A new and efficient route for the synthesis of alkynyl functionalized silicon derivatives

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ABSTRACT

The iridium-based catalytic system, $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]/NEt(i\text{-}Pr)_2$, was examined in the coupling reaction of iodotrisubstituted silanes (R_3SiI) with various terminal arylalkynes ($R^1C\equiv CH$). Under optimum conditions, the process occurs very efficiently (in particular for Me_3SiI and Me_2PhSiI), giving exclusively the respective C_{sp}-silyl functionalized alkynes ($R^1C\equiv CSiR_3$). Additionally, this iridium-based catalytic system was successfully used for the preparation of selected bis(phenylethynyl) disubstituted silanes $[R^2{}_2Si(C\equiv CPh)_2]$ via coupling of phenylacetylene with appropriate diiodo-disubstituted silanes ($R^2{}_2SiI_2$).

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Silyl-functionalized alkynes and diynes play important roles as building blocks in many synthetic transformations. They are common and important precursors for the synthesis of organic and natural products,[1] as well as conjugated oligomers and polymers for the construction of electronic or optoelectronic materials containing a linear carbon–carbon triple bond in their structure, liquid crystals, non-linear materials, molecular wires, and other engineering materials.[2] The known methods for the synthesis of substituted silylalkynes can be divided into two groups of stoichiometric and catalytic reactions. The former comprises protocols which are based on deprotonation of terminal alkynes with strong bases such as n-butyllithium or Grignard reagents, and subsequent treatment of the formed organometallic species of the type $MC\equiv CR^1$ (M = Li, MgX, where X = Cl, Br) with various chlorosilanes ($SiCl_nR_{4-n}$),[3] alkoxysilanes,[4] or even aminosilanes.[5] An organosilyl function may also be introduced with the use of lithium triorganosilylacetylides ($Li^{+-}C\equiv CSiR_3$) by reactions with appropriate ketones, leading to functionalized substituted silylalkynes.[6]

However, presently, synthetic methods based on catalytic transformations are much more common than the classical protocols for the synthesis of such derivatives, and they can be divided into two groups, depending on the strategy applied. The first comprises methods that rely on metal derivative mediated silylation of sp-carbon atom terminal alkynes with various silylating agents, and includes zinc salt catalyzed reactions with employment of aminosilanes,[7a] chlorosilanes,[7b] Me_3SiOTf^{7c} (OTf = $-O_3SCF_3$) or tri-substituted silanes (R_3SiH),[7d] as well as transition metal catalyzed processes such as terminal alkyne dehydrogenative silylation with hydrosilanes,[8] ruthenium-promoted coupling with chlorosilanes,[9] vinylsilanes,[10] palladium-catalyzed coupling with Me_3SiCF_3,[11] or Me_3SiOTf.[12] The second group comprises methods that are based on the incorporation of the whole silylethynyl moiety via palladium-promoted Sonogashira cross-coupling reaction of various silylalkynes ($R_3SiC\equiv CH$),[13] triorganosilylacetylides $[M(C\equiv CSiR_3)_n]$, where M = MgX, n = 1; In, n = 3, ZnCl, n = 1[14] with halogeno functionalized organic compounds or similar nickel-catalyzed reactions.[15]

Our group has also contributed to the development of new catalytic methods for the synthesis of silyl-functionalized terminal alkynes. Since 2006, a series of papers has been published, devoted to the synthesis of silylalkynes via the ruthenium-catalyzed coupling of terminal aliphatic or silyl alkynes ($RC\equiv CH$) with various vinylsilanes ($R'_3SiCH = CH_2$).[10] We have also reported a new and efficient catalytic route for the silylation of terminal alkynes/diynes by Me_3SiI, promoted by an iridium(I) carbonyl precursor in the presence of a tertiary amine.[16,17]
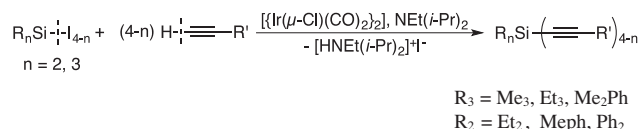
This Letter is a continuation of our earlier research. Here we present the results of our studies in this field, focused on the synthesis of a wide range of silylated terminal alkynes with employment of an iridium-based catalytic system. To demonstrate the powerful synthetic potential of the discovered catalytic method, we extended the portfolio of terminal alkynes, which can be transformed efficiently into silyl derivatives. Additionally, we present the results of a preliminary study on the application of an iridium

