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# Regioselective hydrosilylation of terminal alkynes using pentamethylcyclopentadienyl iridium(III) metallacycle catalysts

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## Abstract

Pentamethylcyclopentadienyl iridium(III) metallacycles catalyse the hydrosilylation of alkynes using triethylsilane and no additive. The reactions proceed rapidly and efficiently at low catalyst loadings and under mild reaction conditions. If catalyses starting from terminal alkynes lead selectively to (*Z*)-alkenylsilanes in high yields, reactions are less efficient and selective starting from internal alkynes due to steric hindrance and the possible formation of isoquinolinium salts. Mass spectrometry highlights up to two consecutive 1,2-insertions of alkynes could take place into the catalyst iridium-carbon bond.

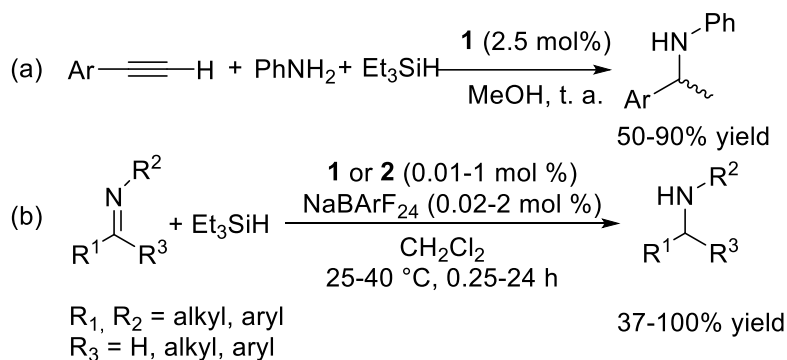
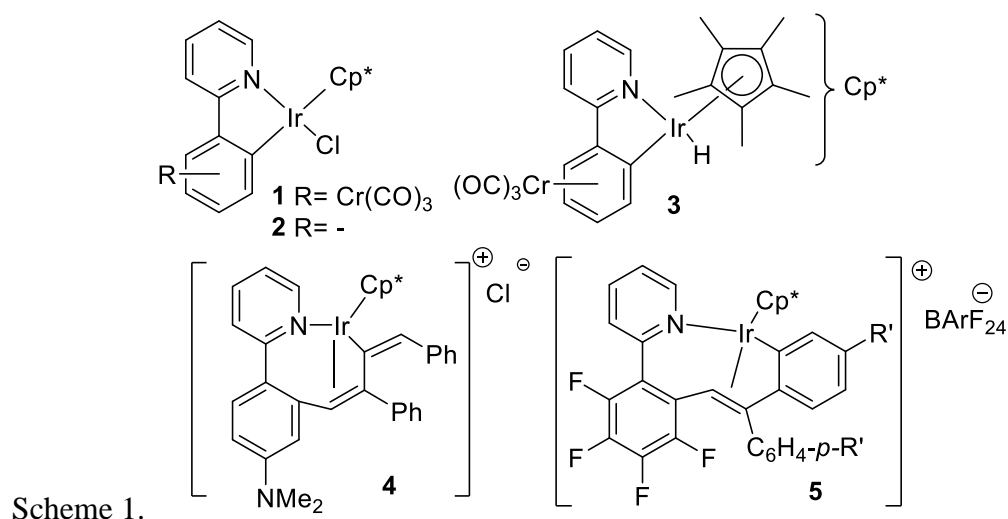
**Keywords:** iridium; metallacycles; half-sandwich; hydrosilylation, alkynes.

## 1. Introduction

Selective reduction of alkynes to alkenes is an important reaction in organic and polymer chemistry [1]. If semihydrogenation of alkynes has been successfully studied mainly by Lindlar reduction [2], the metal-catalysed hydrosilylation of alkynes is an interesting direct and atom-economic reaction which provides versatile alkenylsilanes [3]. However, the control of the reaction's stereo- and regiochemistry remains challenging depending on several factors like the structure of the catalyst, the nature of reagents (e.g. alkyne and silanes) and reaction parameters (e.g. solvent and temperature). The hydrosilylation of terminal alkynes shall lead to  $\beta$ -(*E*)- and less frequent  $\beta$ -(*Z*)-linear vinylsilanes, through respectively anti-Markovnikov

syn-addition and anti-Markovnikov anti-addition [3n,v]. Furthermore, the synthesis of branched  $\alpha$ -vinyl silanes through Markovnikov addition is rare [3a,o,u].

The stereoselective synthesis and reactivity of metallacycles like iridium(III) complex **1** and chromiumtricarbonylbound iridacycle **2** have been studied by some of us for several years (Scheme 1) [4]. Complexes of type **2** were found to display novel catalytic properties for the conversion of terminal aromatic alkynes into racemic *N*-phenyl, 1-arylethylamines by tandem hydroamination and hydrosilylation/protodesilylation reactions under mild “one pot” conditions (Scheme 2 a) [5].



Scheme 2.

The peculiar efficiency of such catalysts in promoting hydrosilylation was assigned to the intervention of iridium–hydrido intermediate **3** (Scheme 1) [4e,5,6], a key species for the transfer of the hydritic H atom to the electrophilic imine substrate. Recently, we showed the combination of iridacycle **1** with sodium tetrakis(3,5-trifluoromethyl)phenyl]borate, NaBARF<sub>24</sub>, as an additive could catalyse the hydrosilylation of various ketimines and aldimines at low catalyst loadings and under mild reaction conditions (Scheme 2 b) [7].

