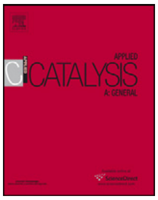
Applied Catalysis A: General 390 (2010) 94–101

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Silylcarbonylation of styrenes catalyzed by iridium(I) siloxide complexes

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ARTICLE INFO

Article history:
Received 6 August 2010
Received in revised form
27 September 2010
Accepted 29 September 2010
Available online 7 October 2010

Keywords:
Silylcarbonylation
Iridium(I) siloxide complexes
Enol silyl ethers of acylsilanes

ABSTRACT

This paper reports the study of iridium(I) catalyzed the incorporation of $HSiMe_2Ph$ and carbon monoxide to styrene and its derivatives. Comparative catalytic tests performed for the various iridium(I) precursors $[\{Ir(\mu\text{-}X)(diene)\}_2]$ (where X = OMe, OAc, $OSiMe_3$; diene = 1,5-cyclooctadiene (cod), tetrafluorobenzobarrelene (tfb)) and $[Ir(CO)_3(PCy_3)(SiPh_3)]$ showed that the binuclear complex $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ is the most efficient catalyst of the process studied and gives the main silylcarbonylation product, i.e. enol silyl ethers of acylsilanes ($RCH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$, where R = Ph, aryl) with relatively good yield. It enabled us to synthesize and isolate the exemplary acylsilane silyl enolates illustrating the potential application of binuclear siloxide iridium(I) complex in the synthesis of so useful in organic synthesis unsaturated organosilicon derivatives. Catalytic results as well as the detailed study of stoichiometric reaction of $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ and $[Ir(CO)_2(PCy_3)(OSiMe_3)]$ with the reaction substrates also under pressure of CO enabled us to propose a general catalytic scheme of the silylcarbonylation process including the formation of enol silyl ethers of acylsilanes as a main product accompanied by silyl enol ethers of aldehydes and products of styrene hydrosilylation.

1. Introduction

TM-catalyzed the incorporation of carbon monoxide into organic molecules has emerged the most elegant and economical synthetic tool for the hydrocarbon chain extension [1]. Cobalt catalyzed the silylcarbonylation reaction as simultaneous incorporation of trisubstituted silanes and carbon monoxide into the various organic molecules, e.g. alkenes [2], aldehydes [3] and cyclic ethers [4] has been successfully explained by Murai et al. [5] to yield silyl enol ethers of the homologous aldehydes as the sole products (Scheme 1).

On the other hand, only a few reports have been found on iridium-catalyzed silylcarbonylation of olefins [6,7] as well as acetylene [8] derivatives. However, iridium complexes, $[Ir_4(CO)_{12}]$ and $[\{Ir(\mu\text{-}Cl)(CO)_3\}_n]$ [6] and $[Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ [7] catalyze the silylcarbonylation of olefins predominantly to enol silyl ethers of acylsilanes only accompanied by enol silyl ethers of aldehydes (Scheme 2).

Enol silyl ethers of acylsilanes are widely used as substrates in organic and organosilicon synthesis (for recent reviews see [9]). These derivatives have been successfully applied as reagents in various reactions, e.g. diastereoselective aldol condensation with acetals [10], preparation of β-amino acids derivatives *via* catalytic Mannich reaction [11] and synthesis of 3-substituted azepanes by Lewis acid-promoted addition to nitroalkenes [12]. They are also very attractive compounds that can be easily converted to acylsilanes by hydrolysis [13] as well as by the reaction with Cl_2 [14], Br_2 [14], PhSCl [15] or acetals [16].

Several effective, stoichiometric procedures for the preparation of various enol silyl ethers of acyl silanes, have been widely described in the literature, such as reaction sequences of (1-silylallyl)lithium [17] or acyllithium [18] with carbon monoxide and chlorosilanes, enolization of acylsilanes [19] and α-substituted acylsilanes [20], following by rearrangement reaction of silenes with trimethylsilylketene [21], reaction of 1,1-bis(trimethylsilyl)substituted lithium alkoxides with benzophenone [22], and reaction of propenoyltrimethylsilane with Me_3Si-Nu [23], e.g. $Me_3Si\text{-}NEt_2$, Me_3Si-SPh, $Me_3Si\text{-}N_3$, etc.

Our recent results on the application of well-defined iridium(I) siloxide complexes in transformation of vinylsilanes to the corresponding enol silyl ethers of acyl silanes [7] encouraged us to continue a detailed study on their catalytic activity in silylcarbonylation of styrene and its mono- and multisubstituted derivatives and their possible application in the synthesis of the appropriate enol silyl ethers of acylsilanes. The aim of this work is to study in detail the catalytic activity to optimize the process studied, in order to establish the effect of the substituents in styrenes on the process efficiency as well as to propose a general mechanistic scheme of iridium(I)-catalyzed incorporation of trisubstituted silanes and carbon monoxide into olefins.

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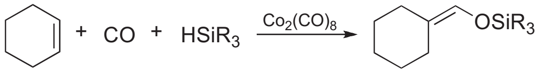
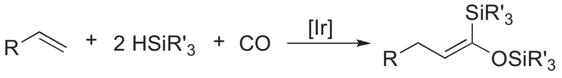
doi:10.1016/j.apcata.2010.09.036



Scheme 1. Cobalt catalyzed silylcarbonylation of olefins.



Scheme 2. Iridium promoted conversion of olefins to enol silyl ethers of acylsilanes.

