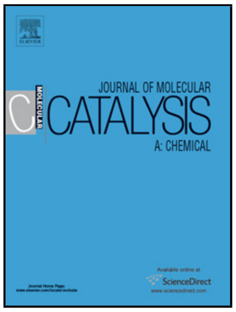

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Iridium-catalysed desilylative acylation of 1-alkenylsilanes

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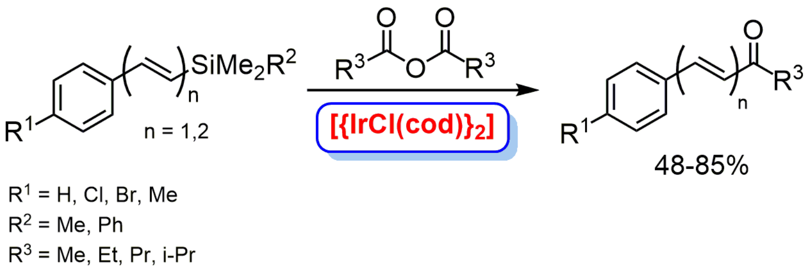
GRAPHICAL ABSTRACT



Highlights:

- The iridium-catalyseddesilylative acylation of vinylsilanes with acid anhydrides.
- Synthesis of (*E*)-styryl and (*E*,*E*)-buta-1,3-dien-1-yl ketones
- Mechanism proposal of the $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$-catalysed acylation of vinylsilanes.

Abstract: *We report the iridium-catalysed desilylative acylation of styryl and dienyl silanes by acid anhydrides to afford (E)-α,β-unsaturated ketones. The* $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ *catalyst is the first non-rhodium complex successfully applied for this type of transformation. Stoichiometric reaction of* $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ *with (E)-trimethyl(4-chlorostyryl)silane was carried out to gain insight into the reaction mechanism.*

Keywords: iridium catalyst, desilylative acylation, anhydride, enone

Introduction

α,*β*-Unsaturated ketones are important reagents for organic synthesis and can be used in many organic transformations.[1] Their synthesis via the classic Claisen-Schmidt condensation as not particularly selective does not fit modern chemistry trends.[2] Some catalytic attempts have been made to synthesise *α*,*β*-unsaturated ketones with allyl alcohols oxidation,[3] Friedel-Crafts acylation with *α*,*β*-unsaturated acyl chlorides,[4,5] carbonylative addition of boronic acids to terminal alkynes,[6] Rupe rearrangement of propargylic alcohols,[7] and metathesis of vinyl ketones with terminal alkenes among them.[8] A variety of chalcones have been synthesized by solid-phase-acid-catalysed condensation of acetophenones with benzaldehydes.[9] On the other hand, visible-light-promoted organocatalysis has been used to obtain linear and cyclic enones bearing both aromatic and aliphatic substituents as well as enals.[10] Acylation of stereodefined vinylsilanes proceeds in a regioselective manner to afford *α*,*β*-unsaturated ketones.[11] Desilylative acylation has been first described by Fleming and Pearce, who used acyl chlorides and $AlCl_3$ as Lewis acid catalyst.[12] Narasaka *et al.* have been the first to report the use of acid anhydrides instead of chlorides in a reaction catalysed by a rhodium complex $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$.[13] The mechanism of the catalytic acylation proceeds via transmetalation between the Rh(I) complex and vinylsilane to afford vinylrhodium intermediate, followed by sequential oxidative addition of acid anhydride and reductive elimination of *α*,*β*-unsaturated ketone with regeneration of Rh(I) catalyst.[13] In our previous work, we have reported a versatile method for the preparation of (*E*)-styryl ketones *via* a sequence of ruthenium-catalysed silylative coupling of styrenes with trimethylvinylsilane and desilylative acylation of silylated products in the presence of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ – in the manner presented by Narasaka *et al*. Knowing the advantages of silylative coupling – its substrate scope and selectivity,[14,15] we decided to make it the starting point on a route to enones. In the subsequent paper we have extended this method by the use of (*E*)-1,2-bis(silyl)ethenes to obtain (*E*)-*β*-silyl-*α,β*-unsaturated ketones.[16] The sequential Hiyama cross-coupling/Narasaka acylation of (*E*)-1,2-bis(silyl)ethene has been also applied to the synthesis of *α,β*-unsaturated carbonyl compounds.[16]

