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Dirhodium(II) Tetrakis(perfluorobutyrate)-Catalyzed 1,4-Hydrosilylation of α,β-Unsaturated Carbonyl Compounds

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The use of dirhodium(II) catalysts in the 1,4-hydrosilylation of α,β-unsaturated ketones and aldehydes was explored. Dirhodium(II) tetrakis(perfluorobutyrate), $Rh_2(pfb)_4$, proved to be the catalyst of choice for this process, providing the corresponding silyl enol ethers in high yields.

Key words dirhodium(II) complex; 1,4-hydrosilylation; silyl enol ether; α,β-enone

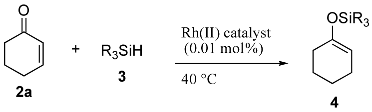
Silyl enol ethers are useful and versatile synthetic intermediates available to the organic chemist.[1,2] The catalytic 1,4-hydrosilylation of α,β-unsaturated carbonyl compounds is generally recognized as a powerful method for the direct and regioselective synthesis of silyl enol ethers. Consequently, a number of transition metal complexes based on rhodium,[3—5] platinum,[6] and copper[7] as well as Lewis acids such as $B(C_6F_5)_3$[8] have been developed for that purpose.

Aside from their effectiveness in diazo decomposition,[9,10] dirhodium(II) complexes are also recognized as Lewis acid catalysts[11,12] as well as catalysts for hydrosilylation of terminal alkynes,[13] terminal alkenes,[14] and enamides,[15] silylformylation of terminal alkynes,[16] and silane alcoholysis.[17] However, to the best of our knowledge, no examples of the dirhodium(II) complex-catalyzed 1,4-hydrosilylation of α,β-unsaturated carbonyl compounds have been reported. As part of a program to explore dirhodium(II) complex-catalyzed transformations,[18] we wish to report herein that dirhodium(II) tetrakis(perfluorobutyrate), $Rh_2(pfb)_4$ (**1a**), is an exceptionally effective catalyst for the 1,4-hydrosilylation of α,β-unsaturated ketones and aldehydes.

At the outset of this work, the 1,4-hydrosilylation of 2-cyclohexen-1-one (**2a**) with triethylsilane (**3a**) in the presence of 0.01 mol% of $Rh_2(pfb)_4$ (**1a**) was examined. The reaction in dichloromethane or dichloroethane proceeded smoothly at 40 °C, giving the corresponding silyl enol ether **4a** in 96% and 95% yields, respectively (Table 1, entries 1, 2).[19] No signs of the 1,2-hydrosilylation product were detected in the crude reaction mixture by NMR spectroscopy. Although other solvents such as benzene, toluene, and THF were also suitable, the reaction times in these solvents were extended (entries 3—5). Using dichloromethane as the solvent, we next evaluated the performance of other dirhodium(II) complexes, $Rh_2(OAc)_4$ (**1b**), $Rh_2(oct)_4$ (**1c**), $Rh_2(tpa)_4$ (**1d**), and $Rh_2(cap)_4$ (**1e**) (entries 6—9). Although these dirhodium(II) complexes could also be used for this process, 0.1 mol% of catalyst was required for completion of the reaction. $Rh_2(pfb)_4$, which features strongly electron-withdrawing carboxylate ligands, proved to be the catalyst of choice in terms of catalyst activity. As expected from the robust nature and high reactivity of $Rh_2(pfb)_4$, the hydrosilylation of **2a** with **3a** proceeded smoothly with very low catalyst loadings (0.0002 mol%) without compromising product yield (entry 10). In addition to triethylsilane, a variety of monohydrosilanes such as diethylmethylsilane (**3b**), dimethylphenylsilane (**3c**), and triethoxysilane (**3d**) could be used in the $Rh_2(pfb)_4$-catalyzed 1,4-hydrosilylation of **2a** (entries 11—13). On the other hand, the reaction of **2a** with diphenylsilane (**3e**) led to the exclusive formation of the 1,2-hydrosilylation product **5**, as observed in the $(Ph_3P)_3RhCl$-catalyzed hydrosilylation with dihydrosilanes (Chart 2).[3]

The applicability of this catalytic system to a range of α,β-unsaturated carbonyl compounds was then investigated