2. Experimental

2.1. General methods and chemicals

All syntheses and manipulations were carried out under argon using standard Schlenk's and vacuum techniques. Pressure reactions were performed in a Parr pressure reactor (300 mL, in 20 mL glass vials). The tfb ligand [24] as well as the following complexes $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ [25], $[Ir(CO)_2(PCy_3)(OSiMe_3)]$ [7], $[Ir(tfb)_2Cl]$ [26], $[\{Ir(\mu\text{-}OMe)(tfb)\}_2]$ [27], $[\{Ir(\mu\text{-}OAc)(tfb)\}_2]$ [28], $[\{Ir(\mu\text{-}Cl)(tfb)\}_2]$ [29] and $[Ir(CO)_3(PCy_3)(SiPh_3)]$ [30] were synthesized according to described methods. Column chromatography was carried out with silica gel 60 from Fluka using C_6H_{12}:^{t}BuOMe = 49:1 or C_6H_{14}:AcOEt = 49:1. ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Gemini 300 VT spectrometer and Varian Mercury 300 VT in C_6D_6. The mass spectra of the products and substrates were determined by GC/MS (Varian Saturn 2100T equipped with a DB-5, 30 m capillary column). GC analyses of organic and organosilicon compounds were carried out on a Varian CP-3800 series gas chromatograph with a capillary column DB-5, 30 m and TCD. Determination of gases was carried out on Varian CP-3800 series gas chromatograph with a capillary column Varian CarboPLOT P7, 25 m with post-column 2.5 m, and TCD detector. As carrier gas argon was used. The chemicals were obtained from the following sources: sodium trimethylsilanolate, C_6D_6, $CDCl_3$ from Aldrich Chemical Co., organosilicone reagents, styrene and substituted styrenes from Gelest Ltd., toluene, hexane, cyclohexane, decane and other solvents from POCH Gliwice (Poland), carbon monoxide (4.7) from Fluka. All solvents and liquid reagents were dried and distilled under argon prior to use.

2.2. General procedure for silylcarbonylation tests

Mixtures of the appropriate olefins $RCH{=}CH_2$ (5.0 mmol), $HSiMe_2Ph$ (10 mmol), decane (internal standard, 5% of the substrates volume) and 15 mL of dried and deoxygenated toluene with the selected iridium(I) precursors (0.025 mmol) were prepared in a Schlenk's flasks under argon. The solutions obtained were placed in 20 mL glass vials equipped with magnetic bars and perforated aluminum caps under argon, and then glass reactors were placed into the Parr pressure reactor (five reactors for one run). Then the reactor was flushed with argon (5.0) and pressurized with CO (4.7). The reaction mixture was magnetically stirred at a given temperature for 60 h. After this time the pressure reactor was allowed to cool to room temperature and the mixture was analyzed by the GC and GC/MS methods. Conversion of the substrates was determined using the internal standard calculation method. Yield of products was calculated based on the conversion of $HSiMe_2Ph$.

2.3. Synthesis of silylcarbonylation products $RCH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$ (***1a***)

Portions of $RCH{=}CH_2$ (5.00 mmol) and $HSiMe_2Ph$ (1.43 g, 10.5 mmol) were dissolved in 15 mL of dried and deoxygenated toluene and 0.01945 g (0.025 mmol) of the catalyst $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ were placed in a Schlenk's flask under argon. Then the solution was transferred by syringe into a glass ampoule, which was placed in the pressure reactor flushed with argon prior to use. The reactor was pressurized to 60 bar with CO. The reaction mixture was magnetically stirred at 120 °C for 60 h. After this time the autoclave was allowed to cool to room temperature and the mixture was analyzed on the GC. The solvent was removed under reduced pressure and the product was isolated by fractional distillation under vacuum or by preparative column chromatography.

2.3.1. Compound $4\text{-}MeC_6H_4CH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$ (Entry 6)

Yield 1.56 g (75%).

Anal. calc. for $C_{26}H_{32}OSi_2$ C 74.94; H 7.74; found C 75.00; H 7.87. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ(ppm) = 7.53 (m, 4H, m-$\underline{Ph}SiMe_2$–); 7.38 (m, 6H, o,p-$\underline{Ph}SiMe_2$–); 7.11 (d, 2H, J_{H-H} = 8.1 Hz, 4-$MeC_6\underline{H_4}$–), 7.05 (d, 2H, J_{H-H} = 8.1 Hz, 4-$MeC_6\underline{H_4}$–); 5.70 (t, 1H, J_{H-H} = 8.1 Hz, –C$\underline{H}$=, Z-isomer), 5.33 (t, 1H, J_{H-H} = 6.8 Hz, –C$\underline{H}$=, E-isomer); 3.41 (d, 2H, J_{H-H} = 6.8 Hz, –CH_2–, E-isomer); 3.19 (d, 2H, J_{H-H} = 8.1 Hz, –CH_2–, Z-isomer); 2.35 (s, 3H, 4-$\underline{Me}C_6H_4$–, E-isomer); 2.33 (s, 3H, 4-$\underline{Me}C_6H_4$–, Z-isomer); 0.46 (s, 6H, –$OSiMe_2Ph$, Z-isomer); 0.44 (s, 6H, –$SiMe_2Ph$, Z-isomer), 0.35 (s, 6H, –$SiMe_2Ph$, E-isomer); 0.33 (s, 6H, –$OSiMe_2Ph$, E-isomer); ^{13}C NMR (75.42 MHz, $CDCl_3$, 300 K) δ(ppm) = 155.78; 138.24; 137.56; 135.44; 134.52; 134.24; 133.88; 133.66; 129.72; 129.38; 129.25; 129.12; 128.51; 128.22; 127.94; 126.05; 125.34; 33.23; 31.92; 21.27; −0.25; −1.63; −2.78. ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ(ppm) = 4.28 (–$OSiMe_2Ph$); −12.40 (–$SiMe_2Ph$).

2.3.2. Compound $4\text{-}MeOC_6H_4CH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$ (Entry 7)

Yield 1.56 g (72%).

Anal. calc. for $C_{26}H_{32}O_2Si_2$ C 72.17; H 7.45; found C 72.24; H 7.63. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ(ppm) = 7.53 (m, 4H, m-$\underline{Ph}SiMe_2$–); 7.18 (m, 6H, o,p-$\underline{Ph}SiMe_2$–); 7.04 (d, 2H, J_{H-H} = 8.8 Hz, 4-$MeOC_6\underline{H_4}$–), 6.74 (d, 2H, J_{H-H} = 8.8 Hz, 4-$MeOC_6\underline{H_4}$–); 5.82 (t, 1H, J_{H-H} = 7.8 Hz, –C$\underline{H}$=, Z-isomer), 5.44 (t, 1H, J_{H-H} = 6.8 Hz, –C$\underline{H}$=, E-isomer); 3.47 (d, 2H, J_{H-H} = 6.8 Hz, –CH_2–, E-isomer); 3.3 (s, 3H, $\underline{Me}OC_6H_4$–); 3.17 (d, 2H, J_{H-H} = 7.8 Hz, –CH_2–, Z-isomer); 0.31 (s, 6H, –$OSiMe_2Ph$); 0.30 (s, 6H, –$SiMe_2Ph$); ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ(ppm) = 160.00; 158.49; 156.75; 155.81; 138.70; 137.53; 134.61; 134.33; 133.72; 133.41; 129.92; 129.51; 129.47; 129.17; 126.37; 125.35; 114.24; 54.73; 33.04; 31.70; −0.30; −0.54; −1.65; −2.92 ($SiCHMe_2$). ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ(ppm) = 4.29 (–$OSiMe_2Ph$); −12.43 (–$SiMe_2Ph$).