In the earlier studies, our effort has been put on extension of the use of rhodium complexes. To the best of our knowledge, no report on other-metal-catalysed desilylative acylation has been published. Moreover, the report of Wagner *et al.* might suggest, that only $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ can be effectively used in the reaction, and no other complex of rhodium offers this opportunity.[17]

Knowing the chemical similarity between rhodium and iridium, we have envisaged that the acylation of vinylsilanes with acid anhydrides can successfully proceed with iridium(I) complexes as catalysts. Given the relatively lower price and commercial availability of iridium precursors, we chose several simple systems containing iridium to be tested in desilylative acylation of styrylsilanes. Although iridium complexes are less frequently used than their rhodium analogues, in some processes e. g. carbonylation, enantioselective hydrogenation of C=N bonds and functionalisation of $C_{(aryl)}$–H bonds, they may be more effective.[18] In this communication we report a preliminary study of iridium(I)-promoted acylation of styrylsilanes..

Results and discussion

We started the studies with optimisation of the reaction conditions. Catalytic screening was applied in the model catalytic process of acylation of (*E*)-*β*-trimethylsilylstyrene with acetic anhydride (Scheme 1). Selected monomeric and dimeric iridium(I) complexes were tested in this process. In a typical procedure, the substrates (1:1 molar ratio) and catalyst (10 mol % corresponding to Ir) were dissolved in toluene (0.5 M concentration) and heated in a

Schlenk flask fitted with a plug valve at 120 °C for 24h under argon atmosphere. The reactions were monitored by GC and GC-MS methods to measure conversion of the substrates and products distribution. The GC-MS analysis of the reaction mixture confirmed the formation of styryl methyl ketone as main product. Despite the use of dry toluene as a solvent, small amounts of the competitive protodesilylation product, i.e. styrene, were detected in the presence of all catalysts tested (Scheme 1). The results are summarised in Table 1.

These results indicate that Ir complex **2** exhibited the highest catalytic activity and selectivity from among the tested group of iridium promoters. Noteworthy is the fact that monomeric species did not lead to any conversion of (*E*)-*β*-trimethylsilylstyrene, whereas all of the tested dimeric complexes showed the ability to catalyse desilylative acylation with at least fairly good effects. The activity of the $IrCl_3/AgPF_6$ system **8** can be related to the ability of $AgPF_6$ to promote protodesilylation in the presence of water since iridium(III) chloride exists as a hydrate. In the light of the preliminary results, we chose complex **2** for further tests. Not only was it the most active one, but also the easiest to synthesise and handle, requiring no special conditions of storage.

A series of catalytic trials were conducted to investigate the activity of complex **2** in desilylative acylation. We chose (*E*)-silylstyrenes containing $SiMe_3$ and $SiMe_2Ph$ groups, known to provide better comparison between iridium and rhodium catalysts [13]. The reactions performed aiming at optimisation of the conditions revealed that a reduction both in the temperature and catalyst loading leads to a significant drop in the observed conversion. A reaction between (*E*)-*β*-trimethylsilylstyrene and acetic anhydride in the presence of 2 mol% of $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ conducted at 120°C caused a decrease in styrylsilane conversion to 28% after 24 h. No reaction occurred at 90°C and only a slight substrate conversion (10%) was observed after 24h, while heating the reactants at 100°C. The best results were obtained when using 0.5 M solution of reagents and 5% of binuclear iridium catalyst **2**.

In the above-optimised conditions, we investigated the scope of this reaction, using various *p*-substituted (*E*)-silylstyrenes and selected acid anhydrides. These results are summarised in Table 2.

The results show that catalyst **2** is active in desilylative acylation of (*E*)-silylstyrenes with various acid anhydrides. Substituted (*E*)-silylstyrenes reacted successfully to give the corresponding (*E*)-styryl ketones in good yields, irrespective of the substituent's electronic character (Table 2, entries 1-8). Aliphatic acid anhydrides can be employed for the iridium-catalysed acylation of (*E*)-styrylsilanes to give corresponding (*E*)-styryl ketones with moderate to high yields (Table 2, entries 1-11, 14-22). Reaction of (*E*)-styrylsilanes with benzoic and methacrylic anhydride let to obtain a mixture of silyl ester ($PhCO_2SiR_3$ or $CH_2=C(Me)CO_2SiR_3$, respectively) and styrene (Table 2 entry 12-13, 23-24). It is worth noting that the $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$-catalysed acylation of (*E*)-styrylsilanes proceeded efficiently using 1 equivalent of acid anhydride, in contrast to the rhodium catalysis which needed 3 equivalents of substrate to achieve satisfactory conversion of silylstyrenes.[12,13] The known products of acylation reactions were detected by a comparison of their GC-MS with the chromatograms of ketones synthesised previously using rhodium catalyst[13] and some of the products were isolated in order to check their structure (Table 2, entries 1-8, 19, 22). However, formation of styryl ketones is almost always accompanied by protodesilylation of their silyl precursors under iridium catalysis (10-30%) and further investigation should be performed to improve the selectivity of the reaction.