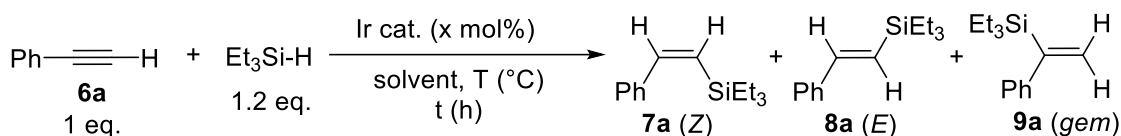
Finally, other reports stated the efficiency of such iridacycles for other reactions [8] like hydrogenation [9] and transfer hydrogenation [10]. Regarding the reactivity of iridacycles with alkynes, we and others demonstrated complexes of type **4** could be obtained from a double 1,2-insertion of a terminal aromatic alkyne like phenylacetylene (Scheme 1) [5,11]. A recent report have revealed such 1,2-alkyne insertion could compete with a vinylidene rearrangement/1,1-insertion depending the nature of the iridium(III) metallacycle. Indeed, the reaction of fluorinated iridacycles with diphenylacetylene derivatives was shown to afford nine-membered metallacycle complexes of type **5** by way of a sequential vinylidene rearrangement, 1,1-insertion of the vinylidene ligand, and the 1,4-iridium migration to the Ar group (Scheme 1) [11a]. Considering our previous results on hydrosilylation of imines as well as on tandem hydroamination-hydrosilylation reactions, we investigated iridium(III) metallacycles as catalysts for the hydrosilylation of alkynes.

## 2. Results and discussion

Screening of reaction conditions (e.g. solvent, temperature, time) and catalysts was performed on the hydrosilylation of phenylacetylene **6a** with triethylsilane (Table 1). Among the various solvents screened, tetrahydrofuran (THF) led to a moderate yield and a poor selectivity (entry 1). If the use of toluene and 1,4-dioxane afforded higher yields and a selectivity for (*E*)-product **8a** (entries 2-4), acetonitrile allowed the reaction to proceed well in favor of the (*Z*)-product **7a** provided the reaction temperature was kept at 80°C for 20 hours, yields being barely not improved at 100°C (entries 5, 6). By comparison, chlorinated solvents had to be preferred considering reactions proceeded well at 40°C in favor of (*Z*)-product **7a**. If dichloromethane led to an almost quantitative yield and a fair selectivity for **7a** in 20 hours without the use of AgBF<sub>4</sub> or NaBARF<sub>24</sub> (entries 7, 8, 9), 1,1',2,2'-tetrachloroethane gave better results in only 2 hours (entry 10). Finally, alcohols could not be used because of their spontaneous reactivity with silanes. Hence, as already noticed in our previous studies [4,5,7], a strong polar solvent had to be preferred to activate the catalyst by dissociation of the Ir-Cl bond. Though the use of acetonitrile, a greener solvent, afforded fair yields and selectivities at 80°C and 20 hours of reaction, the non-coordinating dichloromethane and 1,1',2,2'-tetrachloroethane led to better results in only few hours. In presence of our iridium(III) catalysts, nitrile solvents had another drawback due to their reactivity with silane reagents at high temperatures (entries 5,6) [5,7]. Within the most efficient and selective reaction conditions, catalyst **1** proved to be slightly more active than catalyst **2** (entries 10, 11). Yield and selectivity were also high using 1 mol% of catalyst **1** though the reaction time had to be

extended to 3 hours (entries 12, 13). A preliminary kinetic study performed at 40°C and 1 mol% catalyst loading allowed us to determine a half-life of 1.6 hour (94 minutes) along with a turnover number (TON) of 50 and a turnover frequency (TOF) of 31. However, the data could not be fitted with any simple kinetic law. A further decrease of the catalyst loading to 0.1 mol% led to a much slower reaction with a slightly reduced yield and a significant increase of TON and TOF values (entry 14). However, decreasing the amount of catalyst to 0.01 mol% resulted in a very low yield and showed the catalyst limits (entry 15).

**Table 1:** hydrosilylation of phenylacetylene **6a** - effects of solvent, temperature and time.



Entry	Cat. (%)	Solvent	T (°C)	t (h)	Yield (%) <sup>[a]</sup>	Selectivity <sup>[a]</sup> (Z) / (E) / (gem)			TON <sup>[b]</sup>	TOF <sup>[c]</sup>
1	<b>1</b> (2.5)	THF	60	20	39	51	41	8	16	0.8
2	<b>1</b> (2.5)	toluene	80	20	83	37	57	7	33	1.7
3	<b>1</b> (2.5)	toluene	100	10	87	21	71	8	35	3.5
4	<b>1</b> (2.5)	dioxane <sup>[d]</sup>	80	20	85	1	91	7	34	1.7
5	<b>1</b> (2.5)	CH <sub>3</sub> CN	80	20	72	89	8	3	29	1.5
6	<b>1</b> (2.5)	CH <sub>3</sub> CN	100	20	78	0	92	8	31	1.6
7	<b>1</b> (2.5)	CH <sub>2</sub> Cl <sub>2</sub>	40	20	95	83	12	5	38	1.9
8	<b>1</b> (2.5)	CH <sub>2</sub> Cl <sub>2</sub>	40	2	57	92	3	5	40	20
9 <sup>[e]</sup>	<b>1</b> (2.5)	CH <sub>2</sub> Cl <sub>2</sub>	40	20	0	-	-	-	-	-
10	<b>1</b> (2.5)	TCE	40	2	91	92	6	2	36	18
11	<b>2</b> (2.5)	TCE	40	2	86	91	9	0	36	18
12	<b>1</b> (1.0)	TCE	40	2	71	86	9	5	71	36
13	<b>1</b> (1.0)	TCE	40	3	90	86	9	5	90	30
14	<b>1</b> (0.1)	TCE	40	20	87	81	13	6	870	44
15 <sup>[f]</sup>	<b>1</b> (0.01)	TCE	40	62	11	8	3	0	11	0.2

