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Molybdenum Oxadiene Catalysts for the Chemoselective Hydrosilylation of α,β-Unsaturated Ketones and Aldehydes

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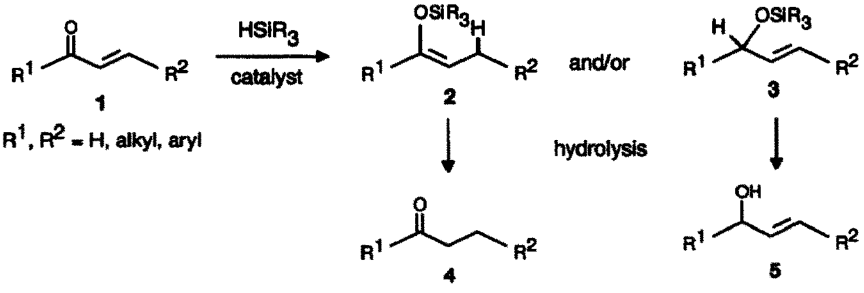
Abstract: Carbonyl molybdenum and tungsten oxadiene complexes exhibit high catalytic activity in hydrosilylation of unsaturated ketones and aldehydes, even those geometrically fixed in *s-trans*-arrangement, using $PhSiH_3$ and Ph_2SiH_2. In the case of 4-phenylbut-3-en-2-one as substrate, variable chemoselectivity is observed depending on the specific catalyst employed.

Hydrosilylation of unsaturated carbonyl compounds provides access not only to saturated and unsaturated silyl ethers. Hydrolysis of these primary products **2** and **3** may also lead to saturated carbonyl compounds **4** and allylic alcohols **5**, as depicted in Scheme 1. Platinum metals, specifically rhodium and platinum complexes are usually employed as catalysts[1] for performing these reactions.

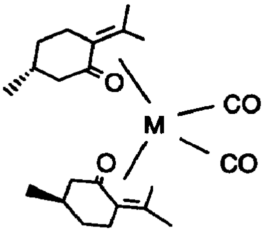


Scheme 1

Hexacarbonyl molybdenum has been reported[2] to catalyze silane additions to unsaturated ketones already some years ago. Unfortunately, relatively large amounts of catalyst (4-9 mol-%) and a large excess of silane were needed to achieve these results. In contrast, molybdenum oxadiene complexes, e.g. compounds **6a**[3], **7a**[4], and **8**, exhibit an improved activity as well as a dramatically changed chemoselectivity in hydrosilylation reactions, even with only a slight excess of silane. These oxadiene complexes are crystalline, orange to brown compounds easily obtained[5] by direct complexation of the oxadienes and air-stable for short periods of time.

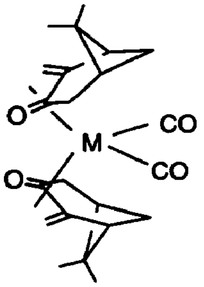
Some important reactivity results are summarised in Table 1. In a typical experiment, the unsaturated carbonyl compound (3 mmol) is dissolved in a solution of the catalyst in benzene or toluene (5 ml) under argon. The silane is added via syringe and the clear yellow to brown mixture kept at reaction temperature with stirring. Then, after dilution with ether (5 ml), 5 % aqueous hydrogen fluoride (5 ml) is added and the two phase mixture stirred for 3 h. Neutralisation, extraction with ether and concentration of the combined extracts affords the crude reaction product. It can further be purified by chromatography, but already turns out to be essentially free of silicon compounds.[6]

Table 1. Hydrosilylation of α,β-Unsaturated Ketones Catalyzed by Dicarbonylbis(oxadiene) Molybdenum and Tungsten Complexes.[a]



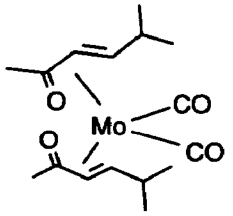
6a (M = Mo)

6b (M = W)

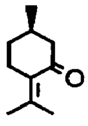
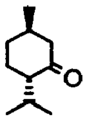
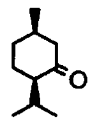
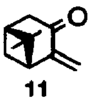
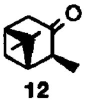
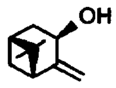
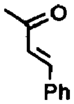
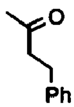
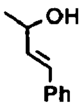


7a (M = Mo)

