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Synthesis, Structure, and Reactivity of [{Ir(cod)(μ-OSiMe$_3$)}$_2$] with Styrene and Vinylsilanes: Catalytic Activation of the Vinylic ═C−H Bond

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This paper reports the first successful synthesis of iridium-siloxide complex [{Ir(cod)(μ-OSiMe$_3$)}$_2$] (**I**), whose structure has been determined by X-ray diffraction. Complex **I** has an A-frame bis-square planar geometry and is a selective catalyst of silylative heterocoupling of styrene with vinyltrisubstituted silanes $CH_2{=}CHSiR_3$ (**A**) (where R_3 = Me$_3$, Me$_2$Ph, (OEt)$_3$), Me$_2$(OSiMe$_3$), Me(OSiMe$_3$)$_2$) and/or of hydrovinylation (co-dimerization) of styrene with vinylsilanes $CH_2{=}CHSi(OR')_3$ (**B**) (where R′ = SiMe$_3$, *tert*-Bu). Results of a stoichiometric study of **I** with substrates and labeling experiments (GC−MS and ^{1}H NMR analysis) with the deuterated styrene indicate the exchange of the vinylic proton and a non-metallacarbene mechanism of the two reactions proceeding via generation of active Ir−H intermediates by oxidative addition of ═C−H to monomeric iridium-siloxide complexes. All the data allowed us to propose a reasonable mechanism of the silylative coupling, which does not involve migratory insertion of olefin into the Ir−Si bond as well as a mechanism of the hydrovinylation (co-dimerization) of styrene with vinyltris(trimethylsiloxy)silane.

Introduction

Molecular complexes incorporating M−O−Si bonds (where M = transition metal) seem to be good models for metal complexes immobilized on silica and/or silicate surfaces.[1] While siloxide complexes of early transition elements are well-characterized, the data on the late transition metal-siloxides in molecular form have been scarce.[2] Siloxy derivatives of ruthenium,[3] nickel,[4] platinum,[5] iron,[6] cobalt,[7] and rhodium[8−11] and to a minor extent also osmium[13] and iridium[5c] have been synthesized and characterized spectroscopically, and the structures of most of them have been resolved by X-ray studies. The complexes containing a Rh−O−Si bond have recently become a subject of great interest. These complexes included [{Rh(cod)(μ-OSiPh$_3$)}$_2$],[7,8] [{Rh(diene)(μ-OSiMe$_3$)}$_2$], where diene = cyclooctadiene (cod)[9a,c] and norbornadiene (nbd),[9c] and [{Rh(CO)$_2$(μ-OSiR$_3$)}$_2$], where R = Me,[10] Ph.[8a] Unfortunately, the reactivity and catalytic activity of the molecular well-defined catalysts have been illustrated in only a few exemplary reactions.[11,12] The complex [{Rh(cod)(μ-OSiMe$_3$)}$_2$] appeared to be a very effective catalyst in hydrosilylation of alkenes[12a] and silylative coupling of vinylsilanes with alkenes.[12b,c] The stoichiometric reactions of the catalyst with the substrates as well as with deuterated substrates enabled us to establish the mechanistic pathways of these catalytic processes.

The Vaska analogue of iridium siloxide, i.e., [Ir(CO)(PPh$_3$)$_2$(OSiMe$_3$)], first synthesized and characterized spectroscopically by Schmidbaur and Adlkofer,[5c] is to our knowledge the only iridium complex containing a

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siloxy ligand. Therefore, the aim of this work is, by analogy with [$\{Rh(cod)(\mu\text{-}OSiMe_3)\}_2$], to prepare a respective iridium siloxide complex and determine its structure and reactivity with α-olefins (vinylsilanes and styrene), to determine conditions for catalytic activation of the vinylic =C−H bond.

Experimental Section

General Methods and Chemicals. All syntheses and manipulations were carried out under argon using standard Schlenk and vacuum techniques. ^1H, ^{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-1, 30 m capillary column). GC analyses were carried out on a Varian 3400 CX series gas chromatograph with a capillary column DB-1, 30 m and TCD. The chemicals were obtained from the following sources: sodium trimethylsilanolate from Aldrich, vinyltrisubstituted silanes from ABCR, benzene from OBR PR Plock (Poland), styrene from Fluka, benzene-d_6 and styrene-d_8 from Dr. Glaser, AG Basel. All solvents and vinyl-substituted silanes were dried and distilled under argon prior to use. [$\{Ir(cod)(\mu\text{-}Cl)\}_2$] was prepared according to the previously reported procedure.[13]

Synthesis of [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$]. Portions of [$\{Ir(cod)(\mu\text{-}Cl)\}_2$] (1.0 g; 1.49 mmol) and $NaOSiMe_3$ (0.347 g; 3.1 mmol) were placed in a Schlenk flask under argon. Then 10 mL of dried and deoxygenated benzene was added. The reaction was conducted for 24 h at room temperature. After this time benzene was evaporated and 15 mL of dried and deoxygenated pentane was added. The entire mixture was filtered off by a cannula system. Evaporation of the filtrate left an orange solid (yield 1.1 g; 94%). ^1H NMR δ (ppm, C_6D_6): 0.31 (s, 18H, $-CH_3$); 1.46 (m, 8H, $-CH_2-$); 2.12, 2.28 (m, 8H, $-CH_2-$); 4.02, 4.13 (m, 8H, $=CH-$). ^{13}C NMR δ (ppm, C_6D_6): 6.03 (OSi−C); 32.64, 33.05 ($-CH_2-$); 55.70, 58.50 ($=CH-$). ^{29}Si NMR (INEPT) δ (ppm, C_6D_6): 17.18 ($-OSiMe_3$). Anal. Calcd for C 33.91; H 5.43. Found: C 33.77; H 5.77.

