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Di-μ-chlorotetrakis(η²-methylenecyclopropane)dirhodium. A Highly Active Catalyst for Hydrosilylation of Alkenes and Alkynes

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Di-μ-chlorotetrakis(η²-methylenecyclopropane)dirhodium, a novel rhodium complex containing the methylenecyclopropane ligand, is a more active catalyst for the hydrosilylation of alkenes and alkynes than either a similar ethylene complex or the Wilkinson catalyst.

Hydrosilylation of alkenes, alkynes and dienes is a subject of current interest, since it is widely used in the preparation of alkyl- and vinyl-silanes, which are important starting materials in organic synthesis. The catalysts commonly used for hydrosilylation are mainly platinum and rhodium complexes. The Wilkinson catalyst,[1–3] π-ethylene,[4,5] carbonyl, [6] hydride[7] and other complexes [9,10] of rhodium show high catalytic activity and a search for more effective and selective catalysts is in progress.

In this Communication we report a novel rhodium complex, di-μ-chlorotetrakis(η²-methylenecyclopropane)dirhodium, containing the methylenecyclopropane ligand, and its catalytic activity in the hydrosilylation reaction. The synthesis of **1** is outlined in Scheme 1. The reaction of di-μ-chlorotetrakis(η²-cyclooctene)dirhodium with an excess of methylenecyclopropane at 10°C affords di-μ-chlorotetrakis(η²-methylenecyclopropane)dirhodium **1**,† which was isolated in 97% yield after evaporation of methylenecyclopropane. Obtained as a second product, cyclooctene was identified by means of ^{1}H NMR spectroscopy and GLC.

$$[(C_8H_{14})_2RhCl]_2 + 2C_4H_6 \xrightarrow{i} [(C_4H_6)_2RhCl]_2 + 2C_8H_{14}$$

Scheme 1 *Reagents and conditions*: i, an excess of methylenecyclopropane, 10°C, 3 h, in argon

The reaction of hex-1-ene with triethyl- and triethoxy-silanes (Scheme 2) was selected to compare the catalytic activity of complex **1** with other well-known rhodium hydrosilylation catalysts (Table 1). The reaction was carried out without solvent at room temperature in an argon atmosphere with a 1.5 molar ratio of alkene/silane. GLC analysis was used to monitor the reaction. Complex **1** ensures a high selectivity of the process. Triethyl-n-hexylsilane was obtained in quantitative yield with 0.1 mol% of catalyst **1** (turnover 2000) (entry 1), Table 1). The yield is lower when the amount of catalyst is decreased. However, even with 0.01 mol% of catalyst the reaction proceeds in 88% yield within 50 h (entry 2). The yield is reduced to 59% on using 0.001 mol% of catalyst (entry 3).

$$C_4H_9CH{=}CH_2 + R_3SiH \longrightarrow C_6H_{13}SiR_3$$
$$R = Et, EtO$$

Scheme 2

† Complex **1** was characterized by elemental analysis, relative molecular mass (M^+, 492) and IR ($\nu_{C=C}$ 1640 cm^{-1}); m.p. (decomp.) 120–122°C.

Table 1 Hydrosilylation of hex-1-ene with triethyl- and triethoxy-silanes in the presence of complex **1**

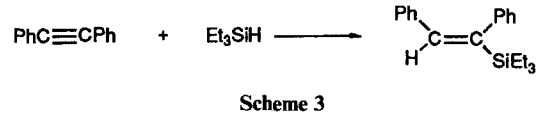
No.	Catalyst	Silane	Amount of catalyst (mol%)	React. temp. /°C	React. time /h	Yield of silane (%)[a]
1	**1**	Et_3SiH	0.1	25	0.5	95
2	**1**	Et_3SiH	0.01	25	40	88
3	**1**	Et_3SiH	0.001	25	25[b]	59
4	$[RhCl(C_2H_4)_2]_2$[c]	Et_3SiH	0.15	85	2	69[d]
5	**1**	$(EtO)_3SiH$	0.2	25	2.5	96
6	$[RhCl(C_2H_4)_2]_2$[c]	$(EtO)_3SiH$	0.15	24	24	90

[a] From GLC data. [b] Starting materials transformed completely. [c] Ref. 4. [d] Reaction with hept-1-ene.

