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Iridium complex catalyzed germylative coupling reaction between alkynes and iodogermanes – a new route to alkynylgermanium and alkynylgermasilicon compounds†

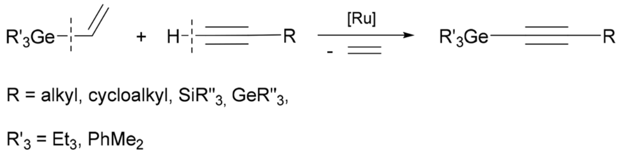
Monika Rzonsowska,[a] Ireneusz Kownacki,[a] Beata Dudziec[a] and Bogdan Marciniec*[a,b]

The new reaction of terminal alkynes with iodogermanes proceeding in the presence of an Ir^I-complex $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$ (**I**) and $NEt(^iPr)_2$, as a hydrogen iodide acceptor, leads to the formation of functionalized alkynylgermanes. This reaction occurs *via* direct activation of the C_{sp}–H bond in the starting alkyne. Detailed stoichiometric experiments using $[Ir(cod)(CCPh)(PCy_3)]$ (**IVa**) and iodogermane were performed and resulted in a proposal of a reasonable mechanism for the germylative coupling reaction between alkynes and iodogermanes.

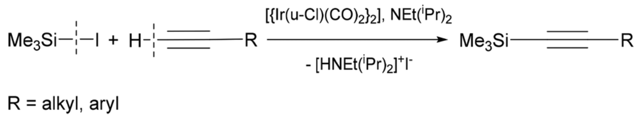
Introduction

The unique properties of unsaturated organogermanes make them an interesting group of compounds. Due to their low toxicity, organogermanes can be used as reagents in organic syntheses, where they can substitute toxic organotin compounds, *i.e.* in the formation of a wide range of molecular and macromolecular organic compounds of complex structure and interesting physicochemical properties.[1] Germanium-based compounds possessing π-conjugated systems (along with their respective silicon compounds) are also considered to be potential candidates for electronic devices as a result of their photo- and electroluminescent properties,[1,2] while the discovery of their biological activities has enabled their application, *e.g.* in anticancer therapy, and hypotensive and immunomodulating medicines.[3]

The literature offers some examples of syntheses of ethynyl- or alkynylgermanes. The methods of their syntheses can be divided into two groups. The first includes classical stoichiometric reactions with organometallic reagents, *i.e.* organogermanium halides with metal acetylides or germylation of terminal alkynes,[4] or redistribution reactions using tin reagents.[5] Catalytic routes to alkynylgermane synthesis are very limited. Recently, we have reported a method for the preparation of alkynylgermanes *via* germylative cross-coupling of selected terminal alkynes with various vinylgermanes catalyzed by complexes containing [Ru]–H and/or [Ru]–Si bonds and occurring according to the following equation (Scheme 1).[6]



Scheme 1 Ruthenium-catalyzed germylative coupling of terminal alkynes with vinyl-substituted organogermane compounds.



Scheme 2 Iridium catalyzed coupling of terminal alkynes with iodotrimethylsilane (Me_3SiI).

Unfortunately, the germylation of phenylacetylene with vinylgermane does not occur due to the competitive dimerization of phenylacetylene under catalytic conditions. In this process, vinylgermane compounds function as germylating agents and hydrogen acceptors.[7] A process of great practical significance is the reaction of the silylation of terminal alkynes with iodosilanes catalyzed by iridium complexes, which has also been developed by our group (Scheme 2).[8]

In this study, this method is applied for the synthesis of new and well-known organogermanium compounds.

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[a] *Faculty of Chemistry, Department of Organometallic Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, Poznan 61-614, Poland. E-mail: Bogdan.Marciniec@amu.edu.pl*

[b] *Center for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, Poznań 61-614, Poland*

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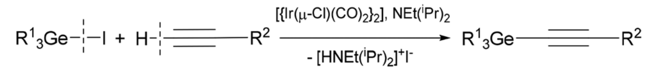


Scheme 3 Coupling of terminal alkynes with iodogermanes (R^1_3GeI).

