fig. 1. Dependence for the dimerisation of phenylacetylene on the concetration of acetic acid. Yield as determined with Raman spectroscopy and ^{1}H-NMR analysis. The experimental error for all reactions is smaller than 4%.

acid seems to act as a proton donor for the reaction process. $HPCy_3^+$ ($pK_a = 9.06$) acts as a weaker acid compared with acetic acid ($pK_a = 4.75$). Acetic acid now acts as the proton donor. The hydrogen needed to free the PhC≡C–CH=CHPh ligand from the Ru-complex is now donated by the acetic acid instead of $HPCy_3^+$. The influence of the acid on the reaction pathway is depicted in Scheme 4.

Addition of acetic acid to the reaction mixture results in a reversed stereoselectivity for the formation of *Z*-isomers. In analogy to the article of Sevin et al. the product distribution can be explained by the following hypothesis [23].

1) Considering the high thermal conditions for the dimerisation reaction (110 °C) and the thermal instability of the alkenyl ruthenium compound **6**, the formation and release of a vinyl carbanion from the intermediate may be expected. The resonance-stabilised molecule should have a V-shaped intermediate, resulting in an unsymmetrical environment on the sp-hybridized carbanion centre. This geometry facilitates the attack of the proton from the less hindered side, thus leading to the formation of the less stable *Z*-isomer (Fig. 2, A).
2) Displacement of the sigma bonds to the ruthenium atom generates an unsymmetrical structure. The attack of the carboxylic acid shows no preference for either side. The dimerisation leads to formation of both the *E*- and *Z*-isomer (Fig. 2, B).
3) Combination of both suggests that it is possible that the generated carbanion remains within the ruthenium complex and is stabilised equally well by the ruthenium atom. Again, the attack of the carboxylic acid leads to the formation of *Z*-isomers (Fig. 2, C).



Scheme 4. Influence of acetic acid on the reaction pathway.

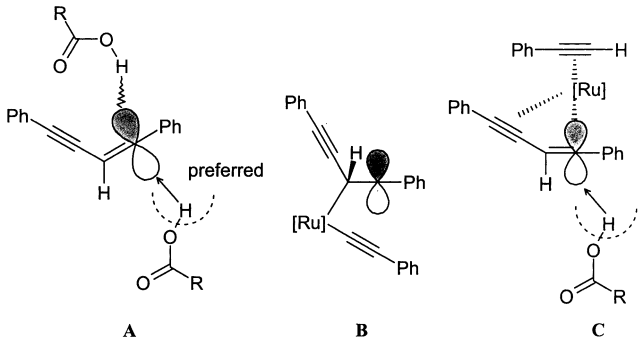


Fig. 2. Dependence of product formation on acetic acid.

When no acetic acid is added, no stabilisation of the carbanion via the COOH-group is possible. The only stabilisation is derived from the Ru-center. The attack of the incoming alkyne can occur via both sides, leading to *E*- and *Z*-isomer. The formation of the thermodynamic stable *E*-isomer is preferred.

This surprising feature of the acid combined with the catalytic activity of complex **1** at elevated temperature, provides a very fast and regioselective catalytic environment for the dimerisation of phenylacetylene.

3. Conclusion

A new and unexpected route towards the dimerisation of phenylacetylene is revealed. Thermal treatment of the alkylidene $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) at 110 °C and subsequent addition of two equivalent of phenylacetylene leads to the formation of a Ru–vinylidene complex **3**. The Ru–vinylidene catalyses the selective tail-to-tail addition of phenylacetylene with an additional preference for *trans*-isomers. Addition of acetic acid, in a stoechiometrical ratio, enhances the reaction rate and yield dramatically. Instead of the decoordinated phosphine, the acid acts as a proton donor. Adding acetic acid results in a reversed stereoselectivity towards the formation of *Z*-isomers. The acid seems to stabilise the released carbanion and generate an unsymmetrical structure, which leads to preferential *Z*-adducts.

4. Experimental

4.1. General remarks

All reactions were performed under inert atmosphere using Schlenck techniques. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. GC–MS analysis were performed on a GC (column SPB^{TM}-5 = 30 m × 0.25 mm × 0.25 μm film thickness, carrier gas: He, 100 kPa, detector = FID, gas chromatograph = Varian 4600) and MS (Finnigan MAT ITD). Toluene-

d_8 (obtained from Acros) and toluene were dried over Na. $Cl_2(PR_3)_2Ru{=}CHPh$ (obtained from Strem Chemicals), phenylacetylene, CH_3COOH and CH_3COOD (obtained from Acros) were used without further purification.

