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The Hydrosilylation of Ald- and Ketimines Catalyzed by Titanocene Complexes

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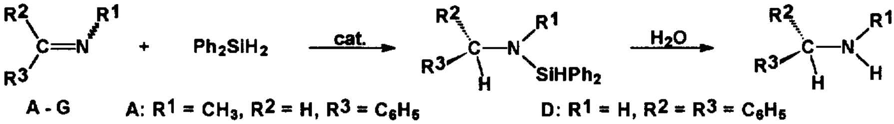
Abstract: Different titanocene complexes **1** - **10** were tested in the catalytic hydrosilylation of ald - and ketimines with Ph_2SiH_2. The highest conversions were obtained with $Cp_2Ti(PhC{\equiv}CSiMe_3)$ **1** up to 98 % at room temperature. © 1997 Elsevier Science Ltd. All rights reserved.

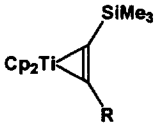
In this work we report our results on the hydrosilylation of several ald- and ketimines **A** - **G** with diphenylsilane in the presence of different titanocene complexes **1** - **10**. As our results show (see Table 1 and 2) two factors, the rest R^1 bound to the imine and the ligand X bound to the metallocene fragment („Cp_2M“) have an essential influence on the conversion. In particular it is evident, that the yield is influenced by changes in the steric properties of the substrate. The substitution pattern at the nitrogen influences the conversion rate in the following order: CH_3 (H) > Ph-CH_2 > Ph. In no example imines with R^1 = Ph were reduced to the corresponding amines with Ph_2SiH_2. We also tried to find a relation between the structure of the leaving group X bound to the metallocene and the activity of the different precatalysts. The nature of the leaving group X plays an important role during the formation of the key intermediate $Cp_2Ti\text{-}H$[6] in the catalytic cycle. The metallocene hydride should be formed easily if the ligand X is bound weakly to the metal. To support this assumption the activity of the less stable titanacyclopropene derivatives is compared with the more stable titanacyclopentadienes. For example the hydrosilylation of **A** with **1** proceeded nearly quantitative at r. t., with **6** a conversion was only observed at 80 °C. Depending on the nature of the substituents R a comparison of the



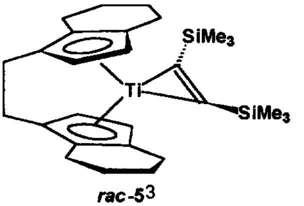
A - G

A: $R^1 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$
B: $R^1 = CH_2C_6H_5$, $R^2 = H$, $R^3 = C_6H_5$
C: $R^1 = C_6H_5$, $R^2 = H$, $R^3 = C_6H_5$
D: $R^1 = H$, $R^2 = R^3 = C_6H_5$
E: $R^1 = CH_2C_6H_5$, $R^2 = CH_3$, $R^3 = C_4H_9$
F: $R^1 = CH_2C_6H_5$, $R^2 = CH_3$, $R^3 = C_6H_{11}$
G: $R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = C_6H_5$

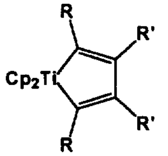
Precatalysts: Cp_2TiX_2



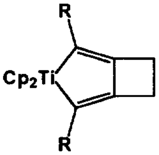
R = Ph **1**[1]
R = nBu **2**[2]
R = $SiMe_3$ **3**[1]
R = tBu **4**[2]



rac-**5**[3]



R = $SiMe_3$, R' = nBu **6**[2]
R = $SiMe_3$, R' = Ph **7**[2]
R = R' = Ph **8**[4]



