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Ruthenium-Catalyzed Synthesis of Alkylidenecyclobutenes via Head-to-Head Dimerization of Propargylic Alcohols and Cyclobutadiene–Ruthenium Intermediates

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Abstract: The reaction of propargylic alcohols with carboxylic acid, or phenol derivatives, in the presence of the precatalyst [RuCl(cod)(C_5Me_5)] leads selectively to a variety of alkylidenecyclobutenes through head-to-head dimerization of propargylic alcohol. The first step is the formation of a cyclobutadiene–ruthenium intermediate resulting from the head-to-head coupling of two molecules of propargylic alcohol. On protonation with strong acids (HPF_6, HBF_4) dehydration of the cyclobutadiene complex leads to formation of an alkylidenecyclobutenyl–ruthenium complex. The X-ray structure of one such complex, [RuCl(C_5Me_5)(η^4-R′CCH–CH–C=CR_2)] (R′ = cyclohexen-1-yl, CR_2 = cyclohexylidene) has been determined. Carboxylate is added at the less substituted carbon of the cyclic allylic ligand. DFT/B3LYP calculations confirm that the intermediate arising from head-to-head coupling of alkyne to the RuClCp* species yields the cyclobutadiene–ruthenium complex more easily with propargylic alcohol than with acetylene.

Keywords: alkylidenecyclobutenes · alkynes · cyclodimerization propargylic alcohols · ruthenium

Introduction

Small strained carbocycles involving three- and four-membered rings attract interest as powerful building blocks in stereoselective reactions and as providers of a rigid and functional neighboring group in synthesis.[1,2] To achieve their selective synthesis in fewer steps still constitutes a challenge. Use in synthesis of cyclobutadienes[3,4] and cyclobutanones,[5] among the four-membered carbocycles, is well documented, whereas use of cyclobutene derivatives[2,6] lacks general access routes although there are examples displaying optical[7] or biological[8] properties. Cyclobutenes are synthetic equivalents of dienes due to their ability to be converted by a concerted ring-opening process into conjugated 1,3-dienes, which can be trapped by a dienophile.[9–11] Recently, advantage has been taken of an alkene metathesis for the transformation of cyclobutene derivatives into 1,5-dienes. This ring-opening catalytic process is particularly useful for the synthesis of unsaturated polymers[12] and of natural products such as appetite suppressants[13] or pheromones.[14]

The most general way to synthesize cyclobutenes is based on the [2+2] cycloaddition reaction between the triple bond of an alkyne and the double bond of an olefin,[15] a transformation that can be promoted thermally,[16] photochemically,[17] with Lewis acids,[18] or with metal-based catalysts.[19,20] Cyclobutenes have also been produced, with a zirconium catalyst, from reaction of alkynyl halides in the presence of Grignard reagents.[21] In the particular case of alkylidenecyclobutenes, no straightforward method is available yet. Isolated examples have been prepared by thermal coupling of

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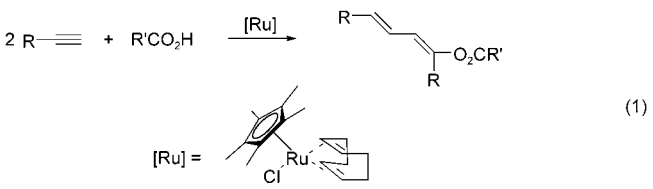
1,5-diynes[22] and by copper-mediated cyclization of 1,4-enynes.[23]

It has been shown recently that the catalyst precursor [RuCl(cod)(Cp*)] (Cp* = C_5Me_5, cod = 1,5-cyclooctadiene) promotes the head-to-head coupling of two terminal alkynes in the presence of carboxylic acid, leading to the stereoselective formation of 1-acyloxybuta-1,3-dienes [Eq. (1)].[24,25]

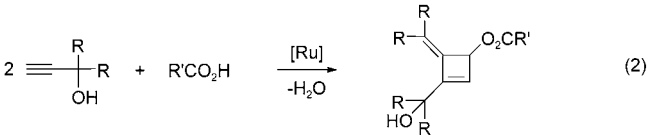
The key intermediate of this reaction was shown to be a



(1)

biscarbene–ruthenium(IV) complex,[26] which undergoes protonation of one carbene carbon atom followed by carboxylate addition at the second carbene carbon atom.[25] Completely different reactivity was observed when propargyl alcohol derivatives were used as functional terminal alkynes.

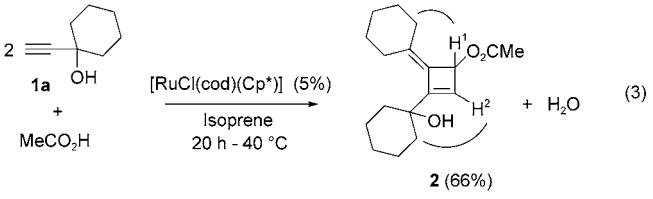
We now report a new catalytic reaction leading to the general formation of alkylidenecyclobutenes.[27] It consists of regioselective combination of two molecules of propargylic alcohol and one of carboxylic acid in the presence of [RuCl(cod)(Cp*)] as catalyst [Eq. (2)] and can be extended to phenols. We show that the reaction takes place by means of head-to-head coupling of the alkynes leading to a cyclobutadiene–ruthenium and then a novel alkylidenecyclobutenyl–ruthenium intermediate.



(2)

Results and Discussion

Evidence for the catalytic formation of alkylidenecyclobutenes from propargylic alcohol: An attempt to apply the dimerization of terminal alkynes in the presence of carboxylic acid [Eq. (1)] to a propargylic alcohol led to the selective formation of alkylidenecyclobutenes. The combination of two molecules of 1-ethynylcyclohexanol (**1a**) with one equivalent of acetic acid in isoprene as solvent in the presence of 5 mol% of the precatalyst [RuCl(cod)(Cp*)] for 20 h at 40 °C led to the selective formation of alkylidenecyclobutene **2** in 66% yield [Eq. (3)].

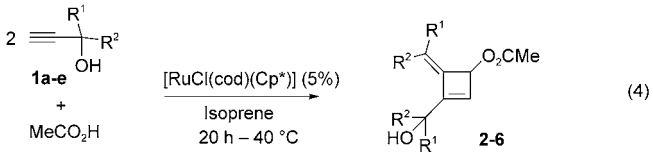


(3)

The structure of **2** has been established by classical NMR techniques and 2D NMR (NOESY) analysis, showing that the alkenyl and the methyne protons on the four-membered ring are in 1,2-positions. The ^{13}C NMR spectrum of **2** shows two signals as doublets of doublets for the two C–H groups of the four-membered ring: at $\delta = 72.4$ (dd, $^1J_{CH} = 162.9$ Hz, $J_{CH} = 4.0$ Hz, CH) and at 130.7 ppm (dd, $^1J_{CH} = 179.3$ Hz, $J_{CH} = 4.0$ Hz,=CH). For both carbon nuclei the first coupling constant is a classical $^1J_{CH}$ value, but the second could be a $^2J_{CH}$ or a $^3J_{CH}$ coupling constant. To overcome this lack of information, a 2D NMR (NOESY) experiment was performed in which a correlation peak was observed between the proton at $\delta = 6.27$ ppm (H2) and a group of protons at $\delta =$ 1.70 ppm, which coincides with the CH_2 of the cyclohexyl group. Furthermore, an additional correlation peak was observed between the proton at $\delta = 5.59$ ppm (H1) and the CH_2 group in the α-position of the cyclohexylidene group. However, no correlation was observed between the two H1 and H2 protons due to the particular geometry of such a strained ring.

The reaction appears to be very dependent on the nature of the solvent. Isoprene was selected after evaluation of a wide range of solvents. Polar solvents, such as dioxane, give only small amounts of the cyclobutene derivative **2**, but it was obtained in good yield when a diene was used as solvent. Isoprene, 1,5-cyclooctadiene, and 1,3-cyclohexadiene respectively led to 80, 65, and 60% conversion of **1a** to **2**.[28] It is noteworthy that isoprene was not incorporated in this transformation, whereas its incorporation into some ruthenium–carbon bonds has been observed,[31] and that the coupling of allyl alcohol with propargylic alcohols has been observed with the same catalyst in the absence of acid.[32]

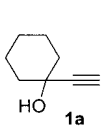
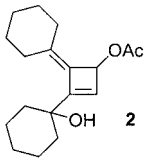
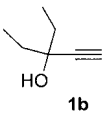
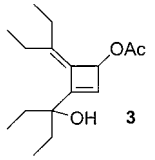
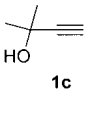
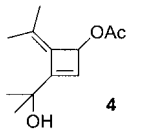
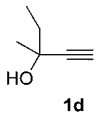
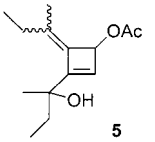
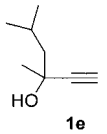
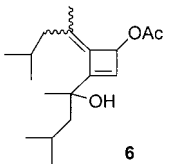
Formation of alkylidenecyclobutenes with various propargylic alcohols: To explore the scope of the above reaction, the reaction of various propargylic alcohols with acetic acid in the presence of 5 mol% of [RuCl(cod)(Cp*)] in isoprene and under the previous conditions was investigated [Eq. (4)] (Table 1).



