DOI: 10.1002/adsc.201000347

One-Pot Desilylation/Dimerization of Terminal Alkynes by Ruthenium and Acid-Promoted (RAP) Catalysis

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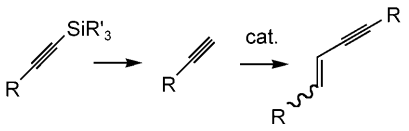
Received: May 4, 2010; Revised: August 24, 2010; Published online: October 12, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000347.

Abstract: The dimerization of terminal arylalkynes promoted by the (*p*-cymene)ruthenium dichloride dimer/acetic acid system {[$RuCl_2$(*p*-cymene)]$_2$/AcOH} can be performed starting from the trimethylsilylethynyl derivatives (12 substrates), deprotected *in situ*, to afford 1,4-disubstituted 1-en-3-ynes with high regio- and (*E*)-stereoselectivity, at room temperature. The extension of this unprecedented two-reaction sequence to a diyne substrate affords a fluorene-based conjugated oligomer. The reaction mixture resulting from the desylilation-dimerization process dimerizes additional aliquots of phenylacetylene. The one-pot protocol results in shorter reaction times due to the presence of acetate salts which increase the concentration of active catalytic species, in which the acetate ligand acts as base toward the bound alkyne. The ruthenium source is transformed into a new trihapto-hexa-1,3-dien-5-yn-3-yl complex, formed by metal-assisted coupling of the enyne product and the terminal alkyne, and still maintaining catalytic activity. Selectivity, endurance, medium and functional group compatibility are the key features of the catalytic system obtained from the *p*-cymene ruthenium dimer under the one-pot conditions.

Keywords: alkyne dimerization; C–C coupling; enynes; polyaddition; ruthenium catalysts

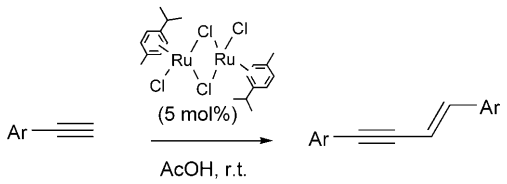
The catalytic dimerization of terminal alkynes is in principle a useful atom-economic methodology for the synthesis of 1,4-disubstituted enynes *via* C(*sp*)–C(sp^2) bond formation.[1] Conjugated 1-en-3-ynes are of particular interest as the grouping occurs in natural products[2] as well as in materials with optoelectronic properties.[1b,3] Notwithstanding the improvements in the optimization of the reaction chemio-/regio-/stereoselectivity, otherwise a major concern, and of catalyst performance,[1,4] the application profile of this process in organic synthesis remains limited.[1,3] With respect to the catalyst, significant restrictions are represented by the need for the transition metal complexes with the desired selectivity to be prepared *ad hoc*, often requiring multistep organometallic syntheses,[1b,4] and by the poor tolerance toward substrate polar groups and moisture in the reaction medium.[5] With regard to the organic substrate, the higher stability of trialkylsilyl-protected ethynyl derivatives with respect to the corresponding free alkynes would imply significant advantages in using the former as starting materials. In fact, the use of the terminal alkyne generated *in situ* can avoid the separation procedures and any implicit handling or stability concerns. Most of all, synthetic ethynyl substrates are most conveniently accessed by Sonogashira-type reactions between trialkylsilylacetylene and aromatic halides,[1b,6] the terminal triple bond being then liberated by removal of the trialkylsilyl group [Eq. (1)].



(1)

While there are no reports regarding the use of this approach in the synthesis of enynes from terminal alkynes, the *in situ* desilylation/oxidative coupling of trialkylsilylacetylenes yielding symmetrically and unsymmetrically substituted 1,3-diynes is a known procedure, successfully employed in the construction of conjugated polyyne materials.[7]

We reported recently that a catalytic system composed of the commercially available ruthenium com-



Scheme 1. Dimerization of arylalkynes catalyzed by **I**/AcOH.

