



New protocol for one-pot synthesis of functionalized symmetrical 1,4-dialkyl- or 1,4-diaryl-1,3-diynes

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ABSTRACT

A new versatile one-pot protocol for preparation of functionalized 1,4-disubstituted-1,3-diynes via a highly selective catalytic silylative coupling of vinylsilanes and terminal alkynes occurring via [Ru] catalyzed reaction and/or [Ir] catalyzed reaction of iodosilanes with alkynes followed by desilylative homocoupling sequence is presented. Contrary to existing stoichiometric systems, the catalytic conditions for the copper salt mediated homocoupling of trimethylsilylalkyne were elaborated that are very tolerant to various functional groups.

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Introduction

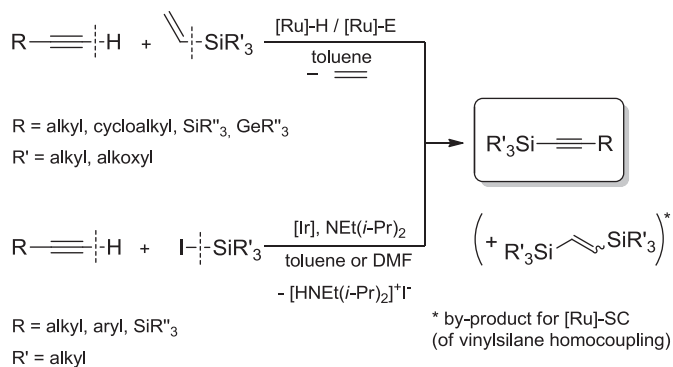
Conjugated 1,4-disubstituted-1,3-diynes are one of recurring building blocks in chemistry, biology and material science as they are key functional groups in preparation of organic compounds [1], natural products [2], pharmaceuticals [3], inorganic/organic composites [4], π -conjugated polymers [5] as well as in molecular recognition processes [6]. Traditionally, 1,3-diynes have been prepared from homocoupling of terminal alkynes which was pioneered by Glaser in 1869 [7], and nowadays, Cu-salt mediated Glaser coupling and related modified methods (e.g. Eglinton coupling, Hay coupling, etc.) [8] are still widely applied in the synthesis of conjugated diynes. The formation of alkynyl copper species and its subsequent oxidative dimerization are proposed in these reactions. In recent years, a number of efficient and convenient methodologies, such as the combination of a palladium catalyst and copper salts or silver oxide have been reported [9]. Attempts have been made with using other transition metals, such as nickel or cobalt in addition with copper salts for the homocoupling of terminal alkynes [10]. In addition to the transition metal

mediated synthesis of 1,3-diynes the “transition-metal-free-Glaser-type coupling” has been also reported [11]. However, this method suffers from the drawbacks of narrow substrate diversity, the alkyne or the coupling reagent often needs to be prefunctionalized and the multistep syntheses can pose additional barriers to their use. A major disadvantage was the required presence of stoichiometric amounts of copper salts or even higher excess of reagents, e.g. KI (Jiang's protocol) [11a,12]. There is much interest in developing methods for direct application of alkynylsilanes as coupling agents. There is also need for new methods that would involve friendly catalytic systems to create 1,3-diynes especially exploiting one-pot procedures that have been rare in the literature on these compounds [13]. These new procedures would be valuable tools not only rising overall efficiency of the reaction, but also preferred from economical and technological points of view. To the best of our knowledge, there is no report of one-pot or sequential reaction for the synthesis of the aforementioned compounds from terminal alkynes and vinylsilanes or iodosilanes.

On the basis of our experience in the field of organosilicon chemistry, we have reported two separate methods for the preparation of organofunctionalized alkynylsilanes via silylative cross-coupling (SC) reactions of selected terminal alkynes in the presence of ruthenium and iridium complexes. The first procedure involves coupling of terminal alkynes with various vinylsilanes catalyzed by complexes containing [Ru]-H and/or [Ru]-Si bonds ([Ru]-SC, i.e. ruthenium catalyzed silylative coupling) [14]. The

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Scheme 1. Ruthenium and iridium catalyzed silylative coupling of terminal alkynes with vinyl- and iodo-substituted organosilicon compounds.

second process occurs between various terminal alkynes and iodosilanes proceeding in the presence of iridium complex ([Ir]-SC, i.e. iridium catalyzed silylative coupling) [15]. The advantage of the iridium catalyzed reaction is the application of both – alkyl and aryl terminal mono- and dialkynes leading to the formation of mono- and bis-silyl-functionalized alkynyl derivatives. Both processes are presented in [Scheme 1](#).

The mechanisms of the above processes are different. The reaction catalyzed by Ru complexes proceeds *via* insertion of vinylsilane into Ru–H bond and β -Si transfer to the metal with elimination of ethylene to generate Ru–Si species, followed by insertion of terminal alkyne and β -H transfer to the metal with elimination of the substituted alkynylsilane ([Scheme 2a](#)) [14a]. The reaction catalyzed by Ir complex proceeds *via* oxidative addition of terminal alkyne into the iridium center, followed by the reaction with NEt(*i*-Pr)₂ with elimination of iodoammonium salt ([HNEt(*i*-Pr)₂]⁺I[−]) and subsequent second oxidative addition, i.e. addition of iodotrimethylsilane and elimination of the substituted alkynylsilane (stoichiometric reactions and information about the ‘real’ catalyst is to be found in Kownacki et al. paper) ([Scheme 2b](#)) [15a].