X-ray Structure Determination. Single crystals of the complex were grown by slow evaporation from the solution. Accurate cell parameters were determined by a least-squares fit of 2842 reflections. Diffraction data were collected by the ω scan technique up to $2\theta = 48°$, on a KUMA KM4CCD four-circle diffractometer[14] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The temperature was kept at −143 °C. All data were corrected for Lorentz−polarization effects[15] and absorption.[16]

The total of 9141 reflections were collected, including 4107 unique ones ($R_{int} = 0.055$); of these 3557 were observed ($I > 2\sigma(I)$). The structures were solved with direct methods with SHELXS97[17] and refined by full-matrix least-squares procedures on F^2 with SHELXL97.[18] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at the calculated positions and refined as a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq}'s of the appropriate carrier atom. Weak restraints were applied to the thermal parameters of carbon atoms. On the refinement, the thermal parameters of oxygen atoms got too low and physically impossible values; therefore we decided to use the scattering factors characteristic of the atom with more electrons (the best results were obtained for aluminum−sulfur). As the geometry of the complex (O−Rh and O−Si bond lengths, etc.) as well as all other analyses exclude the possibility of the presence of other than oxygen atoms, these features must be an artifact. They might be caused by systematic errors such as absorption and/or extinction or the symmetry of the complex (both oxygen atoms lie in the approximate mirror plane of symmetry), inducing a high correlation between parameters, and finally, there may be some disorder in the molecule, which we have not been able to resolve.

Table 1. Crystallographic Data for I

empirical formula	$Ir_2Si_2O_2C_{22}H_{42}$
fw	811.26
cryst size (mm)	0.3 × 0.2 × 0.2
cryst syst	monoclinic
Space group	$P2_1/c$
a, Å	17.0920(14)
b, Å	9.9080(7)
c, Å	16.8493(11)
β, deg	112.707(7)
V, Å^3	2632.2(3)
Z	4
ρ_{calcd}, g cm^{-3}	2.047
μ, mm^{-1}	10.358
R,[a] wR2[b] [$I > 2\sigma(I)$], %	5.78, 11.70

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Significant crystal data are listed in Table 1.

General Procedure for Catalytic Examinations. In a typical catalytic test, iridium complex, olefin, toluene (internal standard), and vinyl trisubstituted silane or vinyl trisubstituted siloxane were placed under argon in a glass ampule ([Ir]:[$CH_2=CHSiR_3$]:[olefin] = 10^{-2}:1:10). The sealed ampule was heated at the specified conditions. The composition of the reaction mixture was analyzed by GC. The conversion, yield, and selectivity were calculated by the internal standard method.

Catalytic Experiments with Deuterated Reagents. Reaction between Styrene-d_0 and Styrene-d_8. [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$] (0.0075 g; 9.64 × 10^{-6} mol) was dissolved under argon in 0.5 mL of C_6D_6 in an NMR tube. Then styrene-d_0 (0.040 g; 3.86 × 10^{-4} mol) and styrene-d_8 (0.043 g; 3.86 × 10^{-4} mol) were added. The tube was sealed and heated at 60 °C for 2 h. The mixture was analyzed by GC−MS and ^1H NMR spectroscopy before and after the reaction.[12c]

Reaction between Styrene-d_8 and Vinyldimethylphenylsilane. [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$] (0.0025 g; 3.2 × 10^{-6} mol) was dissolved under argon in 0.6 mL of benzene in an Supelco vial. To the solution $CH_2=CHSiMe_2Ph$ (0.104 g; 6.43 × 10^{-4} mol) and styrene-d_8 (0.072 g; 6.43 × 10^{-4} mol) were added. The vial was heated in a heating chamber at 80 °C. The reaction was controlled by GC−MS.

Stoichiometric Reactions of [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$] with Styrene and Vinyltrisubstituted Silanes. [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$] (0.035 g; 4.5 × 10^{-5} mol) was dissolved under argon in 0.6 mL of C_6D_6 in a NMR tube. A portion of $CH_2=CHSiMe_2Ph$ (0.146 g; 9 × 10^{-4} mol) was added to the solution. The run of reaction was controlled by ^1H NMR. The corresponding reaction of **I** with styrene (0.094 g; 9 × 10^{-4} mol) and with the mixture of $CH_2=CHSiMe_2Ph$ (0.146 g; 9 × 10^{-4} mol) and styrene (0.094 g; 9 × 10^{-4} mol) were performed using the same procedure as that for $CH_2=CHSiMe_2Ph$.

The reaction of **I** (0.03 g; 3.86 × 10^{-5} mol) with $CH_2=CHSi(OSiMe_3)_3$ (0.248 g; 7.71 × 10^{-4} mol) as well as with the mixture of $CH_2=CH(OSiMe_3)_3$, (0.248 g; 7.71 × 10^{-4} mol) and styrene (0.08 g; 7.71 × 10^{-4} mol) was also performed according to the above-described procedure.

Synthesis of (*E*)-$PhCH=CHSi(OEt)_3$. Portions of $CH_2=CHPh$ (10.9 g; 0.106 mol), [$\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2$] (0.0409 g; 5.26 × 10^{-5} mol), and $CH_2=CHSi(OEt)_3$ (2 g; 0.0105 mol) were placed in a Schlenk flask under argon. The flask was heated in an oil bath at 100 °C for 24 h. After completion of the reaction, the excess of styrene was evaporated. The product