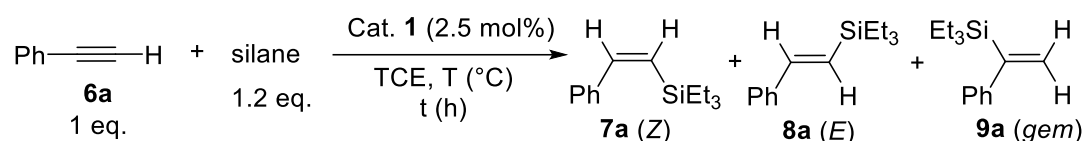
[a] determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal reference. [b] Turnover number = mol of product/mol of catalyst. [c] Turnover frequency = mol of product/mol of catalyst/hour. [d] 1,4-dioxane. [e] reaction with 5 mol% of AgBF<sub>4</sub> or NaBARF<sub>24</sub>, sodium tetrakis(3,5-trifluoromethyl)phenyl]borate. [f] 10 mL solvent and 0.1 eq. of 1,3,5-trimethoxybenzene.

Various silane reagents [12] could be used for the hydrosilylation of phenylacetylene **6a** (Table 2). Interestingly, reactions using affordable triethylsilane could be run in 2 hours and at 40°C affording (Z)-product in good yield, selectivity, TON and TOF (entry 1). However, an increase of temperature and time resulted in the partial isomerization of (Z)-product **7a** into (E)-product **8a** (entry 2). Within the same reaction conditions (e.g. 2 hours and 40°C), the reaction with triphenylsilane allowed also the selective hydrosilylation of **6a**

into (*Z*)-product **7a** but in lower yield, TON and TOF. An increase of the reaction time and temperature led to the complete isomerization of **7a** into (*E*)-product **8a** (entries 3, 4). If sterically hindered 1,1,1,3,5,5,5-heptamethyltrisiloxane afforded selectively (*Z*)-product **7a** at 60°C in 20 hours, a double reaction time led exclusively to the (*E*)-product **8a** (entries 5, 6). Otherwise, the use of triethoxysilane required a stronger heating and showed only the (*E*)-product formation (entries 7, 8). Finally, inexpensive hydrosilylation reagents like tetramethyldisiloxane (TMDS) and polymethylhydroxysiloxane (PMHS) led to complex mixtures (entries 9, 10).

The reaction scope was then studied using the best silane reagent and reaction conditions (Table 3). The hydrosilylation of phenylacetylene **6a** proceeded in fair yields at 40°C with high selectivities for (*Z*)-product **7a** using triethyl- or triphenylsilane. If the use of triethylsilane led to the (*Z*)-alkenylsilane **7b** from para-fluorinated reagent **6b** in good yield and selectivity, triphenylsilane afforded only the (*E*)-product **8b** in a modest yield.

**Table 2:** hydrosilylation of phenylacetylene **6a** - effects of silanes and temperature.



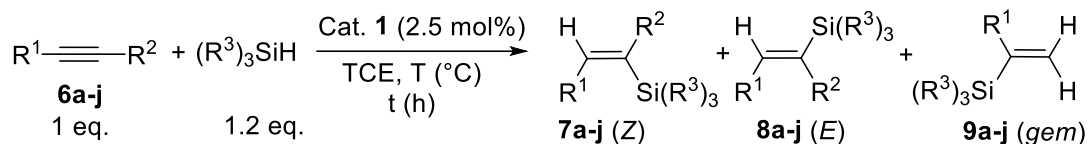
Entry	Silane	Cost <sup>[a]</sup> (€/mmol)	T (°C)	t (h)	Yield (%) <sup>[b]</sup>	Selectivity <sup>[b]</sup> ( <i>Z</i> ) / ( <i>E</i> ) / ( <i>gem</i> )	TON <sup>[c]</sup>	TOF <sup>[d]</sup>
1	Et <sub>3</sub> SiH	0.41	40	2	91	92 / 6 / 2	36	18
2	Et <sub>3</sub> SiH	0.41	60	25	93	38 / 60 / 2	37	1.9
3	Ph <sub>3</sub> SiH	1.64	40	2	80	100 / 0 / 0	32	16
4	Ph <sub>3</sub> SiH	1.64	100	24	65	0 / 100 / 0	26	1.1
5	(Me <sub>3</sub> SiO) <sub>2</sub> - Si(Me)H	0.38	60	20	87	100 / 0 / 0	35	1.8
6	(Me <sub>3</sub> SiO) <sub>2</sub> - Si(Me)H	0.38	60	40	100	0 / 100 / 0	40	1.0
7	(EtO) <sub>3</sub> SiH	0.79	40	2	0	- / - / -	-	-
8	(EtO) <sub>3</sub> SiH	0.79	100	24	63	- / 100 / -	25	1.0
9	TMDS	0.11	70	50	100 <sup>[e]</sup>	unidentified products	-	-
10	PMHS	0.01	60	40	100 <sup>[e]</sup>	unidentified products	-	-

[a] According to ref. 12 and www.sigmaaldrich.com. [b] determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal reference. [c] Turnover number = mol of product/mol of catalyst. [d] Turnover frequency = mol of product/mol of catalyst/hour. [e] determined by GC and GC-MS.