2.3.3. Compound $4\text{-}^tBuOC_6H_4CH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$ (Entry 8)

Yield 1.83 g (77%).

Anal. calc. for $C_{29}H_{38}O_2Si_2$ C 73.36; H 8.07; found 73.43; H 8.25. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ(ppm) = 7.52 (m, 4H, m-$\underline{Ph}SiMe_2$–); 7.36 (m, 6H, o,p-$\underline{Ph}SiMe_2$–); 7.01 (d, 2H, J_{H-H} = 8.3 Hz, 4-$^tBuOC_6\underline{H_4}$–), 6.91 (d, 2H, J_{H-H} = 8.3 Hz, 4-$^tBuOC_6\underline{H_4}$–); 5.67 (t, 1H, J_{H-H} = 8.0 Hz, –C$\underline{H}$=, Z-isomer), 5.33 (t, 1H, J_{H-H} = 7.0 Hz, –C$\underline{H}$=, E-isomer); 3.39 (d, 2H, J_{H-H} = 7.0 Hz, –CH_2–, E-isomer); 3.15 (d, 2H, J_{H-H} = 8.0 Hz, –CH_2–, Z-isomer); 1.35 (s, 9H, 4-$^t\underline{Bu}OC_6H_4$–, E-isomer); 1.34 (s, 9H, 4-$^t\underline{Bu}OC_6H_4$–, Z-isomer); 0.44 (s, 6H, –$SiMe_2Ph$, Z-isomer); 0.43 (s, 6H, –$OSiMe_2Ph$, Z-isomer); 0.35 (s, 6H, –$OSiMe_2Ph$, E-isomer); 0.31 (s, 6H, –$SiMe_2Ph$, E-isomer). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ(ppm) = 155.81; 155.62; 138.46; 137.48; 136.03; 134.43; 134.14; 133.78; 133.63; 133.55; 133.16; 129.70; 129.63; 129.31; 129.23; 128.76; 128.51; 127.86; 125.85; 125.33; 124.28; 124.17; 78.25; 32.97; 31.48; 29.01; −0.34; −0.47; −1.77; −2.84. ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ(ppm) = 4.27 (–$OSiMe_2Ph$); −12.41 (–$SiMe_2Ph$).

2.4. Synthesis of trans-$PhCH_2CH{=}CHOSiMe_3$

Trans-1-trimethylsiloxy-3-phenyl-1-propene were synthesized according to the procedure described for 2-methyl-1-(trimethylsiloxy)propene [31].

2.5. Equimolar reactions of [{Ir(μ-OSiMe$_3$)(cod)}$_2$] (**I**)

With HSiR$_3$. To each of the three Young's NMR tubes containing a solution of 40.00 mg (0.05133 mmol) of complex (**I**) in C_6D_6, the following portions 26.261 mg (0.2258 mmol) of $HSiEt_3$, 30.768 mg (0.2258 mmol) of $HSiMe_2Ph$ and 58.799 mg (0.2258 mmol) of $HSiPh_3$ were introduced under argon. The reactions were conducted for 6 h at room temperature. After this time NMR spectra were recorded.

With HSiR$_3$ and CO. To each of the three NMR tubes containing a solution of 40.00 mg (0.05133 mmol) of complex (I) in C_6D_6, the following portions of the compounds 26.261 mg (0.2258 mmol) of $HSiEt_3$, 30.768 mg (0.2258 mmol) of $HSiMe_2Ph$ and 58.799 mg (0.2258 mmol) of $HSiPh_3$ were added under argon and then immediately CO was introduced to the solutions through a long needle. The reactions were conducted for 6 h at room temperature. After this time ^{1}H NMR spectra were recorded.

2.5.1. Equimolar reactions of [{Ir(CO)$_2$(PCy$_3$)(OSiMe$_3$)] with HSiMe$_2$Ph at room temperature

To the Young's NMR tubes containing a solution of 35.00 mg (0.05664 mmol) of [{Ir(CO)$_2$(PCy$_3$)(OSiMe$_3$)] in C_6D_6, we introduced 15.44 mg (0.1133 mmol) of $HSiMe_2Ph$ under argon. The reaction was conducted for 24 h at room temperature. After this time NMR spectrum was recorded.

2.5.2. Synthesis of [Ir(H)$_2$(CO)$_2$(SiMe$_2$Ph)(PCy$_3$)]

To the Schlenk's tubes containing a solution of 173 mg (0.28 mmol) of [{Ir(CO)$_2$(PCy$_3$)(OSiMe$_3$)] in benzene, the portion of 80.13 mg (0.588 mmol) of $HSiMe_2Ph$ was introduced under argon. The reaction was conducted for 24 h at room temperature. After this time solvent was evaporated and the crude product was washed with three portions of pentane. White solid complex was obtained with a yield of 89% (0.166 g).

Anal. calc. for $C_{28}H_{48}IrO_2PSi$ C 50.35; H 7.24; found 50.39; H 7.32. ^{1}H NMR (400 MHz, C_6D_6, 300 K) δ(ppm) = 7.92 (dd, 2H, m-$\underline{Ph}SiMe_2$–); 7.36 (m, 2H, o-$\underline{Ph}SiMe_2$–); 7.18 (tt, 1H, p-$\underline{Ph}SiMe_2$–); 2.67(m), 2.19(m), 1.75(m), 1.58(m) 1.49(m), 1.22(m), 1.03(m) (33H, –Cy); 0.28 (s, 6H, –$Si\underline{Me_2}Ph$); −10.56 (d, 2H, $J^2_{H-P} = 17.3$ Hz, Ir($\underline{H}$)$_2$). ^{13}C NMR (100.62 MHz, C_6D_6, 300 K) δ(ppm) = 176.55; 149.90; 133.71; 127.88; 127.63; 36.78 (d, $J^1_{C-P} = 21.1$ Hz); 30.55; 30.42; 27.42 (d); 26.56; 9.63(d), 1.36. ^{31}P NMR (161.71 MHz, C_6D_6, 300 K) δ(ppm) = 22.27.