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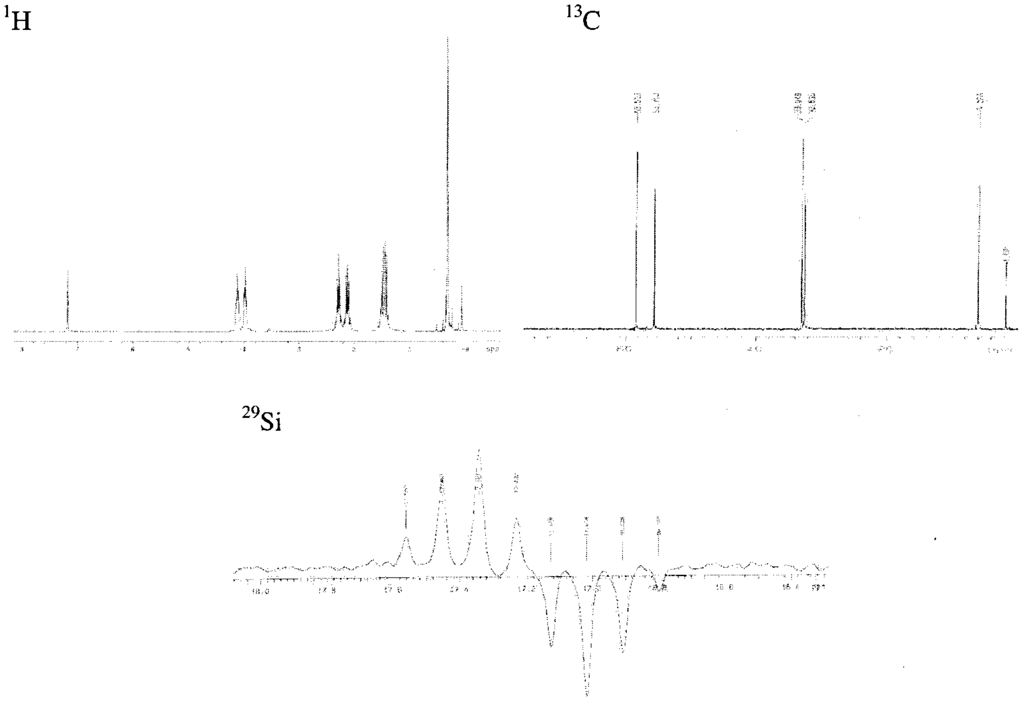

Figure 1. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of [{Ir(cod)(μ-OSiMe$_3$)}$_2$] (**I**) recorded in C$_6$D$_6$ at room temperature.

was extracted from the oily residue with dry pentane. The residue was subjected to fractional distillation under vacuum. The product was collected as a fraction boiling at 94−98 °C, 1 mm, yield 2.37 g (85%) by comparison of the ^{1}H NMR and ^{13}C NMR spectra. The product was identified by comparison with an authentic sample.[22]

Synthesis of (*E*)-PhCH$_2$CH$_2$CH=CHSi(OSiMe$_3$)$_3$. Portions of CH$_2$=CHPh (6.45 g; 0.062 mol), [{Ir(cod)(μ-OSiMe$_3$)}$_2$] (0.0242 g; 3.11×10^{-5} mol), and CH$_2$=CHSi(OSiMe$_3$)$_3$ (2 g; 6.21×10^{-3} mol) were placed in a Schlenk flask under argon. The flask was heated in an oil bath at 100 °C for 48 h. After completion of the reaction the excess styrene was evaporated. The product was extracted from the oily residue with dry pentane. The residue was subjected to fractional distillation under vacuum. The product was collected as a fraction boiling at 124−130 °C (1 mmHg) (yield 1.98 g; 75%). ^{1}H NMR δ (ppm, C$_6$D$_6$): 0.18 (s, 27H, −CH$_3$); 1.27 (t, 2H, −CH$_2$−); 2.81 (q, 2H, −CH$_2$−); 6.15 (d, 1H, =CHSi); 7.19−7.6 (m, 5H, −Ph, 1H, =CH−). ^{13}C NMR δ(ppm, C$_6$D$_6$): 1.93 (−CH$_3$); 15.77 (−CH$_2$−); 26.50 (−CH$_2$−); 128.14, 128.59, 128.74, 136.5 (−C$_6$H$_5$); 130.50 (−CH=), 143.8 (−SiCH=). MS: *m/z* 45(12), 73(50), 189(100), 190(19), 191(12), 207(50), 208(12), 209(12), 279(14), 295(75), 296(25), 297(13), 411(18), 426(11). HRMS: calcd 426.18982, found 426.18921. Anal. Calcd for C 53.46; H 9.97. Found: C 55.00; H 9.17.

(*E*)-PhCH=CHSiMe$_2$Ph was synthesized according to the procedure given previously.[22]

Results and Disscusion

Synthesis and Structure. Reaction of [{Ir(cod)(μ-Cl)}$_2$] with sodium trimethylsilanolate was used effectively for the synthesis of the corresponding iridium-siloxide complex **I** according to the following equation:

$$[\{(\mathrm{cod})\mathrm{Ir}(\mu\text{-Cl})\}_2] + 2\mathrm{NaOSiMe}_3 \rightarrow [\{(\mathrm{cod})\mathrm{Ir}(\mu\text{-OSiMe}_3)\}_2] + 2\mathrm{NaCl} \quad (1)$$

The product was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

The ^{1}H NMR spectrum of [{Ir(cod)(μ-OSiMe$_3$)}$_2$] shows two chemically inequivalent cod-olefinic resonances lines which appear as slightly broadened singlets (presumably owing to the unresolved coupling and not to chemical exchange) at δ = 4.13 and 4.02 ppm (Figure 1).

In the iridium siloxide complex cod-aliphatic signals are observed as three broadened multiplets at δ = 1.46, 2.12, and 2.28 ppm. The Me$_3$Si resonance appears as a singlet at δ = 0.31 ppm. The iridium-chloro precursor [{Ir(cod)(μ-Cl)}$_2$] shows only one type of cod-olefin resonance at δ = 4.28 ppm and the cod-aliphatic multiplet resonances at 1.20 and 1.96 ppm.[13]

The ^{13}C NMR spectrum of [{Ir(cod)(μ-OSiMe$_3$)}$_2$] (Figure 1) is also consistent with a dimeric folded structure, and the cod-olefinic doublet resonance is not equivalent and appears at δ = 55.70 and 58.50 ppm. The cod-aliphatic resonances appear as two singlets at δ = 32.64 and 33.05 ppm. The Me$_3$Si resonance appears as a singlet at δ = 6.03 ppm. The ^{29}Si {^{1}H} INEPT NMR spectrum in C$_6$D$_6$ reveals only a multiplet resonance at 17.18 ppm (Figure 1).