The silylative coupling of olefins with vinylsilanes, in combination with subsequent desilylation reactions *via* one-pot and sequential procedures appears to be a valuable step to provide functionalized unsaturated organic compounds such as (*E*)- β -aryl vinyl halides [16], (*E*)- β -silyl- α,β -unsaturated ketones [17] as well

as unsaturated molecular and macromolecular functionalized arenes [18]. On the other hand, copper salt mediated homocoupling of silylalkynes proceeds in selective manner to afford 1,4-disubstituted-1,3-diynes [19]. Mori and co-workers developed an efficient aerobic synthesis of symmetrical 1,3-diynes from (trimethyl)silyl alkynes with a stoichiometric amount of CuCl [12]. A polar solvent (DMF) is supposed to coordinate to alkynylsilane to form a pentacoordinate species, prone to transmetalation to the corresponding copper derivative.

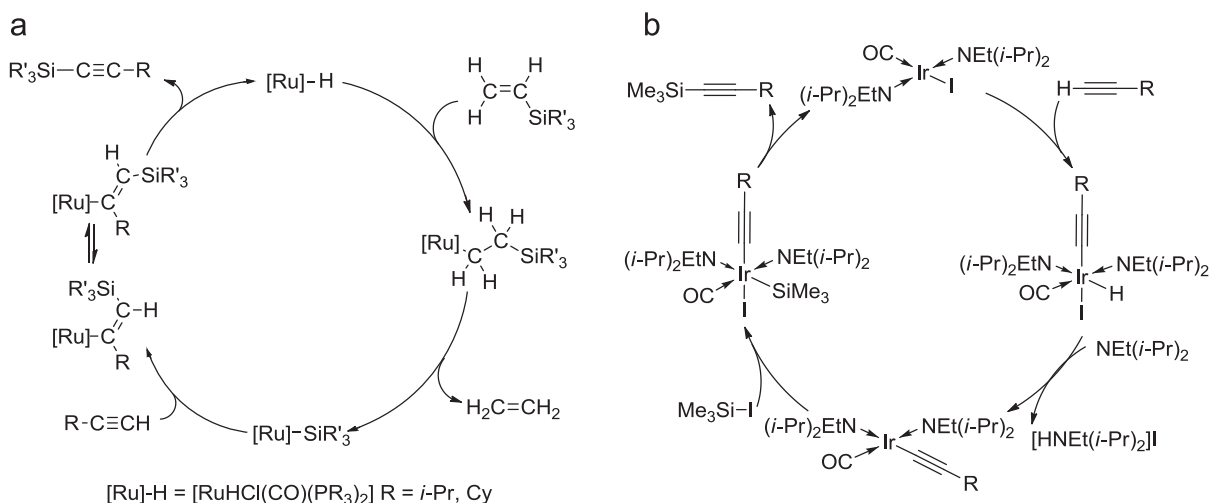
Experimental

General methods and chemicals

All synthesis and manipulations were carried out under argon using standard Schlenk-line and vacuum techniques. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on Varian XL 300 MHz, Bruker Avance 400 MHz and 500 MHz spectrometers in CDCl₃. Chemical shifts are reported in ppm with reference to the residual solvent (CHCl₃) peak for ¹H and ¹³C and to TMS for ²⁹Si. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 400CX instrument with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra were obtained by GC–MS analysis (Varian Saturn 2100T instrument, equipped with a BD-5 capillary column (30 m) and an ion trap detector). Elemental analyses were carried out on a Vario EL III instrument. The chemicals were obtained from the following sources: IrCl₃ × 3H₂O, RuCl₃ × 3H₂O from Pressure Chemicals; cod, PCy₃, CDCl₃, DMF, THF, decane, NEt(*i*-Pr)₂, Me₃SiI, 2-methoxyethanol, ethanol, diethyl ether, n-hexane, toluene from Aldrich; CO from Linde Gas. The column chromatography was performed with silica gel 60 (70–230 mesh; Fluka). The complexes {[Ir(μ -Cl)(CO)₂]₂} [20] and [RuHCl(CO)(PCy₃)₂] [21] were synthesized according to the published methods. All solvents and liquid reagents were dried and distilled under argon prior to use.

General procedure for synthesis of 1,4-disubstituted-1,3-diynes

For [Ru]-SC reaction of alkyl terminal alkynes, e.g. 1-octyne (385.7 mg, 3.5 mmol), trimethylvinylsilane (1.05 g, 10.5 mmol) and of RuHCl(CO)(PCy₃)₂ (50.8 mg, 0.07 mmol) catalyst were dissolved in toluene (7 mL, 0.5 M concentration) and heated in a



Scheme 2. (a). Mechanism of [Ru] – catalyzed silylative coupling of terminal alkynes with R'₃SiCH=CH₂, (b). Mechanism of [Ir] – catalyzed silylative coupling of terminal alkynes with Me₃SiI.

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