(4)

In the case of propargylic alcohols **1a–c** with identical R^1 and R^2 groups, cyclobutenes **2**, **3**, and **4** were obtained selectively in 66, 51, and 57% yield, respectively. Starting from the unsymmetrical propargylic alcohols 3-methylpent-1-yn-3-ol (**1d**) and 3,5-dimethylhex-1-yn-3-ol (**1e**), the cyclobutenes **5** and **6** were isolated in 77 and 68% yields, respectively, but both as mixtures of isomers, due to the presence of two chiral carbon atoms and one double bond. The ^{13}C NMR spectrum of **5** shows the presence of four distinct stereoisomers that are formed without any selectivity. The reaction appears to be completely shut down by use of prop-

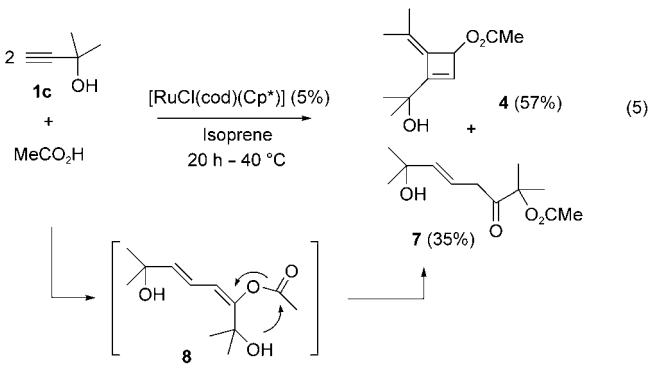
Table 1. Synthesis of alkylidenecyclobutenes **2**–**6** by reaction of propargylic alcohols with acetic acid [Eq. (4)].[a]

Propargylic alcohol	Cyclobutene	Yield [%][b]
 **1a**	 **2**	66
 **1b**	 **3**	51
 **1c**	 **4**	57
 **1d**	 **5**	77
 **1e**	 **6**	68

[a] Conditions: propargylic alcohol (2.5 mmol), acetic acid (1.25 mmol), isoprene (2 mL), catalyst (5%), 20 h at 40°C. [b] Isolated yields.

argylic alcohols bearing bulky substituents, such as *tert*-butyl and phenyl groups. With secondary propargylic alcohols, polymeric compounds were formed. It is also noteworthy that the reaction is restricted to propargylic alcohols bearing a terminal triple bond.

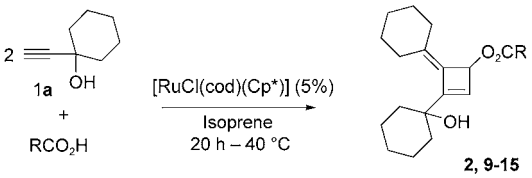
From the less hindered tertiary propargylic alcohol **1c** (2-methylbut-3-yn-2-ol), the reaction led to the formation of the expected cyclobutene derivative **4** (57%), but also to compound **7**, which was isolated in 35% yield and characterized by NMR spectroscopy [Eq. (5)].



(5)

The linear compound **7** has some similarity to the dienol esters depicted in Equation (l).[25] It is feasible that the corresponding dienol ester **8** is formed initially and undergoes a subsequent transesterification leading to **7** [Eq. (5)]. To confirm this hypothesis, the reaction of **1c** with acetic acid was performed under the conditions used for the formation of dienol esters [Eq. (1)] that takes place in dioxane at room temperature for 20 h.[25] We observed the opposite selectivity: the linear product **7** was now the major product and was isolated in 63% yield, whereas the cyclobutene **4** was obtained in 30% yield only. Thus modulation of the **4**/**7** ratio is possible by modifying the reaction conditions. Therefore it may be expected that the formation of dienol ester and that of alkylidenecyclobutene are closely related and may involve the same intermediate. As shown previously, the intermediate leading to the dienol ester is a biscarbene derivative, while the intermediate for cyclobutene formation is expected to be a cyclobutadiene–ruthenium complex, both arising from the head-to-head oxidative coupling of the alkyne, the classical metallacyclopentadiene intermediate. The formation of dienol esters is favored in polar solvents, such as dioxane, and at low temperature with arylacetylenes, compared to the formation of cyclobutenes with propargylic alcohols that mainly occurs at 40°C and in coordinating, nonpolar solvents, such as isoprene.

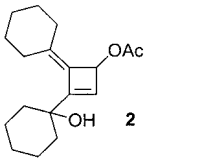
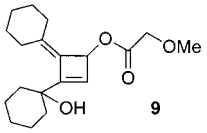
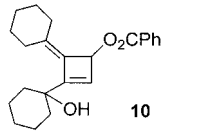
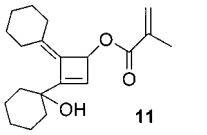
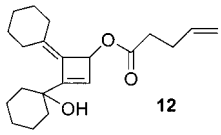
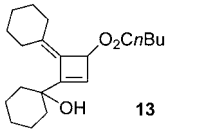
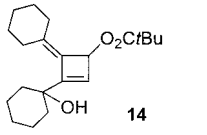
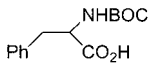
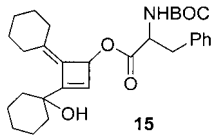
Formation of alkylidenecyclobutenes with various carboxylic acids: Exploration of the reactivity of 1-ethynylcyclohexanol (**1a**) with different carboxylic acids showed that the catalytic formation of alkylidenecyclobutenes can be extended to a variety of carboxylic acids [Eq. (6)] (Table 2).



(6)

Table 2 shows that moderate to good yields are obtained with various carboxylic acids (**2**, **9**–**15**) and that the reaction tolerates a terminal double bond in **11** and **12**. However, the reaction appears to be sensitive to the pK_a of the corresponding carboxylic acids. When the pK_a of the carboxylic acid is low, no reaction is observed. For example, reaction with cyanoacetic acid (pK_a = 2.45) and lactic acid (pK_a = 3.08) did not lead to the formation of the corresponding cyclobutene, whereas reaction does take place with methoxyacetic, benzoic, methacrylic, pent-4-enoic, acetic, valeric, and pivalic acids ($3.5 < pK_a < 5.0$). This observation contrasts with the dimerization of simple terminal alkynes in the presence of carboxylic acids leading to dienol esters [Eq. (1)],[25] which proceeded with carboxylic acids with a rather lower pK_a. An effect of the steric hindrance is also observed as the reaction with pivalic acid (pK_a = 5.03), which possesses a bulky *t*Bu group, gives only a 30% yield of of **14**, whereas 55% of **13** is obtained with valeric acid (pK_a = 4.8, R =

Table 2. Catalytic synthesis of alkylidenecyclobutenes by reaction of propargylic alcohol **1a** with various carboxylic acids [Eq. (6)].[a]

Carboxylic acid	Cyclobutene	Yield [%][b]
$MeCO_2H$ **1'a**	 **2**	66
$MeOCH_2CO_2H$ **1'b**	 **9**	50
$PhCO_2H$ **1'c**	 **10**	66
CO_2H **1'd**	 **11**	45
CO_2H **1'e**	 **12**	65
$nBuCO_2H$ **1'f**	 **13**	55
$tBuCO_2H$ **1'g**	 **14**	30
 **1'h**	 **15**	20

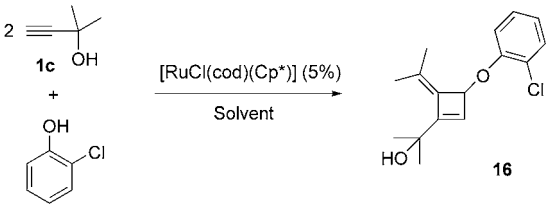
[a] Conditions: 1-ethynylcyclohexanol (2.5 mmol), carboxylic acid (1.25 mmol), isoprene (2 mL), catalyst (5%), 20 h at 40°C. [b] Isolated yields.

*n*Bu). The reaction can take place with N-protected amino acids, but the reactivity seems to be limited by the low solubility of amino acids in isoprene.

Cyclodimerization of propargylic alcohols with addition of phenols: The reaction was investigated with compounds with a higher pK_a, such as phenols. 2-Methylbut-3-yn-2-ol (**1c**) was used for several reasons: firstly, to prevent any purification problems of the cyclobutene derivatives formed from the starting propargylic alcohol; secondly, use of **1c**, which can lead to two compounds, the dienol ester and cyclobutene derivatives analogous to **4** and **7** [Eq. (5)], should allow the selective formation of the cyclobutene derivatives, because phenols are not reactive in the dienol ester transformation.

To optimize the reaction of 2-chlorophenol with **1c** [Eq. (7)] it was performed in different solvents, at various reaction temperatures.

