

Silylcarbonylation of Vinylsilanes Catalyzed by Iridium(I) Siloxide Complexes

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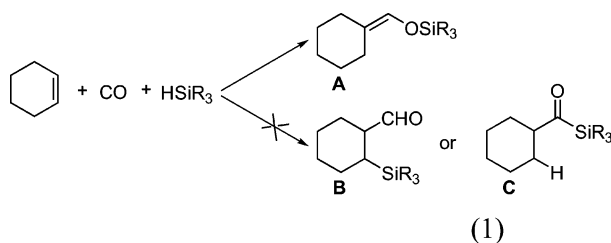
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The iridium siloxide complexes $[\{\text{Ir}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ (**I**) and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{OSiMe}_3)]$ (**II**) were used as catalysts in the silylcarbonylation of $\text{CH}_2=\text{CHSiMe}_3$. While complex **I** effectively catalyzed the highly stereoselective formation of (*E*)-1-(dimethylphenylsiloxy)-1-(dimethylphenylsilyl)-3-(trimethylsilyl)-1-propene (**1a**, $\text{Me}_3\text{SiCH}_2\text{CH}=\text{C}(\text{OSiMe}_2\text{Ph})\text{SiMe}_2\text{Ph}$; yield 82%), complex **II** led the reaction to stereoselective synthesis of (*Z*)-1-(dimethylphenylsiloxy)-3-(trimethylsilyl)-1-propene (**2a**, $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHOSiMe}_2\text{Ph}$; yield 95%). The former product was used for synthesis of the acylsilane ($\text{Me}_3\text{SiCH}_2\text{CH}_2\text{C}(\text{O})\text{SiMe}_2\text{Ph}$) (**4a**; yield 92%), a well-known reagent in organic synthesis. Under a CO atmosphere the cyclooctadiene ligand in both complexes was replaced by CO, and the X-ray structure of $[\text{Ir}(\text{CO})_2(\text{PCy}_3)\text{OSiMe}_3]$ (**IV**) was resolved.

Introduction

Catalytic silylcarbonylation of unsaturated compounds has emerged as a promising, most elegant, and economical synthetic tool for hydrocarbon chain extension via direct introduction of carbon monoxide into organic molecules.¹ Cobalt-catalyzed carbonylation reactions have been explored by Murai and co-workers.² Using $[\text{Co}_2(\text{CO})_8]$ as the catalyst, they have introduced carbon monoxide and trisubstituted silanes into various organic compounds: e.g. alkenes,³ aldehydes,⁴ and cyclic ethers.⁵ The characteristic point in the reaction of alkenes in silylcarbonylation is that enol silyl ethers (**A**) are formed exclusively, and neither β -silyl aldehyde (**B**) nor acylsilane (**C**) is observed in the reaction mixture (eq 1).



While cobalt complexes have been intensively studied in silylcarbonylation reactions, rhodium complexes have

been shown to be efficient catalysts for silylformylation of alkynes and have been effectively used in systems with terminal and internal alkynes,^{6–9} diynes,¹⁰ and enynes,¹¹ giving various unsaturated silyl aldehydes and cyclic compounds containing a carbonyl moiety. On the other hand, rhodium-catalyzed incorporation of CO and organosilane into a C=C bond, e.g. in enamines,¹² leads to formation of enol silyl ethers, exactly as in Murai's study (eq 1), but in reactions of homoallylic alcohol derivatives the aldehydes were observed as products of intramolecular reaction.¹³

In contrast to the case for cobalt and rhodium organometallic precursors, the iridium complexes have not