plex $[RuCl_2(p\text{-cymene})]_2$ (**I**) and acetic acid promotes the dimerization of arylalkynes and affords 1,4-diaryl-1-buten-3-ynes with high (*E*)-stereoselectivity under mild reaction conditions (Scheme 1).[8]

The catalytic species is formed upon interactions of the three components: complex, acetic acid and alkyne. This methodology was then extended to diynic starting materials, thus affording phenylene-ethynylene-vinylene oligomers and polymers *via* a stepwise polyaddition process.[9]

We describe here that the two-reaction sequence involving (i) the deprotection of $ArC{\equiv}CSiMe_3$ substrates and *ii*) the C–C bond forming step promoted by the **I**/AcOH system can be performed consecutively in the same reaction flask.

In the model substrate $PhC{\equiv}CSiMe_3$, silyl deprotection was performed using the common procedure based on aqueous NaOH (5 M) in MeOH/THF (method A):[10] a reaction time of 30 min at room temperature ensured complete conversion into phenylacetylene (**1**). Without further manipulation, a solution of complex **I** in acetic acid was then added into the Schlenk tube, and the dimerization process allowed to proceed under argon. The yield of the enyne product 1,4-diphenyl-1-buten-3-yne (**1a**, 60%, *E*:*Z*, 99:1, determined by ^{1}H NMR and GC) after 6 h was higher than that observed from the catalytic dimerization of **1** in neat AcOH after 45 h (55%).[8] This one-pot protocol was then tested employing *n*-Bu_4NF/AcOH (1 equiv.) in THF (method B),[11,12] as alternative to the desilylation step by NaOH. The same results (within error limits) were obtained regarding yield and stereoselectivity of **1a**. The use of the fluoride source avoids the aqueous highly basic medium which can be incompatible with some functional groups such as nitriles or aldehydes. These results showed the compatibility of the **I**/AcOH catalytic system with the medium and by-products resulting from the desilylation step in either a basic or acidic medium as well as an unexpected higher activity under the one-pot conditions.

In order to assess the functional group compatibility and to expand the scope of the dimerization reaction catalyzed by **I**/AcOH, the one-pot protocols were extended to a new set of various aromatic 1-alkynes. The results are summarized in Table 1. While 3,5-$(MeO)_2C_6H_4C{\equiv}CH$ was consumed within 7 h (entries 1 and 2), substrates bearing *ortho* or electron-withdrawing groups were allowed to react for 24 h. The steric hindrance of a methyl group in the *ortho* position (entry 3) or the coordinating ability of the nitrile moiety toward ruthenium did not inhibit the catalytic activity of the system (entry 6). 4-Ethynylbenzaldehyde was converted selectively into the (*E*)-enyne dimer (entry 7), while only the (*Z*)-isomer is otherwise accessible by ruthenium catalysis.[5a] The dimerization of the protic salicylaldehyde ethynyl derivative afforded a bifunctional aromatic enyne potentially useful for the coordination of transition metal ions (entry 8).

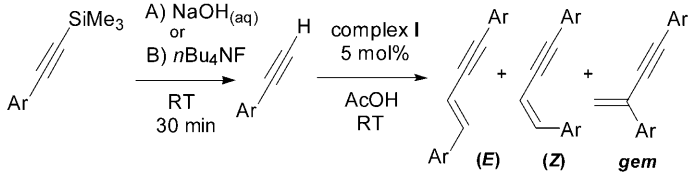
Polycyclic derivatives gave decreased yields of enyne products and progressive loss of selectivity (entries 9 and 10), the *gem* isomer becoming favoured upon increased congestion at the reaction center in the anthracene derivative. However, the reactions of 2- and 3-(trimethylsilylethynyl)thiophene were characterized by competitive cyclotrimerization and dimerization processes (entries 11 and 12).

