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Isomerization of Propargylic Alcohols into α,β-Unsaturated Carbonyl Compounds Catalyzed by the Sixteen-Electron Allyl-Ruthenium(II) Complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]

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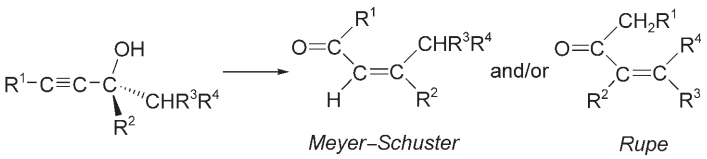
Abstract: The 16-e$^-$ (η^3-allyl)-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] is an efficient catalyst for the regioselective isomerization of terminal propargylic alcohols HC≡CCR^{1}R^2(OH) into α,β-unsaturated aldehydes R^{1}R^{2}C=CHCHO or ketones R^{3}R^{4}C=C(R^1)COMe (if R^2 = CHR^{3}R^4) under mild conditions. This complex has been also used as catalyst for the preparation of conjugated 1,3-enynes *via* dehydration of propargylic alcohols.

Keywords: allenylidene ligands; isomerization; propargylic alcohols; ruthenium; α,β-unsaturated carbonyl compounds; vinylidene ligands

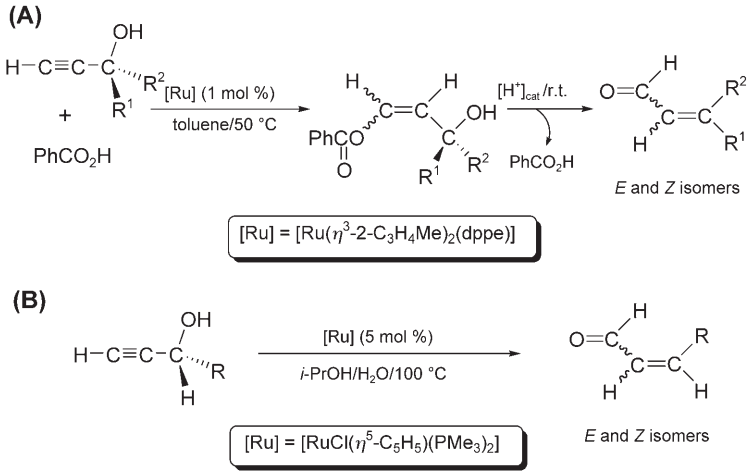
Introduction

The concept of atom economy, i.e., all atoms of the reactant end up in the final product, has emerged as a major goal in synthetic organic chemistry in recent years.[1] Isomerization processes are typical examples of atom economical reactions since no by-products are generated. In this context, the isomerization of easily accessible propargylic alcohols into the valuable raw materials α,β-unsaturated carbonyl compounds (aldehydes or ketones) is a desired synthetic goal. Early achievements in this field are the well-known Meyer–Schuster[2] and Rupe[3] rearrangements (Scheme 1). Both type of reactions are generally carried out in acidic medium or using strong acids as catalysts, which often give rise to non-regioselective transformations.[4] Although more efficient and selective catalytic systems based on transition metal complexes, such as Ti(OR)$_4$/CuCl/RCO$_2$H,[5] Bu$_4$NReO$_4$/*p*-MeC$_6$H$_4$SO$_3$H,[6] MoO$_2$(acac)$_2$/R$_2$SO/ArCO$_2$H[7] and vanadium(V) oxides,[8] have been developed, elevated temperatures (>100 °C) and/or acidic conditions are still needed. With all these oxo-metal catalysts, the suggested key step in the catalytic cycle involves the formation of an allenyloxy intermediate generated by *O*-coordination of the propargylic alcohol to the metal and subsequent addition of the [M]=O oxygen atom to the C(1) carbon atom of the alkyne ([3,3]-sigmatropic rearrangement).

It has been reported that ruthenium(II) complexes are able to catalyze the isomerization of terminal propargylic alcohols into α,β-unsaturated aldehydes (Meyer–Schuster rearrangement) through completely different reaction pathways, i.e., the formation of vinylidene- or allenylidene-ruthenium intermediates resulting from the selective coordination of the C≡C bond of the alkynols to the metal.[9] Thus, Bruneau, Dixneuf and coworkers have developed a one-pot but two-step catalytic procedure based on the *anti*-Markovnikov addition of benzoic acid to the carbon-carbon triple bond of tertiary alkynols catalyzed by [Ru(η^3-2-C_3H_4Me)$_2$(dppe)]. The final enals are obtained after acidic cleavage with PTSA or HBF_4 of the resulting enol esters which can be isolated and characterized (Method **A** in



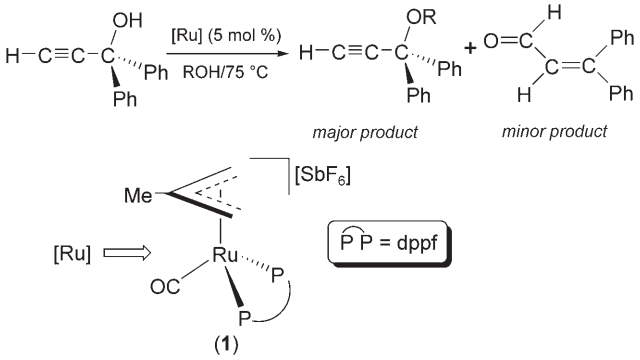
Scheme 1. The Meyer–Schuster and Rupe rearrangement of propargylic alcohols.