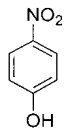
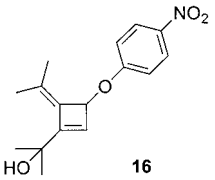
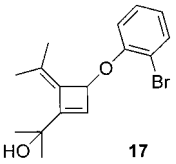
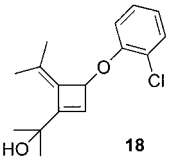
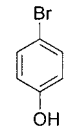
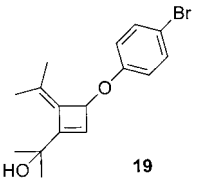
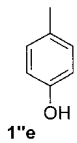
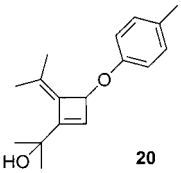
In isoprene at 40°C for 20 h, this reaction leads to 37% of the expected cyclobutene **16**. However, use of dioxane as



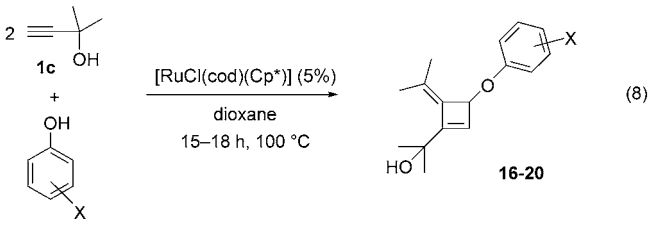
(7)

solvent allows reaction to occur at a higher temperature (100°C), and achieves a better yield (48%) after a reaction time of 18 h. In this case, it is no longer necessary to use isoprene in order to protect the catalyst, probably because phenols are much less acidic than carboxylic acids.[28c] Furthermore, because of the weak reactivity of phenols, yields are better at 100°C than at 40°C. The study was then extended to other phenol derivatives [Eq. (8)] (Table 3).

Table 3. Catalytic synthesis of alkylidenecyclobutenes by reaction of propargylic alcohol **1c** with phenols [Eq. (8)].[a]

Phenol	pK_a	Cyclobutene	Yield [%][b]
 **1"a**	7.15	 **16**	30
 **1"b**	8.43	 **17**	37
 **1"c**	8.49	 **18**	48
 **1"d**	9.34	 **19**	32
 **1"e**	10.26	 **20**	20

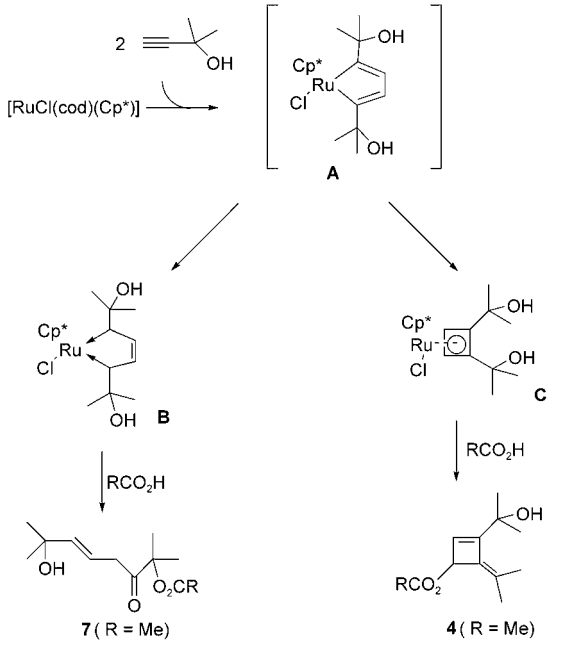
[a] Conditions: 2-methylbut-3-yn-2-ol (2.5 mmol), phenol (1.25 mmol), dioxane (2 mL), catalyst (5%), 15–18 h at 100°C. [b] Isolated yields.



(8)

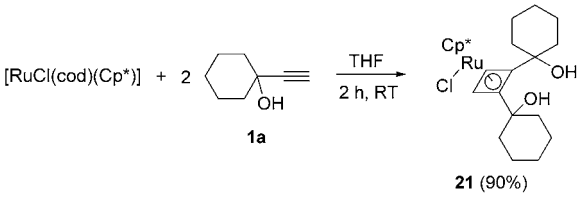
The yields of **16–20** are only moderate compared to those obtained in the reaction with carboxylic acids. The influence of the pK_a is evident in this case also, as the yield decreases as the pK_a of the phenol increases. The reaction does not occur with phenol,[33] aminophenol, or catechol.

Basic mechanism of the catalytic reaction: The reaction leading from **1c** to the compounds **4** and **7** [Eq. (5)] is an interesting transformation from the mechanistic point of view as the two different compounds may arise from the same intermediate. This intermediate can be rationalized as resulting from the head-to-head oxidative coupling of two molecules of propargylic alcohol yielding a 16-electron ruthenacyclopentadiene intermediate **A**. Intermediate **A** should lead to **B** or **C**, two different organometallic derivatives (Scheme 1), in order to complete the 18-electron environment of the ruthenium atom. The first route involves the electronic reorganization of the dienic system **A** into the biscarbene–ruthenium species **B**[25] leading in the presence of acid to the dienyl ester and then to **7**. The second route involves a reductive elimination step leading to the cyclobutadiene–ruthenium(II) complex **C**. The steric hindrance of the CR_2OH group in the alkyne may play an important role in favoring the reductive elimination, but also a conjugated group, such as an aryl group, is absent and therefore cannot contribute to the stabilization of the 18-electron biscarbene species **B**.[25]



Scheme 1. Competitive formation of intermediates **B** and **C** and their derivatives **7** and **4**.

To characterize the intermediates, stoichiometric reactions involving the catalyst precursor and propargylic alcohol **1a** were investigated. Reaction of [RuCl(cod)(Cp*)] with two equivalents of **1a** in THF at room temperature led to the formation of the corresponding cyclobutadiene–ruthenium complex **21**, isolated as a brown powder in 90% yield [Eq. (9)]. Although propargylic alcohols can react to form vinylidene–ruthenium[34] or allenylidene–ruthenium[35] complexes, no traces of such complexes were detected and complex **21** was isolated as a single compound.



(9)

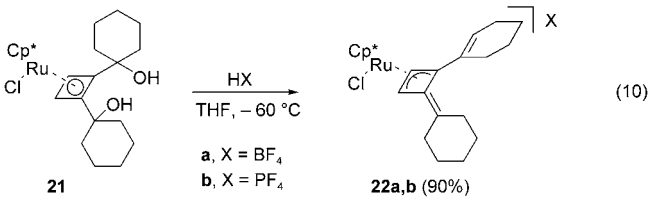
Complex **21** has been successfully characterized by NMR spectroscopy and mass spectrometry. The ^{1}H NMR spectrum showed the two 1-hydroxycyclohexyl groups to be equivalent, and a singlet resonance at $\delta = 3.42$ ppm (2H) for the two protons of the cyclobutadiene ring. The structure was confirmed by the ^{13}C NMR spectrum, which showed two signals for the cyclobutadiene ring at $\delta = 69.8$ and 92.5 ppm, corresponding to the two CH carbon atoms and to the two quaternary carbon atoms, respectively.

Cyclobutadiene complexes are well-known species, since the work of Pettit on the (cyclobutadiene)tricarbonyliron complex.[4,36] Cyclobutadiene–ruthenium complexes usually result from the coupling of two molecules of alkynes at a ruthenium center.[37,38] Thus a {RuCl(Cp*)} fragment arising from [Ru(μ_3-Cl)(Cp*)]$_4$ or [RuCl(Cp*)(tmeda)] reacted with bulky and nonaromatic terminal alkynes such as trimethylsilylacetylene to generate the corresponding cyclobutadiene–ruthenium complexes.[37]

The isolated complex **21** was used as a precatalyst in the transformation of **1a** with acetic acid to give **2**, under similar conditions to those for Equation (3), and a comparable conversion to that obtained with [RuCl(cod)(Cp*)] was observed, suggesting that **21** is a key intermediate in this transformation.

The reactivity of **21** toward acids was then investigated. Addition of acetic acid at room temperature gave no complex; on heating **2** was obtained. More gratifyingly, the reaction with strong acids with noncoordinating anions led to the well-defined derivatives **22a**,**b** [Eq. (10)].

When **21** was treated at −60 °C with one equivalent of HBF_4 or HPF_6 in THF, the ionic ruthenium complex **22a** (X = BF_4) or **22b** (X = PF_6) was isolated, each in 90% yield. Complexes **22a** and **22b** resulted from a single protonation but a double dehydration. The ^{13}C NMR spectrum of **22b** in-



(10)

cludes signals at $\delta = 93.4$ (C=C), 86.3 (=C–H), and 77.3 ppm (=C–H), corresponding to the three allylic carbon nuclei. Another =C–H signal is observed at $\delta = 140.7$ ppm, which corresponds to the tertiary olefinic carbon of the cyclohexenyl ring. Similar data are observed for **22a**.