The same tendency could be observed with para-methoxy and meta-methyl derivatives **6c** and **6d** with higher yields and reduced selectivities. By comparison, dimethylamino substrate **6e** led to an opposite trend. Indeed, whereas the use of triethylsilane led to the (*E*)-alkenylsilane

**8e** in fair yield and selectivity, triphenylsilane afforded both (*Z*)- and (*E*)-products, **7e** and **8e**, in a good yield. We could also notice alkyl substrates **6f** and **6g** displayed poor reactivities.

**Table 3:** substrate scope.



Entry	R <sub>1</sub>	R <sub>2</sub>	Silane	T (°C)	t (h)	Yield (%) <sup>[a]</sup>	Selectivity 7a-j / 8a-j / 9a-j (Z) / (E) / (gem)			
1	<b>6a</b>	Ph	H	Et <sub>3</sub> SiH	40	2	91	92	6	2
2	<b>6a</b>	Ph	H	Ph <sub>3</sub> SiH	40	2	80	100	0	0
3	<b>6b</b>	<i>p</i> -F-(C <sub>6</sub> H <sub>4</sub> )	H	Et <sub>3</sub> SiH	40	2	74	93	5	2
4	<b>6b</b>	<i>p</i> -F-(C <sub>6</sub> H <sub>4</sub> )	H	Ph <sub>3</sub> SiH	40	2	22	0	100	0
5	<b>6c</b>	<i>p</i> -MeO-(C <sub>6</sub> H <sub>4</sub> )	H	Et <sub>3</sub> SiH	40	2	86	69	30	1
6	<b>6c</b>	<i>p</i> -MeO-(C <sub>6</sub> H <sub>4</sub> )	H	Ph <sub>3</sub> SiH	40	2	85	0	98	2
7	<b>6d</b>	<i>m</i> -Me-(C <sub>6</sub> H <sub>4</sub> )	H	Et <sub>3</sub> SiH	40	2	93	93	5	2
8	<b>6d</b>	<i>m</i> -Me-(C <sub>6</sub> H <sub>4</sub> )	H	Ph <sub>3</sub> SiH	40	2	100	0	95	5
9	<b>6e</b>	<i>p</i> -NMe <sub>2</sub> -(C <sub>6</sub> H <sub>4</sub> )	H	Et <sub>3</sub> SiH	40	2	81	19	81	0
10	<b>6e</b>	<i>p</i> -NMe <sub>2</sub> -(C <sub>6</sub> H <sub>4</sub> )	H	Ph <sub>3</sub> SiH	40	12	86	55	41	4
11	<b>6f</b>	<i>n</i> -pentyl	H	Et <sub>3</sub> SiH	40	2	33	0	100	0
12	<b>6f</b>	<i>n</i> -pentyl	H	Ph <sub>3</sub> SiH	40	2	0	-	-	-
13	<b>6g</b>	cyclopropyl	H	Et <sub>3</sub> SiH	40	2	0	-	-	-
14	<b>6g</b>	cyclopropyl	H	Ph <sub>3</sub> SiH	40	2	0	-	-	-
15	<b>6h</b>	CO <sub>2</sub> Et	H	Et <sub>3</sub> SiH	40	2	13 <sup>[b]</sup>	100	0	0
16	<b>6h</b>	CO <sub>2</sub> Et	H	Ph <sub>3</sub> SiH	40	2	0	-	-	-
17	<b>6i</b>	Ph	CO <sub>2</sub> Et	Et <sub>3</sub> SiH	80	20	62 <sup>[c]</sup>	42	58	-
18	<b>6i</b> <sup>[d]</sup>	Ph	CO <sub>2</sub> Et	Et <sub>3</sub> SiH	80	20	6	100	0	0
19	<b>6i</b>	Ph	CO <sub>2</sub> Et	Ph <sub>3</sub> SiH	80	20	0	-	-	-
20	<b>6j</b>	Ph	Me	Et <sub>3</sub> SiH	80	20	35 <sup>[e]</sup>	0	100	0
21	<b>6j</b> <sup>[d]</sup>	Ph	Me	Et <sub>3</sub> SiH	80	20	8	50	50	0
22	<b>6j</b>	Ph	Me	Ph <sub>3</sub> SiH	80	20	0	-	-	-