2.5.3. Equimolar reaction of [Ir(CO)$_3$(PCy$_3$)(SiPh$_3$)]

With HSiMe$_2$Ph. Portion of [Ir(CO)$_3$(PCy$_3$)(SiPh$_3$)] (0.040 g; 0.049 mmol) and 0.6 mL of C_6D_6 were placed in a NMR tube, then 26.72 mg (0.196 mmol) of $HSiMe_2Ph$ was added to the mixture. The reaction was conducted for 24 h at 80 °C. After this time ^{1}H NMR spectrum was recorded.

With trans-$PhCH_2CH{=}CHOSiMe_3$. Portions of [Ir(CO)$_3$(PCy$_3$)(SiPh$_3$)] (0.035 g; 0.0429 mmol) and 0.6 mL of C_6D_6 were placed in the Young's NMR tube under argon, then 26.55 mg (0.1287 mmol) of *trans*-$PhCH_2CH{=}CHOSiMe_3$ was added to the mixture. The reaction was conducted for 24 h at 100 °C. After this time the reaction mixture was analyzed by GC/MS technique.

2.6. Silylcarbonylation of $C_6D_5CD{=}CD_2$ catalyzed by [{Ir(μ-OSiMe$_3$)(cod)}$_2$]

Portions of $C_6D_5CD{=}CD_2$ (0.45 g, 4.00 mmol) and $HSiMe_2Ph$ (1.44 g, 8.4 mmol) were dissolved in 15 mL of dried and deoxygenated toluene and 0.01556 g (0.02 mmol) of the catalyst [{Ir(μ-OSiMe$_3$)(cod)}$_2$] were placed in a Schlenk's flask under argon. Then the solution was transferred by syringe into a glass ampoule, which was placed in the pressure reactor flushed with argon prior to use. The reactor was pressurized to 60 bar with CO. The reaction mixture was magnetically stirred at 80 °C for 48 h. After this time the autoclave was allowed to cool to room temperature and the mixture was analyzed on the GC. The solvent was removed under reduced pressure and the product was isolated by preparative column chromatography using hexane/AcOEt.

^{1}H NMR (400 MHz, C_6D_6, 300 K) δ(ppm) = 7.62 (m, 4H, m-$\underline{Ph}SiMe_2$–); 7.27 (m, 6H, o,p-$\underline{Ph}SiMe_2$–); 3.56 (s, 1H, –CDH–, *E*-isomer); 3.38 (s, 1H, –CDH–, *Z*-isomer); 0.39 (s, 6H, –$OSiMe_2Ph$); 0.38 (s, 6H, –$SiMe_2Ph$).

2.7. Silylcarbonylation of trans-$PhCH_2CH{=}CHOSiMe_3$ catalyzed by [{Ir(μ-OSiMe$_3$)(cod)}$_2$]

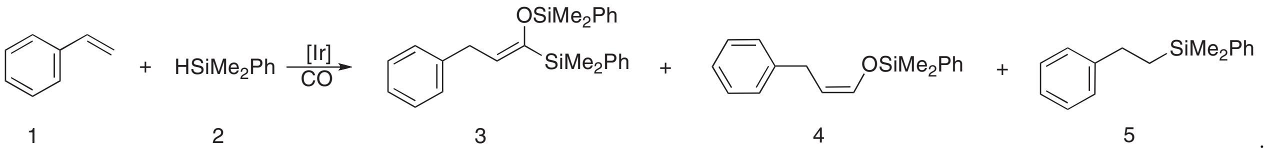
Portions of *trans*-$PhCH_2CH{=}CHOSiMe_3$ (0.5 g, 2.43 mmol) and $HSiMe_2Ph$ (0.33 g, 2.43 mmol) were dissolved in 10 mL of dried and deoxygenated toluene and 9.453 mg (0.0121 mmol) of catalyst [{Ir(μ-OSiMe$_3$)(cod)}$_2$] were placed in a Schlenk's tube under argon. Then the solution was transferred by syringe into a glass ampoule, which was placed in the pressure reactor flushed with argon prior to use. The reactor was pressurized to 60 bar with CO. The reaction mixture was magnetically stirred at 120 °C for 60 h. After this time the autoclave was cooled down to room temperature. The reaction mixture was analyzed by GC/MS technique.

3. Results and discussion

Binuclear iridium(I) siloxide complexes [{Ir(μ-OSiMe$_3$)(cod)}$_2$] and [{Ir(μ-OSiMe$_3$)(tfb)}$_2$] as well as other iridium(I) precursors, consisting O-bridging ligands system, e.g. OAc, OMe were examined in the silylcarbonylation reaction of styrene and its derivatives (see Table 1). In the representative reactions styrene and $HSiMe_2Ph$ under 60 bar of CO, after 60 h at 120 °C, precursors containing bridging-siloxide ligands were characterized with higher efficiency, giving silyl enol ether of acylsilane (**3**) with yields 87% (Entry 1) and 83% (Entry 2), respectively. On the other hand, iridium complexes containing other oxygen-bridging ligands, i.e. OAc, OMe also appeared to be active in the studied reaction, but less selective than the siloxide pre-catalysts ([{Ir(μ-OSiMe$_3$)(cod)}$_2$] and [{Ir(μ-OSiMe$_3$)(tfb)}$_2$]). Moreover, in the presence of iridium(I) precursors with non-silicon containing O-bridging ligands, silylcarbonylation process was accompanied by the increase of styrene polymerization in the adverse reaction. Generally, our iridium(I) siloxide catalytic system more efficiently catalyze the formation of enol silyl ether of acylsilanes, than complexes applied by Murai ([Ir$_4$(CO)$_{12}$], [{Ir(μ-Cl)(CO)$_3$}$_n$]) [6a] in the presence of which, the main product was formed with yield 50%, when tenfold excess of styrene relative to the $HSiEt_2Me$ was used.

