Silylformylation of Alkynes Catalysed by Di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium

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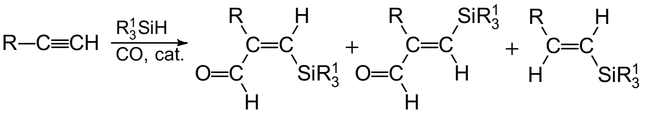
Di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium is proposed as the effective catalyst for the chemo- and regioselective silylformylation of alkynes with triethyl- and dimethylphenylsilanes.

Interaction of unsaturated compounds with silanes and CO catalysed by transition metal complexes, so-called 'silylformylation', has been extensively studied during the last ten years.[1–5] There is great interest in the silylformylation of alkynes as an efficient method for the synthesis of bifunctional olefins – silylated alkenals. This reaction has only been studied on a limited number of catalytic systems. Indeed, [Rh$_4$(CO)$_{12}$],[6–8] [Co$_2$Rh$_2$(CO)$_{12}$],[9] rhodium(II) perfluorobutyrate[10,11] and [Rh(COD)BPh$_4$][12] are described, the latter being used in the reaction with CO in the presence of H$_2$. In the reaction with functionalized alkynes other rhodium(I) complexes may sometimes be used.[13]

The problem of the regio- and stereoselectivity of asymmetric alkynes silylformylation exists, and the possibility of competitive hydrosilylation must be taken into account.



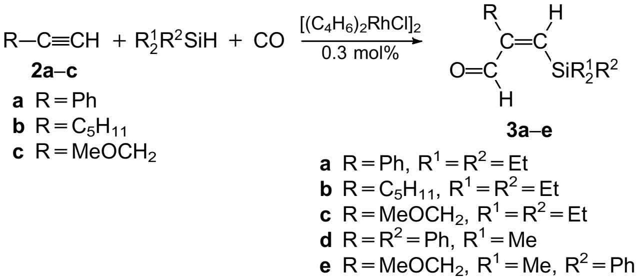
In the case of terminal alkynes silylformylation is very regioselective, with a formyl group in silylalkenals at the substituted carbon atom. Silylformylation occurs as a *cis*-addition with formation of *Z*-isomers.

In the present paper di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium **1**[†] is proposed as the efficient catalyst for terminal alkyne silylformylation with triethyl- and dimethylphenylsilanes.

In a typical procedure, alkyne **2a**–**c** (0.025 mol), organosilane (0.025 mol), dry heptane (75 ml) and 0.3 mol% of complex **1** were placed in an argon stream in a 250 ml stainless steel autoclave with a stirrer and a valve to select the samples. The autoclave was then brought to 30 atm CO, and the reaction mixture was stirred for 2 h at room temperature. The temperature was then raised if required. GLC analysis was used to monitor the reaction. After venting the solution was filtered through a short column with SiO$_2$ to remove the catalyst. The solvent was evaporated, and the residue was distilled under reduced pressure.

The results of silylformylation of alkynes **2a**–**c** are presented in Table 1, which involves the comparative data described in the literature.

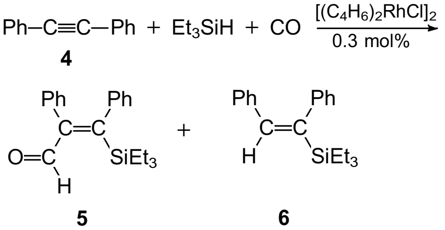
Phenylacetylene reacts with triethylsilane at room temperature and 30 atm CO during 20 h to produce 1-formyl-1-phenyl-2-triethylsilyleth-1-ene **3a**[‡] in 90% total yield and good stereoselectivity (*Z*/*E* = 10:1) (no. 1). 5% of the hydrosilylation products are detected in the reaction mixture before distillation. The process of hydrosilylation is suppressed on increasing the temperature to 50 °C, the practically pure **3a** being formed (no. 2). Further increasing of temperature causes an increase in the reaction rate, but the yield of **3a** is diminished because of its polymerization.



The reaction of hept-1-yne with triethylsilane occurs at a significant rate only on raising the temperature. It is completed during 4 h at 80 °C to form 1-triethylsilyl-2-formylhept-1-ene **3b** (mixture of *Z*/*E* isomers 6:1) in 84% yield and negligible impurity of 1-triethylsilylhept-1-ene (no. 4).

3-Methoxyprop-1-yne **2c** reacts with triethylsilane at 80 °C and 30 atm CO highly chemo- and stereoselectively to produce **3c** in good yield (no. 5).

It is known that internal alkynes are usually less active in silylformylation. The interaction of diphenylacetylene with triethylsilane at 80 °C and 30 atm CO in the presence of catalyst **1** proceeds more slowly and less selectively (no. 6). Overall product yield decreases to 70%, and hydrosilylation occures in competition with silylformylation (21% of **6** in the reaction mixture).



5 **6**

[†] Complex **1** was obtained from di-μ-chlorotetrakis(η^2-cyclooctene)-dirhodium in 97% yield.[14,15]

[‡] Selected spectral characteristics:

Z-**3b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.52 (q, 6H), 0.78 (t, 9H), 1.10 (m, 9H), 2.09 (t, 2H), 6.39 (s, 1H), 9.18 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 3.85, 7.02, 13.61, 22.26, 28.87, 29.13, 32.10, 149.77, 158.36, 194.92.