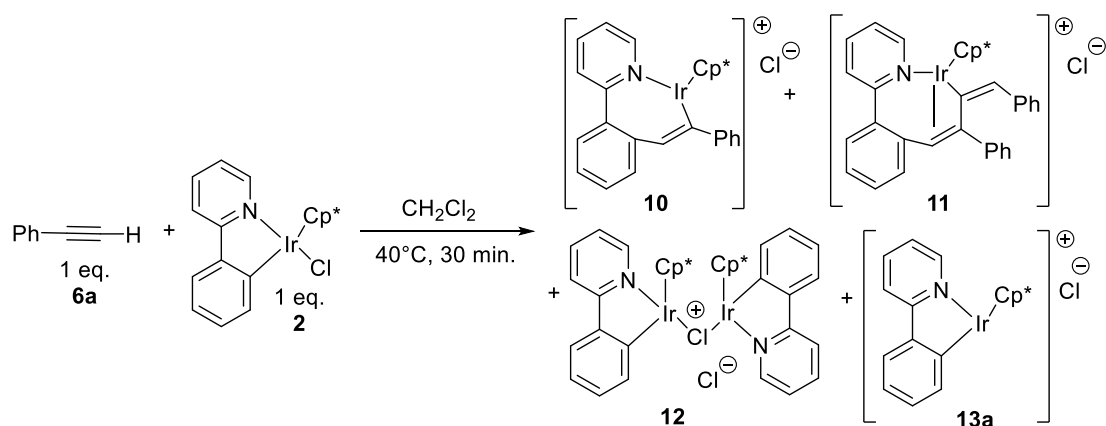
[a] determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal reference and by GC. [b] same result in 20h and 14% yield of (*E*)-selectivity if 80°C during 20h. [c] mixture of α-(*E*)- and α-(*Z*)-products as respect to phenyl substituent. [d] in CH<sub>3</sub>CN. [e] mixture of α- and β-(*E*)-products as respect to phenyl substituent.

Indeed, no reaction was observed with reagent **6g** and the hydrosilylation of **6f** proceeded only with the use of triethylsilane to lead to the (*E*)-product **8f** in a low yield. Ethylpropiolate **6h** displayed also a poor reactivity independently of the reaction time and temperature. Finally, the hydrosilylation of internal alkynes **6i** and **6j** was investigated. If no reactions were observed while using triphenylsilane, modest to average yields were obtained with triethylsilane and the use of acetonitrile as a solvent resulted also in lower reactivities. Reagent **6i** led to both (*Z*)- and (*E*)-products, **7i** and **8i**, in a fair yield, and substrate **6j** afforded exclusively (*E*)-products **8j** in a modest yield.

As a preliminary study regarding the possible active species involved in the catalytic process of such alkyne hydrosilylation reactions [3s, 13, 14], we performed an analysis by electrospray ionization mass spectrometry on the reaction mixture obtained from the quantitative reaction of phenylacetylene **6a** and complex **2** (Scheme 3, Figure 1).

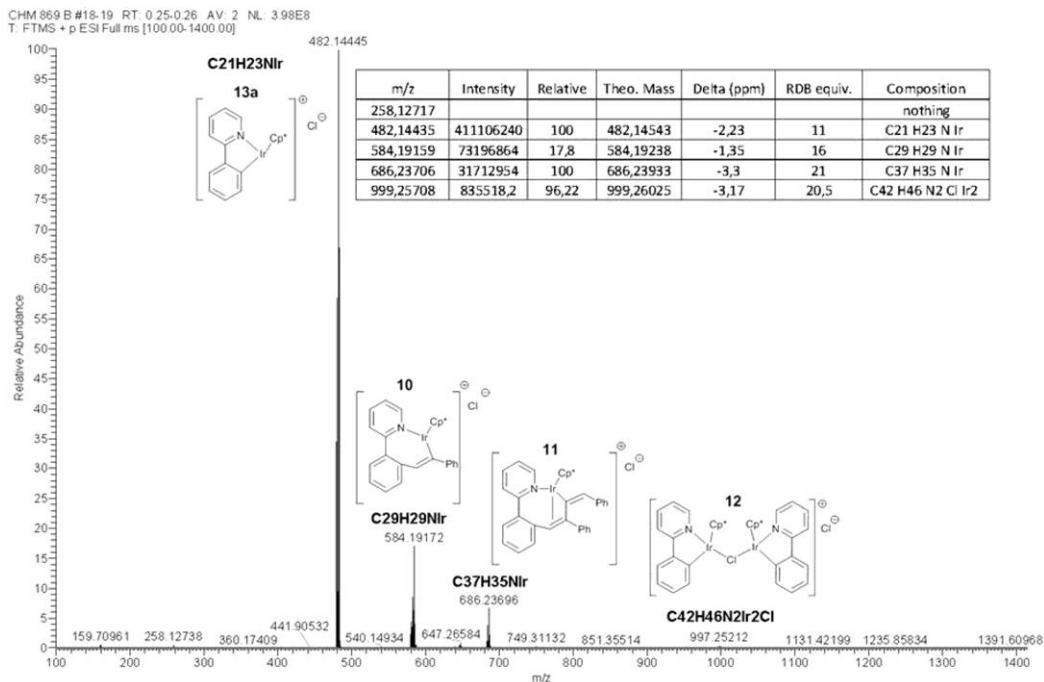
Along this study, complex **2** had to be preferred to **1** because of its higher stability when analysed in methanol by mass spectrometry. Species **10** and **11** could be characterized unambiguously along with complexes **12** and **13a**. Hence, if complex **10** resulted from a single 1,2-insertion of terminal alkyne **6a** into the iridium-C<sub>Ar</sub> bond of complex **2**, species **11** was issued from a double 1,2-insertion of **6a** and no vinylidene rearrangement/1,1-insertion could be evidenced. Our previous studies on tandem hydroamination and hydrosilylation/protodesilylation reactions demonstrated complex **11**, once isolated, had no catalytic activity [5]. Hence, single and double 1,2-insertion of terminal alkyne **6a** proved to compete, one leading to an active catalyst and the other to an inert species. Otherwise, complex **13a** and complex **12** which had been previously linked to the catalyst resting state [7] were also observed.