7b (M = W)



8

Entry	Substrate	Silane[b]	Catalyst (mol-%), Conditions	Conversion [%]	Products[c]	[Product Ratio]
1	 **9**	Et_3SiH	**6b** (1), 48 h, 70°C	2	 **10a** +  **10b**	[66:34]
2		Ph_2SiH_2	**6b** (1), 16 h, 70°C	50		[65:35]
3		$PhSiH_3$	**6a** (1), 16 h, 20°C	95		[55:45]
4		$PhSiH_3$	**6b** (1), 16 h, 70°C	77[d]		[62:38]
5	 **11**	$PhSiH_3$	**7a** (1), 3.5 h, 20°C	86	 **12** +  **13**	[92: 8]
6		$PhSiH_3$	**7b** (1), 7 h, 20°C	100[e]		[50:50[f]]
7	 **14**	Ph_2SiH_2	**6a** (2), 10 h, 50°C	95	 **15** +  **16**	[25:75]
8		Ph_2SiH_2	**6b** (1), 16 h, 70°C	76		[21:79]
9		$PhSiH_3$	**6a** (1), 1 h, 70°C	100		[28:72]
10		$PhSiH_3$	**6b** (1), 12 h, 70°C	98		[23:77]
11		$PhSiH_3$	**7a** (1), 6 h, 50°C	100		[60:40]
12		$PhSiH_3$	**8** (1), 3 h, 50°C	97		[45:55]

[a] additional Experimental Conditions: see text;

[b] the following amounts (mol-%) were used: Et_3SiH (110), Ph_2SiH_2 (70) and $PhSiH_3$ (50);

[c] products and product ratios as determined by NMR and GLC after hydrolytic workup;

[d] 1,4- and 1,2-reduction product obtained in a 3 : 2 ratio;

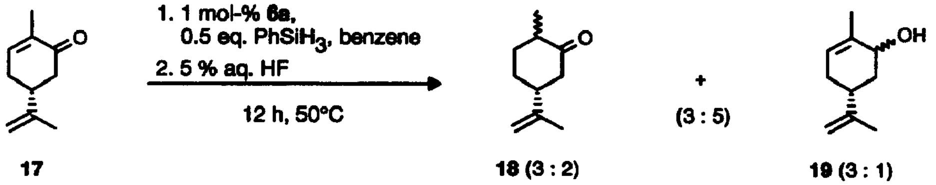
[e] 50 % combined yield of **12** and **13**; several minor products are formed;

[f] **13** is formed as a mixture of diastereomers (3 : 1), major isomer is shown above.

Several conclusions can be deduced from the results in Table 1. Firstly, with sterically hindered, less reactive silanes like triethyl silane, only a stoichiometric reaction could be achieved (entry 1). Reactions with diphenyl silane are again slower than those with phenyl silane (entries 2, 4). Molybdenum complexes, e.g. dicarbonylbis[(R)-(+)-pulegone]molybdenum **6a**, are much more active catalysts than the corresponding, isostructural tungsten complexes (entries 3, 4). Therefore, most of the results presented arise from the use of molybdenum catalysts. Comparison of entries 1, 2 and 3 shows that there is no significant influence of the silane on product distribution, 1,4-addition takes place in all cases, an observation quite unusual for catalytic hydrosilylation.[7] With the pinocarvone complexes **7**, reactions proceed even faster, the tungsten complex again being less active and selective (entries 5, 6). So far, the oxadiene substrates and the oxadiene ligands of the catalyst have been chosen to be identical. Entries 7 to 12 with a different substrate show this selection not to be essential, 4-phenylbut-3-en-2-one (**14**) may serve as example. Most interesting in these cases, the product mixtures obtained with different oxadiene molybdenum carbonyl catalysts (entries 9, 11, 12) widely differ with respect to product ratio (**15**/**16**), ranging from only 21% to about 60% of allylic alcohol **16** at almost complete conversions, thus contrasting previous findings[2] with $Mo(CO)_6$, where the saturated ketone **15** has been reported as exclusive product. Even η^6-benzenetricarbonyl molybdenum shows a relatively low catalytic activity in the above reaction, again leading to a different product ratio, i.e. a 1 : 1 mixture of **15** and **16**.