The X-ray structure of the molecule is shown in Figure 2. To the best of our knowledge complex **I** is the first iridium-siloxide complex whose structure has been determined by the X-ray method. The geometry of the complex is generally similar to that of the rhodium analogue, i.e., [{Rh(cod)(μ-OSiMe$_3$)}$_2$], whose structure was solved previously.[9b]

The complex has an A-frame bis-square planar geometry; a nearly perfect mirror plane of symmetry

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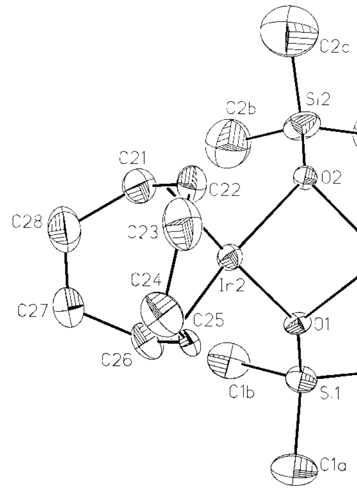


Figure 2. Anisotropic displacement ellipsoid representation of complex **I**. Ellipsoids are drawn at the 33% probability level; hydrogen atoms are omitted for clarity.

Table 2. Relevant Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses[a]

Ir(1)−X(1A)	1.985(14)	Ir(1)−X(1B)	1.999(13)
Ir(1)−O(2)	2.161(3)	Ir(1)−O(1)	2.166(3)
Ir(2)−X(2B)	1.979(11)	Ir(2)−X(2A)	1.983(14)
Ir(2)−O(1)	1.998(3)	Ir(2)−O(2)	2.158(3)
O(1)−Si(1)	1.648(5)	O(2)−Si(2)	1.553(5)
X(1A)−Ir(1)−X(1B)	87.7(6)	X(2B)−Ir(2)−X(2A)	88.4(5)
X(1A)−Ir(1)−O(2)	96.2(4)	X(2B)−Ir(2)−O(1)	92.9(4)
X(1B)−Ir(1)−O(2)	171.2(4)	X(2A)−Ir(2)−O(1)	174.8(4)
X(1A)−Ir(1)−O(1)	171.0(4)	X(2B)−Ir(2)−O(2)	173.1(3)
X(1B)−Ir(1)−O(1)	96.9(4)	X(2A)−Ir(2)−O(2)	96.2(4)
O(2)−Ir(1)−O(1)	78.25(11)	O(1)−Ir(2)−O(2)	82.05(11)
Ir(2)−O(1)−Ir(1)	84.13(11)	Ir(2)−O(2)−Ir(1)	80.56(9)
Si(1)−O(1)−Ir(2)	143.9(2)	Si(2)−O(2)−Ir(2)	134.9(2)

[a] X1A, X1B, X2A, and X2B denote the midpoints of C11−C12, C15−C16, C21−C22, and C25−C26 bonds, respectively (these points are regarded as the coordination sites).

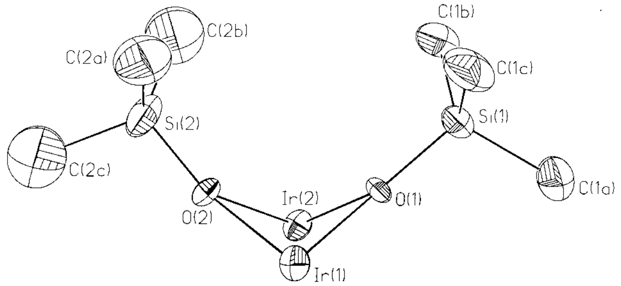
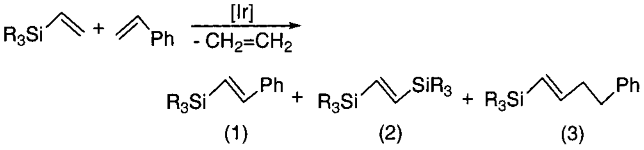


Figure 3. Perspective view of complex **I**.

passes through oxygen and silicon atoms (Figure 2). Selected bond lengths, bond angles, and torsion angles are listed in Table 2.

The roof angle of 119.7 compares well with the value found in a rhodium complex (120.4(2)° [9b]). Also in this case there is a relatively short intramolecular Ir···Ir distance of 2.7923(6) Å (2.812(1) Å for Rh·Rh distance). The cod fragments are close to a C_2 twist boat conformation (Figure 3), the lowest energy conformation found in both experimental[19] and theoretical studies.[20] This can be visualized by small values of asymmetry parameters, ΔC_2,[21] of 1.85° and 2.70° for C11···C18 and C21···C28 rings, respectively.

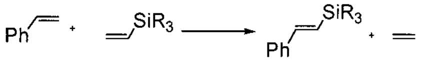
Table 3. Silylative Coupling vs Hydrovinylation (Co-dimerization) of Styrene with Vinyltrisubstituted Silanes Catalyzed by [{Ir(cod)(μ-OSiMe$_3$)}$_2$][a]



compound	conversion (%)	yield (%) (1)	yield (%) (2)	yield (%) (3)
$CH_2{=}CHSiMe_3$	50	2	45	0
$CH_2{=}CHSi(OEt)_3$	90	84	6	0
	59[b]	55	4	0
	7[c]	7	0	0
$CH_2{=}CHSiMe_2Ph$	70	60	4	0
	30[b]	29	traces	0
	2[c]	traces	0	0
$CH_2{=}CHSiMe_2OSiMe_3$	60	6	51	3
	75[d]	7	64	4
$CH_2{=}CHSiMe(OSiMe_3)_2$	9[b]	0	6	3
	44	0	44	0
	65[d]	0	61	4
$CH_2{=}CHSi(OSiMe_3)_3$	46	traces	0	42
$CH_2{=}CHSi(OSiMe_3)_3$	65[d]	traces	0	60
$CH_2{=}CHSi(O^tBu)_3$	7[b]	0	traces	7
	39	0	0	39

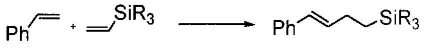
[a] Reaction conditions: [Ir]:[$CH_2{=}CHSi{\equiv}$]:[styrene] = 10^{-2}:1:10, argon, 100 °C, 24 h, ampules. [b] 80 °C, 24 h. [c] [{Ir(cod)(μ-Cl)}$_2$]. [d] 100 °C, 48 h.