We also successfully extended our method for the synthesis of 4-phenyl substituted (*E*,*E*)-buta-1,3-dien-1-yl ketones (Scheme 2). The reaction of 1-phenyl-4-(trimethylsilyl)-1,3-butadiene (mixture of isomers (*E*,*E*)/(*E*,*Z*) = 93:7)[19] with 1 equiv. of acid anhydride in the presence of iridium catalyst **2** (5 mol %) in dry toluene at 120°C for 24-48 h under argon atmosphere allowed isolation of (*E*,*E*)-buta-1,3-dien-1-yl ketones as predominant products in 59-78 % yield (Table 3).

A preliminary mechanistic investigation was carried out. Heating a mixture of complex **2** and 2 equivalents of (*E*)-trimethyl(4-chlorostyryl)silane in toluene-d_8 led to formation of chlorosilane and disiloxane, while no significant change was observed when the mixture contained the catalyst and an acid anhydride. A deduction that comes along is that the reaction studied runs according to the same mechanism as proposed by Narasaka *et al* for $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ complex[13] (Scheme 3).

In the catalytic system created with vinylsilane derivative and appropriate carboxylic acid anhydride, it can be expected that in the first step the initial complex $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ reacts with unsaturated silicon derivative ($R_3Si\text{-}CH{=}CH\text{-}Ar$) yielding a corresponding mononuclear Ir(I) species with π-bonded vinylsilane derivative. It is consistent with studies conducted by Fougeroux, who reported formation of square-planar mononuclear Ir(I) species with allyl derivatives π-bonded to the metallic centre after the reaction of the binuclear iridium precursor $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ with allyl derivatives such as allyl alcohol or allyl ethers.[20] Then, in a further step, the previously formed square-planar Ir(I) species is transformed into five-coordinated silyl-vinylene Ir(III) intermediate *via* $Si\text{-}C_{sp}{}^2$ bond activation followed by evolution of chlorosilane and assumptive formation of vinyliridium complex – the first key intermediate. According to Narasaka [13], should the latter act with an acid anhydride *via* oxidative addition followed by reductive elimination of an α,β-unsaturated ketone with creation of Ir(I) acetyl complex – the second key intermediate.

Experimental

Desilylative acylation of (E)-β-silylstyrenes

In a typical procedure, a previously evacuated and flame-dried Schlenk flask was charged with 2 mL of dry toluene, 176 mg (1 mmol) of (*E*)-β-trimethylsilylstyrene, 96 μL (1 mmol) of distilled acetic anhydride, and 33.6 mg (0.05 mmol) of the iridium complex **2**, under continuous flow of argon. 0.1 mL of decane was added as an internal standard. The reaction vessel was closed tight, then stirred and heated at 120 °C for 24h. Once the specified time had passed, the flask was cooled down to the room temperature, and the sample taken from the mixture was analysed using GC-MS technique to determine the products distribution. Several examples of reactions were selected to be isolated and subjected NMR analysis to determine structure of the products. In such case, the reaction mixture was evaporated on a rotary evaporator and column chromatography purification was carried out (silica gel, hexane – diethyl ether 9:1 $^{v}/_{v}$ used as eluent).

Desilylative acylation of (E)-trimethyl(4-chlorostyryl)silane – an NMR experiment

On the basis of Narasaka's experiment,[13] dried and evacuated NMR tube with a Young valve was charged with 10 mg (0.015 mmol) of the iridium complex **2**, 6.3 mg of (*E*)-β-trimethylsilyl-4-chlorostyrene, and 0.6 mL of dry toluene-d_8. The ^{1}H spectrum was measured, and the tube was heated at 120 °C. Then the spectra were measured after 8 and 24 h of heating.