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catalytic system for the efficient synthesis of bis(arylethynyl-ene)silanes via coupling of terminal alkynes with exemplary gem-inal diiodo-disubstituted silanes.[16]

Employing the most efficient iridium catalytic system, reported in a previous paper,[17] that is [{Ir(μ-Cl)(CO)$_2$}$_2$]/NEt(i-Pr)$_2$, a series of trial coupling experiments using terminal arylalkynes with se-lected iodo-trisubstituted and diiodo-disubstituted silanes were performed.[16] Under the optimized conditions the coupling process occurred smoothly and led to the formation of the desired silyla-tion products in high yields, according to the following scheme:
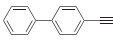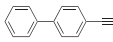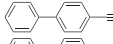
$$R_nSi\text{-}I_{4-n} + (4\text{-}n)\ H\text{—}\equiv\text{—}R' \xrightarrow[\text{- [HNEt}(i\text{-Pr})_2]^+I^-]{[\{Ir(\mu\text{-Cl})(CO)_2\}_2],\ NEt(i\text{-Pr})_2} R_nSi(\text{—}\equiv\text{—}R')_{4-n}$$
$$n = 2, 3$$

$$R_3 = Me_3, Et_3, Me_2Ph$$
$$R_2 = Et_2,\ Meph,\ Ph_2$$
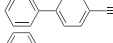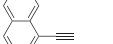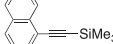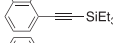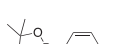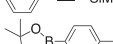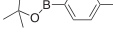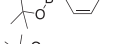
The results compiled in Table 1 show that the iridium(I) pre-catalyst successfully catalyzed the silylation of terminal alkynes with differ-ent trisubstituted iodosilanes. Under the optimum conditions (see Table 1, footnote a) and irrespective of the alkyne applied, the cou-pling occurred efficiently for Me$_3$SiI and Me$_2$PhSiI particularly, giv-ing the respective C$_{sp}$-silyl-functionalized alkynes, exclusively (entries 2, 3, 5, 6, 8, 9, 11 and 12). Lower yields of the products were observed when Et$_3$SiI was used as the silylation agent.

It is presumably an effect of the steric hindrance, resulting from the presence of three ethyl groups at the silicon atom, which signif-icantly hampers the activation of the ≡Si—I bond by the iridium center, and which is also an important process in the proposed catalytic cycle[17] of this coupling reaction.

Considering the results shown in Table 1, the developed method seems to be general and can be utilized efficiently for the silylation of various terminal alkynes, and not only non-functionalized examples. The examples presented in Table 1 show that iridium-

Table 1
Coupling of various terminal alkynes with trisubstituted iodosilanes[a]

Entry	R$_3$	Alkyne	Product	Yield[b] (%)
1	Et$_3$	Ph—≡	Ph—≡—SiEt$_3$	70
2	Me$_2$Ph		Ph—≡—SiMe$_2$Ph	100 (98)
3	Me$_3$		—≡—SiMe$_3$	100 (96)
4	Et$_3$		—≡—SiEt$_3$	75
5	Me$_2$Ph		—≡—SiMe$_2$Ph	98
6	Me$_3$		—≡—SiMe$_3$	100 (97)
7	Et$_3$		—≡—SiEt$_3$	73
8	Me$_2$Ph		—≡—SiMe$_2$Ph	99
9	Me$_3$		—≡—SiMe$_3$	99 (96)
10	Et$_3$		—≡—SiEt$_3$	69
11	Me$_2$Ph		—≡—SiMe$_2$Ph	98
12	Me$_3$		—≡	99 (96)
13			—≡—SiMe$_3$	98 (92)

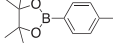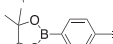[a] Reaction conditions: [alkyne]: [R$_3$SiI]: [NEt(i-Pr)$_2$]: [Ir] = 1: 1.6: 1.8: 10^{-2}, 80 °C, argon, 24 h. Conversion and yield were determined by GC analysis and calculated using the solvent as a standard.
[b] Yield of isolated product in parentheses.