Catalytic Studies. The reaction of styrene with vinyltrisubstituted silanes $CH_2{=}CHSiR_3$ occurs in the presence of **I** according to eq 2:



(2)

where R_3 = $SiMe_2Ph$ and $Si(OEt)_3$. (*E*)-1-Phenyl-2-silylethene, a product of heterocoupling of styrene with vinylsilane, is the main liquid product of the reaction accompanied by traces of 1,2-bis-silylethene as byproduct of the homocoupling of vinylsilane. However, contrary to the [{Rh(cod)(μ-OSiMe$_3$)}$_2$]-catalyzed process,[12b,c] instead of silylative coupling with evolution of ethylene, **I** catalyzes hydrovinylation (co-dimerization) of styrene with $CH_2{=}CHSi(OR')_3$ (where R′ = $SiMe_3$, *t*-Bu) according to eq 3 to get (*E*)-1-silyl-4-phenyl-1-butene as a main



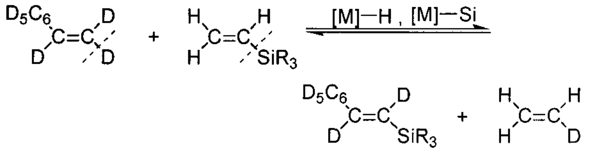
(3)

product accompanied by traces of heterocoupling of vinylsilane with styrene.

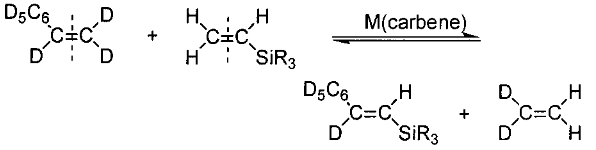
Exemplary catalytic data are compiled in Table 3. All the main products were isolated and characterized by ^1H and ^{13}C NMR and GC−MS analyses.

Apparently, steric hindrance of three siloxy substituents at silicon stops the silylative coupling and promotes the hydrovinylation process. Competitive activation of =C−H in styrene and vinylsilanes by the iridium complex seems to be a crucial point determining different reactivity of these olefins.

Labeling Studies. To learn more about the mechanism of the two above-mentioned reactions, experiments with deuterium-labeled reagents were performed.[22] In the case of a non-metallacarbene mechanism the formation of silylstyrene-d_7 and ethylene-*d* is to be expected (eq 4). In contrast, a metallacarbene mechanism should afford silylstyrene-d_6 and ethylene-d_2 (eq 5).



(4)



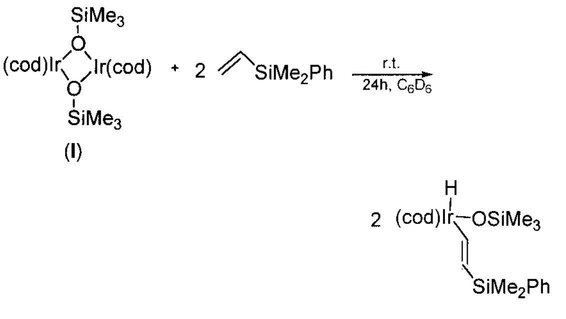
(5)

GC−MS analysis of the reaction mixture in a very early stage shows exclusive formation of silylstyrene-d_7 (and ethylene that has not been analyzed). The peaks $m/z = 245$ ($M^{+\bullet}$) and 230 ($M^{+} - CH_3$) recorded after 0.5 h of the reaction are convincing evidence of the formation of a product containing seven deuterium atoms. No $m/z = 244$ signal was detected at the beginning step of the reaction. This result strongly confirms the non-metallacarbene mechanism of the reaction. It was therefore decided to study the mechanism of hydride (or silyl) complex generation in the system. The reaction between styrene and styrene-d_8 in the presence of catalytic amounts of **I** was tested.

Similarly to the rhodium-siloxide-catalyzed reaction,[12c] also in this system the presence of a mixture of styrenes (d_0, d_1, d_2, d_3, d_5, d_6, d_7, and d_8) was confirmed by GC−MS. The ^1H NMR spectrum clearly shows that H/D exchange takes place in all positions of the vinyl group of styrenes. A similar experiment with the use of *p*-methylstyrene-d_0 and styrene-d_8 confirms this result and shows that there is no other H/D exchange in the aromatic ring or the methyl group. The H/D exchange in the vinyl group of styrene observed in the presence of **I** suggests that generation of active hydride species proceeds by oxidative addition of the vinylic $=C-H$ bond to the iridium atom.

Stoichiometric Study. To characterize the iridium-siloxide complex catalytic performance, a series of pseudostoichiometric reactions between **I** and both substrates were studied. Results of a pseudostoichiometric study of **I** with styrene (where [**I**]:[styrene] = 1:20) at room temperature as well as at 60 °C (after 10 min and 24 h) controlled by ^1H NMR showed no changes in the region of the shifted siloxyl signals. Also no signals assigned to hydrides formed in the process were noted.

