JOC*Note*

Selective Dimerization of Arylalkynes to (*E*)-1,4-Diaryl Enynes Catalyzed by the [Ru(*p*-cymene)Cl_2]$_2$/Acetic Acid System under Phosphine-Free Conditions

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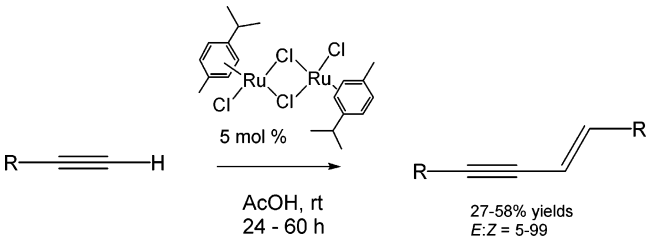
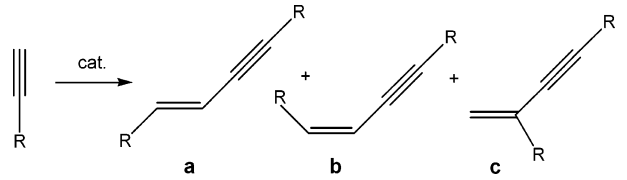


R = C_6H_5, 4-$NO_2C_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$, 3-FC_6H_4, 2-$MeOC_6H_4$, 2-$CF_3C_6H_4$, $C_{10}H_9Fe$

The commercially available di-μ-chlorobis[(*p*-cymene)chlororuthenium(II)] complex catalyzes the dimerization of aromatic alkynes in acetic acid at room temperature to form the corresponding (*E*)-1,4-diarylbut-1-ene-3-yne derivatives, with high stereoselectivity. The procedure does not require the use of additives and can be carried out in the presence of water or aprotic cosolvents, under homogeneous conditions.

The catalytic dimerization of terminal alkynes represents an attractive route for the preparation of 1,4-disubstituted enynes, which are versatile building blocks in organic synthesis.[1] These C-4 unsaturated moieties are key units in naturally occurring compounds,[2] and in organic materials,[3] especially when derived from aromatic alkynes. Due to competition among head to head coupling to give 1,4-disubstituted *E* and *Z* enynes (**a** or **b**, Scheme 1) or butatrienes, head to tail coupling yielding 2,4-disubstituted enynes (**c**), cyclotrimerization, or polymerization, there is an increasing demand for improving the efficiency and the selectivity of the dimerization process. Catalytic systems easily accessible and tolerant toward substituents and reaction conditions are also highly desirable for extending the application profile of this atom economical reaction in organic synthesis.

SCHEME 1. Products from Catalytic Dimerization of Terminal Alkynes



Active catalytic systems for this reaction are found in main group elements,[4] rare-earth,[5] or transition metal complexes.[6] Among these, palladium complexes afford predominantly 2,4-disubstituted enynes,[6a] while appropriate additives can shift the selectivity toward 1,4-disubstitution.[7] Rhodium complexes catalyze the dimerization of alkylalkynes,[8] but the reactions of arylalkynes require the presence of excess phosphine,[9a] of MeI,[9b] or of bulky diarylamino based PNP ligands.[9c] Ruthenium complexes are excellent catalysts, with preference for head to head coupling and *Z*-selectivity.[1a,b,10] Important breakthroughs are the *Z*-selective dimerization in aqueous media,[11] or the