Scheme 2. Ru-catalyzed isomerization of propargylic alcohols into enals.

Scheme 2).[10] Formation of these enol esters involves the nucleophilic attack of the benzoate anion at the α-carbon of hydroxy-vinylidene intermediates [Ru]=C=C(H)C(OH)R^1R^2. A more direct route has been reported by Wakatsuki and co-workers using the cyclopentadienyl complex [RuCl(η^5-C_5H_5)(PMe_3)$_2$], which is able to catalyze the isomerization process in only one step and under neutral conditions (Method **B** in Scheme 2).[11] In this case the proposed key-intermediate is an allenylidene derivative [Ru]=C=C=CHR, generated by dehydration of the propargylic alcohol upon coordination to the metal,[9] which probably undergoes the nucleophilic attack of the previously eliminated molecule of water at the electrophilic α-carbon atom of the allenylidene chain.[9] We note that, while method **A** has been exclusively applied to the isomerization of tertiary propargylic alcohols (R^1 and $R^2 \neq$ H), method **B** is only operative when secondary alkynols are used, the tertiary ones remaining unreactive. Moreover, both methodologies are not stereoselective since enals are in all cases obtained as mixtures of the corresponding *E* and *Z* isomers.[12]

Recently, we have reported that the cationic 16-e$^-$ (η^3-allyl)-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] [dppf = 1,1′-bis(diphenylphosphino)ferrocene] (**1**) is able to catalyze the propargylic substitution reaction of 1,1-diphenyl-2-propyn-1ol with a large variety of alcohols to afford propargylic ethers HC≡CCPh_2(OR) in good yields (Scheme 3).[13] Remarkably, the formation of minor amounts of 3,3-diphenyl-2-propen-1-al, resulting from the formal isomerization of the alkynol, was observed by GC/MS in almost all of the reactions. This fact prompted us to investigate the potential of complex **1** as a catalyst for the isomerization of propargylic alcohols into α,β-unsaturated carbonyl compounds. Thus, herein we describe the successful application of **1** to the isomerization of a large variety terminal alkynols. The present paper brings novelty with



Scheme 3. Ru-catalyzed propargylic substitution reactions of 1,1-diphenyl-2-propyn-1-ol with alcohols.

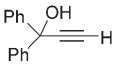
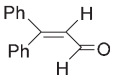
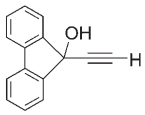
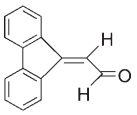
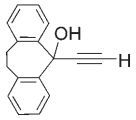
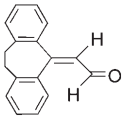
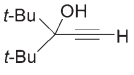
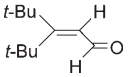
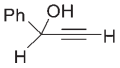
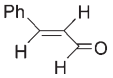
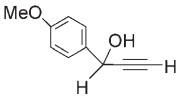
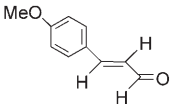
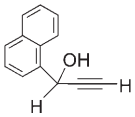
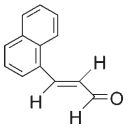
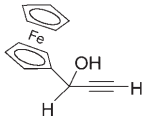
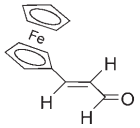
respect to the previously reported Ru-based catalytic systems[10,11] since, depending on the nature of the propargylic alcohol, enals (Meyer–Schuster rearrangement) or enones (Rupe rearrangement) can be selectively obtained.

Results and Discussion

Isomerization of Propargylic Alcohols into α,β-Unsaturated Aldehydes (Meyer–Schuster Rearrangement)

Since the favoured formation of the propargylic ethers *vs.* the enals (Scheme 3) is due to the presence of alcohols, which act both as solvents and nucleophiles, we have explored the catalytic activity of the allyl-Ru(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) in THF as solvent to form the enals selectively. The isomerization of 1,1-diphenyl-2-propyn-1-ol (**2a**) into 3,3-diphenyl-2-propen-1-al (**3a**) was used as a model reaction.