X-ray diffraction of the alkylidenecyclobutenyl–ruthenium complex 22b: Crystals of **22b** suitable for X-ray analysis were obtained from a biphasic system based on dichloromethane/diethyl ether mixtures. The structure is presented in Figure 1 and Table 4 gives the more representative bond lengths and angles.[39]

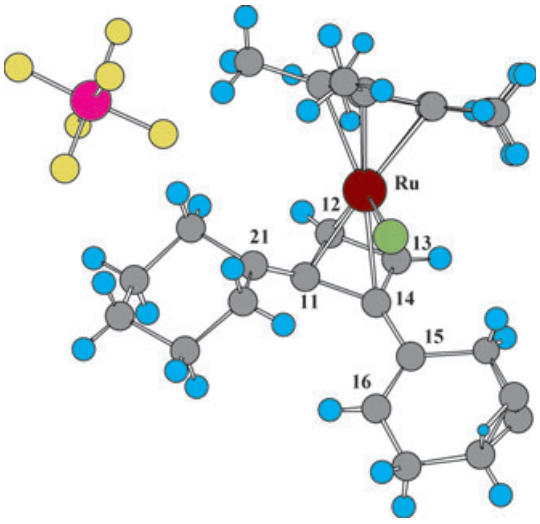
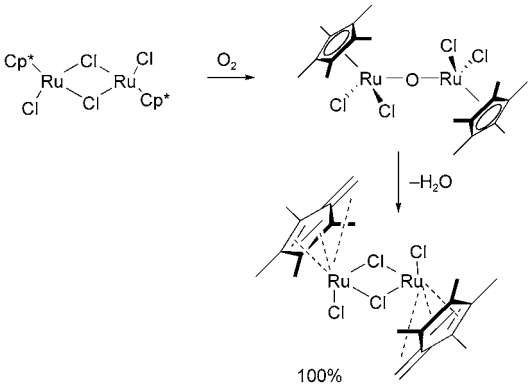


Figure 1. X-ray structure of the cyclobutenyl–ruthenium complex **22b**.

The cationic complex **22b** bears an alkylidenecyclobutenyl ligand coordinated to the ruthenium; it confirms the general structure of the cyclobutenyl derivative proposed on the basis of NMR spectroscopy. The two substituents of the cyclobutene ring consist of a cyclohexenyl group bonded to the C14 carbon of the four-membered ring (C15=C16 1.330(7) Å) and a cyclohexylidene group bonded to the C11 carbon of the ring (C11=C21 1.364(8) Å). The C12, C13, and C14 carbon atoms are bonded to the metal in an allylic mode, since the shortest bond lengths of the ring are C12–C13 1.426(9) Å and C13–C14 1.428(7) Å. The four-membered ring appears to be planar. Furthermore, the Ru–C11 bond length (2.194(4) Å) is comparable to the allyl Ru–C bond lengths (Ru–C12 2.114(4) Å, Ru–C13 2.237(5) Å, and Ru–C14 2.315(4) Å). The coordination of the Cp*, chloride, and allyl ligands leads to an unsaturated ruthenium(IV) complex with 16 electrons. To complete its coordination sphere of 18 electrons the additional coordination of the double bond C11=C21 is observed, but the interaction remains weak, as indicated by the long Ru–C21 distance (Ru–C21 2.674(4) Å). An inclination of approximately 30° is observed for the C11=C21 bond bending toward the ruthenium atom with respect to the plane of the four-membered ring (28.8 and 33.0° inclination to the respective C11-C12-C13 and C11-C14-C13 planes). However, the Ru–C21 distance is too long to be a part of a real (η^2-C=C)–Ru bond system.

The coordination of exocyclic double bonds is already known in ruthenium chemistry, especially in fulvene–ruthenium complexes [Eq. (11)].[40] Air oxidation of the precursor [{$RuCl_2$(Cp*)}$_2$] led to a fulvene complex, the structure of which showed the bending of the C=C bond toward the ruthenium atom.

However, in the fulvene complex the Ru–CH_2 distances



(11)

(2.268(4) and 2.271(4) Å) in the (C=CH_2)–Ru bonds for the two ligands of the dimer are still close to a normal (η^2-C=C)–Ru bond length, as the other Ru–C bonds in this complex are in the range between 2.172(4) and 2.166(4) Å for both rings. In the case of the fulvene complex [Eq. (11)] the exocyclic double bond is η^2-coordinated, while in the complex **22b** it is only η^1-coordinated through the C11 carbon, and not with C21: Ru–C21 is 2.674(4) Å (Figure 2).

Table 4. A selection of bond lengths and bond angles for **22b**.

Bond lengths [Å]				Angles [°]		Dihedral angles [°]	
Ru–Cl	2.3845(12)	C11–C12	1.499(7)	C11-C12-C13	90.7(4)	C11-C12-C13-C14	0.4(4)
		C12–C13	1.426(9)	C12-C13-C14	92.4(5)	C14-C11-C12-C13	–0.3(3)
Ru–C11	2.194(4)	C13–C14	1.428(7)	C13-C14-C11	90.3(4)	C12-C11-C14-C13	0.3(3)
Ru–C12	2.114(4)	C14–C11	1.506(7)	C14-C11-C12	86.6(4)	C12-C13-C14-C11	–0.3(4)
Ru–C13	2.237(5)			C11-C14-C15	135.6(5)	C12-C13-C14-C15	171.3(5)
Ru–C14	2.315(4)	C14–C15	1.448(7)	C12-C11-C21	128.6(4)	C12-C11-C14-C15	–171.0(6)
		C15–C16	1.330(7)	C13-C14-C15	133.5(5)	C21-C11-C12-C13	151.2(5)
Ru–C21	2.674(4)	C21–C11	1.364(8)	C14-C11-C21	136.3(4)	C21-C11-C14-C13	–147.0(6)
						C21-C11-C14-C15	41.6(9)

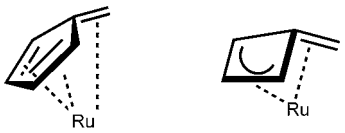


Figure 2. η^2- and η^1-coordination of the (C=C)–Ru bonds.

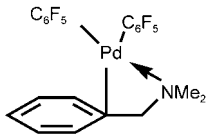
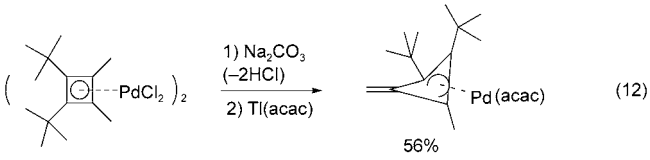


Figure 3. η^1-interaction in the complex *cis*-$[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)]$.

To our knowledge no ruthenium complex with an allylic ligand in a four-membered ring has been described so far, whereas a (η^3-methylenecyclobutenyl)–palladium complex has already been synthesized and characterized [Eq. (12)].[41]



(12)

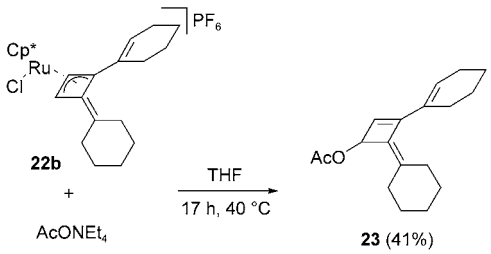
The main difference from **22b** is that in this allyl–palladium complex the four-membered ring is not planar and the double bond moves away from the metal center. This can be explained by the stability of this 16-electron palladium complex not requiring further stabilization by coordination of the exocyclic C=C bond.

Some complexes exhibiting interaction between the metal center and only one carbon of a C=C double bond are known, especially in the case of an aromatic group maintained close to the metal.[41] For example, in the complex *cis*-$[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)]$ there is η^1-arene interaction between the *ipso* carbon atom of the phenyl ring of the *N*-dimethylbenzylamine ligand and the palladium center (Figure 3).

In **22b**, the η^1-coordination of the double bond could result from the steric difficulty for the exocyclic C=C carbon to coordinate to the metal center. The alkylidenecyclobutadienyl ligand in **22b** should be considered as an η^4-coordinated ligand, which gives five electrons to the ruthenium atom.

To confirm that a complex similar to **22b**, but only monodehydrated, is a model intermediate for the reaction **1a**→**2**, the stoichiometric reaction of **22b** in the presence of ammonium acetate ($AcONEt_4$) in THF for 17 h at 40 °C led to the decomposition of the organometallic complex and to the formation of an organic compound **23** isolated in 41 % yield [Eq. (13)]; compound **23** is the dehydrated analogue of the corresponding cyclobutene **2** previously obtained in the presence of acetic acid.

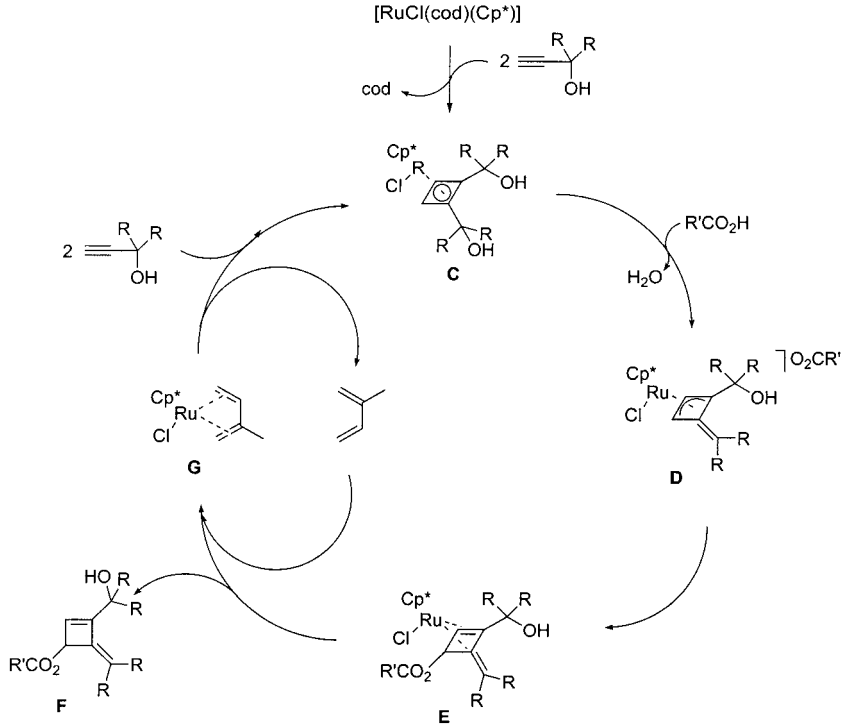
Compound **23** shows a similar ^{1}H NMR spectrum as that



(13)

of **2**, except for the presence of a new signal as a multiplet at $\delta = 5.92$ ppm corresponding to the vinylic proton of the cyclohexenyl group. This compound was also detected during the catalytic formation of **2**, but in a very small amount.