Results obtained for two binuclear siloxide precursors (Entries 1 and 2) showed that different diene ligands bonded to the iridium center do not amend their catalytic activity. We found previously [7], that under carbonylation conditions in the first step the diene ligand is replaced by carbonyl ligands, so in both pre-catalysts the same siloxide-carbonyl intermediate is formed, therefore no differences in the catalytic efficiency between [{Ir(μ-OSiMe$_3$)(cod)}$_2$] and [{Ir(μ-OSiMe$_3$)(tfb)}$_2$] should be observed.

Table 1
Catalytic activity of various iridium(I) precursors in silylcarbonylation of styrene



Entry	Complex	Conversion (%)		Yield (%)		
		1	2	3	4	5
1	[{Ir(μ-OSiMe$_3$)(cod)}$_2$]	99	97	87	6	4
2	[{Ir(μ-OSiMe$_3$)(TFB)}$_2$]	95	93	83	7	3
3	[{Ir(μ-OMe)(TFB)}$_2$]	99	83	64	12	7
4	[{Ir(μ-OAc)(TFB)}$_2$]	99	67	52	8	6
5	[Ir(CO)$_3$(PCy$_3$)(SiPh$_3$)]	99	91	62	18	10

[styrene]:[HSiMe$_2$Ph]:[Ir] = 1:2:10^{-2}, argon, toluene, 60 h, T = 120 °C, 60 bar.

Iridium(I) silyl complex [Ir(CO)$_3$(PCy$_3$)(SiPh$_3$)] was also found very active but less selective (Entry 5).

According to data collected in Table 1, iridium(I) binuclear siloxide complex [{Ir(μ-OSiMe$_3$)(cod)}$_2$] was chosen for further study of silylcarbonylation of various monosubstituted styrene derivatives (Table 2). Silylcarbonylation carried out in the presence of selected precursor led to formation of the target product of **3a** type, in most cases with good yields (82–86%) (Entries 6–10). It allowed isolation and characterization of new compounds illustrating the possibility of iridium siloxide complexes application in the synthesis of new acylsilane derivatives.

In the catalytic tests performed, the effect of different electronic properties of substituents bonded to aromatic ring in 4-position on the selectivity of the main product **3a** was not observed (Entries 6–10). Significant effect was approved in the case of 2-chlorostyrene (Entry 11). The presence of one electron-withdrawing substituent in *ortho* position caused a decrease in the substrates conversion and in consequence also in the yield of the products.

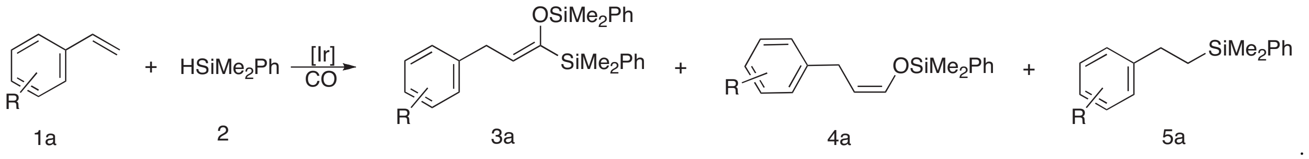
The efficiency of iridium(I) binuclear siloxide complex [{Ir(μ-OSiMe$_3$)(cod)}$_2$] in silylcarbonylation of multi-substituted styrenes was also examined. Results of the catalytic tests are compiled in Table 3. While, as expected, one substituent bonded in *ortho* position lowered the yield of the corresponding enol silyl ethers of acylsilanes, two substituents bonded to the aromatic ring dramatically suppressed the formation of the main products of **3b** type. However, in the case of *ortho*- and di-*ortho*-substituted styrenes, the presence of two effects, i.e. electronic and steric could significantly influence the reactivity of the vinyl group. We suggest (Entries 12 and 14) that steric effects play the key role. Substituents attached to the aromatic ring in two *ortho* positions block the vinyl group effectively, making the incorporation of carbon monoxide and HSiMe$_2$Ph very difficult. In 3,4-dimethoxystyrene (Entry 13), two methoxy radicals make the vinyl group active mainly in polymerization of starting olefin under reaction conditions.

As we mentioned above, Murai and coworkers [6a] published for the first time the results on the iridium catalyzed reaction of olefins with trisubstituted silanes under pressure of carbon monoxide, but the mechanism of enol silyl ether of acylsilanes formation in the presence of iridium complexes is yet unknown. These authors suggested, that iridium carbine complex (Ir≡C–OSiR$_3$), similarly to ruthenium carbine complex [6b], is the intermediate responsible for formation of silyl enol ether of acylsilane in the catalysis of HSiR$_3$ and CO simultaneous incorporation into olefins.

To identify the catalytically active iridium species formed from iridium-siloxide precursor under silylcarbonylation conditions as well as to characterize the catalytic performance of siloxide pre-catalyst, a series of stoichiometric reactions of siloxide precursors with the reaction substrates was studied. Our preliminary NMR study of transformations of iridium(I) siloxide precursors [Ir(cod)(PCy$_3$)(OSiMe$_3$)] under silylcarbonylation reaction conditions has revealed that in the presence of CO, the cyclooctadiene ligand is replaced by carbon monoxide [7]. Unfortunately, isolation of the product after the reaction of [{Ir(μ-OSiMe$_3$)(cod)}$_2$] (**I**) with CO was not possible because during evaporation of the solvent the product was observed to be decomposed.