Results and discussion

The coupling of terminal alkynes with iodotrimethylgermanes in the presence of an iridium(I) chlorocarbonyl complex $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$ (**I**) and $NEt(^iPr)_2$ as a hydrogen iodide acceptor leads to the formation of alkynyl-substituted germanes (Scheme 3).[9]

The optimization of reaction conditions was performed successfully for the model reaction, *i.e.* germylation of phenylacetylene with Me_3GeI. Several parameters were tested, *e.g.* first of all, the type of solvent (toluene, DMF, THF), which showed that the highest conversion of alkyne was achieved in toluene (98%) and an unacceptably low conversion in THF and DMF. Other factors affecting the yield of alkynylgermane included the amount of catalyst, temperature and the type of base. A small loading of (**I**), *i.e.* $<1 \times 10^{-2}$, and low temperature (lower than 80 °C) require the reaction time of 48 hours for complete phenylacetylene consumption. However, a temperature increase to 110 °C results in a drop in the yield of the targeted product due to side dimerization and trimerization of the initial alkyne. We also speculate that the iridium species (**IV**) (see Scheme 6) is thermally unstable. Further tests performed for model amines, *e.g.* $NEt(^iPr)_2$ (98% phenylacetylene conversion), NEt_3 (78%), $C_5H_{11}N$ (40%), and C_5H_5N (0%), proved that less hindered amines efficiently blocked the catalytic activity of the initial iridium complex and the best choice was $NEt(^iPr)_2$. The steric and electronic effect of the R^1 substituent at iodogermane was also tested. Several attempts for application of *n*-Bu and Ph germanium derivatives revealed their lower activity resulting in longer reaction time, *i.e.* 48 h, to obtain very good product yield.

The application of the $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$ (**I**) catalyst for the germylative coupling of selected terminal alkynes, *i.e.* alkyl, cycloalkyl, aryl and silyl, and germylethynes with R^1_3GeI, under the optimum conditions enables the respective alkynylsilanes to be generated as exclusive products (see the data presented in Table 1).

The reaction was successfully performed under an argon atmosphere (Schlenk flask) in a closed system, in toluene at 80 °C. Most of the new alkynylgermane derivatives were isolated and fully characterized by spectroscopic methods (GC-MS, ^1H, ^{13}C NMR, HRMS (see ESI†)). The proposed procedure appears to be universal, as it can be used for both non-functionalized and functionalized alkynes. The iridium catalyst (**I**) seems to be resistant to terminal alkynes with initial functional groups, *e.g.* –OH, and no preliminary germylation of alcohol is observed (in contrast to the results of the analogous silylation[8]).

The available literature presents a scheme for the mechanism of iridium-catalyzed silylative coupling of terminal alkynes with iodosilanes, which proposes as an initial step the generation of the hexacoordinate Ir^{III} (**IIIa**) complex *via* oxidative addition of terminal alkyne into the tetracoordinate Ir^I precursor (**II**) (Scheme 4).[8] The structure of complex **IIIa** was solved by X-ray analysis (for R = $Si(i\text{-}Pr)_3$ and NR'_3 = pyridine) providing direct evidence of the activation of the C_{sp}–H by the Ir^I carbonyl complex. The spatial configuration of the ligand attached to the iridium center assumed the elimination of the respective amine hydrochlorides (dehydrohalogenation occurring in the presence of amines is a well-known process[10]) and formation of iridium complex **IV**.

In view of these mechanistic observations for silylative coupling, detailed studies were performed to determine the mechanism of the germylative coupling of terminal alkynes with iodogermane involving oxidative addition/reductive elimination or σ-bond metathesis. For further stoichiometric investigations, the tetracoordinate Ir^I complex $[Ir(cod)(CCPh)(PCy_3)]$ (**IVa**) was chosen, as previously used in a study of oxidative addition by Oro *et al.*[11] Detailed stoichiometric experiments using **IVa** and iodogermane were performed with ^1H, ^{13}C, ^{31}P NMR and GC-MS monitoring – the results are presented below.