4.1.1. Ru Complex **2**

$Cl_2(PR_3)_2Ru{=}CHPh$ was heated at 110 °C in toluene for 60 min. ^{1}H-NMR (tol-d_8, 300 MHz, 25 °C, ppm): δ 1.95–1.20 (m, PCy_3). ^{13}C{H}-NMR (tol-d_8, 75 MHz, 25 °C, ppm): δ 35.76, 30.34, 28.1, 27.02 (all m, PCy_3). ^{31}P{H}-NMR (tol-d_8, 129 MHz, 25 °C, ppm): δ 46.9, 30.68.

4.1.2. Ru Complex **3**

To Ru-complex (**2**) two equivalents of phenylacetylene were added. The reaction was stirred at 110 °C for 1 h. ^{1}H-NMR (tol-d_8, 300 MHz, 25 °C, ppm): δ 7.99–7.21 (m, H of Ph), 5.34 (s, Ru=C=C*H*Ph), 2.20–1.39(m, PCy_3). ^{13}C{H}-NMR (tol-d_8, 75 MHz, 25 °C, ppm): δ 341.4 (Ru=*C*=CHPh), 132.72, 131.76, 130.85, 123.26 (C of Ph), 118.80 (Ru=C=*C*HPh), 37.48, 37.13, 36.34, 25.62, 34.03, 30.68, 27.73 (PCy_3). ^{31}P{H}-NMR (tol-d_8, 129 MHz, 25 °C, ppm): δ 52.92.

Dimerisation of phenylacetylene catalysed by the $Cl_2(PR_3)_2Ru{=}CHPh$ precursor: A solution of the Grubb's catalyst $Cl_2(PR_3)_2Ru{=}CHPh$ (0.032 mmol) in toluene (3 ml) is treated at 110 °C for 1 h. Hundred equivalent phenylacetylene (3.20 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by ^{1}H-NMR and GC–MS.

Reaction of phenylacetylene and CH_3COOH catalysed by the $Cl_2(PR_3)_2Ru{=}CHPh$ precursor. A solution of the Grubb's catalyst $Cl_2(PR_3)_2Ru{=}CHPh$ (0.032 mmol) in toluene (3 ml) is treated at 110 °C for 1 h. Hundred equivalents phenylacetylene (3.2 mmol) and 100 equivalent acetic acid (3.2 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by ^{1}H-NMR and GC–MS.

Reaction of phenylacetylene and CH_3COOD catalysed by $Cl_2(PR_3)_2Ru{=}CHPh$ precursor: In a glove box, a 5 mm Wilmad NMR tube is charged with Grubb's catalyst (0.056 mmol, 0.046 g) and phenylacetylene (0.56 mmol, 0.057 g) and toluene-d_8 (1 ml). The reaction mixture is treated at 110 °C for 60 min. Acetic acid-*d* (0.56 mmol, 0.034 g) is added to the solution and the sealed NMR tube was kept at 110 °C. Product formation and ^{2}H-exchange is monitored by ^{1}H-NMR and GC–MS.

4.2. Spectroscopic data for dimeric products

4.2.1. Tail-to-tail adducts

cis-Ph–CH=CHC≡CPh: ^{1}H-NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.10–6.80 (m, Ph) 6.48 (d, $J = 12.0$ Hz, =C*H*Ph) 5.84 (d, $J = 12.0$ Hz, =C*H*C≡C); GC–MS = $m/z = 204$ [M^+].

trans-Ph–CH=CHC≡CPh: ^{1}H-NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.10–6.80 (m, Ph) 7.04 (d, $J = 16.6$ Hz, =C*H*Ph) 6.33 (d, $J = 16.6$ Hz, =C*H*C≡C); GC–MS = $m/z = 204$ [M^+].

4.2.2. Head-to-tail adduct

^{1}H-NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.10–6.80 (m, Ph) 5.37 (s, =CH_2) 4.92 (s, =CH_2); GC–MS = $m/z = 205$ [M^+].

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