**Scheme 3.**



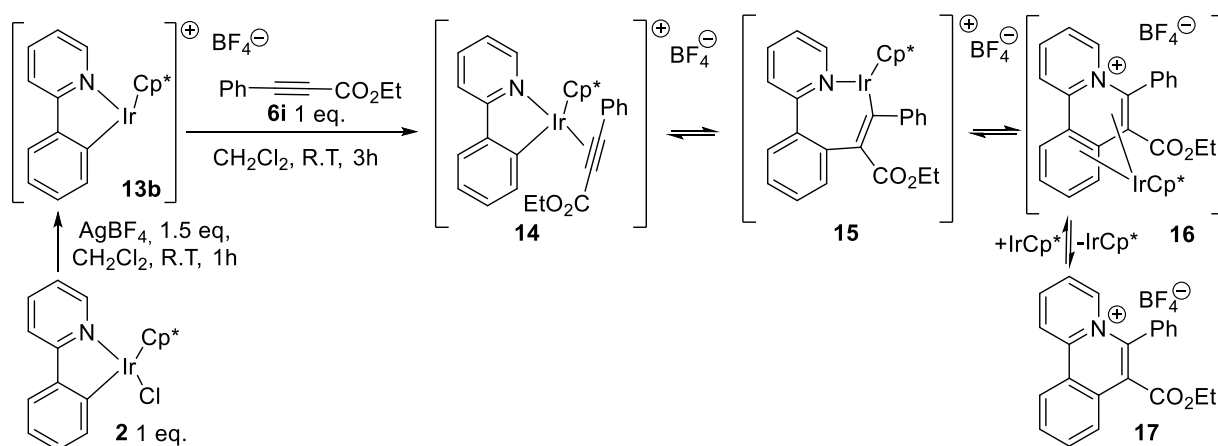


**Figure 1.** ESI(+)-MS analysis in methanol of the crude mixture resulting from the catalytic hydrosilylation of reagent **6a**.

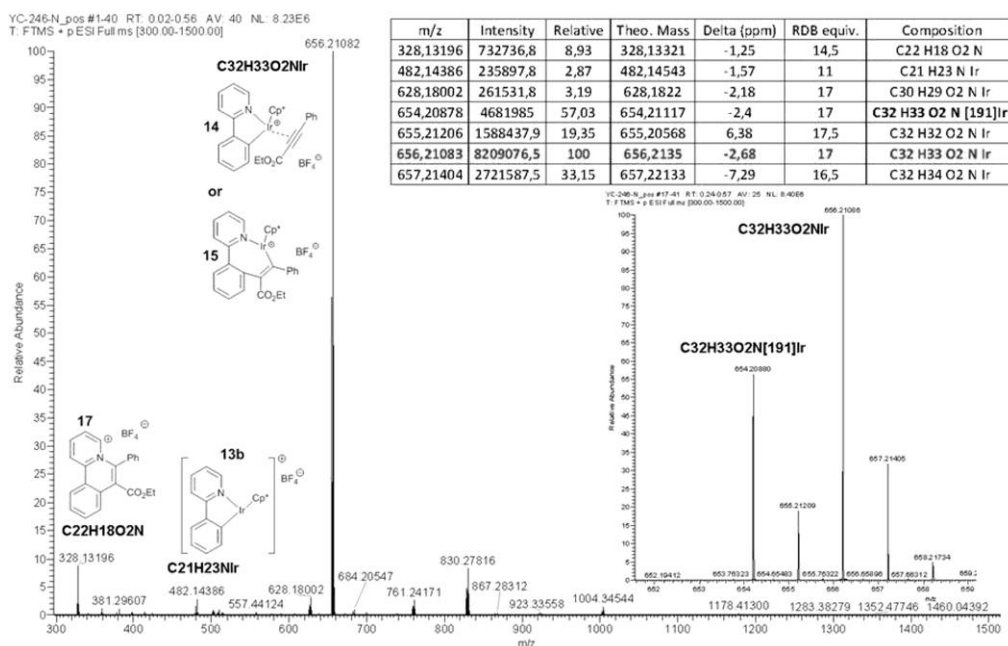


Another analysis by electrospray ionization mass spectrometry was performed on the crude mixture resulting from the quantitative reaction of iridium(III) complex **2** with internal alkyne **6i** (Scheme 4, Figure 2). The use of silver tetrafluoroborate was shown to be critical to stabilize the formed species. If complex **13b** appeared as the first reaction intermediate linked to the catalyst resting state [7], the main species observed at m/w 656 was likely to be complex **14** and/or **15** as the result of a single 1,2-insertion of internal alkyne **6i** into complex **2** iridium-C<sub>Ar</sub> bond.

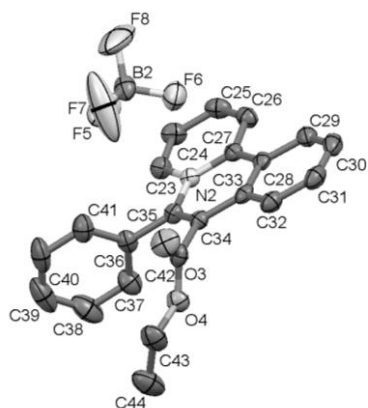
**Scheme 4.** Reaction of complex **2** with AgBF<sub>4</sub> and phenylpropiolate.



**Figure 2.** ESI(+)-MS analysis in methanol of the crude mixture resulting from the stoichiometric hydrosilylation of reagent **6i**.