Mechanistically, these results can be taken as evidence for at least one of the oxadiene ligands staying coordinated to the metal centre during the catalytic cycle. As complexes **6** and **7** are enantiomerically pure, this might allow for their use in asymmetric hydrosilylation. Experiments in order to explore this possibility are underway. Loss of both oxadiene ligands, on the other hand, should lead to the formation of identical catalytically active species even from different oxadiene complexes and therefore give rise to identical product ratios, which is not observed. It yet remains unclear if the ligand stays in a η^4-coordination mode which might be essential in order to produce sufficient rigidity to allow asymmetric induction in this catalysis.

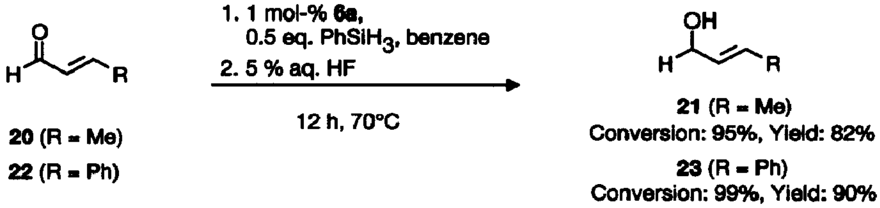
The terpene ketone R-(-)-carvone (**17**) with an oxadiene fragment fixed in *s-trans* geometry is another interesting substrate in several respects. Its reaction in the presence of phenyl silane leads to the formation of a mixture of diastereomers of 1,2- and 1,4-addition products (Scheme 2). Especially the formation of the latter is remarkable, as it has not been observed so far with group VI metal catalysts. A simultaneous interaction of the metal with both carbonyl and alkene fragment, which is unlikely in *s-trans* oxadienes, has previously[2,8] been assumed as being necessary for the hydrosilylation to proceed in order to explain why *s-trans* oxadienes could not be 1,4-hydrosilylated or -hydrogenated with those catalysts. Secondly, the carvone reaction shown here is specific for the oxadiene fragment, no hydrosilylation takes place at the isopropenyl group. The overall reactivity thus strongly parallels that observed with noble metal catalysts, e.g. of rhodium or palladium .[9]



Conversion: 100%, Yield: 95%

Scheme 2

With unsaturated aldehydes **20** or **22** as substrates, the reactions exclusively produce the corresponding allylic alcohols **21** and **23** in high yields (Scheme 3). This selectivity might be arising from the formation of an intermediate η^1- or η^2-bound aldehyde complexes leading to an exclusive activation of the carbonyl fragment of the oxadiene. Such η^1- and η^2-aldehyde complexes are known as stable compounds for a variety of metals[10] including tungsten, whereas only few iron complexes with η^4-bound unsaturated aldehydes exist.



20 (R = Me)
22 (R = Ph)

21 (R = Me)
Conversion: 95%, Yield: 82%
23 (R = Ph)
Conversion: 99%, Yield: 90%

Scheme 3

In conclusion, molybdenum oxadiene complexes are not only active catalysts for the hydrosilylation of unsaturated carbonyl compounds, but allow a tuning of chemoselectivity by selection of the catalysts ligands. This may lead to interesting preparative applications as well as to an improved understanding of the influences arising from the ligand sphere in an active hydrosilylation catalyst.

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4. Schmidt, Th., Bienewald, F. *GIT Fachz. Lab.* **1993**, 37, 761-762.
5. The complexes of pinocarvone and 5-methylhex-3-en-2-one are prepared similar to those of pulegone (as described in Ref. 3) in comparable yields.
6. When mono- or diphenyl silane are used, more than one of the hydrogen atoms at silicon is active in the hydrosilylation reaction, permitting the use of substoichiometric amounts (50 and 70 mol-%, respectively) of these silanes.
7. e.g.: Ojima, I.: The Hydrosilylation Reaction. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z. Eds.; John Wiley & Sons: Chichester, 1989; Part 2, pp. 1479-1526.
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   b) Keinan, E., Greenspoon, N. *J. Am. Chem. Soc.* **1986**, 108, 7314-7325.
10. e.g.: Honeychuck, R.V., Bonnesen, P.V., Farahi, J., Hersh, W.H. *J. Org. Chem.* **1987**, 52, 5296-5298; Gladysz, J.A., Huang, Y.-H. *J. Chem. Educat.* **1988**, 65, 298-303; Bullock, R.M., Rappoli, B.J. *J. Am. Chem. Soc.* **1991**, 113, 1659-1669.

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