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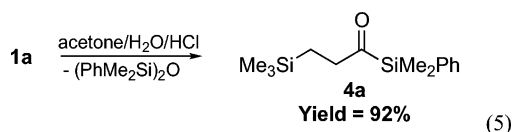
Table 2. Reaction of Vinyltrimethylphenylsilane with Dimethylphenylsilane and Carbon Monoxide in the Presence of Iridium(I) Siloxide Complexes I and II^a

molar ratio [H ₂ C=CHSiMe ₂ Ph]: [HSiMe ₂ Ph]	pressure of CO (bar)	conversion (%)		yield (%)		
		H ₂ C=CHSi- Me ₂ Ph	HSiMe ₂ - Ph	1b	2b	3b
1:2 ^c	10	94	99	31	47	15
1:2 ^c	60	72	81	40	18	14
1:2 ^d	10	0	0	0	0	0
1:2 ^{b,d}	10	80	78	0	0	80

^a Conditions: [H₂C=CHSiMe₂Ph]:[Ir] = 1:5 × 10⁻³, argon, 24 h, T = 120 °C, toluene, unless specified otherwise. ^b In air. ^c [Ir(cod)(μ-OSiMe₃)₂]. ^d [Ir(cod)(PCy₃)(OSiMe₃)].

molar ratio of substrates and pressure of the carbon monoxide, as well as the structure of the catalyst used. The catalytic activity of the iridium(I) siloxide complexes was studied in the reaction systems of two vinylsilanes, vinyltrimethylsilane and vinyltrimethylphenylsilane.

The data given in Table 1 indicate that for a mixture of substrates (**a**), complex **I** catalyzes the formation of the enol silyl ether of the acylsilane (**1a**) in high yield. Under the optimal reaction conditions (*p*_{CO} = 60 bar, *t* = 60 h, *T* = 80 °C) and with equimolar quantities of the substrates, compound **1a** was formed with a yield of 82%, accompanied by 14% of the side product **1b**. However, distillation under vacuum enabled us to isolate pure **1a** (see the Experimental Section). The siloxy precursor **I** appeared to be more effective and selective under conditions milder than for the complexes used previously ([Ir(μ-Cl)(CO)₂]₂], yield = 53%, *E/Z* = 79/21, *p*_{CO} = 50 bar, *T* = 140 °C using 10 equiv of olefins)^{2d} and also than for the analogous chloro complex [Ir(μ-Cl)(cod)]₂. The high efficiency of **I** can be applied to the synthesis of acylsilanes, which proceeds via hydrolysis¹⁴ of product **1**: e.g., the synthesis of **4a** according to eq 5.



Acylsilanes are useful and are widely used as reagents in organic synthesis: e.g., acylation of allylic esters or unsaturated ketones, *Z*-olefination of acylsilanes etc.,^{16b-1} and synthesis of organosilicon derivatives.^{16a}

Under the same reaction conditions complex **II** leads to exclusive and stereoselective formation of (*Z*)-1-(dimethylphenylsiloxy)-3-(trimethylsilyl)propene (**2a**; Table 1), which has been isolated and spectroscopically characterized.

When vinyltrimethylphenylsilane (mixture **b**) was used instead of vinyltrimethylsilane, the yield of silylcarbonylation products dramatically decreased (**1b**, **2b**). In the presence of complex **I** and under low pressure of CO (10 bar) compound **2b** was formed as the main product in 47% yield, but when the system was pressurized to 60 bar, a higher yield of compound **1b** was observed, not exceeding 40%. When the precursor **II** was used as the catalyst, the hydrosilylation product was exclusively formed, but only when a small amount of air was introduced into the reaction system (Table 2).

A preliminary NMR study on transformations of iridium(I) siloxide precursors under silylcarbonylation