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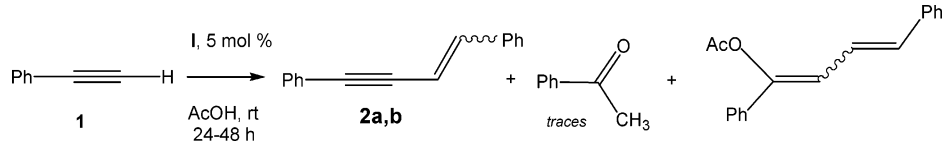
SCHEME 2. Reaction of Phenylacetylene in the Presence of Complex [Ru(*p*-cymene)Cl_2]$_2$ (I) in Acetic Acid



extension of the reaction to the cross-dimerization process between different alkynes.[4,6c,8c,12] However, *E*-selective dimerization by ruthenium catalysis has been achieved only in few cases and using homemade complexes, which are the expression of the synthetic organometallic expertise of various groups. In fact, 1,4-disubstituted but-1-ene-3-yne derivatives have been isolated as reaction products, with *E*-selectivity larger than 90%, only in the case of *t*-BuC≡CH,[10a] PhC≡CH,[10a,e,j,l] and HC≡CCO_2Me.[10g,i] High *E*-selectivity was observed by GC-MS for *t*-BuC≡CH[10k] and PhC≡CH.[10d]

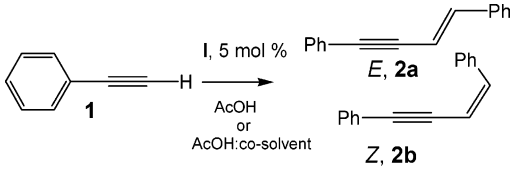
It is known from the literature that the ruthenium catalyzed dimerization can be further assisted by a proton donor, either phenylacetylene itself[13] or a carboxylic acid,[14] which promotes the formation of vinylidene species or the release of the enyne from a Ru-enynyl intermediate in the final σ bond metathesis step.[13,14,15] On these bases, we have carried out the reaction of different alkynes in acidic media. We report here on our findings that the commercially available [Ru(*p*-cymene)Cl_2]$_2$ (**I**) complex catalyzes the dimerization of aromatic alkynes, with excellent stereoselectivity toward formation of (*E*)-1,4-diarylbut-1-ene-3-yne compounds.

Treatment of phenylacetylene (**1**) in aqueous ethanol in the presence of complex **I** and excesses of various acids (CF_3CO_2H, $MeCO_2H$, *p*-toluenesulfonic; reflux, 24 h) gave only traces of the hydration product acetophenone. On the other hand, when a solution of PhC≡CH (0.45 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (0.023 mmol) in 5 mL of acetic acid/water (4:1, v:v) was warmed up to 50 °C, the GC analysis of the reaction mixture after 4 h showed some unreacted alkyne, *p*-cymene from the complex, clean formation of the dimeric products (*E*,*Z*)-1,4-diphenylbut-1-ene-3-yne (**2a**:**2b** = 23:1), and only traces of acetophenone. The reaction proceeded also at room temperature in neat acetic acid (**1**, 0.91 mmol, 0.18 M; **I**, 5 mol %), affording after 48 h 1,4-diphenylbut-1-ene-3-yne (**2a**:**2b** = 98:2 in the reaction mixture), which was isolated with excellent *E*/*Z* stereoselectivity (99.6%) after column chromatography in 45% yield. Further chromatographic elution yielded a complex mixture of products derived from solvent addition to dimeric species and related hydrated derivatives,[16] none of them in preparative useful quantities, which were identified by GC-MS analysis (Scheme 2).

A larger scale preparation was performed using 2.0 g of phenylacetylene in acetic acid:water (4:1), which afforded 1,4-diphenylbut-1-ene-3-yne in 36% of isolated yield (overnight, 80 °C). Several runs were performed using phenylacetylene as the model substrate and changing some reaction parameters, in the presence of an internal standard in order to evaluate the effective conversion into the products **2a** and **2b** by GC analysis (Table 1). The data indicate that although the consumption of PhC≡CH, at the same substrate to catalyst ratio (20:1), increases at either increasing substrate concentration (entries 1, 2, 4 and 10, 12) or reaction time (entries 2, 3; 4, 5; and 10, 11), the conversions of the alkyne into the dimeric products remain in the range of 38−57% yield. This may be due to the undesired processes becoming increasingly relevant in both cases. The change from [**1**] = 0.09 to 0.40 M is accompanied by a small decrease in *E*-stereoselectivity (entries 1, 4). The reaction carried out in the mixed aqueous medium shows a larger consumption of substrate at comparable times but affords a similar conversion into the enynes as that in neat acetic acid (entries 1, 6). The formation of the enyne as well as the stereoselectivity are reduced significantly upon increasing the temperature (entries 6−8), which evidently assists the undesired reactions to a large extent. Some experiments were performed using a different cosolvent instead of water, namely tetrahydrofuran or dichloromethane, without observing significant increases of the reaction yield. A procedure for the recycling of the catalytic system from the reactions in AcOH:H_2O is described in the Supporting Information.