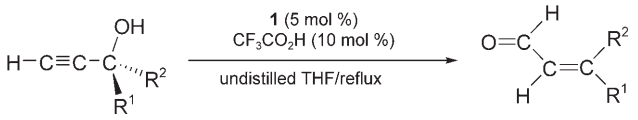
Table 1. Isomerization of propargylic alcohols **2a**–**h** into α,β-unsaturated aldehydes **3a**–**h** catalyzed by complex **1** in the presence of CF_3CO_2H.[a]

Entry	Substrate		Product		Time	Yield[b]
1		**2a**		**3a**	10 min	95%
2		**2b**		**3b**	30 min	96%
3		**2c**		**3c**	15 min	96%
4		**2d**		**3d**	30 min	91%
5		**2e**		**3e**	3.5 h	95%
6		**2f**		**3f**	2.5 h	93%
7		**2g**		**3g**	1.5 h	94%
8		**2h**		**3h**	45 min	92%

[a] *Reaction conditions:* reactions were carried out in refluxing THF (wet; undistilled) using 1 mmol of the corresponding propargylic alcohol (1.0 M solution). [Substrate]:[Ru]:[CF_3CO_2H] ratio = 20:1:2.
[b] Isolated yield (quantitative yields were observed by GC in all cases).

Thus, we have found that when a 1.0 M solution of **2a** in distilled THF was refluxed for 24 h in the presence of a catalytic amount of **1** (5 mol %), enal **3a** was selectively obtained in 78% yield (determined by GC). Remarkably, a dramatic rate enhancement was observed when wet THF (undistilled) was used as solvent under the same reaction conditions, resulting in the quantitative transformation of **2a** into **3a** in 1.5 h. Nevertheless, the addition of different acidic co-catalysts including NH_4Cl, NH_4PF_6, $(CH_3CO)_2O$, $(CF_3CO)_2O$, CH_3CO_2H and CF_3CO_2H, resulted in an improved catalytic activity. The best results were obtained using trifluoroacetic acid (1.0 M solution in wet THF; [**2a**]:[**1**]:[CF_3CO_2H] ratio = 20:1:2; reflux) allowing the quantitative formation of 3,3-diphenyl-2-propen-1-al (**3a**) in only 10 min (95% isolated yield; see entry 1 in Table 1).[14]

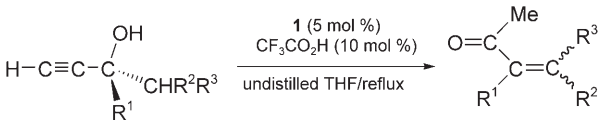
Under these optimized reaction conditions (1.0 M solution in wet THF; [substrate]:[**1**]:[CF_3CO_2H] ratio = 20:1:2; reflux) the catalytic activity of complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) was tested for a number of other propargylic alcohols (Scheme 4; results are summarized in Table 1). Thus, as observed for 1,1-diphenyl-2-propyn-1-ol (**2a**), other tertiary alkynols (**2b**–**d**) undergo a fast ($\leq$30 min) and efficient isomerization into the corresponding enals (**3b**–**d**) ($\geq$91% isolated yields; quantitative yields were in all cases observed by GC) regardless the presence of aryl (entries 2 and 3) or alkyl (entry 4) substituents. Secondary alkynols (**2e**–**h**; entries 5–8 in Table 1) can also be efficiently isomerized ($\geq$92% isolated yields within 3.5 h), demonstrating the generality of this catalytic transformation.[15] Remarkably, the resulting enals **3e**–**h** are in all cases stereoselectively formed as the thermodynamically more stable *E* isomer. This fact contrasts with the results previously reported by Bruneau, Dixneuf and Wakatsuki using the related Ru-based catalytic systems [Ru(η^3-2-C_3H_4Me)$_2$(dppe)]/$PhCO_2H$ and [RuCl(η^5-C_5H_5)(PPh_3)$_2$],[10,11] from which enals are generated as mixtures of the corresponding *E* and *Z* stereoisomers.



Scheme 4. The Meyer–Schuster rearrangement catalyzed by complex **1**.

Isomerization of Propargylic Alcohols into α,β-Unsaturated Ketones (Rupe Rearrangement)

The catalytic isomerization of propargylic alcohols bearing a C–H bond in the β-position with respect to the alcohol group proceeds in a different way, giving instead α,β-unsaturated methyl ketones as the result of a formal Rupe-type rearrangement of the alkynol (see Scheme 5 and Table 2). Thus, enones **5a–g** have been selectively obtained in 78–94% yield (quantitative transformations by GC) starting from the alkynols 3-isopropyl-4-methyl-1-pentyn-3-ol (**4a**; entry 1), 3-ethyl-1-pentyn-3-ol (**4b**; entry 2), 3-methyl-1-pentyn-3-ol (**4c**; entry 3) and the 1-ethynylcycloalkanols **4d–g** (entries 4–7), using the optimized conditions described above (1.0 M solution in wet THF; [substrate]:[**1**]:[CF_3CO_2H] ratio = 20:1:2; reflux).[16] In contrast to the stereoselective formation of aldehydes **3e–h**, the ketones **5b–c** are obtained as a 1:1 mixture of the *E* and *Z* stereoisomers (see entries 2 and 3), suggesting that different intermediates are now involved in the catalytic cycle.