The catalytic cycle: On the basis of the previous stoichiometric reactions, the catalytic cycle in Scheme 2 may account for the catalytic combination of two molecules of



Scheme 2. Catalytic cycle for alkylidenecyclobutene formation.

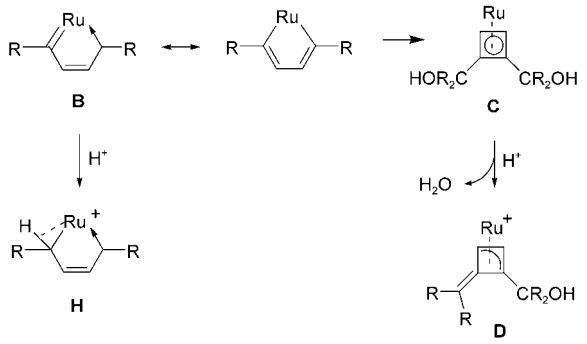
propargylic alcohol allowing the formation of an alkylidenecyclobutene **2**. The characterization of the first complex **21** shows the first step of the cycle to consist of the formation of a cyclobutadiene–ruthenium complex **C** with head-to-head C≡C bond coupling. The addition of carboxylic acid is thus expected to give the intermediate **D**, resulting from protonation and monodehydration. Intermediate **D** is thus analogous to **22**, which is obtained from **21** with a strong acid, except that the monodehydration is observed only in the presence of a carboxylate anion. Then, the addition of the carboxylate at the less-substituted terminal carbon atom of the cyclic allylic group gives the intermediate **E**, analogously to the transformation **22b**→**23** [Eq. (13)].

This reaction is similar to a classic allylic substitution reaction.[43] Such a process is already known with ruthenium complexes, in both stoichiometric[44] and catalytic roles.[45] The catalytic allylation of phenol derivatives is not a common process and only a few metal complexes have been used for this purpose.[46] Moreover, the phenolate addition to allyl groups promoted by a ruthenium complex in both stoichiometric[47] and catalytic reactions has only recently been observed.[45a,48]

The spontaneous displacement of the cyclobutene **F** from the ruthenium intermediate **E** may regenerate the catalyst precursor, which again combines with two propargylic alcohol molecules to give **C**. Alternatively, as we observed a strong beneficial influence of isoprene as solvent, it is possible that the weakly bonded cyclobutene **F** in intermediate **E** may be displaced by isoprene present in high concentration to give the intermediate **G** as a catalytic relay. This process would allow the stabilization of the ruthenium catalyst at the end of the catalytic cycle. This may indicate that coordination of the solvent (isoprene) prevents the decomposition of the catalyst. This complex **G** can react with two molecules of propargylic alcohol similarly to the precatalyst [RuCl(cod)(Cp*)] to generate a cyclobutadiene–ruthenium complex **C**.

The use of isoprene is essential, probably because the reaction of propargylic alcohols at the metal center is relatively slow, mainly due to steric hindrance; thus the catalyst is exposed to protonation by the carboxylic acid. The intermediate coordination of isoprene, forming complex **G**, would avoid the protonation of the ruthenium species and let the transformation occur.

Oxidative coupling of alkynes—biscarbene versus cyclobutadiene–ruthenium intermediate: The above transformation of propargylic alcohols [Eq. (2)] contrasts well with that of arylacetylenes [Eq. (1)]. Actually, the key intermediates leading to cyclobutenes from the oxidative coupling of alkynes on the {RuCl(Cp*)} moiety are quite different. From arylacetylenes the oxidative coupling leads to a stable, isolable biscarbene–ruthenium complex;[26a–c] Calhorda, Kirchner, and co-workers[26d] have shown by computational studies that it corresponds to the biscarbene–ruthenium(IV) complex **B**. Eisenstein, Clot, and co-workers have provided evidence that the protonation of intermediate **B** takes place at the carbene carbon to give a mixed (alkyl)(carbene)ruthenium species **H**[25] (Scheme 3).



Scheme 3. Biscarbene–ruthenium intermediate **H** versus cyclobutadiene–ruthenium intermediate **D**.

To explain why the initial oxidative coupling intermediate **B** gives cyclobutadiene–ruthenium complex **C** with propargylic alcohols, the reductive elimination in the **B**→**C** pathway has been studied computationally.

Computational studies of the reaction of alkynes with the RuCl(Cp) and RuCl(Cp) fragments*: The formation of the η^4-cyclobutadiene complex **C** from a metallacycle **B**, the latter being generated through oxidative coupling of two acetylene molecules to the RuCl(Cp) fragment, has been investigated by means of DFT/B3LYP calculations.[49] As a result, a one-step transformation featuring the replacement of one carbenic M=C bond by two M–C single bonds has been suggested for the transition state (Figure 4). This sym-

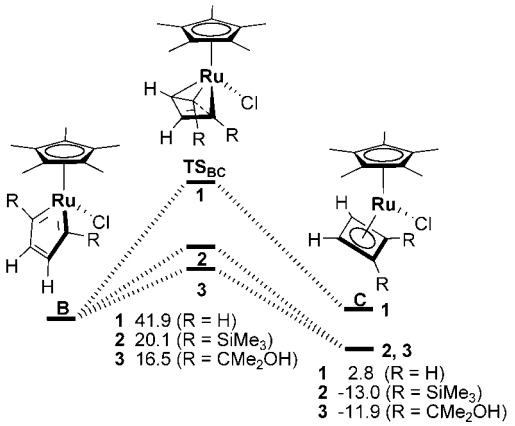


Figure 4. Activation energy for dimerization of various alkynes.

metry-forbidden pathway is energetically prohibitive,[50] unless the substituents on the acetylene are changed. We have therefore compared the activation energy of formation of the cyclobutadiene–ruthenium complex with propargylic alcohol to that with a simple terminal alkyne. For the RuCl(Cp) system the energy barrier (in kcal mol^{-1}) for the

transformation of **B** into **C** varies strongly with the nature of R in the starting alkyne HC≡CR in the series: H (41.1) ≈ Ph (40.4) > Me (35.6) ≫ $SiMe_3$ (26.8). In the case of propargylic alcohols, with HC≡$CCMe_2OH$ as the model alkyne, the decrease in the activation energy is calculated to be 28.7 kcal mol^{-1}. Relative to the substituents of acetylene, the variation of those of the Cp ligand are also important. While there is no significant difference between Cp and Cp* for the reaction with the parent acetylene, with HC≡$CSiMe_3$ and the propargylic alcohol HC≡$CCMe_2OH$ the activation energy decreases significantly and this effect is more pronounced in the case of RuCl(Cp*): from 41.9 for acetylene to 20.1 and 16.5 kcal mol^{-1} for HC≡$CSiMe_3$ and the propargylic alcohol, respectively (Figure 4).

These last values can be attained experimentally, thus becoming competitive with those for other processes such as the addition of carboxylic acids. They explain the accessibility of cyclobutadiene–ruthenium intermediates for HC≡C-CR_2OH alkynes, leading to alkylidenecyclobutenes, whereas this accessibilty does not exist for arylacetylenes.

Conclusion

The combination of two molecules of propargylic alcohol and one molecule of carboxylic acid, catalyzed by a simple ruthenium complex, affords alkylidenecyclobutenes. This original synthetic method was also applied to phenols, in which case it represents a rare example of the catalytic addition of phenol to allyl groups, especially with ruthenium complexes as the catalyst. It is a new example of C–C bond formation by triple-bond activation and has been shown to proceed via a cyclobutadiene–ruthenium complex and a novel type of alkylidenecyclobutenylruthenium derivative displaying an unusual mode of coordination. This single-step access route to strained four-membered functional cyclic compounds, satisfying the atom economy concept as it results from combination of three molecules into one with elimination of one molecule of water, is likely to be extended to other propargylic fragments or alkynes, as long as the reductive elimination leading to a cyclobutadiene intermediate is energetically favored.

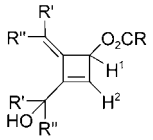
Experimental Section

All catalytic reactions were carried out under an inert atmosphere in Schlenk tubes. Chemicals were obtained commercially and used as supplied. [RuCl(cod)(Cp*)] was prepared according to the reported method.[44e] Products were isolated by silica gel (70–230 mesh) flash column chromatography with mixed solvents (pentane/diethyl ether mixtures). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 300 WB and DPX 200 spectrometers in deuterated chloroform at 298 K. IR spectra were recorded on a Bruker IFS28 spectrometer. Elemental analysis was performed for the selected compound **19** (white powder) by the Service de Microanalyse du CNRS, Lyon (France). The high-resolution mass spectra of the other compounds, which were too hygroscopic for elemental analysis, were recorded on a Varian MATT 311 high-resolution spectrometer at the Centre Regional de Mesures Physiques de l'Ouest (CRMPO), University of Rennes 1, France.