Although water is compatible with the dimerization, the reaction performed in air does not afford the desired products. A change of the solution color from dark orange to green

TABLE 1. Product Analyses and Stereoselectivity of the Dimerization Reaction of Phenylacetylene (1),[a] Catalyzed by Complex [Ru(*p*-cymene)Cl_2]$_2$ (I), in AcOH or AcOH:Cosolvent



entry	[**1**]/M	solvent	temp/°C	time/h	**1**[b]	yield/%[c]	*E*/%
1	0.09	AcOH	rt	22	45	38	99.0
2	0.18	AcOH	rt	22	45	42	99.0
3	0.18	AcOH	rt	45	28	55	98.7
4	0.40	AcOH	rt	25	28	42	97.8
5	0.40	AcOH	rt	44	10	43	97.5
6[d]	0.09	AcOH:H_2O	rt	23	10	40	99.1
7[d]	0.09	AcOH:H_2O	50	24	3	22	96.7
8[d]	0.09	AcOH:H_2O	80	24	−	24	93.9
9[e]	0.18	AcOH:THF	rt	24	50	40	97.4
10[e]	0.18	AcOH:CH_2Cl_2	rt	24	32	55	98.3
11[e]	0.18	AcOH:CH_2Cl_2	rt	45	19	57	98.5
12[e]	1.0	AcOH:CH_2Cl_2	rt	22	13	46	97.1
13[e]	0.18	AcOH:CH_2Cl_2	40	16	10	62	97.0
14	0.18	CD_3CO_2D	rt	24	65[f]	9	97.5

[a] A total of 50−100 μL in 5 mL of solvent. [b] GC, relative % of **1** in the reaction mixture. [c] *E* + *Z* yields calculated using 1,2-diphenylethane as internal standard. [d] AcOH:H_2O (4:1). [e] AcOH:cosolvent (3:2). [f] Detected as PhC≡CD.

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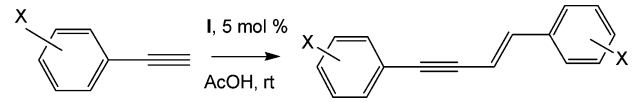
TABLE 2. Syntheses of 1,4-Diarylbut-1-ene-3-yne Compounds Catalyzed by Complex [Ru(*p*-cymene)Cl$_2$]$_2$ (I), in Acetic Acid at Room Temperature[a]



entry	X	time/h	product	yield/%[b]	*E*/%[c]
1	H, (**1**)	48	**2**	45	>99[d]
2	4-NO$_2$ (**3**)	48	**4**	58	98[e,f], 92[e,g]
3	4-Cl (**5**)	48	**6**	44	99[d]
4	3-F (**7**)	24	**8**	50	94[d]
5	4-MeO (**9**)	48	**10**	43	97[d,f], 87[d,g]
6	2-MeO (**11**)	60	**12**	54	83[d]
7	4-CF$_3$ (**13**)	24	**14**	32	98[d]
8	2-CF$_3$ (**15**)	40	**16**	~20[h]	95[d]