Scheme 5. The Rupe rearrangement catalyzed by complex **1**.

This catalytic transformation can be also successfully applied to more elaborate substrates such as the hormonal steroids ethistherone (**4h**; entry 8), 17α-ethynylestradiol (**4i**; entry 9) and mestranol (**4j**; entry 10). The resulting enones **5h–j**, which are important building blocks in the chemistry of steroids,[17] have been obtained in pure form in excellent yields (96–97% yields).

It is worthy of note that no transformations were observed when internal propargylic alcohols such as $MeC{\equiv}CCH_2(OH)$ and $(HO)MeHCC{\equiv}CCHMe(OH)$ were used as substrates. The absence of catalytic activity with these particular alkynes is based on their lack of ability to undergo tautomerization to form vinylidene species, a process which is well-documented for terminal alkynes (see mechanistic proposal below).[9]

Synthesis of Terminal 1,3-Enynes *via* Catalytic Dehydration of Propargylic Alcohols

Monitoring the catalytic isomerization of propargylic alcohols **4** into enones **5** by GC/MS the intermediate formation of the terminal 1,3-enynes **6** is observed (Scheme 6).

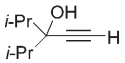
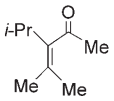
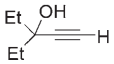
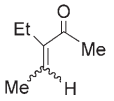
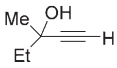
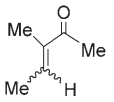
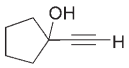
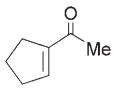
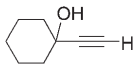
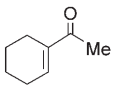
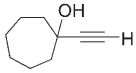
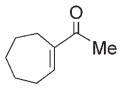
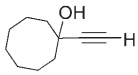
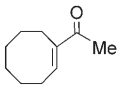
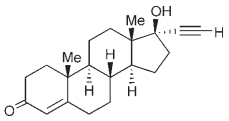
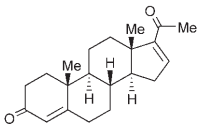
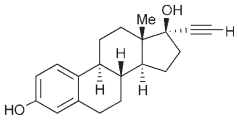
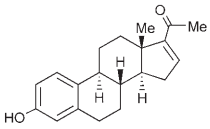
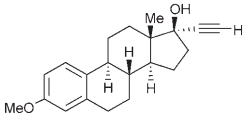
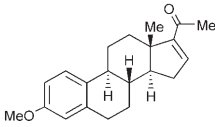
An example of the reaction profile for the isomerization of 1-ethynylcyclopentanol (**4d**) into 1-acetylcyclopentene (**5d**) is shown in Figure 1. The overall transformation involves two well-separated steps, i.e., the initial formation of the terminal enyne 1-ethynylcyclopentene (**6d**) after *ca.* one hour (87% yield), which slowly evolves into the final product 1-acetylcyclopentene (quantitative yield after 20 hours). Taking into account that the first step is considerably faster than the second one, we envisaged the possibility to use the catalyst [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) not only for the isomerization of propargylic alcohols **4** into ketones **5** but also for the catalytic synthesis of 1,3-enynes **6** which are important synthetic intermediates in organic chemistry.[18,19]

Such a transformation has been achieved efficiently at 60 °C by using anhydrous THF (distilled) as solvent. Selected results are summarized in Table 3 (all reactions performed using 1.0 M solutions of **4**; [**4**]:[**1**]:[CF_3CO_2H] ratio = 20:1:2).[20] Among the different alkynols used, the dehydration of the hormonal steroids ethisterone (**4h**; entry 3) and mestranol (**4j**; entry 4) is noteworthy, the corresponding conjugated enynes **6h** and **6j** being obtained in pure form in excellent yields (96–97%). Moreover, in accord with the absence of stereoselectivity observed in the formation of enone **5c** (entry 3 in Table 2), we have found that the dehydration of propargylic alcohol **4c** (entry 1 in Table 3) does not proceed in a stereoselective manner, the enyne **6c** being obtained as 1:1 mixture of the corresponding *E* and *Z* isomers (see also entry 7). As expected, when the catalytic reactions are performed in undistilled THF the hydration of the *in situ* formed 1,3-enynes **6** generates enones **5**. The ability of complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) to catalyze the direct hydration of 1,3-enynes has been confirmed in the transformation of 1-ethynylcyclohexane into 1-acetylcyclohexene.[21]

Mechanistic Proposal for the Isomerization and Dehydration Reactions

Schemes 7 and 8 show plausible mechanisms for the formation for enals **3a–h** and enones **5a–j**, respectively, as well as for the dehydration process yielding 1,3-enynes **6** (Scheme 8). Although no catalytically active species could be isolated or *in situ* characterized by NMR techniques, we assume that the key intermediate is in all the cases an hydroxyvinylidene complex $[Ru]^+{=}C{=}C(H)C(OH)R^1R^2$ (**A**). This species results