A study of stoichiometric reactions of [{Ir(μ-OSiMe$_3$)(cod)}$_2$] with various trisubstituted silanes (HSiR$_3$, where R$_3$ = Me$_2$Ph, Ph$_3$,

Table 2
Results on [{Ir(μ-OSiMe$_3$)(cod)}$_2$] catalyzed silylcarbonylation of monosubstituted styrenes

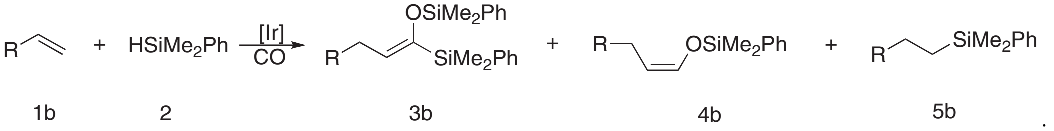


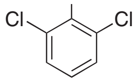
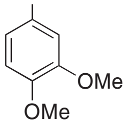
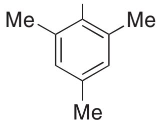
Entry	R	Conversion (%)		Yield (%)		
		1a	**2**	**3a**, Z/E	**4a**	**5a**
6	4-Me	98	97	84(75[a]), 1/3.7	8	2
7	4-OMe	95	93	83(72[a]), 1/4.0	6	3
8	4-O^{t}Bu	96	94	82(77[a]), 1/3.0	7	2
9	4-Cl	97	94	86	4	2
10	4-Br	96	94	83	8	3
11	2-Cl	75	65	50	8	5

[RC$_6$H$_4$CH=CH$_2$]:[HSiMe$_2$Ph]:[Ir] = 1:2:10^{-2}, argon, toluene, 60 h, T = 120 °C, 60 bar.

[a] Isolated yield.

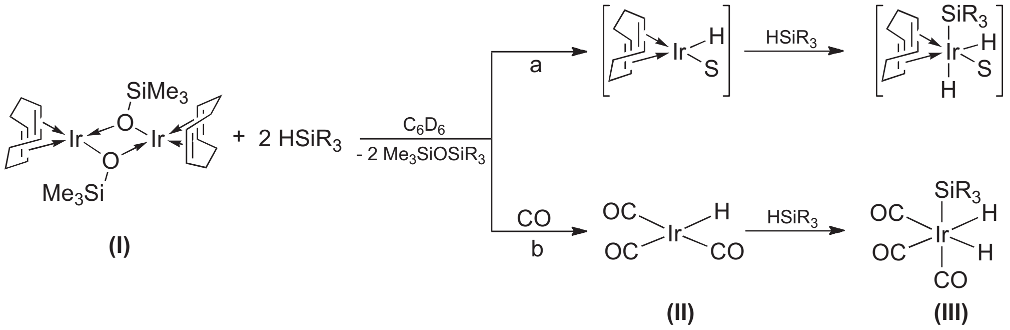
Table 3
Results on [{Ir(μ-OSiMe$_3$)(cod)}$_2$] catalyzed silylcarbonylation of multisubstituted styrenes



Entry	R	Conversion (%)		Yield (%)		
		1b	**2**	**3b**	**4b**	**5b**
12		54	45	24	11	10
13[a]		100	15	10	3	2
14		27	25	18	3	4

[RCH=CH$_2$]:[HSiMe$_2$Ph]:[Ir] = 1:2:10^{-2}, argon, toluene, 60 h, T = 120 °C, 60 bar.

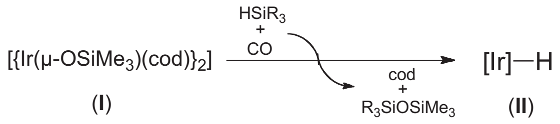
[a] Polymerization as main process.



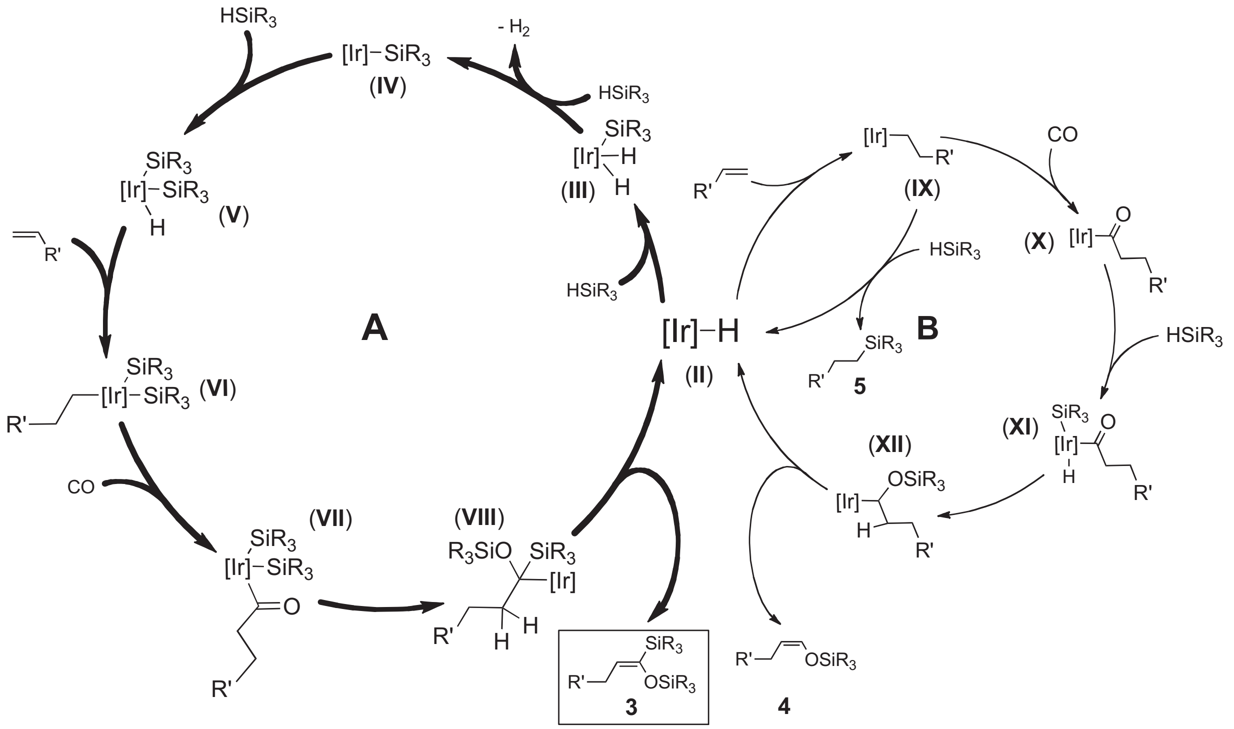
Scheme 3. Reaction of the precursor **I** with trisubstituted silanes.