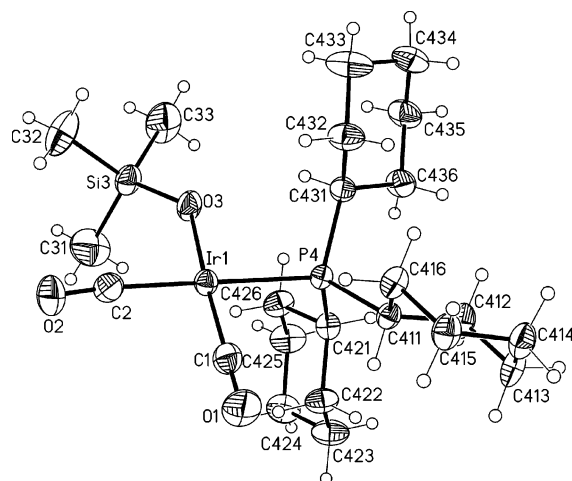
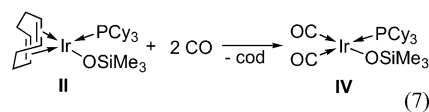
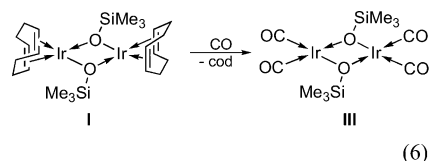


Figure 1. Perspective view of the complex, along with the numbering scheme. Selected geometrical parameters (distances in Å and angles in deg), with esd's in parentheses are as follows. Distances: C1–Ir1–C2, 1.827(8); Ir1–C2, 1.906(8); Ir1–O3, 1.995(5); Ir1–P4, 2.381(1); C1–O1, 1.146(9); C2–O2, 1.109(10); Si3–O3, 1.607(5); Si3–C31, 1.843(12); Si3–C32, 1.841(12); Si3–C33, 1.855(11); P4–C411, 1.836(6); P4–C421, 1.854(7); P4–C431, 1.853(6); <C(sp³)–C(sp³)>, 1.52(2). Angles: C1–Ir1–C2, 88.8(3); C1–Ir1–O3, 176.9(3); C1–Ir1–P4, 91.9(2); C2–Ir1–O3, 94.3(3); C2–Ir1–P4, 178.5(2); O3–Ir1–P4, 85.0(1); Ir1–C1–O1, 179.2(9); Ir1–C2–O2, 175.2(8); Ir1–O3–Si3, 136.9(3); Ir1–P4–C411, 112.2(2); Ir1–P4–C421, 111.9(2); Ir1–P4–C431, 110.7(2). The anisotropic displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms are depicted as spheres with arbitrary radii.

reaction conditions has revealed that, in the presence of CO, the cyclooctadiene ligand is replaced by carbon monoxide. The synthetic reaction performed according to eq 7 allowed the isolation of compound **IV**. Unfortunately, isolation of compound **III** was not possible, because during evaporation of the solvent the product was observed to decompose.



The structure of complex **IV** was determined by ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectroscopy and X-ray analysis. Figure 1 shows a perspective view of the complex with the numbering scheme.

The coordination of iridium is square planar, as is the case in the majority of the four-coordinated iridium complexes. The carbonyl groups are situated *cis* with respect to each other, and Ir–C–O angles are close to 180°. Cyclohexyl rings are close to the ideal chair conformations, and the distortions from the ideal C_{3v} symmetry are small. The geometry of the siloxy group is similar to that described for other transition-metal–

siloxo complexes (the mean value of the Si–O bond length from the 44 fragments is 1.60(2) Å).²²

Conclusions

While the iridium siloxide dimeric iridium complex **I** appeared to be a very efficient catalyst for the silylcarbonylation of vinyltrimethylsilane, giving highly stereoselectively enol silyl ethers of acylsilanes, Me₃SiCH₂CH=C(OSiMe₂Ph)SiMe₃Ph (**1a**; 82%, *E/Z* = 93/7), the monomeric iridium siloxide complex **II** proved to be a stereoselective catalyst in the exclusive synthesis of the silyl-substituted enol silyl ether (*Z*)-Me₃SiCH₂CH=CHOSiMe₂Ph (**2a**; yield 95%). Compound **1a** can be effectively used for the synthesis of Me₃SiCH₂CH₂C(OSiMe₂Ph) (**4a**; yield 92%).