Table 2. Isomerization of propargylic alcohols **4a–j** into α,β-unsaturated ketones **5a–j** catalyzed by complex **1** in the presence of CF_3CO_2H.[a]

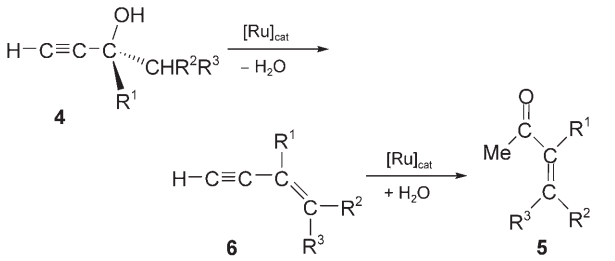
Entry	Substrate		Product		Time	Yield[b]
1		**4a**		**5a**	2 h	93%
2[c]		**4b**		**5b**	6.5 h	81%
3[c]		**4c**		**5c**	11 h	78%
4		**4d**		**5d**	20 h	94%
5		**4e**		**5e**	2 h	93%
6		**4f**		**5f**	1.25 h	89%
7		**4g**		**5g**	1.5 h	91%
8		**4h**		**5h**	26 h	97%
9		**4i**		**5i**	5 h	96%
10		**4j**		**5j**	4 h	96%

[a] *Reaction conditions:* reactions were carried out in refluxing THF (wet; undistilled) using 1 mmol of the corresponding propargylic alcohol (1.0 M solution). [Substrate]:[Ru]:[CF_3CO_2H] ratio = 20:1:2.
[b] Isolated yield (quantitative yields were observed by GC in all cases).
[c] [*E*]:[*Z*] ratio = 1:1.

from the initial formation of an unstable η^2-alkyne complex (*via* π-coordination of the C≡C bond of the propargylic alcohol to the metal) which tautomerizes into the thermodynamically more stable vinylidene isomer **A**.[9] The proposed formation of hydroxyvinylidene **A** is in accord with the absence of catalytic activity observed when internal propargylic alcohols are used as substrates [i.e., $MeC{\equiv}CCH_2(OH)$ or (HO)MeHCC≡CCHMe(OH)] since they are not able to undergo the required tautomerization into a vinylidene species.[9] This fact seems to discard also the involvement of ruthenium-stabilized propargylic cations in these isomerization reactions.[22]

Then, the fate of the catalytic cycle is depending on the nature of the propargylic alcohol substituents R^1 and R^2:

i. If no C–H bonds are present in the β-position with respect to the alcohol group (R^1 and $R^2 \neq CHR^3R^4$; propargylic alcohols **2a**– **h**), dehydration of **A** generates an allenylidene complex **B** (see Scheme 7). The electrophilicity of the C_α carbon of the unsaturated chain in **B**, typical of allenylidene complexes,[9] favours the re-addition of water to give



Scheme 6. The two steps in the isomerization of propargylic alcohols into enones.

the hydroxy-carbene derivative **C**. Finally, the demetallation of carbene **C** takes place, involving probably an acyl intermediate **D**, affording the corresponding enals **3a**–**h** and regenerating the 16-e$^-$ catalyst. The stereoselectivity observed in the formation of aldehydes **3e**–**h**, starting from the secondary alkynols **2e**–**h**, strongly supports the involvement of an allenylidene intermediate since it is well-documented that the addition of RO–H bonds (water or alcohols) across the C_α=C_β unit of monosubstituted allenylidenes [M]=C=C=C(H)R usually generates Fischer-type alkenyl-carbene complexes [M]=C(OR)-C(H)=C(H)R with *E* stereochemistry.[23]

ii. If a C–H bond is present in the β-position with respect to the alcohol group (R^2 = CHR^3R^4; propargylic alcohols **4a**–**m**) the reaction proceeds in a different way since no allenylidene **B** is formed. The dehydration of hydroxyvinylidene **A** leads instead to the thermodinamically favoured alkenyl-vinylidene tautomer **E** (see Scheme 8),[24] which is in equilibrium with its π-enyne isomer **F**.[9] Provided that an excess of water is present in the reaction media, complex **F** can undergo the Markovnikov addition of water to the coordinated C≡C bond to afford the corresponding enones **5a**–**j**. This final step most probably involves the intermediate formation of complexes of type **G** and **H** (such intermediates are commonly proposed on metal-catalyzed alkyne hydrations).[25] The alternative demetallation of the π-enyne complex **F** explains the formation of the terminal 1,3-enynes **6c**–**d**, **h**, **j**–**m**. In accord with this, the catalytic process performed in distilled THF yield selectively the 1,3-enynes since the absence of water precludes the addition reaction to give the ketones.