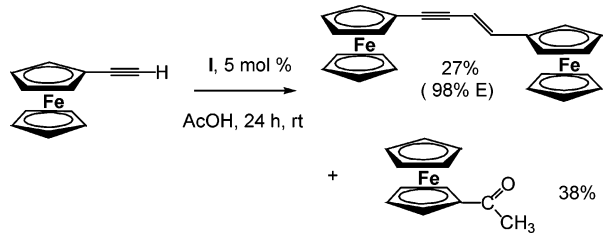
[a] Reactions performed on 100−400 mg scale of alkyne; [ArC≡CH] = 0.17−0.20 M; 5 mol % of **I**. [b] Isolated yields. [c] Over *E* + *Z*. [d] By GC or GC-MS from the peak areas of the *E* and *Z* isomers. [e] By ^{1}H NMR, from integration of the lower frequency olefinic doublets of the *E* and *Z* isomers. [f] The precipitate in the reaction mixture. [g] Extracted from the mother liquor. [h] In a mixture with the regioisomers of tris(2-trifluoromethylphenyl)benzene.

indicates degradation of the catalytic system. The method exhibits a remarkable medium selectivity. In fact, we observed only formation of acetophenone (54% yield) upon treatment of PhC≡CH with 5 mol % of **I** in trifluoroacetic acid (24 h, rt). The same hydration product and no enynes were observed in formic acid. Therefore, phenylacetylene can dimerize, while resisting the hydration process, through a catalytic species provided by acetic acid. This was also the solvent of choice in the original Straus reaction, performed upon heating copper(I) phenylacetylide in acetic acid under inert gas.[3a,6c] The phosphine-rich complex [RuCl$_2$(PPh$_3$)$_3$] does not promote either dimerization or hydration of phenylacetylene under the conditions of this work.

Trimethylsilylacetylene or 1-octyne in the presence of **I** does not exhibit any reactivity, either at rt or at 80 °C, except for traces of 2-octanone, indicating that the procedure is limited to aromatic alkynes. We extended the reaction to a series of ring substituted arylacetylenes and to ethynylferrocene. Table 2 lists the substrates, the yields, and the stereoselectivity of the isolated 1,4-diarylbut-1-ene-3-yne products. In the case of the 1-ethynyl-4-nitro-, -4-chloro-, and -4-methoxy-benzene derivatives, the products precipitated out of the reaction mixture, thus allowing an easy separation. The procedure is compatible with the presence of various substituents on the aryl ring and, in particular, of either strong electron-withdrawing or electron-donating groups. The *E*-stereoselectivity appears satisfactory (>97%) regardless of the electronic features of the group in the *para* position, although it is reduced slightly for substitution in *meta* and *ortho* (entries 4, 6, 8). In the case of the *ortho*-CF$_3$ derivative, the conversion into the dimers is poor and accompanied by consistent formation of the three isomers of alkyne cyclotrimerization, tris(2-CF$_3$C$_6$H$_4$)C$_6$H$_3$.

So far, the compatibility with ring substituents of largely different electronic properties, from NO$_2$ to OMe, was not observed in ruthenium catalysis but only in the case of rhodium[9] or lanthanide half-metallocene catalysts.[5b] When the triple bond is electron rich, as in the case of ethynylferrocene (**17**), (*E*)-1,4-diferrocenylbut-1-ene-3-yne (**18a**) is obtained with high stereoselectivity (98%) but in lower yields (27%) with respect to the arylic alkynes, due to consistent formation of acetylferrocene, isolated in 38% yield (Scheme 3).

SCHEME 3. Products from Competitive Dimerization and Hydration Reactions of Ethynylferrocene in the Presence of Complex I



The dimerization of **17** in the presence of dinuclear ruthenium complexes afforded selectively the *Z* isomer of 1,4-diferrocenylbut-1-ene-3-yne,[17] while an *E* and *Z* mixture in roughly equivalent amounts was obtained in the presence of Cp*Ru complexes.[18] The formal hydration of ethynylferrocene[19] and of other alkynes is known to occur in protic but not necessarily aqueous media, in the presence or absence of a metal catalyst under acidic conditions.[20]