Et$_3$) (Scheme 3a) and in the presence of CO (Scheme 3b) followed by ^{1}H NMR technique, confirmed the formation of iridium silyldihydrido complexes *via* elimination step of appropriate siloxanes whose structures were confirmed by GC/MS analysis.

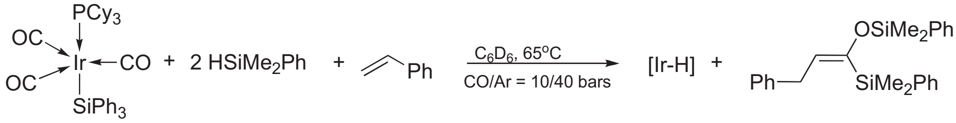
On the ^{1}H NMR spectra recorded to monitor the reactions of siloxide precursor with HSiMe$_2$Ph and HSiPh$_3$, performed according to Scheme 3 by path (**a**), revealed a number of signals assigned to hydrides −15.46, −15.49, −15.59, −15.93, −15.76 ppm for HSiMe$_2$Ph and respectively −7.50, −7.87, −8.03, −10.05 ppm for HSiPh$_3$. A large number of organometallic species containing hydride ligands and their undergoing transformations in time made the isolation of compounds not possible. To stabilize the yielded iridium hydride species, appropriate trisubstituted silanes and carbon monoxide were introduced simultaneously to the solution of binuclear siloxide complex. ^{1}H NMR spectra recorded of the reaction mixtures obtained, showed the resonance lines assigned to a number of various hydride species R$_3$ = Et$_3$ (−8.49, −9.01, −11.35, −11.99 (dominant)), Me$_2$Ph (−5.95, −9.25, −14.31), Ph$_3$ (−7.33, −9.75, −11.58, −19.07 ppm), respectively. Unsuccessful isolation trials of hydride-silyl complexes obtained during the reactions of iridium binuclear precursor with HSiR$_3$ and CO prompted us to apply a more stable siloxide precursor [Ir(CO)$_2$(PCy$_3$)(OSiMe$_3$)] [7] to study of dihydrido-silyl complexes formation. Stoichiometric reaction of binuclear iridium siloxide precursor (**I**) confirmed that in the initial step each iridium center in complex (**I**) reacts with one molecule of trisubstituted silane and carbon monoxide. As a result of elemental reaction sequence i.e. oxidative addition of HSiR$_3$, substitution of cyclooctadiene ligand by CO, and then elimination of disiloxane Me$_3$SiOSiR$_3$ molecule, iridium(I)-hydride species (**II**) are formed as in the case of iridium(I) siloxide catalyzed hydrosilylation reaction [32] (Scheme 4). The equimolar experiments on the reactivity of **I** with reaction substrates as well as all catalytic results provided the basis for a general mechanistic scheme to be proposed (Scheme 5). The iridium(I) hydride species (**II**), stabilized by excess of CO, can initiate two catalytic cycles. After the reaction of (**II**) with the next molecule of H–Si derivative, the formation of dihydride-silyl complex [Ir](H)$_2$(SiR$_3$) (**III**) initiates cycle **A** in which the main product of (**3**) type is formed. Iridium(I) hydride complex is also responsible for the formation of a side product (**4**) in cycle **B**. Formation of type



Scheme 4. Initial transformation of the precursor **I**.



Scheme 5. Catalytic performance of complex $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ (**I**) in transformation of olefins to enol silyl ethers of acylsilanes (cycle **A**) accompanied by enol silyl ethers of aldehydes (cycle **B**) and hydrosilylation of olefins.



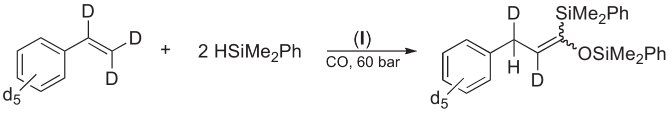
Scheme 6. Equimolar reaction of $[Ir(CO)_3(PCy_3)(SiPh_3)]$ with $HSiMe_2Ph$ and $H_2C{=}CHPh$ under pressure of carbon monoxide.

(**III**) species was confirmed by the reaction of one equivalent of $[Ir(CO)_2(PCy_3)(OSiMe_3)]$ with two equivalents of $HSiMe_2Ph$ in the reaction sequence (**I**) → (**II**) → (**III**), which results the formation of dihydride-silyl complex $[Ir(H)_2(CO)_2(SiMe_2Ph)(PCy_3)]$ quantitatively. The ^1H NMR spectrum of the isolated iridium(III) silyl-dihydride complex showed a doublet at −10.58 ppm with a coupling constant $J_{H-P} = 17.10$ Hz assigned to two hydride ligands bonded to iridium center, while the ^{31}P NMR spectrum revealed a singlet at 22.27 ppm (see Section 2). Additionally, GC/MS analysis confirmed the presence of disiloxane ($Me_3SiOSiMe_2Ph$) in the reaction mixture obtained.

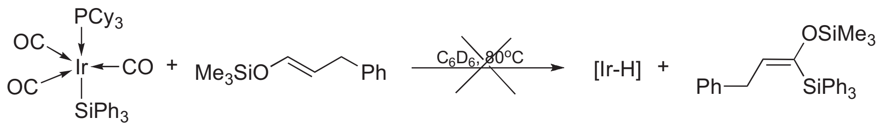
We assumed, that in the catalytic cycle (**A**) proposed, the dihydride-silyl complex (**III**) under silylcarbonylation conditions is transformed to iridium(I)-silyl complex (**IV**), which is responsible for the formation of final product, i.e. enol silyl ethers of acylsilanes (type **3** product). GC analysis of the gas mixture left after the reaction confirmed the presence of hydrogen (there was no presence of formaldehyde); which implied that from complex (**III**) silyl species (**IV**) is yielded.