On the other hand, the reaction of **I** with $CH_2{=}CHSiMe_2Ph$ was carried out to yield a complex containing an Ir−H bond according to eq 6:



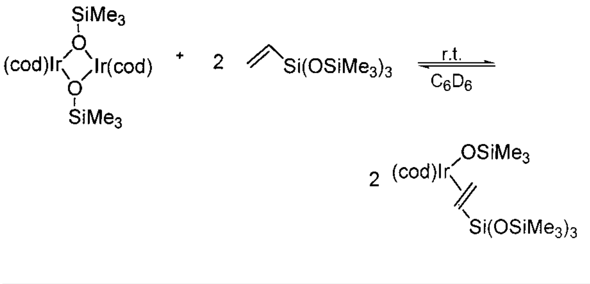
(6)

where $[Ir]:[CH_2{=}CHSiMe_2Ph] = 1:10$.

An ^1H NMR study showed no dissociation of cod from the iridium complex and signals assigned to hydrides of which the most intense was that of the chemical shift at −11.19 ppm. A doublet of low intensity around of 8.9 ppm is suggested to correspond to the protons from the vinylidene ligand fragment [Ir]C*H*═CHSi. The reported ^1H NMR characterization of iridium complexes with $[Ir(acac)(H)\{(E)\text{-}CH{=}CHC(O)Me\}(PCy_3)_2]$[23] (two doublets at 10.91 and 6.48 ppm) implies that it was impossible to observe the second coupled doublet assigned to the proton (IrCH═C*H*Si), as most probably its chemical shift is the same as that of the signals observed in the spectrum of the initial vinylsilane used in excess. Lower values of the chemical shift for the proton attached to the carbon atom adjacent to the iridium atom can be interpreted as due to electron-donor properties of the silicon atom. When at the next step styrene was introduced to such a mixture at the molar ratio $[Ir]:[CH_2{=}CHSiMe_2Ph]:[styrene] = 1:10:10$, the ^1H NMR spectrum recorded after 24h showed additional resonance lines at −16.05 and −18.38 ppm. The measurements were controlled after 5 days, and the line at −18.38 ppm disappeared, while the signal at −16.05 remained. Moreover, GC−MS study in the same conditions ($[Ir]:[CH_2{=}CHSiMe_2Ph]:[styrene] = 1:10:10$) revealed formation of (*E*)-$PhMe_2SiCH{=}CHPh$, $PhMe_2SiCH{=}CHSiMe_2Ph$, and no traces of siloxane $PhMe_2SiOSiMe_3$, which would have been the evidence for reductive elimination from the $[Ir(cod)(CH{=}CHPh)(SiMe_2Ph)(OSiMe_3)]$ intermediate.

On the other hand, when styrene was added prior to vinyldimethylphenylsilane, similar results were observed. The ^1H NMR spectrum recorded after 1 h showed the line at −11.20 ppm, but after 24 h additional peaks (−11.69, −12.78, and −13.69 ppm) were detected, emphasizing the lability of iridium(hydride)(siloxide) complexes containing ligands forming from both substrates under the reaction conditions.

When vinyltris(trimethylsiloxy)silane ($CH_2{=}CHSi(OSiMe_3)_3$) was subjected to a reaction with **I** (where $[Ir]:[CH_2{=}CHSi(OSiMe_3)_3] = 1:10$), at room temperature after 10 min, the resonance line assigned to the $OSiMe_3$ dimer (0.312 ppm) disappeared and two signals assigned to the siloxy group of the monomeric siloxide complex with a coordinated vinylsilane molecule (characterized by the chemical shifts 0.271 and 0.267 ppm) appeared. Simultaneously, the chemical shifts of the signals from the cyclooctadiene ligand changed by about 0.04 ppm. No signals assigned to hydrides were observed. If the sample was heated for 2 h at 60 °C, no changes in the ^1H NMR spectrum were noted, so the reaction can be formulated as follows:



(7)

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[23] Castarlenas, R.; Esteruelas, M. A.; Martin, M.; Oro, L. A. *J. Organomet. Chem.* **1998**, *564*, 241.

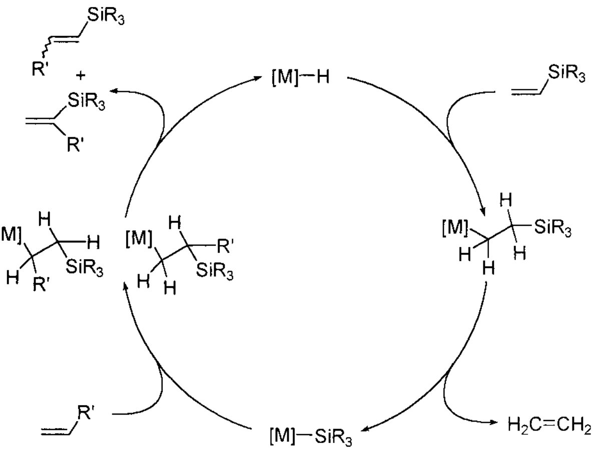
If subsequently styrene was added to the same sample and the mixture was heated for 2 h at 60 °C, the NMR spectrum showed also no signals in the hydride region; however, the spectrum recorded after 24 h showed a singlet at −18.87 ppm, which still remained after 48 h. Results of the GC−MS and ^{1}H NMR study evidenced formation of $PhCH_2CH_2CH{=}CHSi(OSiMe_3)_3$. The ^{1}H NMR spectrum of the compound obtained did not reveal signals characteristic of the R_3SiCH_2 system, whose chemical shift usually is 0.4−0.7 ppm. Therefore, we have proposed a structure of a vinylsilane and not styrene derivative.

Mechanistic Implications. All pseudo-stoichiometric reactions of **I** with styrene and two types of vinyltrisubstituted silanes provided the evidence that mechanisms of the two reactions observed, i.e., silylative coupling (trans-silylation, silyl group transfer) (**A**) and hydrovinylation (co-dimerization) (**B**) of styrene with vinylsilane, involve iridium−hydrogen intermediates.