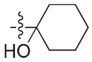
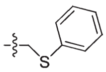
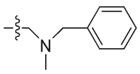
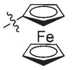
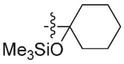
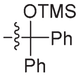
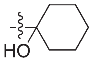
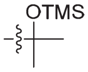
The synthesized and isolated tetracoordinate Ir^I complex (**IVa**) was fully characterized by NMR spectroscopy. There is only one singlet at 19.54 ppm in the ^{31}P NMR spectrum, coming from coordinated tricyclohexylphosphine. The ^{13}C NMR spectrum reveals a specific resonance line at 67.30 ppm assigned to $=CH$ of the cyclooctadiene coordinated to the Ir^I square planar coordination area. Two doublets assigned to the triple bond of the phenylethynyl moiety are present at 126.41 ppm for $-CC$-Ph with a coupling constant $^2J_{C-P}$ = 13.6 Hz and 83.25 ppm for $-CC$-Ph with a coupling constant $^3J_{C-P}$ = 12.7 Hz. There are also five additional signals assigned to the phenyl group: 131.21, 129.85, 128.39, 125.18, 121.63. The ^1H NMR spectrum reveals groups of signals corresponding to the phenyl ring (7.68 ppm (dd), 7.16 ppm (tr), 6.97 ppm (dd)), two multiplets at 5.27 ppm and 3.76 ppm assigned to the $=CH$ of the coordinated cyclooctadiene and 2.44–1.10 ppm of the cyclohexyl substituent on phosphorus. Direct addition of iodogermane to complex **IVa** was performed in benzene-d_6 in a J. Young NMR tube (Scheme 5).

The system was maintained at room temperature for 12 hours and then the reaction temperature was increased to 45 °C for a further 24 hours. After each change in the process conditions, a series of NMR analyses were carried out.

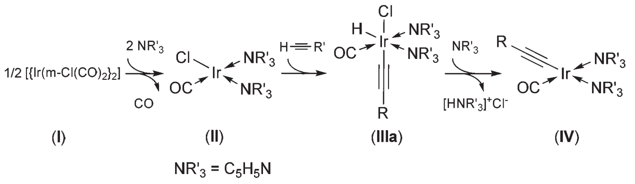
After 12 hours at room temperature, the ^{31}P NMR spectrum revealed (besides the peak at 19.55 ppm assigned to the tetracoordinate Ir^I complex (**IVa**)) an additional resonance line at 14.69 ppm coming from a new coordinative species, probably hexacoordinate Ir^{III} complex (**Va**), *i.e.* a product of the oxidative addition of iodogermane to **IVa** (Fig. 1 ESI†). The ^{13}C NMR analysis also disclosed changes in the resonance lines assigned to the carbon-containing ligands, confirming a new coordination sphere, *i.e.* formation of **Va**. A new resonance line assigned to $=CH$ cyclooctadiene coordinated to the Ir^{III} octahedral coordination area appeared at 53.9 ppm. There are

Table 1 Iridium(I)-catalyzed germylation of terminal alkynes[a]

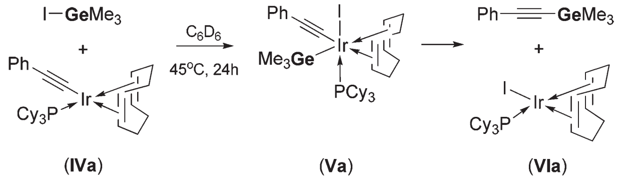
$$R^1_3Ge{-}I \;+\; {\equiv}{-}R^2 \xrightarrow[\text{toluene}]{\text{cat. [Ir], NEt(}^i\text{Pr)}_2} R^1_3Ge{-}{\equiv}{-}R^2$$