Conclusions

In summary, the first iridium-catalysed protocol for efficient desilylative acylation of substituted vinylsilanes with acid anhydrides has been reported. Di-μ-chlorobis(1,5-cyclooctadiene)diiridium(I) proved to be an efficient catalyst for desilylative acylation of substituted (*E*)-styrylsilanes and (*E*,*E*)-1-phenyl-4-(trimethylsilyl)-1,3-butadiene to yield (*E*)-styryl ketones and (*E*,*E*)-4-phenylbuta-1,3-dien-1-yl ketones, respectively. The catalytic activity of the iridium catalyst $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ in the acylation of substituted vinylsilanes by acid ahydrides was similar to that of the earlier reported rhodium catalyst $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ [13], however, the reaction over the Ir complex required higher temperature (120 °C) than that needed for Rh catalysis activity (90 °C). Although, under optimum conditions the Ir complex promoted competitive protodesilylation of styrylsilanes, the isolation yields of acylation products (58-85%) were slightly better in most cases than those obtained with Rh catalyst (18-84%). Moreover, in the reactions performed over Rh catalysis, the competitive decarbonylation, isomerisation and polymerisation were also observed. The iridium catalyst $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ seems to be also more effective for acylation of silylated dienes. Preliminary mechanistic studies indicate that iridium catalysis proceeds according to the transmetalation mechanism, analogous to that reported previously for rhodium(I) complexes.

Acknowledgment

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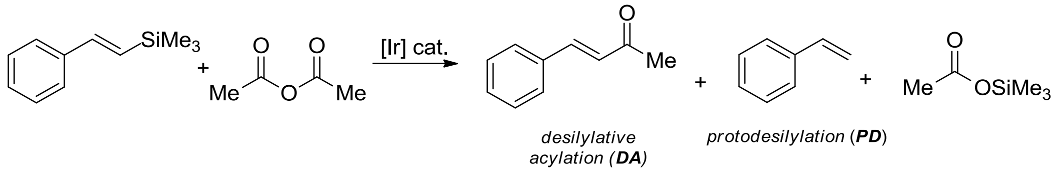
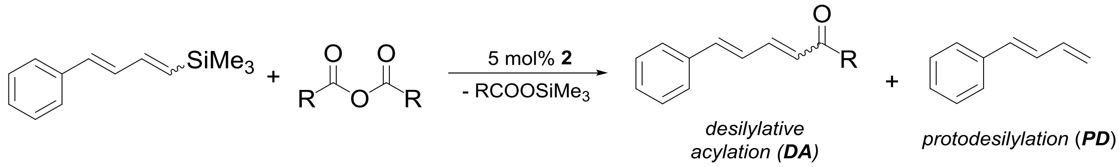
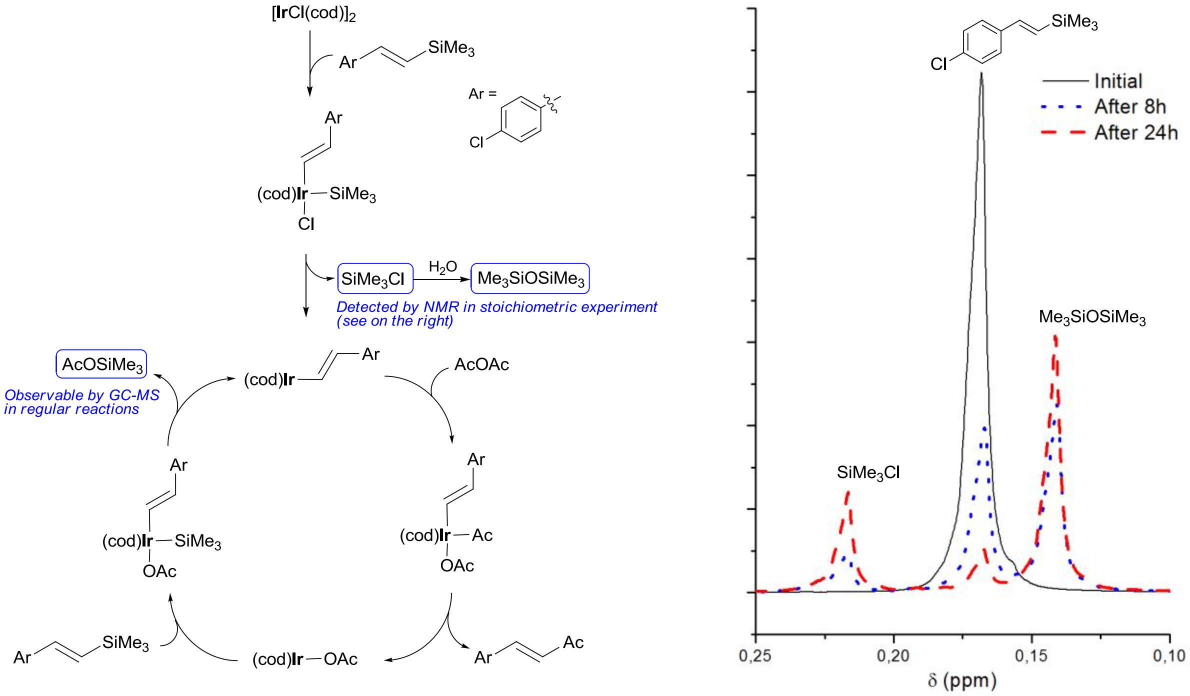