Our methylenecyclopropane–rhodium complex is a more effective hydrosilylation catalyst than other rhodium complexes. For example, with a similar π-ethylene rhodium complex, the reaction of Scheme 2 proceeds at a higher temperature and with a lower yield (Table 1, entry 4). Complex **1** is also more active in the reaction of hex-1-ene with triethoxysilane: triethoxy-n-hexylsilane was obtained in quantitative yield within 2.5 h with 0.2 mol% of **1** (entry 5).

We have studied the catalytic activity of methylenecyclopropanerhodium complex **1** in the hydrosilylation of alkynes. The reaction of diphenylacetylene with triethylsilane in hexane solution went to completion within 3 h at room temperature with 0.1 mol% of **1** and led to (*Z*)-1,2-diphenyl-1-(triethylsilyl)ethene in 82% preparative yield (Scheme 3). It is worth noting that hydrosilylation with **1** proceeds under milder conditions than with the Speier catalyst.[11]

In the hydrosilylation of phenylacetylene three isomeric adducts are possible (Scheme 4). We have studied the reaction of phenylacetylene with triethyl- and triethoxy-silanes at room temperature in hexane solution with 0.1 mol% of catalyst **1**. Identification of the phenylacetylene adducts was accom-

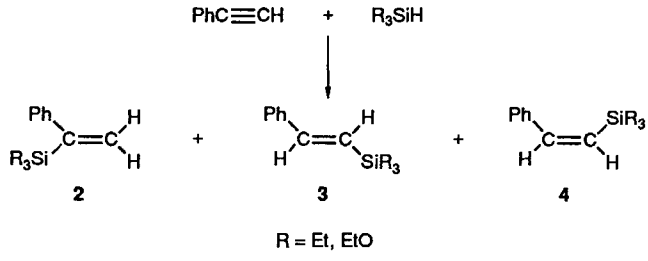


Scheme 3

Table 2 Hydrosilylation of phenylacetylene with triethyl- and triethoxy-silanes in the presence of complex **1**

No.	Catalyst	Silane	Amount of catalyst (mol%)	Time /h	Temp. /°C	Products			
						Yield (%)	Ratio		
							2	**4**	**3**
1	**1**	Et_3SiH	0.1	7	25	85	1	—	2
2	**1**	$(EtO)_3SiH$	0.1	12	25	75	1	2	1
3	**1**	$(EtO)_3SiH$	0.5	2	25	80	4	1	4
4	$Rh(PPh_3)_3Cl$[a]	$MeEt_2SiH$	3.0	10	100	24	1	4	2

[a] Ref. 2.



Scheme 4

plished by means of ^1H NMR spectra, the spectroscopic parameters being taken from ref. 2.

A mixture of 1-phenyl-1-(triethylsilyl)ethane **2** and (*E*)-1-phenyl-2-(triethylsilyl)ethene **3** in a 1:2 ratio and 85% total yield (GLC) was obtained in the reaction with triethylsilane. The amount of (*Z*)-1-phenyl-2-(triethylsilyl)ethene **4** did not exceed 5% (entry 1, Table 2). The reaction of phenylacetylene with triethoxysilane proceeds with a significantly lower selectivity: all three possible adducts are obtained in similar amounts in this case. However, it can be seen from Table 2 that the methylenecyclopropane complex is significantly more effective in the hydrosilylation of phenylacetylene than *e.g.* the Wilkinson catalyst (entry 4). The use of **1** requires a lower reaction temperature and gives a substantially higher yield of adducts.

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