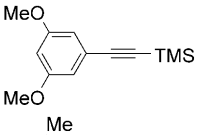
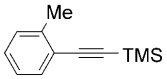
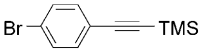
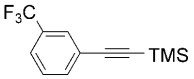
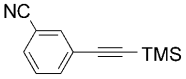
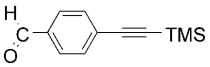
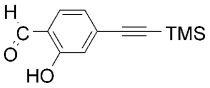
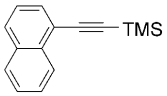
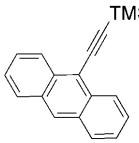
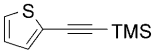
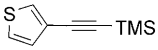
The extension of the one-pot protocol to the diyne **2** afforded the corresponding fluorene-(*E*)-enyne oligomer (**2a**, Scheme 2),[9b] as the first example of a polyaddition process performed on a trialkylsilyl-protected substrate.[1b,3b] Isolated as wholly soluble material in 55% yield, **2a** is characterized by a number-averaged molecular weight (M_n) of 2100 g mol^{-1} with a polydispersity index (M_w/M_n) of 1.8 (M_w = weight-averaged molecular weight), as determined by gel permeation chromatography, and by an average number of repeat units (n_{AV}) of 5.3, as determined by ^{1}H NMR spectroscopy. Due to the interest in using easily handled bis-ethynylsilanes under simplified procedures for the synthesis of conjugated polymers,[13] this finding opens the way to further developments.

Following the one-pot desylilation-dimerization of $PhC{\equiv}CSiMe_3$, the reaction mixture remained catalytically active. Sequential additions of $PhC{\equiv}CH$ were converted in each run into **1a** by the initial catalyst load, as shown in Table 2. The GC analysis of the reaction mixture performed after 46 h of overall reaction time showed 15 mol% of residual alkyne and 76 mol% conversion into the enyne (run 5). This corresponds to the conversion of 3.5 mmol of $PhC{\equiv}CH$ catalyzed by 1 mol% of the dinuclear ruthenium precatalyst **I** (or 2 mol% of a mononuclear ruthenium species), with a turnover number (TON) of 73. The residual alkyne was further converted into the enyne (run 5′). These sequential transformations of **1** show the robustness of the catalytic system $[RuCl_2(p\text{-cymene})]_2$/AcOH under the one-pot conditions.

Due to the moderate yields of dimers, we extended further the product analysis, and details are given here for the reaction of 1-trifluoromethyl-3-trimethylsilylethynylbenzene (entry 5 in Table 1). Following the separation of the desired enyne from the chroma-

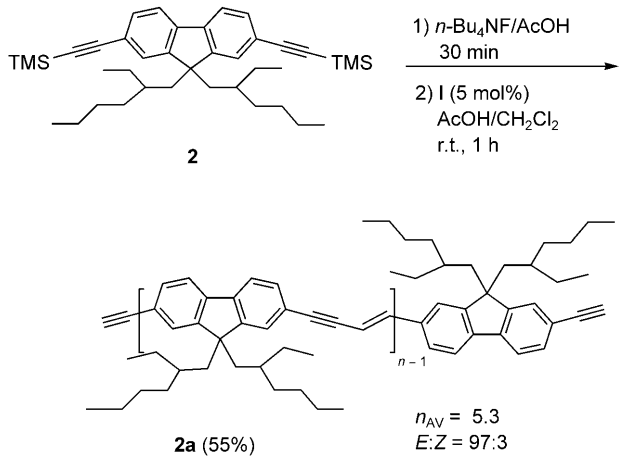
Table 1. One-pot desilylation/dimerization of aromatic 1-alkynes.



Entry	Substrate[a]	Step 1[b]	Time [h][c]	Yield[d] [%]	*E*:*Z*:*gem*[e]
1		A	7	48	99:1:0
2		B	7	47	90:10:0
3		A	24	47	96:4:0
4		A	24	69	99:0:0
5		A	24	35	84:16:0
6		B	6	42	99:1:0
7		B	24	47	96:4:0
8		B[f]	24	51	99:0:0
9		A	24	25	92:8:0
10		A	24	29	29:23:47
11		B	6	64[g]	81:19:0
12		A	6	67[h]	98:2:0

[a] 1.0–1.7 mmol (entry 8: 2.75 mmol).
[b] Method of desilylation.
[c] Step 2: reaction time after addition of **I** dissolved in AcOH.
[d] Isolated yields.
[e] Determined by ^{1}H NMR.
[f] 3 h.
[g] Combined yields of dimerization and cyclotrimerization products (22% of enynes).
[h] Combined yields of dimerization and cyclotrimerization products (57% of enynes).