The H/D processes occurring in the presence of **I** between styrene-d_8 and styrene-d_8 as well as *p*-methylstyrene-d_0 and styrene-d_0 are the convincing evidence for oxidative addition of the ═C−H bond of styrenes and vinylsilanes to the iridium siloxide complex **I**.

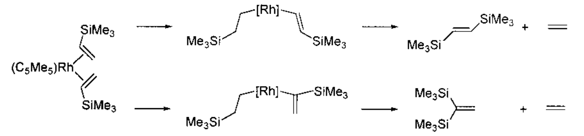
The silylative homocoupling of vinyl-substituted silicon compounds and their heterocoupling with olefin can be effectively catalyzed by ruthenium,[24] rhodium,[12a,b,23b,d,25] cobalt,[26] and iron[27] complexes. Results of the catalytic, synthetic, and mechanistic studies of the process have shown that in the presence of catalysts containing initially M−H or M−Si bonds (or those in which these bonds can be generated in situ) the reaction occurs through the cleavage of the ═C−Si bond of the vinyl silicon compound and the ═C−H bond of the olefin (also the vinyl-silicon compound in homocoupling; see eq 4). The catalytic cycle of this new type of silylolefin conversion involves the migratory insertion of olefin (or vinylsilane) into the M−Si bond, where M = Ru,[24f,i] Rh,[25] and Co[26] (and vinylsilane into the M−H bond), followed by β-H (and β-Si) transfer to the metal atom with elimination of phenyl(silyl)ethene (and ethene)[28] (Scheme 1).

Scheme 1



where: M = Ru, Rh, Co; R = alkyl, aryl, alkoxyl, siloxyl
R' = Ph, alkyl, silyl

Experiments performed by Brookhart et al.[29] under thermolysis conditions (140 °C, cyclohexane-d_{12}) and in 10-fold excess of $CH_2{=}CHSiMe_3$ showed the occurrence of the following process:



(8)

These reactions provide precedents for hydrovinylation of one of the coordinated molecules of vinylsilane followed by the insertion of the second molecule into the generated Rh−H bond (not observed in this system), subsequent elimination of ethylene, and reductive elimination of two types of bis(silyl)ethenes.

Our earlier study on the application of siloxy-rhodium complexes in homo-[12b] and heterocoupling[12c] of vinylsilanes with olefins revealed that contrary to the previously reported silylative coupling of olefins by complexes containing initially M−H and M−Si bonds, the proposed catalytic cycle does not involve migratory insertion of olefin into the Rh−Si bond (the associative mechanism) since the final step of the product formation occurs via reductive elimination of the final product (the dissociative mechanism).

The hydrovinylation is originally defined as the addition of ═C−H of ethylene to the C═C bond of a second alkene molecule[2] and has been catalyzed by nickel or palladium compounds. Ruthenium, rhodium, and cobalt complexes were also reported as catalysts, but the reaction was usually accompanied by considerable isomerization of the primary product.[30] Per analogy to the historical hydrovinylation, in this paper the observed reaction of codimerization (**B**) is understood as an addition of ═C−H of vinyltris(trimethylsiloxy)silane (also vinyltri(*tert*-butoxy)silane) to C═C of styrene

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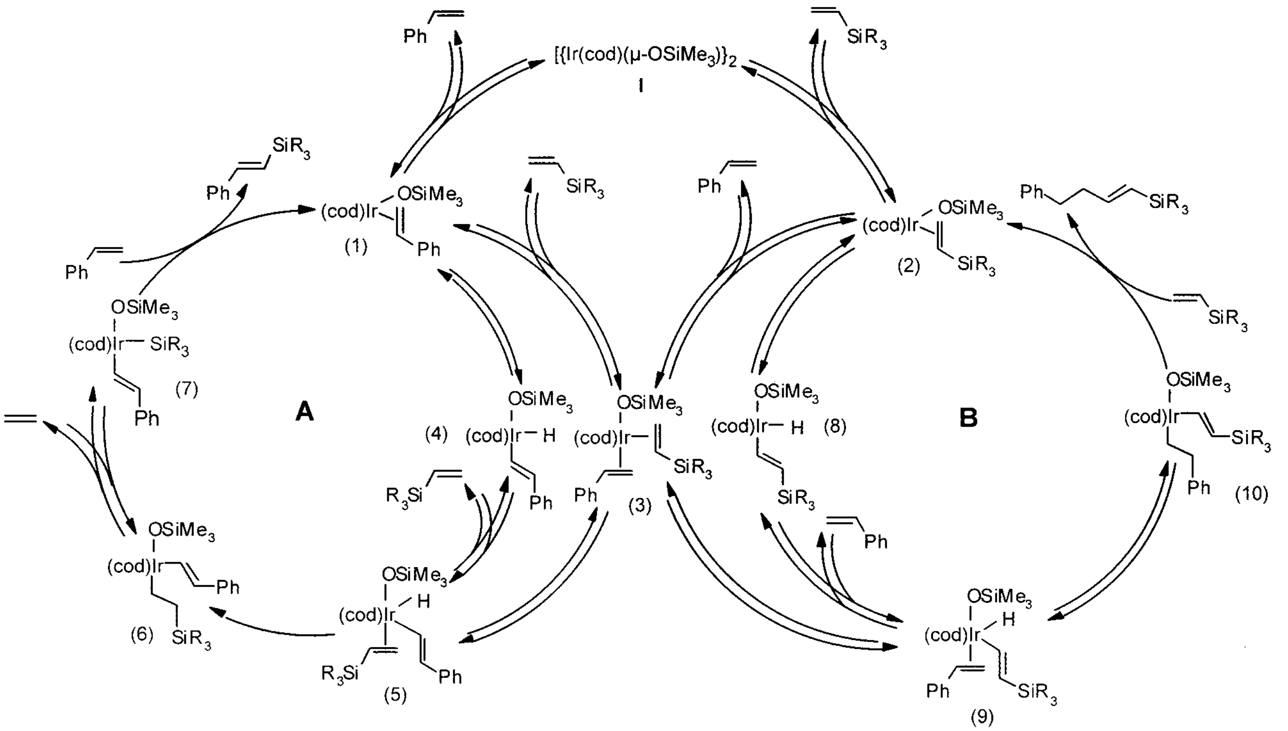
Scheme 2. Catalytic Activation of =C−H of Styrene and Vinylsilane



to get the products (E)-$PhCH_2CH_2CH{=}CHSi(OSiMe_3)_3$ and (E)-$PhCH_2CH_2CH{=}CHSi(O\text{-}tert\text{-}Bu)_3$ (1-silyl-4-phenyl-1-butene); so adapting the classical name we can call this reaction hydro(silyl)vinylation.