Table 2
Coupling of selected diiodo-disubstituted silanes with phenylacetylene[a]

Entry	R$_2$	Product	Yield[b] (%)
1	Et$_3$	Ph—≡—Si(Et)(Et)—≡—Ph	99
2	Me$_2$Ph	Ph—≡—Si(Ph)(Me)—≡—Ph	99 (96)
3	Ph$_2$	Ph—≡—Si(Ph)(Ph)—≡—Ph	99 (95)[c]

[a] Reaction conditions: [alkyne]: [R$_2$SiI$_2$]: [NEt(i-Pr)$_2$]: [Ir] = 2.6: 1: 2.8: 2 × 10^{-2}, 90 °C, argon, 48 h. Conversion and yield were determined by GC analysis and cal-culated using the solvent as a standard.
[b] Yield of isolated product in parentheses.
[c] Reaction at 100 °C.

promoted silylative coupling can be successfully used for the preparation of a wide range of terminal alkyne silyl derivatives, even those containing reactive functional groups such as —B(OCMe$_2$CMe$_2$O), —N(SiMe$_3$)$_2$ (entries 9–13) in their structures.[16]

In the case of the H$_2$N-functionalized alkyne (entry 13), it was also possible to prepare the final product via a 'one-pot' protocol, where both non-catalytic N-silylation and catalytic C-silylation processes occurred.[16]

In order to demonstrate the synthetic potential of this reaction, the iridium-based catalytic system was also successfully used for the preparation of selected bis(alkynyl)disubstituted silanes via coupling of phenylacetylene (as a model reagent) with appropriate diiodo-disubstituted silanes (see Table 2, entries 1–3). Generally, for diiodosilanes used as reagents, under the optimum reaction condi-tions (see Table 2, footnote a), the complete transformation of the initial dihalosilanes, and almost quantitative formation of bis(phen-ylethynylene)disubstituted silicon derivatives were observed after 48 hours. The high activity of the iridium-based catalytic system in the coupling of diiodosilanes (R$_2$SiI$_2$) with phenylacetylene clearly illustrates the high potential of this reaction, not only in the synthesis of various molecular bis(arylethynyl)silanes, but also ethynylene-silylene or arylene-ethynylene-silylene oligomers, if in-stead of terminal alkynes, organic or silicon diethynyl derivatives are used. Several silyl-functionalized alkynes and bis(phenylethyn-ylene) disubstituted silicon derivatives were isolated and character-ized by spectroscopic methods (see Supplementary data), to show the scope of this new and efficient catalytic reaction.

In conclusion, we have presented the application of a novel, iridium-promoted silylative coupling of terminal alkynes with iodosilanes (ISiR$_3$) for the synthesis of various arylethynylene functionalized silicon derivatives. The iridium-based catalytic system, [{Ir(μ-Cl)(CO)$_2$}$_2$]/NEt^{i}Pr$_2$, under optimum conditions, catalyzed efficiently the transformation of a wide range of various terminal alkynes, even those containing reactive functional groups such as —NH$_2$, —B(OCMe$_2$CMe$_2$O), to give the desired silylated product. Various (arylethynyl)trisubstituted silanes were isolated and characterized by spectroscopic methods. Moreover, we found that the iridium catalytic system could be used in the double alkynylation of diiodosilanes. Using reaction conditions similar to those employed for the reactions with monoiodosilanes, bis(pheny-lethynylene)silanes were yielded almost quantitatively. Selected compounds were also isolated and characterized by spectroscopic methods.

General procedure

A glass Schlenk reactor (10 mL) equipped with a magnetic stir bar was evacuated and flushed with argon. The calculated amount of [{Ir(μ-Cl)(CO)$_2$}$_2$] complex (0.005 or 0.0025 mmol) was placed in the reactor under the flow of argon, then 3 mL of solvent and amine

(1.8 mmol) were added. The obtained mixture was stirred for about 10 min. In the next step, the terminal alkyne (1 mmol) and R$_3$SiI (1.6 mmol) were added, and the reaction was conducted at the given temperature. The mixture was analyzed by GC and GC/MS at the beginning and after 24 or 48 h. The conversions and yields were calculated using the internal standard calculation method.

Acknowledgment

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.11.103.

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