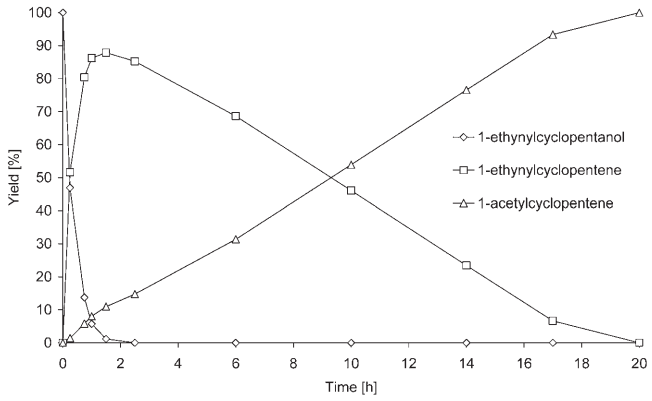
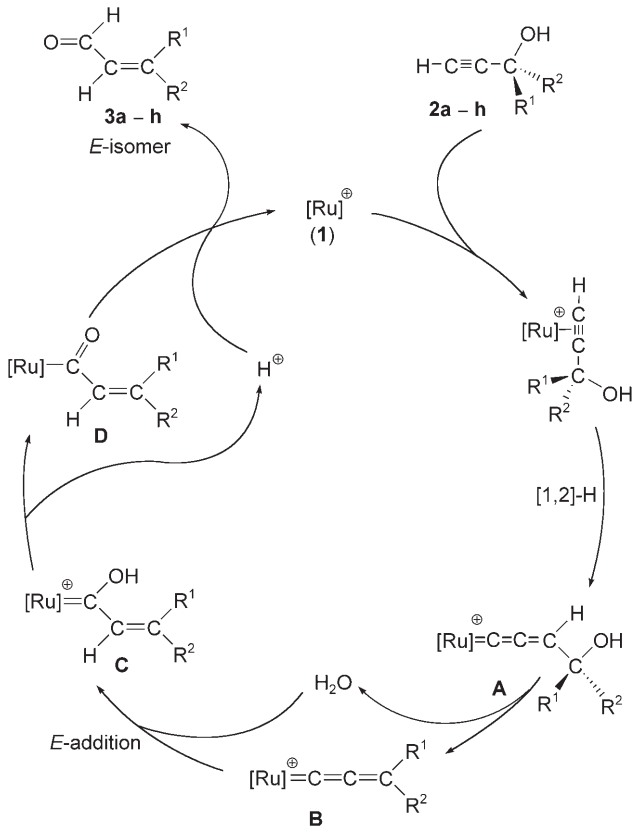


Figure 1. Product distribution as a function of time for the isomerization of **4d**.



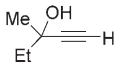
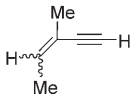
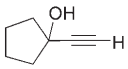
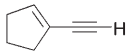
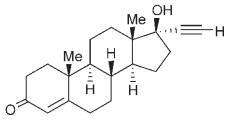
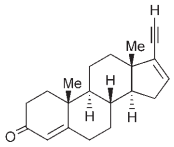
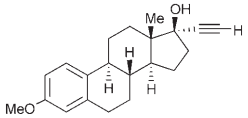
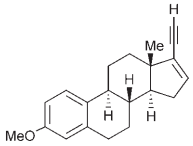
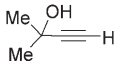
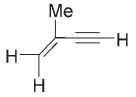
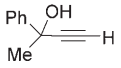
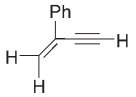
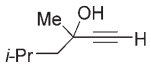
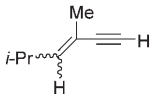
Scheme 7. Reaction pathway for Ru-catalyzed Meyer–Schuster rearrangement.

Concerning the role of the co-catalyst, it is well-known that dehydration of hydroxyvinylidene derivatives to form both allenylidene or alkenyl-vinylidene complexes can be promoted by Brønsted or Lewis acids.[26] Thus, the rate enhancement observed in our catalytic reactions upon addition of CF_3CO_2H can be explained by assuming that the dedydration of intermediate **A** into **B** (Scheme 7) or **E** (Scheme 8) is favoured in the presence of acid.[27]

Conclusion

In this work it has been shown that the sixteen-electron allyl-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**), in the presence of acid, is a high-

Table 3. Dehydration of propargylic alcohols catalyzed by complex **1** in the presence of CF_3CO_2H.[a]

Entry	Substrate		Product		Time	Yield[b]
1[c]		**4c**		**6c**	5 h	91%
2		**4d**		**6d**	5 h	94%
3		**4h**		**6h**	7 h	97%
4		**4j**		**6j**	2.5 h	96%
5		**4k**		**6k**	6 h	75%
6		**4l**		**6l**	3 h	97%
7[c]		**4m**		**6m**	2 h	92%

[a] *Reaction conditions:* reactions were carried out in THF (dry; distilled) at 60 °C using 1 mmol of the corresponding propargylic alcohol (1.0 M solution). [Substrate]:[Ru]:[CF_3CO_2H] ratio = 20:1:2.
[b] Isolated yield (quantitative yields were observed by GC in all cases).
[c] [*E*]:[*Z*] ratio = 1:1.