Computational details: All calculations were performed using the Gaussian 98 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology.[51] The geometries and energies of the model complexes were optimized at the B3LYP level[52] with the Stuttgart/Dresden ECP (SDD) basis set[53] to describe the electrons of Ru; for all other atoms the 6-31G(d,p) basis set was employed except for the CH_3 groups of the Cp* ligand and the CH_3 and OH groups of the propargylic alcohol, for which an STO-3G basis set was used.[54,55] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides, and obtaining the minima presented on the reaction energy profile. All geometries were optimized without symmetry constraints and the energies were zero-point corrected.

Typical procedure for ruthenium-catalyzed dimerization of terminal propargylic alcohols with carboxylic acids: [RuCl(cod)(Cp*)] (0.125 mmol, 5%) and carboxylic acid (1.25 mmol, 0.5 equiv) were added to a solution of the terminal alkyne (2.5 mmol, 1 equiv) in degassed isoprene (2 mL) under an inert atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 20 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent: pentane/diethyl ether mixtures) to give the dimerization adduct as a viscous oil in 20–77% yield. The adducts, general formula **24**, were analyzed by NMR (^{1}H and ^{13}C), IR, and mass spectrometry.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl acetate (**2**)*:



Yield: 66%; ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 1.4–1.75 (m, 17H; cyclohexyl OH), 2.01 (s, 3H; MeCO), 1.96–2.08 (m, 2H; cyclohexyl CH_2), 2.37–2.47 (m, 2H; cyclohexyl CH_2), 5.59 (d, J = 0.5 Hz, 1H; H1), 6.2 ppm7 (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 171.3, 162.0, 130.7, 129.3, 127.8, 72.4, 69.4, 35.8, 35.6, 31.4, 30.8, 27.9, 27.7, 26.4, 25.5, 21.7, 21.6, 21.2 ppm; MS (EI): m/z calcd for $C_{18}H_{26}O_3$: 290.1882; found: 290.1879; FTIR (neat): $\tilde{\nu}$ = 3462, 2928, 1732, 1577 cm^{-1}.

*3-(1-Ethyl-1-hydroxypropyl)-4-(1-ethylpropylidene)cyclobut-2-enyl acetate (**3**)*: Yield: 51%; ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 0.78 (t, J = 7.6 Hz, 3H; ethyl Me), 0.82 (t, J = 7.6 Hz, 3H; ethyl Me), 0.93 (t, J = 7.5 Hz, 3H; ethyl Me), 0.95 (t, J = 7.5 Hz, 3H; ethyl Me), 1.62 (q, J = 7.5 Hz, 2H; ethyl CH_2), 1.63 (q, J = 7.4 Hz, 2H; ethyl CH_2), 1.84 (s, 1H; OH), 1.98 (q, J = 7.5 Hz, 2H; ethyl CH_2), 2.00 (s, 3H; MeCO), 2.31 (m, 2H; ethyl CH_2), 5.57 (s, 1H; H^1), 6.30 ppm (s, 1H; H^2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 171.3, 160.1, 133.1, 132.0, 130.9, 74.2, 72.1, 30.4, 30.2, 23.5, 23.3, 21.2, 13.1, 12.7, 8.0, 7.7 ppm; MS (EI): m/z calcd for $C_{16}H_{26}O_3$: 266.1881; found: 266.1875; FTIR (neat): $\tilde{\nu}$ = 3466, 2967, 1720, 1573 cm^{-1}.

*3-(1-Hydroxymethylethyl)-4-methylethylidenecyclobut-2-enyl acetate (**4**)*: Yield: 57%; ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 1.36 (s, 3H; Me), 1.40 (s, 3H; Me), 1.63 (s, 3H; Me), 1.83 (s, 1H; OH), 1.90 (s, 3H; Me), 2.03 (s, 3H; $MeCO_2$), 5.55 (s, 1H; H1), 6.27 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 171.3, 162.0, 132.4, 130.1, 119.7, 72.4, 68.2, 28.3, 28.2, 21.2, 20.8, 20.3 ppm; MS (EI): m/z calcd for $C_{12}H_{18}O_3$: 210.1256; found: 210.1258; FTIR (neat): $\tilde{\nu}$ = 3445, 2978, 1737, 1644 cm^{-1}.

*3-(1-Hydroxy-1-methylpropyl)-4-(1-methylpropylidene)cyclobut-2-enyl acetate (**5**)*: Yield: 77% (mixture of several isomers); ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 0.75–1.00 (m, 6H; 2Me), 1.29–1.31 (3s, 3H; 1Me), 1.60–1.69 (m, 2H; 1CH_2), 1.58, 1.85 (3s, 3H; 1Me), 1.99 (2s, 3H; 1Me), 2.0–1.95 (m, 2H; 1H; CH_2, OH), 2.24–2.31 (m, 1H; CH_2), 5.52–5.56 (3s, 1H; H1), 6.25–6.27 ppm (2s, 1H; H2); ^{13}C NMR (totally decoupled and dept 135; 50.329 MHz, $CDCl_3$): δ = 171.41, 171.33 (CO), 161.54, 161.49, 161.23 (=Cq), 132.36, 132.28, 131.90, 131.84 (=Cq), 131.72, 131.47,

131.20 (=CH), 125.24, 125.18, 125.09, 124.99 (=Cq), 72.40, 72.38, 72.30, 72.24 (CH−O), 71.41, 71.32, 71.20 (Cq−O), 32.98, 32.89, 32.79 (CH_2), 27.56, 27.21 (CH_2), 25.72, 25.39 (CH_3), 21.19 (CH_3), 17.77, 16.76 (CH_3), 12.77, 12.52 (CH_3), 8.30, 8.10 ppm (CH_3); MS (EI): *m/z* calcd for $C_{14}H_{22}O_3$: 238.1569; found: 238.1570; FTIR (neat): $\tilde{\nu}$ = 3454, 2969, 1721, 1580 cm^{-1}.

*3-(1-Hydroxy-1,3-dimethylbutyl)-4-(1,3-dimethylbutylidene)cyclobut-2-enyl acetate (**6**)*: Yield: 68% (mixture of several isomers); ^1H NMR (200.131 MHz, $CDCl_3$): δ = 0.78–0.92 (m, 12H; 4Me), 1.37–1.38 (2s, 3H; 1Me), 1.58–1.59, 1.82–1.85 (4s, 3H; 1 Me), 1.57–1.87 (m, 6H; 1CH_2, 1H (CH_2), OH, 2CH), 2.01–2.02 (2s, 3H; 1Me), 2.15–2.22 (m, 1H; CH_2), 5.54–5.56 (2s, 1H; H1), 6.32–6.33 ppm (3s, 1H; H2); FTIR (neat): $\tilde{\nu}$ = 3473, 2926, 1732, 1579 cm^{-1}.

*6-Hydroxy-1,1,6-trimethyl-2-oxohept-4-enyl acetate (**7**)*: Yield: 35%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.26 (s, 6H; Me), 1.42 (s, 6H; Me), 2.03 (s, 3H; $MeCO_2$), 2.08 (s, 1H; OH), 3.15 (m, 2H; CH_2), 5.64 ppm (m, 2H; HC=); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 207.1, 170.4, 142.0, 119.7, 83.6, 70.6, 39.0, 29.5, 23.5, 21.2 ppm; MS (EI): *m/z* calcd for $C_9H_{13}O_2$: 153.0912; found: 153.0916; FTIR (neat): $\tilde{\nu}$ = 3441, 2976, 1732, 1716, 1645 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl methoxyacetate (**9**)*: Yield: 50%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.35–1.75 (m, 17H; cyclohexyl, OH), 1.95–2.05 (m, 2H; cyclohexyl CH_2), 2.30–2.45 (m, 2H; cyclohexyl CH_2), 3.38 (s, 3H; O−Me), 3.96 (s, 2H; O−CH_2), 5.68 (s, 1H; H1), 6.25 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 170.5, 162.5, 130.2, 129.0, 128.0, 72.7, 69.8, 69.4, 59.3, 35.7, 35.6, 31.3, 30.9, 28.0, 27.6, 26.4, 25.5, 21.7, 21.6 ppm; MS (EI): *m/z* calcd for $C_{19}H_{28}O_4$: 320.1987; found: 320.1977; FTIR (neat) $\tilde{\nu}$ = 3467, 2929, 1749, 1576 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl benzoate (**10**)*: Yield: 66%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.40–1.80 (m, 16H; cyclohexyl), 1.90 (s, 1H; OH), 2.00–2.20 (m, 2H; cyclohexyl CH_2), 2.40–2.55 (m, 2H; cyclohexyl CH_2), 5.78 (s, 1H; H1), 6.40 (s, 1H; H2), 7.23–7.54 (m, 3H; Ph), 7.97–8.03 ppm (m, 2H; Ph); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 166.8, 162.0, 132.9, 131.0, 130.4, 129.6, 129.3, 128.3, 127.7, 73.1, 69.5, 35.8, 35.7, 31.4, 31.0, 28.2, 27.8, 26.5, 25.5, 21.8, 21.7 ppm; MS (EI): *m/z* calcd for $C_{23}H_{28}O_3$: 352.2038; found: 352.2039; FTIR (neat): $\tilde{\nu}$ = 3481, 3069, 2931, 1717, 1602, 1584 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl methacrylate (**11**)*: Yield: 45%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.25–1.80 (m, 17H; cyclohexyl, OH), 1.93 (s, 3H; Me), 2.07–2.12 (m, 2H; cyclohexyl CH_2), 2.43–2.50 (m, 2H; cyclohexyl CH_2), 5.54 (d, J = 1.4 Hz, 1H; =CH_2), 5.61 (s, 1H; H1), 6.09 (d, J = 1.4 Hz, 1H; =CH_2), 6.37 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 168.1, 162.1, 136.9, 131.4, 129.7, 128.0, 126.0, 73.2, 69.9, 36.2, 36.1, 31.8, 31.4, 28.5, 28.2, 26.9, 25.9, 22.2, 22.1, 18.7 ppm; MS (EI): *m/z* calcd for $C_{16}H_{22}O_2$: 246.1620 [M^+ −CHOCCH$_2$CH$_3$]; found: 246.1608; FTIR (neat): $\tilde{\nu}$ = 3447, 3181, 2982, 1713, 1632 cm^{-1}.

