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RHODIUM-DIPHOSPHINE COMPLEXES AS CATALYSTS IN ALDOL ADDITIONS

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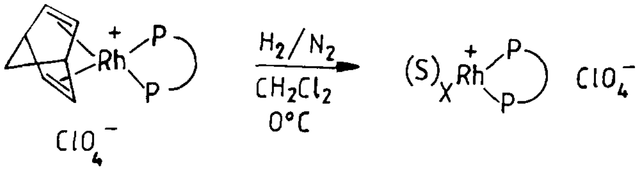
Summary: Rhodium(I)-diphosphine complexes catalyze the aldol addition of enolsilanes to aldehydes, an enantioselective version being possible if chiral phosphines are used.

The recent report by Sato, Matsuda and Izumi$^{1)}$ concerning the first example of rhodium-catalyzed crossed aldol additions of enolsilanes to aldehydes prompts us to report our results in this area. Using known procedures$^{2-4)}$, we prepared the complexes 1, 2$^{5)}$ and 3 and discovered that they catalyze the aldol addition of enolsilanes 5 to aldehydes 4 in dichloromethane (Table 1).



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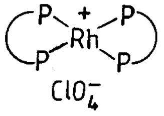
$P_2 = Ph_2P(CH_2)_nPPh_2$

S = Solvent

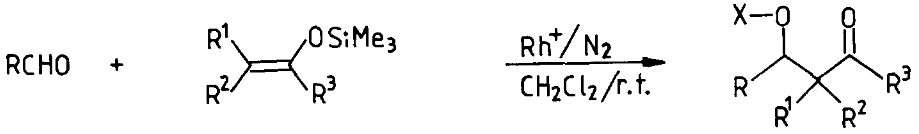
a) n = 2; b) n = 4



$P_2 = Ph_2P(CH_2)_nPPh_2$

a) n = 2; b) n = 4

3



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a) $x=SiMe_3$

b) x=H

Table 1. Rh(I)-catalyzed aldol addition at 22°C in CH_2Cl_2

Entry	R	R^1	R^2	R^3	catalyst[a] (mol-%)	reaction time (h)	isol. yield[b] (%)
1	Ph	CH_3	CH_3	OMe	1a (5)	2	75
2	Ph	CH_3	CH_3	OMe	2a (3)	18	63
3	Ph	CH_3	CH_3	OMe	3a (10)	18	57
4	n-C_6H_{13}	CH_3	CH_3	OMe	1a (10)	6	71
5	Ph	CH_3	CH_3	OMe	1b (5)	2	81
6	Ph	CH_3	CH_3	OMe	2b (5)	18	62
7	Ph	OEt	$OSiMe_3$	OEt	1a (10)	1	92
8	n-C_3H_7	OEt	$OSiMe_3$	OEt	1a (10)	24	91
9	n-C_6H_{13}	OEt	$OSiMe_3$	OEt	1a (10)	6	82
10	$CH_2=CH(CH_2)_8$	OEt	$OSiMe_3$	OEt	1a (10)	2	74
11	Ph	H	H	Ph	1a (10)	48	35

a) In the generation of 2a there is always a minor amount of 3a present as observed by ^{31}P NMR spectroscopy.

b) Products following chromatography on SiO_2 (pet.-ether 40-60/ethyl acetate 10:1). In case of entries 1-6 mixtures of 6a and 6b are formed, the former predominating. Complete desilylation using $HF/H_2O/THF$ is possible. Products in entries 7-10 occur as 6a (diastereomeric mixtures). Yields were not optimized.

None of the above reactions[6)] proceed in strongly coordinating solvents such as THF, acetonitrile or methanol, which are known to form Lewis acid/Lewis base adducts with rhodium[7)]. This may be an indication that the mechanism of aldol addition in CH_2Cl_2 involves coordination of one or more aldehyde molecules at the metal according to 7, leading to an activation of the carbonyl function$^{8)}$. Control experiments show that R_3SiClO_4 (which could be formed under the reaction conditions) does not catalyze the aldol addition. Also, $[Ph_2P(CH_2)_2PPh_2]_2RhCl$ is a much less effective catalyst, i.e., the aldol addition requires considerably longer reactions times. Alternatively, intermediate rhodium enolates may be formed which in turn undergo aldol additions$^{9)}$

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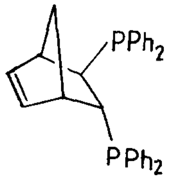
Preliminary experiments on asymmetric induction were also performed using commercially available (R,R)-NORPHOS (8)$^{10)}$ and (S,S)-CHIRAPHOS (9)$^{11)}$ in the reaction of 5 ($R^1=R^2=CH_3$; $R^3=OCH_3$) with benzaldehyde (Table 2). These are the first examples of enantioselective aldol additions using chiral rhodium catalysts$^{12)}$.



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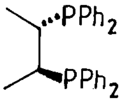

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Table 2. Catalytic Asymmetric Aldol Additions of 5($R^1=R^2=CH_3$; $R^3=OCH_3$) to Benzaldehyde

Catalyst	Mol-% of catalyst	ee (%)^a	Configuration^b
1 (CHIRAPHOS)	5	5	S
2 (NORPHOS)	5	7	R
3 (NORPHOS)	5	12	R

a) Aldolization proceeded to >75% in all cases. The crude product was desilylated and the ee value of the aldol determined by NMR shift experiments ($Eu(tfc)_3$).

b) Absolute configuration: Lit.$^{13)}$.

In summary, rhodium-diphosphine complexes are useful catalysts for aldol additions of enolsilanes to aldehydes, as little as 3-5 mol-% often being sufficient. It remains to be seen whether more efficient chiral ligands for asymmetric catalytic C-C bond formation can be developed. They could also be useful in the Rh-catalyzed cyanohydrin-forming addition of Me_3SiCN to aldehydes14).

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References and Notes:

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3) K. Tani, K. Suwa, T. Yamagata and S. Otsuka, Chem. Lett. 265 (1982).
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5) Hydrogenation of 1 to form 2 was carried out in CH_2Cl_2, not in donor solvents as previously reported2). 2 is therefore only a formal representation and may be covalent. See: J. Peone jr. and L. Vaska, Angew. Chem. Int. Ed. Engl. 10, 511 (1971).
6) A typical procedure involves the solution of an aldehyde (2 mmol) and an enolsilane (2 mmol) in CH_2Cl_2 (2 ml) in the presence of freshly prepared Rh-catalyst (5 mol-%). After the given amount of time the solvent was stripped off and the residue extracted with pet.-ether/ethyl acetate (10:1) followed by chromatography on SiO_2.
7) J.P. Collman and L.S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry"; Univ. Sci. Books, CA, USA, 1980, p. 338 ff.
8) Concerning the structure and electronic nature of the $PhCHO/BF_3$ adduct, see M.T. Reetz, M. Hüllmann, W. Massa, S. Berger, P. Rademacher and P. Heymanns, J. Am. Chem. Soc. 108, 2405 (1986).
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13) M. Guette, J. Capillon and J.P. Guette, Tetrahedron 29, 3659 (1973).
14) We have observed that Me_3SiCN adds smoothly to aldehydes at room temperature in the presence of catalytic amounts (5%) of 1 or 2, conversion being 90%.

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