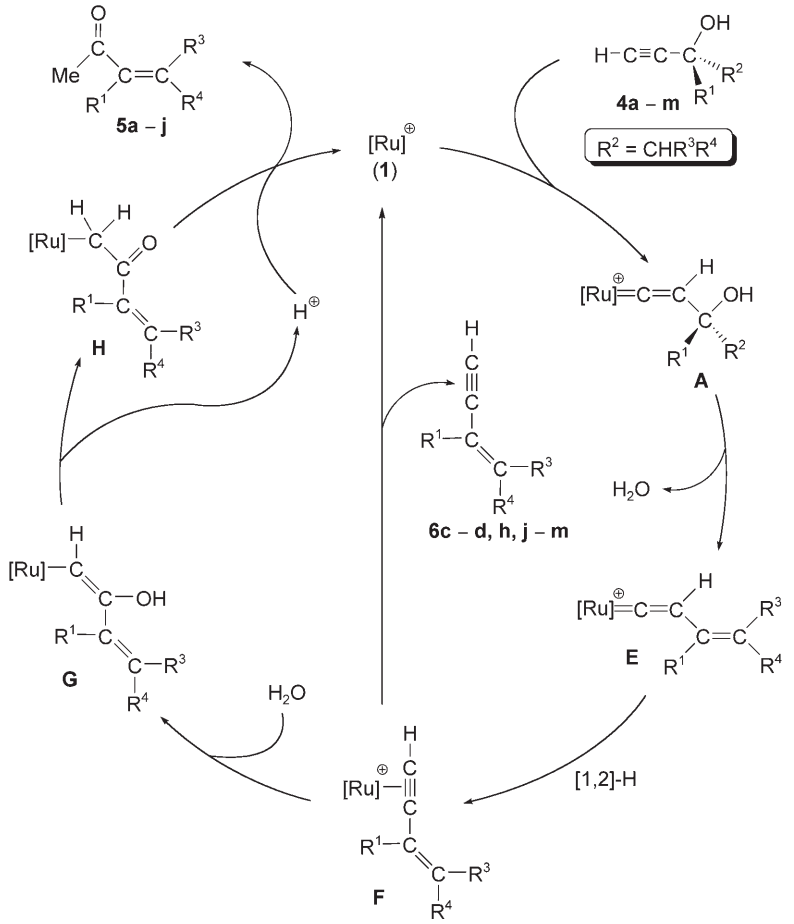
ly efficient catalyst for the isomerization of terminal propargylic alcohols into α,β-unsaturated carbonyl compounds, which can be obtained in excellent yields (78–97%). This complex has also proven to promote chemoselective transformations giving rise to enals (Meyer–Schuster rearrangement) or enones (Rupe rearrangement) depending on the nature of the propargylic alcohol. To the best of our knowledge, complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) represents the first example of a ruthenium catalyst for the Rupe-type rearrangement of propargylic alcohols. Moreover, **1** has also proven to be highly stereoselective in the isomerization of secondary propargylic alcohols yielding *E*-enals exclusively. Although it has been described that complexes [Ru(η^3-2-$C_3H_4Me)_2$(dppe)]/$PhCO_2H$ and [RuCl(η^5-C_5H_5)($PPh_3)_2$] are also active in the synthesis of enals,[10,11] in contrast to catalyst **1**, they always lead to mixtures of *E* and *Z* stereoisomers.

We also note that the catalytic behaviour towards propargylic alcohols HC≡CCR^1R^2(OH) shown by the allyl-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)-(CO)(dppf)][SbF_6] (**1**) contrasts with that previously observed in our group using the indenyl-ruthenium(II) catalyst [RuCl(η^5-C_9H_7)($PPh_3)_2$] which, in the presence of water, leads to the selective formation of hydroxy-aldehydes $R^1R^2C(OH)CH_2CHO$.[28] Although the formation of a hydroxyvinylidene-ruthenium complex as key intermediate in the catalytic cycle is in both cases proposed, its subsequent dehydration to generate allenylidene or alkenyl-vinylidene species seems to be strongly dependent on the electronic properties of the ruthenium moieties, being favoured in the case of **1**.

In summary, the catalytic procedure for the synthesis of α,β-unsaturated carbonyl compounds reported here represents a very simple, efficient and selective methodology, involving readily available propargylic alcohols as precursors and proceeding in an overall atom economical manner.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification with the exception of com-



Scheme 8. Reaction pathway for Ru-catalyzed Rupe rearrangement.

plex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**)[13] and propargylic alcohols **2c**, **d**, **f**, **g**, **h**[29] which were prepared by following the methods reported in the literature. Gas chromatographic measurements were made on a Hewlett-Packard HP6890 equipment using an HP-INNOWAX cross-linked polyethylene glycol (30 m, 250 μm) or a Supelco Beta-Dex™ 120 (30 m, 250 μm) column.