tographic column in hexane, a dark red solid was then eluted using increasing portions of acetone. The ^{1}H NMR spectrum of this material showed the well defined signals of ruthenium-coordinated *p*-cymene, in the range 5.8–4.7 ppm, and a multiplet of 3-$CF_3C_6H_4$- moieties in the aromatic region, in the relative ratio 1:3 (*p*-cymene/$CF_3C_6H_4$). The signals at lower frequencies of the *p*-cymene ring were superimposed by the doublets (5.16 and 4.67 ppm, J = 11.1 Hz) of two *trans* protons of a η^3-allylic moiety.[4h] The ^{13}C NMR spectrum exhibited a signal at 181.8 ppm, due to a vinylic =C–Ru carbon atom, whereas the presence of an unbound triple bond was observed as a band at 2202 cm^{-1} in the infrared spectrum. These data are consistent with the structure of a η^3-hexa-1,3-dien-5-yn-3-yl complex in which the or-



Scheme 2. One-pot synthesis of oligo-fluorene-ethynylene-vinylene **2a**.

Table 2. Series of catalytic cycles performed by $[RuCl_2(p\text{-cymene})]_2$ under the one-pot conditions, upon sequential additions of phenylacetylene (**1**).[a]

Run	Alkyne	Time [h][b]	**1** [mmol][c]	Conversion [mmol][d]
1	PhC≡CSiMe$_3$	4	0.03	0.72
2[e]	PhC≡CH	4	0.10	1.81
3[e]	PhC≡CH	15	0.18	2.31
4[e]	PhC≡CH	5	0.47	2.70
5[e]	PhC≡CH	18	0.69	3.50
5′	–	8	0.57	3.63

[a] *Reaction conditions in run 1*: 1) PhC≡CSiMe$_3$ (0.95 mmol), TBAF (1.0 mmol) in THF (1.05 mL), AcOH (45 μL), bibenzyl (0.10 mmol), 30 min; 2) **I** (0.048 mmol), AcOH (5 mL).
[b] Reaction time of each cycle.
[c] Residual **1**.
[d] mmol of **1** (overall) converted into **1a**, on the basis of GC-analysis with reference to bibenzyl as internal standard.
[e] **1** (100 μL, 0.91 mmol).

ganic ligand arises by the coupling of three molecules of alkyne. The ESI-TOF mass spectrum, with a cluster of peaks centered at $m/z = 803.1$ ($[M+Na]^+$) and a most intense one at $m/z = 745.2$ ($[M-Cl]^+$) establishes the molecular formula {Ru(η^6-*p*-cymene)Cl[η^3-ArCHCHC=C(Ar)C≡CAr]} (**3**, Ar = 3-$CF_3C_6H_4$) of this new ruthenium complex. The isolated amount of **3** accounts for 51 mol% of the ruthenium source and for 15 mol% of the terminal alkyne. Complex **3** was observed by ^{1}H NMR in the crude reaction mixture, so that it did not form upon chromatography. A similar hexadienylyne complex with η^3-allyl coordination was isolated and fully characterized in the course of the dimerization of phenylacetylene catalyzed by the vinylidene complex [Ru(η^5-C_5Me_5)Cl(PPh_3)(=C=CHPh)] in the presence of Et_3N.[4h] Compound **3** is still a dimerization catalyst, converting phenylacetylene into the enyne **1a** (70%) after 24 h in acetic acid (at room temperature). Red complexes with similar spectroscopic features were isolated from the reactions of other substrates in Table 1, and their characterization will be reported in due course.