Table 1. 1,4-Hydrosilylation of 2-Cyclohexen-1-one (**2a**) Catalyzed by Dirhodium(II) Complexes[a)]



Entry	Rh(II) complex	Silane	Solvent	Time (h)	Product	
						Yield[b)] (%)
1	$Rh_2(pfb)_4$ (**1a**)	Et_3SiH (**3a**)	CH_2Cl_2	1	**4a**	96
2	$Rh_2(pfb)_4$ (**1a**)	Et_3SiH (**3a**)	$(CH_2Cl)_2$	1	**4a**	95
3	$Rh_2(pfb)_4$ (**1a**)	Et_3SiH (**3a**)	Benzene	2	**4a**	93
4	$Rh_2(pfb)_4$ (**1a**)	Et_3SiH (**3a**)	Toluene	2	**4a**	94
5	$Rh_2(pfb)_4$ (**1a**)	Et_3SiH (**3a**)	THF	2	**4a**	92
6	$Rh_2(OAc)_4$ (**1b**)[c)]	Et_3SiH (**3a**)	CH_2Cl_2	1	**4a**	95
7	$Rh_2(oct)_4$ (**1c**)[c)]	Et_3SiH (**3a**)	CH_2Cl_2	1	**4a**	95
8	$Rh_2(tpa)_4$ (**1d**)[c)]	Et_3SiH (**3a**)	CH_2Cl_2	8	**4a**	88
9	$Rh_2(cap)_4$ (**1e**)[c)]	Et_3SiH (**3a**)	CH_2Cl_2	3	**4a**	88
10	$Rh_2(pfb)_4$ (**1a**)[d)]	Et_3SiH (**3a**)	CH_2Cl_2	12	**4a**	92
11	$Rh_2(pfb)_4$ (**1a**)	Et_2MeSiH (**3b**)	CH_2Cl_2	0.5	**4b**	96
12	$Rh_2(pfb)_4$ (**1a**)	Me_2PhSiH (**3c**)	CH_2Cl_2	1	**4c**	94
13	$Rh_2(pfb)_4$ (**1a**)	$(EtO)_3SiH$ (**3d**)	CH_2Cl_2	6	**4d**	90

a) Unless otherwise noted, reactions were carried out as follows: **3** (1.2 eq) was added to a solution of **2a** (960 mg, 10 mmol) and Rh(II) complex (0.01 mol%) in the indicated solvent (3 ml) and the mixture was stirred at 40 °C. *b*) Isolated yield. *c*) 0.1 mol% of catalyst was used. *d*) 0.0002 mol% of catalyst was used.

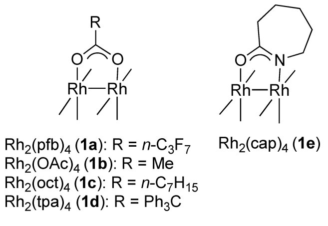


Chart 1

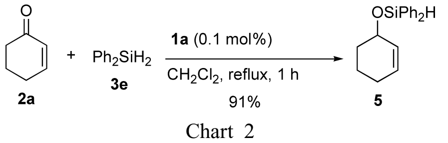


Chart 2

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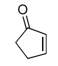
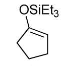
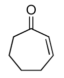
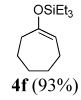
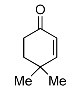
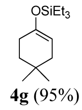
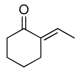
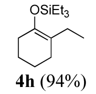
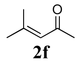
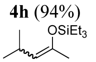
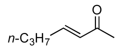
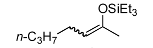
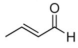
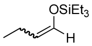
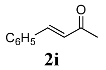
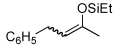
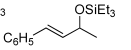
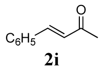
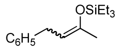
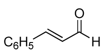
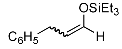
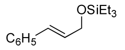
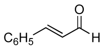
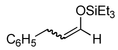
Table 2. 1,4-Hydrosilylation of α,β-Unsaturated Carbonyl Compounds Catalyzed by Dirhodium(II) Carboxylates[a]