General Procedure for the Catalytic Isomerization of Propargylic Alcohols 2a–h into α,β-Unsaturated Aldehydes 3a–h

In a Schlenk tube, the catalyst [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) (0.049 g, 0.05 mmol), the corresponding propargylic alcohol **2a–h** (1 mmol) and CF_3CO_2H (7.4 μL, 0.1 mmol) were dissolved, under a nitrogen atmosphere, in undistilled THF (1 mL) and the reaction mixture was refluxed for the indicated time (see Table 1; the course of the reaction was monitored by regular sampling and analysis by GC). After removal of the solvent under vacuum, flash chromatography (silica gel) of the residue using a mixture of EtOAc/hexane (1/5) as eluent afforded enals **3a–h**.

General Procedure for the Catalytic Isomerization of Propargylic Alcohols 4a–j into α,β-Unsaturated Ketones 5a–j

In a Schlenk tube, the catalyst [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) (0.049 g, 0.05 mmol), the corresponding propargylic alcohol **4a–h** (1 mmol) and CF_3CO_2H (7.4 μL, 0.1 mmol) were dissolved, under a nitrogen atmosphere, in undistilled THF (1 mL) and the reaction mixture was refluxed for the indicated time (see Table 2; the course of the reaction was monitored by regular sampling and analysis by GC). After removal of the solvent under vacuum, flash chromatography (silica gel) of the residue using a mixture of EtOAc/hexane (1/5) as eluent afforded enones **5a–h**.

General Procedure for the Catalytic Dehydration of Propargylic Alcohols

In a Schlenk tube, the catalyst [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) (0.049 g, 0.05 mmol) and the corresponding propargylic alcohol **4d**, **h**, **j**, **l**, **m** (1 mmol) were dissolved, under a nitrogen atmosphere, in dry THF (1 mL) and the reaction mixture was refluxed for the indicated time (see Table 3; the course of the reaction was monitored by regular sampling and analysis by GC). After removal of the solvent under vacuum, flash chromatography (silica gel) of the residue us-

ing a mixture of EtOAc/hexane (1/10) as eluent afforded 1,3-enynes **6d, h**, **j**, **l**, **m**. The synthesis of enynes **6c** and **6k** was performed in a sealed tube and the product isolated from the reaction mixture by fractional distillation (bp 59 and 34 °C/760 mm Hg, respectively).

Characterization data for compounds **3a**–**h**, **5a**–**j** and **6c**, **d**, **h**, **j**–**m** can be found in the Supporting Information.

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[15] Although the sixteen-electron complex $[Ru(\eta^3\text{-}C_3H_5)(CO)(dppf)][SbF_6]$ is also an active catalyst for these isomerization reactions, its efficiency is lower when compared to complex **1**. As an example, using $[Ru(\eta^3\text{-}C_3H_5)(CO)(dppf)][SbF_6]$ only 62% of conversion was achieved in the isomerization reaction of 1,1-diphenyl-2-propyn-1-ol (**2a**) (1.0 M solution in wet THF; [**2a**]:[Ru]:[CF_3CO_2H] ratio = 20:1:2; reflux) into 3,3-diphenyl-2-propen-1-al (**3a**) after 4 hours (to be compared with entry 1 in Table 1). Moreover, it should be noted that the presence of the 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand in the catalyst seems to be crucial since the closely related complexes $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dippf)][SbF_6]$ and $[Ru(\eta^3\text{-}C_3H_5)(CO)(dippf)][SbF_6]$ (dippf = 1,1′-bis(diisopropylphosphino)ferrocene) have found to be completely inactive.

[16] Likewise, as observed in the formation of enals, longer reaction times are required if the catalytic reactions are performed in the absence of CF_3CO_2H. As an example, quantitative isomerization of 3-isopropyl-4-methyl-1-pentyn-3-ol (**4a**) (1.0 M solution in wet THF; [**4a**]:[**1**] ratio = 20:1; reflux) into 3-isopropyl-4-methyl-3-penten-2-one (**5a**) was achieved only after 22 h (to be compared with entry 1 in Table 2).

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[20] Dehydration of propargylic alcohols **4a**, **b**, **e**, **f**, **g**, **i** has also been checked under these reaction conditions. Although the corresponding enynes are readily formed (yields up to 70%; GC determined), the re-addition of water to the C≡C bond cannot be completely suppressed in these cases (see mechanism in Scheme 8) and concomitant formation of enones **5a**, **b**, **e**, **f**, **g**, **i** is also observed.

[21] Quantitative transformation of commercially available 1-ethynylcyclohexene (**6e**) (1.0 M solution in wet THF; [**6e**]:[**1**]:[CF_3CO_2H] ratio = 20:1:2; reflux) into 1-acetylcyclohexene (**5e**) was achieved after *ca.* 2.5 h (to be compared with entry 5 in Table 2).

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