E-**3b**: ^{1}H NMR δ 0.38 (q, 6H), 0.76 (t, 9H), 1.10 (m, 9H), 2.28 (t, 2H), 6.69 (s, 1H), 9.10 (s, 1H). ^{13}C NMR δ 3.98, 7.07, 13.65, 22.31, 28.87, 29.13, 32.03, 148.53, 157.76, 192.77.

Z-**3d**: ^{1}H NMR δ 0.66 (s, 6H), 7.30 (s, 1H), 7.38–7.68 (m, 10H), 10.13 (s, 1H). ^{13}C NMR δ –0.35, 128.18, 128.35, 128.62, 129.36, 129.56, 129.70, 134.06, 137.50, 137.94, 151.67, 154.49, 192.20.

E-**3d**: ^{1}H NMR δ 0.53 (s, 6H), 7.25 (s, 1H), 7.38–7.68 (m, 10H), 9.76 (s, 1H).^{13}C NMR δ –2.04, 128.18, 128.35, 128.41, 128.62, 129.36, 129.56, 129.70, 134.06, 138.20, 138.73, 153.80, 157.10, 194.12.

Z-**3e**: ^{1}H NMR δ 0.43 (s, 6H), 3.25 (s, 3H), 4.05 (d, 2H, *J* = 1.8 Hz), 7.13 (t, 1H, *J* = 1.8 Hz), 7.27 (m, 5H), 9.68 (s, 1H). ^{13}C NMR δ 0.29, 59.80, 70.36, 128.30, 129.66, 133.68, 137.62, 148.57, 152.22, 192.39.

E-**3e**: ^{1}H NMR δ 0.40 (s, 6H), 3.06 (s, 3H), 3.94 (s, 2H), 6.93 (s, 1H), 7.43 (m, 5H), 9.36 (s, 1H). ^{13}C NMR δ –1.64, 59.21, 66.77, 129.03, 129.38, 133.68, 144.09, 153.35, 155.56, 194.31.

Spectral characteristics of compounds **3a** and **3c** correspond to literature data.[11]

Table 1 Silylformylation of alkynes **2a–c** and **4** in the presence of 0.3 mol% of di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium.

Entry no.	Substrate	Silane	$T/°\mathrm{C}$	$P_{\mathrm{CO}}/\mathrm{atm}$	t/h	Products		
						Yield[a] (%)	Aldehydes (Z/E)	Silanes (%)
1	PhC≡CH	$\mathrm{Et_3SiH}$	20	30	20	90	10/1	5
2	PhC≡CH	$\mathrm{Et_3SiH}$	50	30	20	83	15/1	2
3	PhC≡CH	$\mathrm{Et_3SiH}$	80	30	8	67	16/1	3
4	$\mathrm{C_5H_{11}C{\equiv}CH}$	$\mathrm{Et_3SiH}$	80	30	4	84	8/1	8
5	$\mathrm{MeOCH_2C{\equiv}CH}$	$\mathrm{Et_3SiH}$	80	30	5	68	40/1	5
6	PhC≡CPh	$\mathrm{Et_3SiH}$	80	30	19	41	> 99/1	29
7	PhC≡CH	$\mathrm{Me_2PhSiH}$	20	30	3	74	8/1	20
8	PhC≡CH	$\mathrm{Me_2PhSiH}$	20	60	3	91	30/1	4
9	PhC≡CH[b]	$\mathrm{Me_2PhSiH/Rh_4(pfb)_2}$	20	10	16	73	12/1	1
10	PhC≡CH[c]	$\mathrm{Me_2PhSiH/Rh_4(CO)_{12}}$	100	30	2	89	88/12	–
11	$\mathrm{MeOCH_2C{\equiv}CH}$	$\mathrm{Me_2PhSiH}$	20	60	7	90	17/2	4

[a] Yield after distillation. [b] Ref. 11. [c] Ref. 6.

Silylformylation of alkynes with dimethylphenylsilane is known to proceed generally more quickly and more selectively.[9–11] Phenylacetylene reacts with dimethylphenylsilane in the presence of catalyst **1** at room temperature and 30 atm CO during 3 h, but the amount of hydrosilylation products increases significantly as compared with the reaction with triethylsilane (no. 7). The reduction in chemoselectivity of the reaction is connected with the high activity of complex **1** as the catalyst for alkyne hydrosilylation with dimethylphenylsilane.[§] We succeeded in suppressing the competitive hydrosilylation reaction on increasing the CO pressure to 60 atm. Under these conditions silylformylation of alkynes **2a** and **2c** is completed at room temperature during 3 and 7 h, respectively, leading to the formation of the almost pure Z isomers of **3d** and **3e** in excellent yields (nos. 8, 9).

As is seen from the results in Table 1, di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium is an efficient catalyst for the silylformylation of terminal alkynes. In the reaction with dimethylphenylsilane it shows a higher catalytic activity and selectivity compared to other rhodium catalysts. The time of reaction of phenylacetylene, for example, is diminished by a factor of 5 as compared to dirhodium perfluorobutyrate.[11]

It should be noted that silylformylation catalysed by **1** begins only after some period of induction. We suppose that the catalytic intermediate is formed from di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium by its interaction with CO. The investigation of the mechanism of the catalysis is in progress.

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[§] It was established in specially designed experiments that hydrosilylation reactions of phenylacetylene and 3-methoxyprop-1-yne with dimethylphenylsilane in the presence of complex **1** are completed during 0.5 h at room temperature.