Entry	R^1	R^2	Isolated yield [%]	Entry	R^1	R^2	Isolated yield [%]
1	$-CH_3$	–Ph	94	12	$-CH_3$		97
2		$-CH_2CH_2Ph$	92	13		$-Si(^iPr)_3$	93
3			79^b	14		$-Ge(^iPr)_3$	34
4			65^b	15	$-n\text{-}C_4H_9$	–Ph	99^b
5			80^b	16		$-CH_2CH_2Ph$	97^b
6		$-n\text{-}C_6H_{13}$	95	17		$-SiEt_3$	99^b
7		$-SiMe_2Ph$	95	18		$-SiMe_2Ph$	90^b
8			96	19		$-n\text{-}C_6H_{13}$	95^b
9			65^b	20			70^b
10			65	21	Ph	$-SiEt_3$	76^b
11			93				

[a] Reaction conditions: [Ir] : [alkyne] : [R^1_3GeI] : [base] = 10^{-2} : 1 : 1.2 : 1.8, 24 h, 80 °C. [b] 48 h, closed system.



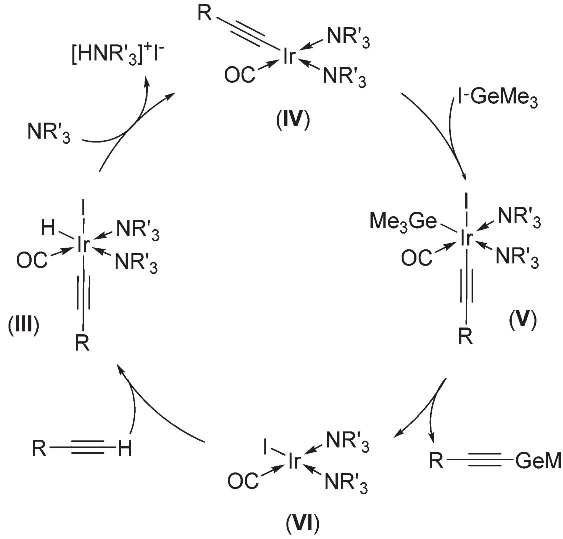
Scheme 4 Activation of the $_{sp}$C–H bond in terminal alkynes.



Scheme 5 Stoichiometric reaction of **IVa** with iodotrimethylgermane with respective products (observed in NMR and GC-MS spectra).

also new, additional doublets for the triple bond of the phenylethynyl moiety at 128.65 ppm for –*C*C-Ph with a coupling constant $^2J_{C-P}$ = 29.4 Hz and 88.01 ppm for –C*C*-Ph with a coupling constant $^3J_{C-P}$ = 13.1 Hz, which is consistent with a position adjacent (*cis*) to the trimethylgermyl group (Fig. 2 see ESI,† p. S-28).

Also, the ^{1}H NMR data confirm the appearance of a new coordinative species of Ir^{III}. There are additional resonance lines assigned to the phenyl ring at 7.50 ppm (m), 7.14 ppm (m), 6.95 ppm (m) as well as three multiplets at 5.58 ppm, 5.44 ppm and 3.28 ppm assigned to the =CH of coordinated cyclooctadiene in a new hexacoordinate Ir^{III} complex (**Va**) (Fig. 3 – see ESI,† p. S-29). After heating at 45 °C for an additional 24 hours, the changes in the ^{31}P, ^{13}C and ^{1}H spectra become even more intense. The resonance lines coming from complex **IVa** are less intense, in contrast to the strong signals from the hexacoordinate Ir^{III} complex (**Va**). There are also new resonance lines in the ^{13}C NMR spectrum at 105.42 ppm and 96.12 ppm that can be assigned to trimethyl(phenylethynyl)germane, *i.e.* the product of the reductive elimination from complex **Va**. The GC-MS analysis of the resulting reaction



Scheme 6 Mechanism of the germylative coupling of terminal alkynes with iodogermane.

mixture verifies this observation and simultaneously suggests the formation of a new tetracoordinate Ir^I complex (**VIa**) (Scheme 5).

Detailed stoichiometric studies were also performed for the $[Ir(CO)_2(CCPh)(PCy_3)]$ complex and similar results were obtained.[12] However, this complex seemed to exhibit higher reactivity. The presence of the hexacoordinate Ir^{III} complex (produced *via* oxidative addition of iodogermane) was much less visible (less intense resonance lines in the NMR spectra) due to a rapid, consecutive reductive elimination of the product, *i.e.* trimethyl(phenylethynyl)germane (GS-MS detection). This result may suggest further application of the complex as an effective catalyst in germylative coupling reactions.