Entry	Substrate	Rh(II) (mol%)	Time (h)	Product Yield[b] (%)
1	 **2b**	**1a** (0.05)	0.3	 **4e** (91%)
2	 **2c**	**1a** (0.01)	0.5	 **4f** (93%)
3	 **2d**	**1a** (0.01)	0.5	 **4g** (95%)
4	 **2e**	**1a** (0.01)	0.5	 **4h** (94%)
5	 **2f**	**1a** (0.01)	0.3	 **4i** (97%, Z:E[c] = 92:8)
6	 **2g**	**1a** (0.01)	1	 **4j** (94%, Z:E[c] = 78:22)
7	 **2h**	**1a** (0.01)	1	 **4k** (94%, Z:E[c] = 80:20)
8	 **2i**	**1a** (0.01)	2	 **4l**  **6a** (94%[d], Z-**4l**:E-**4l**:**6a**[c] = 81:14:5)
9	 **2i**	**1b** (0.1)	3	 **4l** (96%, Z:E[c] = 85:15)
10	 **2j**	**1a** (0.01)	1	 **4m**  **6b** (93%[d], Z-**4m**:E-**4m**:**6b**[c] = 94:2:4)
11	 **2j**	**1b** (0.1)	2	 **4m** (96%, Z:E[c] = 95:5)

a) All reactions were performed on a 5 mmol scale with 1.2 eq of **3a** in CH_2Cl_2 under reflux. *b*) Isolated yield. *c*) Determined by ^1H-NMR. *d*) Combined yield of 1,4-adduct and 1,2-adduct.

and the results are summarized in Table 2. The use of cyclic α,β-enones, including 2-cyclopenten-1-one (**2b**), 2-cyclohepten-1-one (**2c**), and 4,4-dimethyl-2-cyclohexen-1-one (**2d**), afforded the corresponding silyl enol ethers **4e**—**g** in high yields (entries 1—3).[20] (E)-2-Ethylidenecyclohexanone (**2e**) was converted to silyl enol ether **4g** in high yield (entry 4). The 1,4-hydrosilylation also proceeded smoothly with mesityl oxide (**2f**), 3-heptene-2-one (**2g**), and crotonaldehyde (**2h**), although the products were a mixture of stereoisomers (entries 5—7). However, in the cases of benzalacetone (**2i**) and (E)-cinnamaldehyde (**2j**), containing a phenyl group at the β-position, reactions with **3a** gave predominantly silyl enol ethers **4l, m**, along with very small amounts of 1,2-hydrosilylation products **6a, b** (entries 8, 10). Gratifyingly, this problem could be overcome by changing the catalyst from $Rh_2(pfb)_4$ to $Rh_2(OAc)_4$. The reactions in the presence of 0.1 mol% of $Rh_2(OAc)_4$ afforded exclusively silyl enol ethers **4l, m** in high yields with no evidence of 1,2-hydrosilylation (entries 9, 11).

In summary, we have reported the first example of the 1,4-hydrosilylation of α,β-unsaturated ketones and aldehydes catalyzed by dirhodium(II) complexes and have shown that $Rh_2(pfb)_4$ is an exceptionally effective catalyst for this process. The effective use of $Rh_2(OAc)_4$ as a backup catalyst for $Rh_2(pfb)_4$ was also demonstrated, in cases where β-phenyl substituted substrates are used. The dirhodium(II) carboxylate catalysts are air-stable, and easily handled. Further studies of the scope of the reaction as well as mechanistic studies are currently in progress.

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19) Typical procedure (Table 1, entry 1): Et_3SiH (**3a**) (1.9 ml, 12 mmol) was added to a solution of 2-cyclohexen-1-one (**2a**) (960 mg, 10 mmol) and $Rh_2(pfb)_4$ (**1a**) (1.1 mg, 0.001 mmol, 0.01 mol%) in CH_2Cl_2 (3 ml) and the mixture was refluxed for 1 h. Evaporation *in vacuo* gave the crude product (2.2 g), which was purified by short-path column chromatography (5 g of WAKO-gel C-200, 94.3 : 4.7 : 1 hexane/ether/Et_3N) followed by Kugelrohr distillation (5 mmHg, 100 °C) to provide **4a** (2.05 g, 96%) as a colorless oil.
20) The present method was found to be somewhat sensitive to the structure of the substrate; 3-methyl-2-cyclohexen-1-one and 2-methyl-2-cyclohexen-1-one were recovered unchanged.