Under a CO atmosphere, the cyclooctadiene ligand in complexes **I** and **II** is replaced by CO. [Ir(CO)₂(PCy₃)₂(OSiMe₃)] (**IV**) was synthesized (yield 70%), and its square-planar iridium coordination was confirmed by X-ray crystallography.

Experimental Section

General Methods and Chemicals. All synthesis and manipulations were carried out under argon using standard Schlenk and vacuum techniques. Pressure reactions were performed in an autoclave (100 mL, equipped with a PTFE insert). The catalyst precursors {[Ir(μ -OSiMe₃)(cod)]₂} (**I**)¹⁷ and [Ir(cod)(PCy₃)(OSiMe₃)] (**II**)¹⁸ were synthesized as we described previously. Column chromatography was carried out with silica gel 60 from Fluka. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers in C₆D₆. The mass spectra of the products and substrates were determined by GC-MS (Varian Saturn 2100T equipped with a 30 m DB-1 capillary column). GC analyses were carried out on a Varian 3800 series gas chromatograph with a 30 m DB-1 capillary column and TCD. The chemicals were obtained from the following sources: sodium trimethylsilanolate, benzene-*d*₆, CDCl₃, and hydrochloric acid diethyl ether solution from Aldrich Chemical Co., trisubstituted and vinyl trisubstituted silanes from Gelest Ltd., toluene, hexane, and acetone from POCH Gliwice (Poland), and carbon monoxide from Fluka. All solvents and vinyl-substituted silanes were dried and distilled under argon prior to use.

Synthesis of the Complex [Ir(CO)₂(PCy₃)(OSiMe₃)] (IV**).** A portion of complex **II** (0.2 g, 0.3 mmol) was dissolved in 3 mL of dried and deoxygenated benzene in a Schlenk tube. Then, 10 mL of carbon monoxide was introduced into a vigorously stirred solution. The reaction was carried out for 0.5 h at room temperature. After that time, the mixture was filtered off by a cannula system. From the filtrate obtained, solvent and cyclooctadiene were evaporated. The pale yellow solid was dissolved in pentane and cooled to –20 °C for crystallization. The crystals obtained were washed with two small portions of pentane at –60 °C and dried under vacuum (yield 0.129 g (70%)). Anal. Calcd for C₂₃H₄₄IrO₃PSi: C, 44.57; H, 7.15. Found: C, 44.77; H, 7.91. ¹H NMR (δ (ppm), C₆D₆): 0.39 (s, 9H, Me); 1.12, 1.55, 1.90, 2.15 (m, 33H, Cy). ¹³C NMR (δ (ppm), C₆D₆): 4.47 (–Me); 26.79, 27.92, 28.06, 30.24, 32.65, 32.99 (–Cy); 176.38, 179.97 (CO). ³¹P NMR (δ (ppm), C₆D₆): 32.01 (PCy₃). ²⁹Si NMR (δ (ppm), C₆D₆): 10.64 (–OSiMe₃).

X-ray Structure Determination of IV. Single crystals of **IV** were grown by slow evaporation of pentane from the solution. Diffraction data were collected at room temperature by the ω -scan technique, on a KUMA-KM4CCD diffractome-