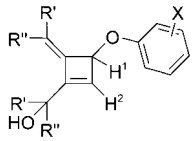
*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl pent-4-enoate (**12**)*: Yield: 65%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.40–1.80 (m, 17H; cyclohexyl, OH), 1.95–2.10 (m, 2H; cyclohexyl CH_2), 2.27–2.42 (m, 6H; cyclohexyl CH_2, $(CH_2)_2CO$), 4.95 (dm, J = 10.2 Hz, 1H; =CH_2), 5.00 (dm, J = 17.1 Hz, 1H; =CH_2), 5.61 (s, 1H; H1), 5.75 (m, 1H; =CH), 6.26 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 173.3, 162.0, 136.6, 130.8, 129.3, 127.7, 115.4, 72.4, 69.4, 35.8, 35.7, 33.7, 31.4, 30.9, 28.9, 28.0, 27.7, 26.4, 25.5, 21.7, 21.6 ppm; MS (EI): *m/z* calcd for $C_{21}H_{30}O_3$: 330.2194; found: 330.2197; FTIR (neat): $\tilde{\nu}$ = 3474, 3080, 2931, 1722, 1641, 1574 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl pentanoate (**13**)*: Yield: 55%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3H; CH_3) 1.24–1.76 (m, 21H; cyclohexyl, $(CH_2)_2$, OH), 2.05 (m, 2H; cyclohexyl CH_2), 2.30 (t, J = 7.2 Hz, 2H; CH_2), 2.46 (m, 2H; cyclohexyl CH_2), 5.65 (s, 1H; H1), 6.31 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 174.5, 162.3, 131.3, 129.9, 128.0, 72.6, 69.8, 36.2, 36.1, 34.7, 31.8, 31.3, 28.4, 28.1, 27.5, 26.9, 25.9, 22.7, 22.1, 22.0, 14.1 ppm; MS (EI): *m/z* calcd for $C_{21}H_{32}O_3$: 332.2352; found: 332.2380; FTIR (neat): $\tilde{\nu}$ = 3469, 2960, 2930, 1728, 1610 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl 2,2-dimethylpropanoate (**14**)*: Yield: 30%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.20 (s, 9H; *t*Bu), 1.25–1.8 (m, 17H; cyclohexyl, OH), 1.95–2.1 (m, 2H; cyclohexyl CH_2), 2.3–2.6 (m, 2H; cyclohexyl CH_2), 5.61 (s, 1H; H1), 6.31 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 179.3, 161.8, 131.5, 130.0, 127.6, 72.6, 69.9, 39.2, 36.2, 36.1, 31.8, 31.3, 28.5, 28.2, 27.6, 26.9, 25.9, 22.2, 22.1 ppm; FTIR (neat): $\tilde{\nu}$ = 3447, 2989, 2930, 1735, 1617 cm^{-1}.

*4-Cyclohexylidene-3-(1-hydroxycyclohexyl)cyclobut-2-enyl BOC-phenylalaninate (**15**)*: Yield: 20%; ^1H NMR (200.131 MHz, $CDCl_3$): major diastereoisomer: δ = 1.41 (s, 9H; *t*Bu), 1.2–1.75 (m, 17H; cyclohexyl, OH), 1.9–2.0 (m, 2H; cyclohexyl CH_2), 2.4–2.5 (m, 2H; cyclohexyl CH_2), 2.9–3.2 (m, 2H; CH_2Ph), 4.6 (m, 1H; CH), 5.0 (m, 1H; NH), 5.60 (s, 1H; H1), 6.32 (s, 1H; H2), 7.13–7.31 ppm (m, 5H; Ph); minor diastereoisomer: δ = 1.43 (s, 9H; *t*Bu), 1.2–1.75 (m, 17H; cyclohexyl, OH), 1.9–2.0 (m, 2H; cyclohexyl CH_2), 2.4–2.5 (m, 2H; cyclohexyl CH_2), 1.9–3.2 (m, 2H; CH_2Ph), 4.6 (m, 1H; CH), 5.0 (m, 1H; NH), 5.62 (s, 1H; H1), 6.27 (s, 1H; H2), 7.13–7.31 ppm (m, 5H; Ph); ^{13}C NMR (50.329 MHz, $CDCl_3$): major diastereoisomer: δ = 172.6, 162.7, 155.4, 136.6, 130.5, 129.8, 129.1, 128.9, 128.6, 127.4, 80.2, 73.8, 69.9, 55.0, 39.0, 36.2, 36.1, 31.7, 31.4, 28.7, 28.4, 28.1, 26.8, 25.9, 22.1 ppm; minor diastereoisomer: δ = 172.2, 162.9, 155.5, 136.5, 130.8, 130.0, 129.1, 128.8, 128.4, 127.4, 80.2, 74.0, 69.9, 54.8, 38.6, 36.2, 36.1, 31.7, 31.3, 28.7, 28.4, 28.1, 26.8, 25.9, 22.1 ppm; FTIR (neat): $\tilde{\nu}$ = 3373, 2975, 1750, 1720, 1602 cm^{-1}.

Typical procedure for ruthenium-catalyzed dimerization of terminal propargylic alcohols with phenols: [RuCl(cod)(Cp*)] (0.125 mmol, 5%) and carboxylic acid (1.25 mmol, 0.5 equiv) were added to a solution of the terminal alkyne (2.5 mmol, 1 equiv) in degassed dioxane (2 mL) under an inert atmosphere at room temperature. The reaction mixture was stirred at 100 °C for 20 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent: pentane/diethyl ether mixtures) to give the dimerization adduct in 20–48% yield. The compounds (general formula **25**) were analyzed by NMR (^1H and ^{13}C) and IR spectroscopy, mass spectrometry, or elemental analysis.



*2-[-3-(4-Nitrophenoxy)-4-methylethylidenecyclobut-1-enyl)]propan-2-ol (**16**)*: Yield: 30%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.42 (s, 3H; Me), 1.44 (s, 3H; Me), 1.75 (s, 3H; Me), 1.80 (s, 1H; OH), 1.97 (s, 3H; Me), 5.27 (s, 1H; H1), 6.46 (s, 1H; H2), 6.96 (d, J = 9.3 Hz, 2H; Ar), 8.16 ppm (d, J = 9.3 Hz, 2H; Ar); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 163.4, 163.1, 141.5, 131.9, 128.6, 126.0, 121.0, 115.1, 76.0, 68.8, 28.4, 28.3, 21.0, 20.5 ppm; MS (EI): *m/z* calcd for $C_{16}H_{19}NO_4$: 289.1314; found: 289.1312; FTIR (KBr): $\tilde{\nu}$ = 3430, 3085, 2978, 1607, 1591 cm^{-1}.

*2-[-3-(2-Bromophenoxy)-4-methylethylidenecyclobut-1-enyl)]propan-2-ol (**17**)*: Yield: 37%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.41 (s, 3H; Me), 1.43 (s, 3H; Me), 1.84 (s, 3H; Me), 1.87 (s, 1H; OH), 1.97 (s, 3H; Me), 5.14 (s, 1H; H1), 6.48 (s, 1H; H2), 6.77–6.95 (m, 2H; Ar), 7.17–7.26 (m, 1H; Ar), 7.48–7.53 (m, 1H; Ar); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 162.2, 154.8, 133.5, 132.7, 129.9, 128.3, 122.2, 120.4, 115.0, 112.8, 76.9, 68.7, 28.4, 28.2, 21.1, 20.7; MS (EI): *m/z* 322.0582 (calcd for $C_{16}H_{19}O_2{}^{79}Br$: 322.0568); FTIR (KBr): $\tilde{\nu}$ = 3381, 3065, 2976, 1585, 1571 cm^{-1}.