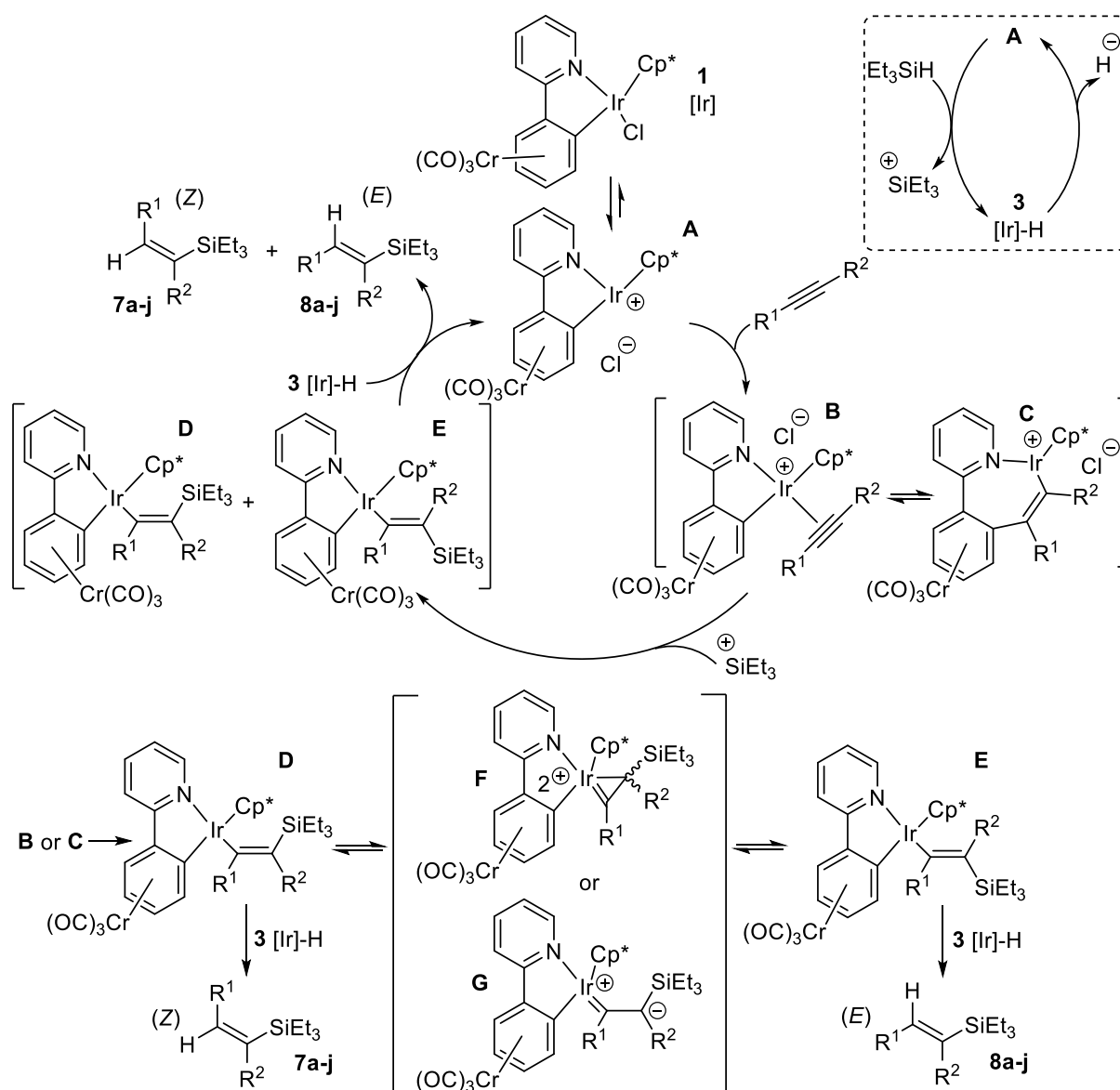
In addition, thanks to the stabilizing effect of tetrafluoroborate anion, minor species **17** was observed at m/w 328 and confirmed by X-ray diffraction analysis. Indeed, characterization of single crystals grown by diffusion of the reaction crude mixture (dichloromethane solution) in hexane helped to confirm the synthesis of species **17** (Figure 3, Table 4). That compound shall be prepared from complex **15** by, first, the formation of intermediate **16**, which is a pyridoisquinolinium moiety bound to the iridium center and, second, the release of pentamethylcyclopentadienyl iridium(III) fragment (Scheme 3). It is worth to note such reaction pathway was already observed when pentamethylcyclopentadienyl rhodium(III) complexes and O<sub>2</sub> were used to catalyse oxidative C–H activation/annulation reactions and produce various related isoquinolinium salts [15].



**Figure 3.** Ortep plot of **17** in the solid state. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. CCDC 1473938 [16].

On the whole, if isoquinolinium salt **17** could be synthesised to the detriment of the catalytic hydrosilylation of alkynes, its characterization confirmed a single 1,2-insertion of internal alkyne into the catalyst iridium-C<sub>Ar</sub> bond was likely to occur. However, we could not find evidences of a double 1,2-insertion of internal alkynes or of a vinylidene rearrangement/1,1-insertion. Hence, the reaction mechanism shall start by the insertion of alkyne reagent into the iridium-C<sub>Ar</sub> bond of the dechlorinated species **A** (Scheme 5).