Scheme 1. *Reaction of (E)-β-trimethylsilylstyrene with acetic anhydride in the presence of iridium catalysts*



Scheme 2. Synthesis of 4-phenyl-(E,E)-buta-1,3-dien-1-yl ketones with the use of complex ***2***



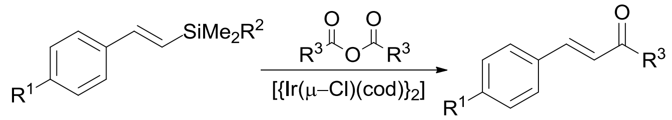
Scheme 3. Proposed mechanism of desilylative acylation of silylstyrenes by acid anhydride using complex ***2***

Table 1. *The results of catalyst screening in the desilylative acylation of (E)-β-trimethylsilylstyrene with acetic anhydride.*

Entry	**Catalyst**	**Styrylsilane conversion, %** [a]	**DA/PD ratio**
1	$[\{Ir(\mu\text{-}Cl)(CO)_2\}_n]$ **1**	64	85:15
2	$[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ **2**	90	90:10
3	$[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$ **3**	88	90:10
4	$[Ir(coe)_2(\mu\text{-}OMe)\}_2]$ **4**	67	80:20
5	$[IrCl(CO)(PPh_3)_2]$ **5**	0	-
6	$IrCl_3$ **6**	0	-
7	$IrCl_3$ / 2 eq PPh_3 **7**	0	-
8	$IrCl_3$ / $AgPF_6$ **8**	25	20:80

[a] *Measured by GC. Reaction conditions: toluene, 24h, 120 °C*

Table 2. *Results of iridium-catalysed acylation of (E)-styrylsilanes.*



Entry	**R^1**	**R^2**	**R^3**	**Styrylsilane Conversion [%][a] (isolated yield)**	**DA/PD [%][a]**
1	H	CH_3	CH_3	90 (72)	90:10
2	CH_3			76 (65)	90:10
3	Cl			78 (59)	90:10
4	Br			99 (85)	90:10
5	H		C_2H_5	98 (58)	90:10
6	CH_3			94 (76)	90:10
7	Cl			81 (67)	90:10
8	Br			88 (62)	90:10
9	Br		C_3H_7	79	80:20
10	H		*i*-C_3H_7	97	90:10
11	CH_3			99	100:0
12	H		-$C(CH_3)=CH_2$	58	80:20[b]
13	H		C_6H_5	99	90:10[c]
14	H	C_6H_5	CH_3	98	85:15
15	CH_3			63	90:10
16	Cl			83	90:10
17	H		C_2H_5	97	70:30
18	CH_3			93	80:20
19	Cl			99 (70)	80:20
20	H		*i*-C_3H_7	85	90:10
21	CH_3			92	70:30
22	Cl			91 (61)	80:20
23	H		-$C(CH_3)=CH_2$	99	85:15[b]
24	H		C_6H_5	66	90:10[c]

*Reaction conditions: [silylstyrene]:[acid anhydride]:[**2**] = 1:1:0.05, toluene (0.5 M), 24h, 120 C;* [a]*Measured by GC.* [b] *[$CH_2=C(Me)CO_2SiR_3$]:[styrene] ratio.* [c] *[$PhCO_2SiR_3$]:[styrene] ratio.*

Table 3. *Results of iridium-catalysed acylation of 1-phenyl-4-(trimethylsilyl)-1,3-butadiene*

Entry	**R**	**Time [h]**	**Isolated yield [%]**	***EE/EZ***[a]	**DA/PD**
1	CH_3	24	78	90:10	9:1
2	C_2H_5	24	67	90:10	8:2
3	C_6H_5	48	59	85:15	8:2

*Reaction conditions: [silyldiene]:[acid anhydride]:[**2**] = 1:1:0.05, toluene (0.5 M), 120 C;* [a]*Measured by* ^1H *NMR.*