ter²³ with graphite-monochromatized Mo K α radiation (λ = 0.710 73 Å). The data were corrected for Lorentz–polarization effects²⁴ as well as for absorption by SORTAV.²⁵ Accurate unit-cell parameters were determined by a least-squares fit of 6595 reflections of highest intensity, chosen from the whole experiment. The structure was solved with SHELXS97²⁶ and refined by the full-matrix least-squares procedure on *F*² by SHELXL97.²⁷ Scattering factors incorporated in SHELXL97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + 0.0724P^2]$ ($P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups. The *U*_{iso} values of hydrogen atoms were set as 1.2 (1.3 for methyl groups) times the *U*_{eq} value of the appropriate carrier atom. Relevant crystal data and data collection parameters together with structure refinement details for complex **IV** are as follows: formula, Ir(CO)₂OSi(CH₃)₃P(C₆H₁₁)₃; formula weight, 617.83; crystal system, triclinic; space group, *P*1; *a*, 9.8328(6) Å; *b*, 10.2516(6) Å; *c*, 14.9852(9) Å; α , 80.797(5)°; β , 85.881(5)°; γ , 66.447(6)°; *V*, 1366.82(14) Å³; *Z*, 2; *D*_x, 1.501 g cm^{–3}; *F*(000), 620; μ , 5.006 mm^{–1}; crystal size, 0.3 $\times$ 0.2 $\times$ 0.2 mm; θ range, 3.26–27.5°; *hkl* range, –12 $\leq h \leq$ 12, –13 $\leq k \leq$ 13, –19 $\leq l \leq$ 19; number of reflections collected, 13 042; number of unique reflections (*R*_{int}), 6212 (0.074); number of reflections with *I* > 2 σ (*I*), 5126; number of parameters, 262; *R*(*F*) (*I* > 2 σ (*I*)), 0.048; *R*_w(*F*²) (*I* > 2 σ (*I*)), 0.114; *R*(*F*) (all data), 0.056; *R*_w(*F*²) (all data), 0.119; goodness of fit, 1.075; max/min $\Delta\rho$, 1.27/–3.13 e Å^{–3}.

General Procedure for Silylcarbonylation. A mixture of CH₂=CHSiR₃ (3.93 mmol), HSiMe₂Ph (3.93 mmol), and 10 mL of dried and deoxygenated benzene or of CH₂=CHSiR₃ (3.93 mmol), HSiMe₂Ph (7.86 mmol), and 20 mL of dried and deoxygenated toluene with the iridium catalyst (0.01965 mmol) precursor was prepared in a Schlenk flask under argon. The solution was transferred by a cannula system into the autoclave, which was flushed with argon prior to use. Then the reactor was pressurized with CO. The reaction mixture was magnetically stirred at the given temperature for 48–60 h. After this time the autoclave was cooled to room temperature and the mixture was analyzed on the GC.

Synthesis of (*E*)-1-(Dimethylphenylsiloxy)-1-(dimethylphenylsilyl)-3-(trimethylsilyl)-1-propene (1a**, Me₃SiCH₂CH=C(OSiMe₂Ph)SiMe₂Ph).** Portions of CH₂=CHSiMe₃ (1.572 g, 15.72 mmol) and HSiMe₂Ph (4.28 g, 31.44 mmol) were dissolved in 50 mL of dried and deoxygenated benzene; this solution and 0.0305 g (0.0393 mmol) of catalyst **I** were placed in a Schlenk flask under argon. Then the solution was transferred by a cannula system into the autoclave, which was 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 60 h. After this time the autoclave was cooled to room temperature. The solvent was removed under reduced pressure, and the product was isolated by fractional distillation under vacuum (120 °C/1 mmHg, 72% yield). Anal. Calcd for C₂₂H₃₄OSi₃: C, 66.26; H, 8.59. Found: C, 66.52; H, 9.11. ¹H NMR (δ (ppm), C₆D₆): 0.016 (s, 9H, Me); 0.34 (s, 6H, Me); 0.36 (s, 6H, Me); 1.56 (d, *J*_{H–H} = 8.4 Hz, 2H, –CH₂–); 5.24 (t, *J*_{H–H} = 8.4 Hz, 1H, –CH=); 7.22, 7.59 (m, 10H, Ph). ¹³C NMR (δ (ppm), C₆D₆): –2.74, –1.64, 0.52 (Me); 17.53 (–CH₂–); 123.6 (=CH–); 129.43, 129.7, 133.81, 134.66, 138.16, 139.31 (Ph); 153.76 (=C(Si)OSi). ²⁹Si NMR (δ (ppm), C₆D₆): –12.68, 1.37, 3.64. MS (*m/z* (relative intensity)): 400 (6), 399 (8), 398 (31, M⁺), 271 (15), 248 (7), 247 (7), 243 (7), 234 (10),

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233 (41), 211 (30), 210 (24), 209 (100), 195 (10), 194 (22), 193 (24), 149 (17), 148 (6), 147 (23), 136 (11), 135 (18), 117 (5), 107 (8), 105 (6), 75 (5), 73 (31), 45 (12).