*2-[-3-(2-Chlorophenoxy)-4-methylethylidenecyclobut-1-enyl)]propan-2-ol (**18**)*: Yield: 48%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.41 (s, 3H; Me), 1.43 (s, 3H; Me), 1.82 (s, 3H; Me), 1.92 (s, 1H; OH), 1.96 (s, 3H; Me), 5.15 (s, 1H; H1), 6.47 (s, 1H; H2), 6.83–6.97 (m, 2H; Ar), 7.12–7.23 (m, 1H; Ar), 7.31–7.35 ppm (m, 1H; Ar); ^{13}C NMR (50.329 MHz, $CDCl_3$): δ = 162.2, 153.9, 132.8, 130.4, 129.9, 127.6, 123.6, 121.8, 120.4, 115.3, 76.9, 68.7, 28.4, 28.2, 21.1, 20.6 ppm; MS (EI): *m/z* calcd for $C_{16}H_{19}O_2{}^{35}Cl$: 278.1073; found: 278.1068; FTIR (KBr): $\tilde{\nu}$ = 3410, 3068, 2977, 1587, 1572 cm^{-1}.

*2-[-3-(4-Bromophenoxy)-4-methylethylidenecyclobut-1-enyl)]propan-2-ol (**19**)*: Yield: 32%; ^1H NMR (200.131 MHz, $CDCl_3$): δ = 1.46 (s, 3H; Me),

1.48 (s, 3H; Me), 1.81 (s, 3H; Me), 1.88 (s, 1H; OH), 2.01 (s, 3H; Me), 5.19 (s, 1H; H1), 6.51 (s, 1H; H2), 6.85 (d, $J=8.9$ Hz, 2H; Ar), 7.39 ppm (d, $J=8.8$ Hz, 2H; Ar); ^{13}C NMR (50.329 MHz, $CDCl_3$): $\delta=162.7$, 157.6, 133.2, 132.7, 130.3, 120.7, 117.7, 113.6, 76.1, 69.2, 28.8, 28.7, 21.4, 21.0 ppm; elemental analysis calcd (%) for $C_{16}H_{19}O_2Br$: C 59.20, H 6.38; found: C 59.70, H 6.25; FTIR (neat): $\tilde{\nu}=3336$, 2975, 1625, 1588 cm^{-1}.

2-[-3-(4-Methylphenoxy)-4-methylethylidenecyclobut-1-enyl)]propan-2-ol (***20***): Yield: 20%; ^{1}H NMR (200.131 MHz, $CDCl_3$): $\delta=1.36$ (s, 3H; Me), 1.41 (s, 3H; Me), 1.78 (s, 3H; Me), 1.86 (s, 1H; OH), 1.96 (s, 3H; Me), 2.26 (s, 3H; Me), 5.15 (s, 1H; H1), 6.51 (s, 1H; H2), 6.83 (d, $J=8.2$ Hz, 2H; Ar), 7.06 ppm (d, $J=8.2$ Hz, 2H; Ar); ^{13}C NMR (50.329 MHz, $CDCl_3$): $\delta=161.7$, 156.0, 133.2, 130.7, 130.2, 129.9, 119.9, 115.3, 75.6, 68.7, 28.4, 28.3, 28.2, 21.0, 20.5 ppm; MS (EI): m/z calcd for $C_{17}H_{22}O_3$: 258.1619; found: 258.1603; FTIR (KBr): $\tilde{\nu}=3436$, 3023, 2977, 1611, 1593 cm^{-1}.

Chloro{η^4-[1,2-di(1-hydroxycyclohexyl)cyclobutadienyl]}pentamethylcyclopentadienylruthenium (21): 1-Ethynylcyclohexanol (3.7 mmol, 460 mg, 5 equiv) was added to a solution of [RuCl(cod)(Cp*)] (0.74 mmol, 282 mg) in THF (10 mL) under a nitrogen atmosphere. After being stirred at room temperature for 2 h the solvent was removed under vacuum, the solid residue was washed with anhydrous diethyl ether (3×15 mL), and dried under vacuum. The complex **21** was obtained as a brown powder (350 mg). Yield: 90%; ^{1}H NMR (200.131 MHz, CD_2Cl_2): $\delta=$ 0.94–1.09 (m, 4H; cyclohexyl CH_2), 1.30–1.65 (m, 14H; cyclohexyl CH_2), 1.68 (s, 15H; C_5Me_5), 2.08–2.14 (m, 2H; cyclohexyl CH_2), 3.42 (s, 2H; =CH), 3.93 ppm (s, 2H; OH): ^{13}C NMR (50.329 MHz, CD_2Cl_2): $\delta=99.6$, 92.5, 69.8, 69.4, 42.2, 36.0, 25.8, 21.9, 21.7, 10.5 ppm; MS (FAB): m/z calcd for $C_{26}H_{39}O_2ClRu$: 520.1686; found: 520.1660; FTIR (nujol): $\tilde{\nu}=$ 3443, 3403, 3023, 2977, 1654 cm^{-1}.

Chloro[η^3-(1-cyclohex-1-enyl-2-cyclohexylidenecyclobutenyl)]pentamethylcyclopentadienylruthenium complexes (22a, 22b): Acid HX (HBF_4 or HPF_6 1.1 equiv) was added to a solution of complex **21** (1 mmol, 520 mg) in THF (20 mL) under a nitrogen atmosphere at −60 °C. The stirred reaction mixture was allowed to warm to room temperature and kept at this temperature for 3 h. The solvent was removed under vacuum, then the solid was washed with diethyl ether (3×15 mL) and dried under vacuum. For **22a** a solution of HBF_4 (155 mL; 60% w/w in diethyl ether) was used and **22a** was obtained as a dark red powder (510 mg). Yield: 90%; ^{1}H NMR (200.131 MHz, CD_2Cl_2): $\delta=1.46$–1.58 (m, 14H; cyclohexyl CH_2), 1.83–1.90 (m, 2H; cyclohexyl CH_2), 1.83 (s, 15H; C_5Me_5), 2.23–2.29 (m, 2H; cyclohexyl CH_2), 5.06 (s, 1H; =CH), 5.56 (s, 1H; =CH), 6.05 ppm (t, $J=3.8$ Hz, 1H; cyclohexenyl =CH); ^{13}C NMR (50.329 MHz, CD_2Cl_2): $\delta=149.1$, 140.2, 134.7, 128.9, 103.8, 93.5, 86.8, 77.6, 35.9, 33.9, 31.4, 28.8, 26.3, 25.6, 24.2, 21.8, 21.5, 10.6 ppm; elemental analysis calcd (%) for $C_{26}H_{36}RuClBF_4$: C 54.60, H 6.34, Cl 6.19; found: C 54.25, H 6.77, Cl 6.32; FTIR (nujol): $\tilde{\nu}=3095$, 1632, 1559, 1041 cm^{-1}.

For **22b** a solution of HPF_6 (175 mL, 60% w/w in water) was used and **22b** was obtained as a dark red powder (570 mg). Yield: 90%; ^{1}H NMR (200.131 MHz, CD_2Cl_2): $\delta=1.46$–1.59 (m, 14H; cyclohexyl CH_2), 1.83–1.90 (m, 2H; cyclohexyl CH_2), 1.82 (s, 15H; C_5Me_5), 2.24–2.30 (m, 2H; cyclohexyl CH_2), 4.89 (s, 1H; =CH), 5.48 (s, 1H; =CH), 6.06 ppm (t, $J=$ 3.8 Hz, 1H; cyclohexenyl =CH); ^{13}C NMR (50.329 MHz, CD_2Cl_2): $\delta=$ 149.3, 140.7, 135.3, 128.8, 103.8, 93.4, 86.3, 77.3, 35.4, 34.0, 31.5, 28.9, 26.3, 25.6, 24.2, 21.7, 21.4, 10.6 ppm; elemental analysis calcd (%) for $C_{26}H_{36}RuClPF_6$: C 49.57, H 5.76, Cl 5.63; found: C 49.23, H 5.50, Cl 6.27; FTIR (nujol): $\tilde{\nu}=3103$, 1630, 1561, 844 cm^{-1}. Microcrystals of complex **22b** were obtained in a dichloromethane/diethyl ether biphasic system.

3-Cyclohex-1-enyl-4-cyclohexylidenecyclobut-2-enyl acetate (23): $AcONEt_4$ (83 mg, 0.44 mmol, 1.13 equiv) was added to a solution of complex **22a** (220 mg, 0.34 mmol) in degassed THF (5 mL) under an inert atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 17 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent: pentane/diethyl ether) to give the cyclobutene **23** adduct as a viscous oil (38 mg). Yield: 41%; ^{1}H NMR (200.131 MHz, CD_2Cl_2): $\delta=1.40$–1.70 (m, 10H; cyclohexyl), 2.02 (s, 3H; Me), 2.04–2.15 (m, 6H; cyclohexyl), 2.25–2.27 (m, 2H; cyclohexyl CH_2), 5.71 (s, 1H; H1), 5.92 (m, 1H; cyclohexenyl =CH), 6.24 ppm (s, 1H; H2); ^{13}C NMR (50.329 MHz, CD_2Cl_2): $\delta=171.2$, 155.7, 131.1, 130.4, 129.4, 128.8, 127.2, 72.9, 30.8, 30.3, 27.8, 27.7, 26.4, 25.9, 25.3, 22.4, 21.9, 21.2 ppm; MS (EI): m/z calcd for $C_{18}H_{24}O_2$: 272.1776; found: 272.1726; FTIR (neat): $\tilde{\nu}=3052$, 2925, 1733, 1646, 1588 cm^{-1}.

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