R = Me **9**[5]
R = nBu **10**[5]

titanacyclopropene derivatives **1** - **4** shows the hydrosilylation activity in the following order: ^{t}Bu (**4**) < Me_3Si (**3**) < ^{n}Bu (**2**) < Ph (**1**). Complex **1** is the most active catalyst, which achieved a conversion of 98 % already at r. t. in 24 h. Analogous zirconocene complexes[1] to **3** are completely inactive. A comparison of the titanacyclopentadiene derivatives **6** - **8** with the bicyclic titanacyclopentadienes of type **9** and **10** indicates, that the strained bicyclic complexes are more active. The results of ketimine hydrosilylation are summarized in Table 2. As shown, the ketimines are significantly less reactive than the aldimines. There is no evident difference in the imine conversion in the presence of investigated catalysts **1**, **3** and **9**, but a significant difference was observed for the *ansa*-titanocene alkyne complex **5**. Unfortunately, this complex gave only a very low activity at relative extreme conditions. Consequently, the enantiomerically pure form of this complex is unsuitable for enantioselective imine hydrosilylation under these conditions. In contrast Buchwald and coworkers obtained excellent results in the imine hydrosilylation (up to 97 % chemical yields and 99 % ee at r. t.) with a modified *ansa*-titanocene complex (S,S)-(EBTHI)TiF_2.[6]

Table 1: Hydrosilylation* of aldimines with diphenylsilane catalyzed by titanocene complexes

	C_6H_5-CH=N-CH_3 **A**					C_6H_5-CH=N-CH_3 **A**					C_6H_5-CH=N-CH_3 **A**			
catalyst	conv. (%)	time (h)	temp. (°C)	[subst.] / [cat.]	catalyst	conv. (%)	time (h)	temp. (°C)	[subst.] / [cat.]	catalyst	conv. (%)	time (h)	temp. (°C)	[subst.] / [cat.]
1	98	24	r.t.	30	**4**	5	24	r.t.	30	**7**	5	6	80	30
	100	1	50	30		86	6	50	30		21	24	80	30
	100	3	50	60		100	1	80	30	**8**	4	6	80	30
	51	6	50	100	**5**	0	24	r.t.	30	**9**	56	24	r.t.	30
2	75	24	r.t.	30		0	6	50	30		98	6	50	30
	100	6	50	30		74	6	80	30		74	6	50	60
3	21	24	r.t.	30		100	24	80	30		100	1	80	30
	98	6	50	30	**6**	0	24	r.t.	30	**10**	6	24	r.t.	30
	100	1	80	30		0	6	50	30		40	6	50	30
						96	6	80	30		100	1	80	30

	C_6H_5-CH=N-$CH_2C_6H_5$ **B**					C_6H_5-CH=N-C_6H_5 **C**			
catalyst	conv. (%)	time (h)	temp. (°C)	[subst.] / [cat.]	catalyst	conv. (%)	time (h)	temp. (°C)	[subst.] / [cat.]
1	52	6	80	30	**1**	0	24	80	30
3	56	6	80	30	**3**	0	24	80	30
	100	24	80	30					
9	43	6	80	30	**9**	0	24	80	30

*general reaction conditions: 0.033 mmol catalyst (or as in the Table described) and 1.2 mmol Ph_2SiH_2 were stirred for 10 min at r. t.. Then 1 mmol imine was added. Reaction temperature and time are indicated in Table 1 and 2. After hydrolysis the product distribution was determined by GC on 12.5 m OV101 column (programme: 50 °C, 8 °/ min, 250 °C).

Table 2: Hydrosilylation* of ketimines with Ph_2SiH_2 catalyzed by titanocene complexes at 80 °C and [substrate]:[catalyst] = 30

	$C_6H_5(C_6H_5)C$=NH **D**		$CH_3(C_4H_9)C$=$NCH_2C_6H_5$ **E**		$CH_3(C_6H_{11})C$=$NCH_2C_6H_5$ **F**		$CH_3(C_6H_5)C$=NC_6H_5 **G**	
catalyst	conv. (%)	time (h)	conv. (%)	time (h)	conv. (%)	time (h)	conv. (%)	time (h)
1	77	24	21	24				
3	75	24	20	24	21	24	0	24
5			3	24				
9	75	24	23	24				

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