Synthesis of (Z)-1-(Dimethylphenylsiloxy)-3-(trimethylsilyl)-1-propene (2a, Me₃SiCH₂CH=CHOSiMe₂Ph). Portions of CH₂=CHSiMe₃ (1.572 g, 15.72 mmol) and HSiMe₂Ph (2.14 g, 15.72 mmol) were dissolved in 50 mL of dried and deoxygenated benzene; this solution and 0.053 g (0.079 mmol) of catalyst **II** were placed in a Schlenk flask under argon. Then the solution was transferred by a cannula system into the autoclave, which was flushed with argon prior to use. The reactor was pressurized to 60 bar with CO. The reaction mixture was magnetically stirred at 100 °C for 24 h. After this time the autoclave was cooled to room temperature. The solvent was removed under reduced pressure, and the product was isolated by fractional distillation under vacuum (80 °C/1 mmHg, 90% yield). Anal. Calcd for C₁₄H₂₄OSi₂: C, 44.57; H, 9.15. Found: C, 44.83; H, 9.91. ¹H NMR (δ (ppm), C₆D₆): 0.079 (s, 9H, Me); 0.26 (s, 6H, Me); 1.69 (d, *J*_{H-H} = 9.3 Hz, 2H, -CH₂-); 4.55 (m, *J*_{H-H} = 6.6 Hz and *J*_{H-H} = 9.3 Hz, 1H, -CH=); 6.23 (d, 1H, *J*_{H-H} = 6.6 Hz =CH-); 7.22, 7.57 (m, 5H, Ph). MS (*m/z* (relative intensity)): 264 (2, M⁺), 249 (7), 161 (10), 149 (16), 148 (8), 147 (41), 136 (14), 135 (100), 107 (5), 105 (6), 75 (8), 73 (31).

Synthesis of [3-(Trimethylsilyl)propionyl]dimethylphenylsilane (4a). A portion of **1a** (1.0 g, 2.5 mmol) and 6 mL of acetone were placed in a single-neck flask (10 mL) equipped with a magnetic stirrer. Then to the mixture obtained was added 2 mL of 0.4 mol/L hydrochloric acid solution in Et₂O. The reaction was conducted for 4 h at room temperature. After

this time the solvent was removed under reduced pressure and product **4a** was isolated from the residue on a silica gel column, where hexane was used as a mobile phase the hexane (yield 0.61 g (92%)). Anal. Calcd for C₁₄H₂₄OSi₂: C, 63.57; H, 9.15. Found: C, 63.69; H, 10.12. ¹H NMR (δ (ppm), C₆D₆): -0.09 (s, 9H, Me); 0.50 (s, 6H, Me); 0.59 (m, 2H, -CH₂Si≡); 2.52 (-CH₂C(O)-); 7.40, 7.56 (Ph). ¹³C NMR (δ (ppm), C₆D₆): -4.51 (Me); -1.89 (Me); 8.29 (-CH₂Si≡); 43.04 (-CH₂C(O)-); 128.11, 129.81, 133.94, 134.73 (Ph); 245.92 (-C(O)-). MS (*m/z* (relative intensity)): 249 (38), 209 (5), 193 (5), 191 (6), 187 (13), 163 (18), 138 (5), 136 (14), 135 (100), 107 (9), 105 (7), 75 (7), 73 (13), 45 (6).

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Supporting Information Available: A CIF file, giving crystallographic data for complex **IV**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (excluding structure factors) for the structural analysis have also been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-264289. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax +44(1223)336-033; e-mail deposit@ccdc.cam.ac.uk; web www.ccdc.cam.ac.uk.

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