The results of the above experiments allow us to propose a reasonable mechanism for the germylative coupling of terminal alkynes with iodogermanes proceeding in the presence of the active species **IV** (Scheme 6).

Identification of complexes **IVa**, **Va** and **VIa** enabled the proposal of the respective intermediates **IV**, **V** and **VI** in this catalytic mechanism. Germylative coupling of terminal alkynes with iodogermanes involves the oxidative addition of iodogermane to tetracoordinate complex **IV** (generated analogously to a documented reaction path for silylative coupling – see Scheme 4) followed by reductive elimination of the product, *i.e.* trimethyl(alkynyl)germane. The next step is the known process of consecutive oxidative addition of terminal alkyne to **VI**, generating hexacoordinate species **III**, undergoing reductive elimination, recovering **IV** and closing the whole catalytic cycle.

Experimental

General methods

All synthesis and manipulations were carried out under an argon atmosphere using regular Schlenk techniques. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Ultra Shield spectrometer (600 MHz) and a Varian Mercury spectrometer (300 HMz), and Bruker Avance II (400 MHz) and Bruker Avance III (500 MHz) spectrometers in benzene-d_6 and $CDCl_3$. High resolution mass spectra (HRMS) were obtained by electron impact ionization (EI) using an AMD Intectra Mass AMD 402 instrument. Some of the products gave significant fragmentation which made them difficult to analyze by the HRMS method. For a few of them HRMS analysis was impossible to perform or have been obtained for fragmented ions. The chemicals were purchased from the following sources: $IrCl_3 \times 33H_2O$ from Pressure Chemicals; cod, C_6D_6, $CDCl_3$, toluene from Sigma Aldrich; Me_3GeI, $NEt(^iPr)_2$ from ABCR; CO from Linde Gas. The complex $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$,[13] Bu_3GeI and Ph_3GeI,[14] ethynyltriisopropylgermane,[15] (1-trimethylsiloxycyclohexyl)ethyne[16] were synthesized according to published methods. All solvents and liquid reagents were purchased from commercial sources, dried and distilled under an argon atmosphere prior to use (in case of iodogermanes, they were additionally kept at 4–8 °C).

General synthetic procedure for germylative coupling of terminal alkynes

The glass Schlenk reactor equipped with a magnetic stirring bar was evacuated and flushed with argon. A given amount of the complex $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$ was placed in the reactor under a flow of argon; then toluene and a precise amount of $NEt(^iPr)_2$ were added. The mixture was then stirred for 10 min. Next, appropriate amounts of terminal alkyne and $R^1{}_3GeI$ were added. The reaction was conducted in a closed system at 80 °C upon stirring for 24 hours (or 48 hours). After the reaction was complete, toluene and any excess of other reagents were removed under reduced pressure. The crude product was isolated by purification using column chromatography (SiO_2) with hexane as an eluent.

Stoichiometric reaction of complex IVa with iodotrimethylgermane

An amount of **IV** (0.073 g, 11 mmol) was introduced into an NMR tube along with 0.6 mL benzene-d6 at room temperature under a dry argon atmosphere. Iodotrimethylgermane (0.031–0.034 g, 13–14 mmol) was added. The reaction was carried out at room temperature for 12 h with NMR detection; after that, it was continued for an additional 24 h at 45 °C, followed by subsequent NMR analysis.

Conclusions

We have reported a new and universal (considering iodogermane compounds) catalytic method for the synthesis of unsaturated organogermanium compounds, analogous to that of silicon compound synthesis, involving the activation of C_{sp}–H bonds in terminal alkynes in the presence of an iridium catalyst. Our tests have shown the formation of products that are mostly new compounds which could play a very important role in organogermanium chemistry and organic synthesis as well as being precursors for optoelectronic materials.

Acknowledgements

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