The dimerization processes proceed in the presence of tetrabutylammonium or sodium acetate, which form as the by-product of the desilylation by the fluoride source (method B), or upon addition of **I**/AcOH (method A), respectively. In attempts to rationalize the observed faster conversion of the free alkynes with respect to the reactions catalyzed by complex **I** in neat acetic acid,[8] the reactivity of PhC≡CH was checked upon addition of equimolar NaOAc, in order to simulate the one-pot conditions, other factors such as the precise medium composition remaining different. The rates of consumption of the alkyne **1** and formation of the enyne (*E*)-**1a**, as followed by ^{1}H NMR in the presence or absence of NaOAc, are shown in the plot of Figure 1. The first order analysis of the disappearance of **1** yields half-life ($t_{1/2}$) values of 394 and 44 min for the reactions in the absence or presence of the acetate salt, respectively. A higher rate of formation of **1a** was also observed in the presence of *n*-Bu_4NOAc (see the Supporting Information). In addition, there is no evidence for a slow activation stage, which is otherwise apparent in the early stages of the reaction without added acetate.

These results highlight the dramatic effect of the acetate anion as a promoter of the catalytic activity. More detailed kinetic and mechanistic studies will allow us to distinguish the contributions of specific

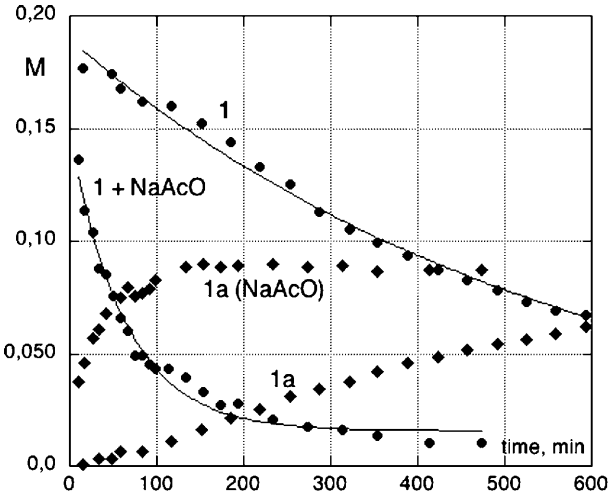
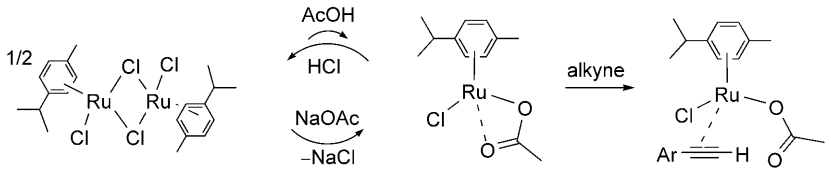
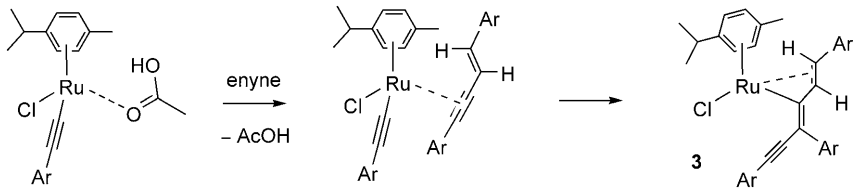


Figure 1. Time evolution of PhC≡CH (**1**, circles, 10 μL, 0.178 M) and of (*E*)-PhCH=CH–C≡CPh (**1a**, squares) in the reactions catalyzed by complex **I** (2.4 mg, 7.8 mM, 4.3%), in the absence or presence of NaOAc (8 mg, 0.19 M) in CD_3CO_2H (0.50 mL), at 29.1 °C. The solid lines represent the fitting with the first-order rate equation.



Scheme 3. Proposed activation stage in RAP catalysis.