The above precedents together with the present results and the MS study of the products of the deuterated styrene reaction with vinyldimethylphenylsilane support the non-metallacarbene mechanism for the competitive reaction of vinylsilanes with styrene proceeding in the presence of iridium complex **I** as a precursor, shown in Scheme 2.

The very fast H/D exchange process occurring in **I**−styrene d_0−styrene d_8 mixtures of both stoichiometric and catalytic conditions and the observation (by ^{1}H NMR) of unstable complexes containing an Ir−H bond in the pseudo-stoichiometric examination of **I** with styrene have allowed us to assume that coordination of styrene to iridium is responsible for the cleavage of the dimeric iridium complex **I** to form **1** followed by an oxidative addition of =C−H of styrene to iridium (complex **4**). The latter initiates, in the presence of $CH_2{=}CHSiMe_2Ph$ as a second substrate, a catalytic process observed by GC−MS (see Scheme 2, cycle **A**). On the other hand, a coordination of vinylsilane to iridium observed by ^{1}H NMR is also evidence for the cleavage of dimeric **I** by vinylsilane (**I** → **2**) followed by an oxidative addition of =C−H vinylsilane to iridium to form complex **9**, initiating, in the presence of styrene, the catalytic hydrovinylation (co-dimerization process) (see cycle **B**). 16e monomeric iridium complexes of square planar geometry (**1** and **2**), under catalytic conditions can coordinate the second (not bulky) molecule of the olefin (complex **3**).

In the cases of $CH_2{=}CHSiMe_2Ph$, $CH_2{=}CHSiMe_3$, and $CH_2{=}CHSi(OEt)_3$, where process **A** occurs exclusively, the formation of intermediate **5** seems to be a crucial step for the whole stereoselective process of (E)-styrylsilane production. All of the stoichiometric and catalytic results (by GC−MS and ^{1}H NMR) indicate that the reaction can proceed either via **1** → **4** → **5** or **1** → **3** → **5** pathways. When vinylsilane is added prior to styrene, a sequence of reversible pathways **2** → **8** → **9** → **3** → **5** must also be regarded.

The next insertion of vinylsilane into the Ir−H bond of **5** is followed by elimination of ethylene (β-Si transfer) to give the Ir−Si intermediate **7**. Then according to the dissociative mechanism observed also for rhodium-siloxide catalyst,[12c] the reductive elimination of (E)-silylstyrene takes place in an excess of styrene, regenerating complex **1**. The side reaction of homocoupling of vinylsilanes to yield bis(silyl)ethene can occur according to the same mechanism that involves an iridium intermediate containing two vinylsilane molecules coordinated to the iridium (cf. eq 8).

On the other hand, the intermediate **2**, i.e., 16e monomeric iridium complex with a coordinated molecule of vinyltris(siloxy)silane, which is observed (by ^{1}H NMR) even under pseudo-stoichiometric study, initiates an activation of =C−H of vinylsilane (complex **9**) that predominates over the activation of styrene. For the case of such a bulky vinylsilane (see also vinyltri(*tert*-butoxy)silane) it seems probable that the reaction occurs rather via preliminary oxidative addition of =C−H of vinylsilane **2** → **8** → **9** than via formation of five-coordinated iridium complex **3** with two π-bonding olefin molecules **2** → **3** → **9**. The next insertion of styrene into the Ir−H bond is followed by direct elimination of phenylethyl(silyl)ethene as a main product of the hydrovinylation (mechanism **B**) and regeneration (in the presence of silane with bulky substituents, such as vinyltris(siloxy)silane and vinyltri(*tert*-butoxy)silane) of complex **2**. The side reaction of heterocoupling of styrene with this vinylsilane is also observed as an effect of the mechanism **A**.

The above considerations explain why silylative heterocoupling of styrene (cycle (**A**)) in the presence of **I** occurs much more easily with relatively small substituents at silicon in the vinylsilane, while the bulky substituent prefers the hydrovinylation (hydro(silyl)-vinylation) of styrene proceeding via mechanism (**B**).

Conclusions

(i) [{Ir(cod)(μ-OSiMe$_3$)}$_2$] (**I**), the first iridium-siloxide complex whose structure has been successfully determined, has been synthesized and spectroscopically characterized.

(ii) **I** is a precursor of the stoichiometric and catalytic activation of =C−H bond of styrene and vinylsilanes.

(iii) Catalytic labeling and stoichiometric study of the system **I** + vinylsilane + styrene (styrene-d_8) allowed us to propose a reasonable mechanism of the competitive reaction of the silylative coupling (**A**) and hydrovinylation (co-dimerization) (**B**) of styrene with vinylsilanes catalyzed initially by **I**.

(iv) While phenyl, methyl, and not bulky alkoxy substituted vinylsilanes at silicon lead to stereo- and regioselective synthesis of styrylsilane via silylative coupling (**A**), bulk siloxy and *tert*-butoxy substituents at silicon have been found to give also stereo- and regioselectively, (*E*)-1-silyl-4-phenyl-1-butene (co-dimerization) (**B**).

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