**Scheme 5.** Proposed reaction mechanism.



While a first equivalent of **A** inserts the alkyne reagent forming species **B** and **C**, a second equivalent of **A** reacts with triethylsilane to afford iridium hydride complex **3** (Schemes 1 and 5) and triethylsilyl cation. The latter can then react with species **B** and **C** to lead to intermediates **D** and **E** which react further with hydride **3** to form (Z)- and (E)-alkenylsilane

products and release cationic iridium species **A**. If the low reactivity and selectivity observed for the hydrosilylation of internal alkynes may be related to their implicit steric hindrance and the possible formation of isoquinolinium salts, the selective synthesis of (*Z*)-alkenylsilanes from terminal alkynes proved to depend on both electronic and steric parameters of the substrates as well as on the reaction temperature (Tables 2 and 3, Scheme 5). According previous studies on iridium and rhodium catalysts [13c-e], (*Z*)-alkenylsilanes **7a-j** shall be the kinetic products formed through anti-additions leading to intermediates **D** (Scheme 5). Isomerization appeared privileged by high reaction temperature and time (Table 1). It may occur through  $\eta^2$ -vinyl species **F** or zwitterionic carbenes **G** to generate intermediates **E** which shall then react with iridium hydride **3** and afford (*E*)-alkenylsilanes **8a-j** as the thermodynamic products (Scheme 5).

## Conclusion

Pentamethylcyclopentadienyl iridium(III) metallacycles were shown to catalyse the hydrosilylation of alkynes using triethylsilane and no additive. The reactions could proceed rapidly and efficiently at low catalyst loading and under mild conditions. If the catalyses starting from terminal alkynes led selectively to (*Z*)-alkenylsilanes in high yields, reactions were less efficient and selective starting from internal alkynes due to steric hindrance and the possible formation of isoquinolinium salts. Isomerization from (*Z*)- to (*E*)-alkenylsilanes appeared privileged by high reaction temperature and time. A study by mass spectrometry showed single and double alkyne 1,2-insertion could take place into the catalyst iridium-carbon bond but no vinylidene rearrangement/1,1-insertion could be evidenced. Whereas a single insertion was observed for internal alkynes, a double 1,2-insertion was possible using terminal alkynes but led to an inert catalytic species.

## 3. Experimental section

### 3.1. General data

All solvents were dried using standard methods. All commercial reagents were used as received unless otherwise stated. Unless stated, all reactions were carried out under a dry nitrogen atmosphere.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  (75 MHz) spectra were acquired on a Bruker Avance spectrometer. Chemical shifts are reported downfield of  $\text{Me}_4\text{Si}$  in ppm and coupling constants are expressed in Hz. Gas chromatography analyses were done on GC Shimadzu

2010+ with FID detectors using Supelco SPB-5 column (30 m, 0.25 mm, 0.25  $\mu\text{m}$ ) and with nitrogen as gas carrier. GC-MS analyses were performed on a Shimadzu QP2010+ (EI mode) using Supelco column SLBTM-5ms (30 m, 0.25 mm, 0.25  $\mu\text{m}$ ). Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. Flash chromatography was carried out with Macherey silica gel (Kieselgel 60). MS-ESI and HRMS-ESI analyses were performed at CUMA-University Lille Nord de-France.

**Table 4.** Crystal data and structure refinement compound **17**.

	<b>Compound 17 CCDC</b>
Temperature	173 K
Empirical formula	$\text{C}_{22}\text{H}_{18}\text{NO}_2\text{BF}_4$
Formula weight	415.18
Wavelength	0.71073 (MoK $\alpha$ )
Crystal system	Monoclinic
Space group	P21/c
a ( $\text{\AA}$ )	27.6525 (14)
b ( $\text{\AA}$ )	10.2341 (5)
c ( $\text{\AA}$ )	14.1072 (7)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	102.6830(10)
$\gamma$ ( $^\circ$ )	90
Volume( $\text{\AA}^3$ )	3894.9(3)
Z	8
Crystal dim (mm)	0.40 x 0.25 x 0.18
Density ( $\text{g}\cdot\text{cm}^{-3}$ )	1.416
Absorption coefficient	$0.115 \text{ mm}^{-1}$
Absorption (max. and min. transmission)	0.7458 and 0.6373
F(000)	1712
$2\theta$ limits (deg)	1.510 to 29.050
Limits $hkl$	-37, 37 / -13, 13 / -19, 19
Reflections collected	31007
Independent reflections	10348 [R(eq.) = 0.0841]
Num. of var.	543
GOF	0.876
Final R indices	R = 0.0552, wR = 0.1293
R indices (all data)	R <sub>all</sub> = 0.1593, wR <sub>all</sub> = 0.1652

### 3.2. General procedure for the catalysis

Under nitrogen, alkyne reagent (0.15 mmol, 1 eq.) and selected iridium(III) catalyst (x mol%) were introduced in a Schlenk tube along with internal reference 1,3,5-trimethoxybenzene (1 eq.). TCE solvent (2 mL) was added followed by silane reagent

(0.18 mmol, 1.2 eq.). The reaction mixture was then heated at the selected temperature under stirring. In order to follow the progress of the reaction, aliquots (0.1 mL) were taken at defined times, filtered through Celite with a CH<sub>2</sub>Cl<sub>2</sub> wash (3 mL), evaporated under vacuum and analysed by <sup>1</sup>H NMR.

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- [16] CCDC 1473938 for compound 17. Selected bond lengths (Å): C27-N2 1.383(3), C27-C28 1.442(3), C28-C33 1.403(3), C33-C34 1.435(3), C34-C35 1.347(3), C35-N2 1.426(3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).