Relatively high catalytic activity of iridium complex $[Ir(CO)_3(PCy_3)(SiPh_3)]$ (Table 1, Entry 5) in the studied process suggests that an iridium(I)-silyl intermediate (**IV**) plays an important role in catalytic cycle (**A**) and it must be generated *in situ* in the presence of carbon monoxide. Followed by ^1H NMR, equimolar reaction of $[Ir(CO)_3(PCy_3)(SiPh_3)]$ with $HSiMe_2Ph$ at 60 °C confirmed formation Ir–H species. The spectrum recorded showed two doublets in the hydride region, i.e. at −10.28 ppm ($J^2_{H-P} = 16.2$ Hz) and a major one at −10.44 ppm ($J^2_{H-P} = 16.8$ Hz). Traces of the complex $[Ir(H)_2(CO)_2(PCy_3)(SiMe_2Ph)]$ were also observed (−10.56 ppm, $J^2_{H-P} = 17.3$ Hz, $Ir(\underline{H})_2$). Additionally, the GC/MS analysis of the reaction mixture obtained after the stoichiometric reaction of iridium(I) silyl complex $[Ir(CO)_3(PCy_3)(SiPh_3)]$ with $HSiMe_2Ph$ and styrene under carbonylation conditions confirmed the formation of appropriate enol silyl ether of acyl silane (Scheme 6) (see Section 2).

Instead of silylcarbonylation product containing two different silyl substituents, the product with two $SiMe_2Ph$ groups was observed. The presence of the same two silyl groups in the final derivative can be explained by the exchange of $SiPh_3$ ligand in the initial precursor under reaction conditions. Using GC/MS technique the presence of free $HSiPh_3$ as well as PCy_3 in the reaction mixture was detected. Formation of Ir–H species as well as the enol silyl ether of acylsilane in the stoichiometric experiments with $[Ir(CO)_3(PCy_3)(SiPh_3)]$ suggests that iridium(III) bissilyl-hydride intermediate ($IrH(SiR_3)_2$) (**V**) is active in this process. Then after the insertion of the olefin into Ir–H bond, complex (**VI**) can be formed. Subsequent insertion of CO takes place into Ir–C bond giving the acyl complex (**VII**). The formation of iridium acyl deriva-



Scheme 7. $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ (**I**) catalyzed silylcarbonylation of styrene-d_8.



Scheme 8. Stoichiometric reaction of *trans*-$PhCH_2CH{=}CHOSiMe_3$ with $[Ir(CO)_3(PCy_3)(SiPh_3)]$.

tive (**VII**) was indirectly confirmed by the NMR study of type (**3**) product structure obtained in the silylcarbonylation of styrene-d_8 with $HSiMe_2Ph$ catalyzed by complex (**I**) (Scheme 7) (see Section 2).

Singlets located at 3.56 ppm and 3.38 ppm in the ^1H NMR spectrum of silylcarbonylation product obtained were assigned to the benzyl position in the product examined (*E* and *Z* isomers), which confirms formation of the intermediate (**VII**) in the sequence (**V**) → (**VI**) → (**VII**). In the next step as a result of transition complex (**VII**) formation, the rearranged intermediate (**VIII**) appears. The rearrangement proposed in our catalytic scheme ((**VII**) → (**VIII**)) is based on the transformation recognized by Murai and coworkers [2,5a] for conversion of olefins to silyl enol ethers of aldehydes catalyzed by $[Co_2(CO)_8]$. Moreover, in the hydrosilylation of carbonyl compounds the mechanism based on the Chalk Harrod's concept involves just the insertion of the carbonyl substrates into the rhodium-silicon bond to produce the silylalkoxylrhodium intermediate of the (**VIII**) type [33]. However, we suppose that in the case of iridium intermediate (**VII**), the shift of two silyl moieties to acyl function bonded to iridium center and formation of transition complex (**VIII**) occurs. As a consequence of hydrogen transfer, the final product (**3**) is eliminated from (**VIII**) species and the initial iridium-hydride complex (**II**) is recovered.

We also assume that by-products (**4** and **5** type) are produced by the sequence of reactions (**II**) → (**IX**) → (**X**) → (**XI**) → (**XII**) → (**II**) and (**II**) → (**IX**) → (**II**) as shown in cycle **B**, which is analogous to the scheme presented for cobalt [2,5a] catalyzed conversion of olefins to silyl enol ethers of aldehydes under the silylcarbonylation conditions.

The catalytic silylcarbonylation reaction of synthesized *trans*-$PhCH_2CH{=}CHOSiMe_3$ with $HSiMe_2Ph$ in the presence of (**I**) confirmed that the starting compound cannot be transformed to the appropriate silyl enol ether of acylsilane (no silylcarbonylation product has been detected), but only isomerization products were observed. Additionally, no insertion–elimination sequence product was observed on the GC/MS and NMR spectra after the reaction of *trans*-$PhCH_2CH{=}CHOSiMe_3$ with $[Ir(CO)_3(PCy_3)(SiPh_3)]$ (Scheme 8).

Thus, it is evidenced that cycles **A** and **B** operate independently, and enol silyl ether of aldehyde (side product (**4**)) produced in cycle **B** cannot be converted into the reaction product (**3**).

4. Conclusions

Catalytic tests performed on various iridium(I) precursors confirmed high efficiency of the binuclear siloxide complex $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ in transformation of styrene and its *para*-substituted derivatives to appropriate enol silyl ethers of acylsilanes ($RCH_2CH{=}C(OSiMe_2Ph)SiMe_2Ph$, where R = Ph, aryl) *via* incorporation of trisubstituted silane and carbon monoxide into the starting olefin. Some of the exemplary new organosilicon derivatives were isolated and fully characterized by the spectroscopic methods. However, in the case of *ortho*- and di-*ortho*-substituted styrenes the presence of the halogen or organic groups at the positions mentioned blocks the vinyl group effectively, making the incorporation of carbon monoxide and $HSiMe_2Ph$ very difficult.

Catalytic results on silylcarbonylation and stoichiometric studies of $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$, $[Ir(CO)_2(PCy_3)(OSiMe_3)]$ and $[Ir(CO)_3(PCy_3)(SiPh_3)]$ with the reaction substrates allowed us to propose a reasonable scheme of the catalytic performance of binuclear siloxide complex $[\{Ir(\mu\text{-}OSiMe_3)(cod)\}_2]$ in transformation of olefins to enol silyl ethers of acylsilanes as well as competitive reactions.

Acknowledgements

This work was made possible by a grant (N204 162 32/4248) from the Ministry of Science and Higher Education, and postdoctoral fellowship from Foundation for Polish Science (I. Kownacki).

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