The transformation of complex **I** into catalytic species presumably occurs by (*i*) solvolytic cleavage of the dimer with formation of HCl and of [RuCl(*p*-cymene)(κ^2-OAc)] and [Ru(*p*-cymene)(κ^1-OAc)(κ^2-OAc)] species,[21] which allow (*ii*) addition of the alkyne to ruthenium when the carboxylate groups are monodentate. Coordinative unsaturation around the metal center can also occur by release of the η^6-bound arene, as suggested by the presence of free *p*-cymene in the reaction mixture. (*iii*) The effective carbon−carbon bond-forming step involves either alkynyl/η^2-alkyne or *cis*-alkynyl/vinylidene species, the latter being most common in ruthenium catalysis.[1] A catalytic cycle for the dimerization promoted by complex **I** is postulated in a simplified version in Scheme 4. The lack of 2,4-disubstituted enynes **c**, which cannot form by vinylidene coupling, and the large *E*-selectivity suggest 1,2 migration of an alkynyl to a vinylidene group in the stereo-determining step (d).[1a] This is affected by the transoid or cisoid configuration of the arylvinylidene moiety with respect to the alkynyl, where the former arrangement can be favored in this system by the absence of bulky ligands, often present in the complexes giving high *Z*-stereoselectivity.[10b,d,h,m,11,13]

The fact that this catalytic dimerization does not proceed with aliphatic alkynes further supports the occurrence of a vinylidene species in the catalytic cycle, this moiety being favored by conjugation with the aryl group on the β-carbon. The lower yield of enyne in the reaction performed in deuterated acetic acid (Table 1, entry 14) suggests a kinetic isotopic effect due to hydrogen transfer in slow steps of either the initiation stage or the catalytic cycle, as anticipated from the literature information.

The low chemical selectivity of this process which yields hydration and butadiene derivatives as byproducts (Scheme 2)

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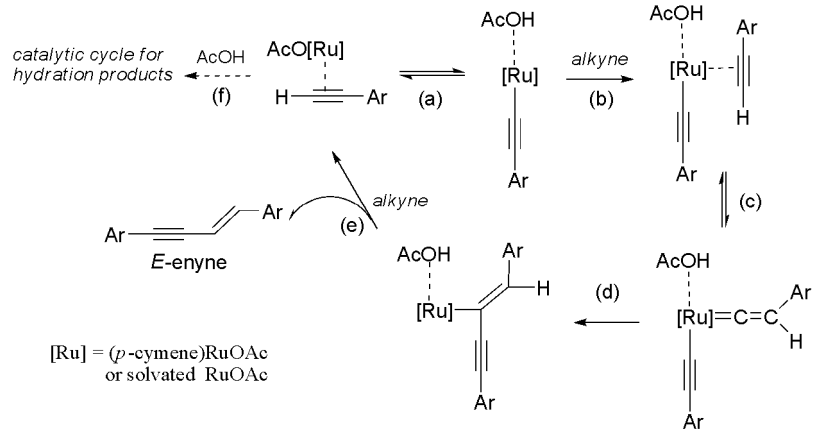
SCHEME 4. Catalytic Cycle for the Dimerization Reaction Catalyzed by Complex I



indicates the existence of different metal−organic species in solution producing competitive catalytic processes. In particular, the formal hydration of the triple bond arises from equilibria involving π-η^2-alkyne species (a and c).[1] In fact, the electron-rich triple bond of ethynylferrocene favors these η^2-adducts yielding larger amounts of the corresponding ketone. The formation of butadiene derivatives should arise from a 1−4 stepwise addition of acetic acid to a bis-carbene ruthenium species, in analogy to the case of the selective synthesis of functionalized butadienes catalyzed by [RuCl(COD)(C_5Me_5)].[16b] In the present work, these byproducts are formed in kinetic competition with the enynes, since the percent yield of **2a**,**b** remained constant upon checking the reaction mixture over several days.