Scheme 4. Proposed formation of complex **3** (Ar = 3-$CF_3C_6H_4$).

counteranions and of generic polarity effects. However, it can be anticipated that the reaction of phenylacetylene did not give any evidence of improved reactivity in a saturated solution of *n*-Bu_4NPF_6. To explain the catalytic behaviour of the **I**/AcOH system, taking into account the role of acetic acid, we previously proposed an initiation stage involving release of HCl from complex **I** and formation of monomeric [RuCl(*p*-cymene)(OAc)] or [Ru(*p*-cymene)$(OAc)_2$]. Such complexes, in particular the chloride species, are known to form under mild conditions from the ruthenium dimeric precursor in polar protic solvents.[14] Fast exchange between bidentate (18-e) and monodentate (16-e) acetato species allows then the coordination of the alkyne and the onset of the catalytic cycle.[9a] As depicted in Scheme 3, the new observations support this hypothesis: excess sodium acetate provides a higher concentration of the active species, thus enhancing the overall catalytic performance. The bound acetate can act as intramolecular base toward the π-alkyne and generate AcOH and an arylacetylide derivative. Substitution by the second alkyne molecule, most likely rapid π-alkyne-vinylidene tautomerization, and subsequent C–C bond formation *via* acetylide-vinylidene coupling, afford a σ-enynyl species, from which the organic enyne is then liberated by protonation.[1b,8]

The same acetylide species involved in the catalytic cycle accounts for the formation of the hexa-1,3-dien-5-yn-3-yl complex **3**, generated by alkyne insertion into the ruthenium acetylide bond (Scheme 4).

The role of the acetate ligand in base-assisted proton abstraction finds various analogies in the literature, in particular in the case of the activation of sp^2-C–H bonds by oxygenated anions, a phenomenon which is gaining increasing recognition and interest in organometallic catalysis.[15] To the best of our knowledge, this work reports the first case of activation of terminal alkynes by bound acetate.

In summary, 1,4-diarylsubstituted enynes with diverse functional groups can be obtained under mild conditions from silane substrates. The catalytic system resulting from $[RuCl_2(p\text{-cymene})]_2$/AcOH, active at room temperature and (*E*)-stereoselective, tolerates aqueous reagents, the by-products of the deprotection step, and polar/protic substituents in the aryl ring. The RAP procedure, based on readily available starting materials and simple experimental protocols, can therefore be regarded as a promising and practical tool for the synthesis of *E*-enyne systems.

Experimental Section

General Procedures of Desilylation/Dimerization

To a stirring solution of the aromatic trimethylsilylethynyl substrate in THF (1 equiv., 0.7 M), an equal volume of a methanolic mixture of aqueous NaOH (1.25 equiv., 5 M) was added dropwise (method A). Alternatively, the substrate, acetic acid (1 equiv.) and tetrabutylammonium fluoride (1.1 equiv.) in THF (1 M) were introduced into a Schlenk tube (method B). The mixture was then stirred at room temperature for 30 min. Unless stated otherwise (see Table 1), the GC analysis of a sample withdrawn from the reaction mixture showed quantitative transformation into the corresponding terminal alkyne, under the conditions of both methods A and B. Acetic acid and $[RuCl_2(p\text{-cymene})]_2$ (5 mol%) into separate Schlenk tubes were degassed by argon/vacuum cycles. Then, (i) acetic acid (2.5 mL per mmol of substrate) and (ii) a solution of **I** in acetic acid (3.1 mL per mmol of substrate) were transferred in sequence into the reaction tube *via* cannula. The solution was stirred at room temperature and the reaction progress was followed by means of GC and GC-MS analyses. Unless stated otherwise, the reaction was interrupted when the conversion of the terminal alkyne was estimated to be over 90%. The reaction mixture was poored into dichloromethane, and extracted with water and aqueous $NaHCO_3$. The organic layers were dried over sodium sulfate, then filtered and

evaporated to dryness. The crude mixtures were then purified by column chromatography (silica/hexanes or silica/hexanes/CH_2Cl_2). See the Supporting Information for details on each synthesis.

Supporting Information

Experimental procedures and characterization data of the enyne products and of complex **3**, with figures of ^1H and ^{13}C NMR spectra, plot for the reaction of **1** in the presence of *n*-Bu_4NOAc, synthesis and fluorescence spectra of **2a** are given in the Supporting Information.

Acknowledgements

The authors are grateful to Dr. Silvia Bartocci for the synthesis of 4-(trimethylsilylethynyl)salicylaldehyde. The invitation of the reviewers to describe the catalytic activity in additional cycles and the fate of the ruthenium catalyst is greatly appreciated.

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