Among the dimerization processes promoted by ruthenium catalysis, this is the first report in which the procedure employs a commercially available complex,[22] and under phosphine-free conditions, which are not common.[10h,i] Although the yields of the dimeric products are only moderate, the simplicity of the catalytic system/reaction conditions, the compatibility with aqueous media, and the excellent *E*-stereoselectivity may expand the synthetic applicability of the dimerization of terminal alkynes. High *E*-stereoselectivity, not previously observed in aqueous systems, is a relevant feature for organic conducting materials,[3c,10m] and studies along this perspective will be reported in due course.

Experimental Section

General Synthetic Procedure. The complex [Ru(*p*-cymene)-$Cl_2]_2$ (**I**, 55−60 mg) and the alkyne (1.7 − 1.8 mmol), when solid as for compounds **3**, **5**, and **17**, were weighed and introduced into a 100 mL Schlenk tube. After three vacuum/argon cycles, glacial acetic acid (10 mL) was added to the tube and the alkyne, when liquid, using a microsyringe. After additional vacuum/argon cycles, the solution was left stirring under argon atmosphere for the time indicated in Table 2 for each substrate. In the presence of a precipitate, this was separated by transferring the mother liquor via cannula, washed with mixtures of methanol−hexane, and then purified by column chromatography. The mother liquor including the washings, or the reaction solution in the absence of a precipitate, was poured into water/chloroform, and the water phase was extracted twice with chloroform. The collected organic phases were washed until neutrality and dried over sodium sulfate. The residue was then purified by column chromatography.

(*E*)-1,4-Di-*m*-fluorophenylbut-1-ene-3-yne (8a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−6.95 (m, 9H), 6.35 (d, J = 16.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (d, J_{CF} = 245 Hz), 162.4 (d, J_{CF} = 246 Hz), 140.5, 138.4 (d, J_{CF} = 7 Hz), 130.1 (d, J_{CF} = 24 Hz), 130.0 (d, J_{CF} = 24 Hz), 127.4 (d, J_{CF} = 4 Hz), 125.0, 122.3 (d, J_{CF} = 4 Hz), 118.2 (d, J_{CF} = 23 Hz), 115.6 (d, J_{CF} = 21 Hz), 115.4 (d, J_{CF} = 21 Hz), 112.7 (d, J_{CF} = 23 Hz), 109.1, 91.2 (d, J_{CF} = 3 Hz), 89.3. FT-IR (dichloromethane): 2198, 1939, 1861, 1702, 1582, 1486, 1447. GC-MS (*m*/*z*): 240 (6.3%, *Z*), 240, 220, 144, 119 (93.7%, *E*). Anal. Calcd. for $C_{16}H_{10}F_2$: C, 79.99; H, 4.20. Found: C, 79.78; H, 4.25.

(*E*)-1,4-Diferrocenylbut-1-ene-3-yne (18a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (d, J = 15.9 Hz, 1H), 5.84 (d, J = 15.9 Hz, 1H), 4.42 (vt, J = 1.8 Hz, 2H) 4.37 (vt, J = 1.8 Hz, 2H) 4.27 (vt, J = 1.8 Hz, 2H), 4.22 (s, 5H), 4.20 (vt, J = 1.8 Hz, 2H), 4.14 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 105.9, 89.0, 85.4, 71.1, 70.0, 68.8, 67.0, 66.1. FT-IR (dichloromethane): 3100, 3031, 2195, 1612, 1411, 1106, 1043, 1027, 1003, 937 cm^{-1}; (mineral oil): 948, 817, 722 cm^{-1}. Anal. Calcd. for $C_{24}H_{20}Fe_2$: C, 68.62; H, 4.80. Found: C, 68.19; H, 5.16.

Supporting Information Available: General experimental section, procedure for recycling of the catalytic system, full experimental procedures, and characterization data of the dimerization products, including GC-MS, FT-IR, and charts of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) The dimerization of phenylacetylene has been reported to occur after thermolysis (110 °C) of either first- or second-generation Grubbs catalysts.[14]