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Dehydrocoupling of Silanes Catalyzed by Zirconocene- and Titanocene Alkyne Complexes

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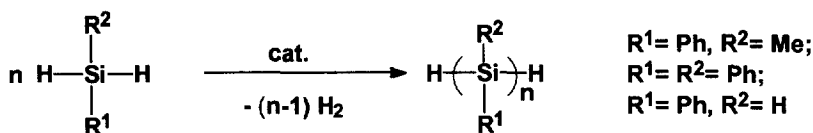
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Abstract: The zirconocene- and titanocene alkyne complexes **1-10** were tested to be effective catalysts in the dehydrocoupling of hydrosilanes like PhMeSiH_2 and Ph_2SiH_2 to give oligomers and of other examples, e.g., PhSiH_3 polymers with cyclic oligosilanes as byproducts. © 1997 Elsevier Science Ltd.

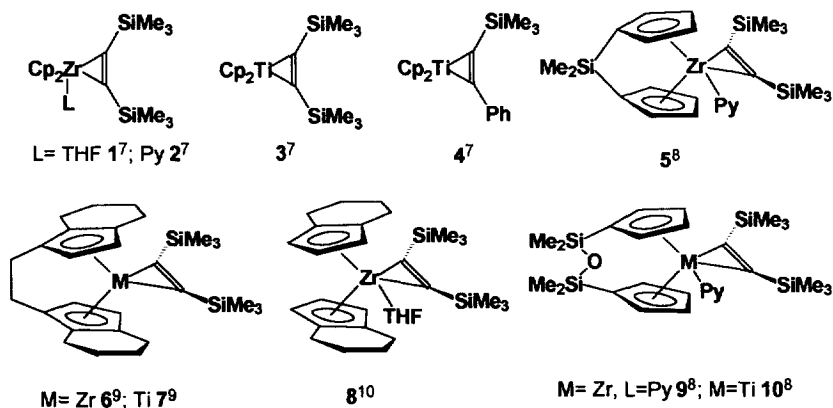
Zirconocene- and titanocene alkyne complexes are active catalysts or precatalysts in the isomerization of olefins,¹ polymerization of acetylene,² hydrosilylation of ald- and ketimines,³ and ring opening polymerization of lactones.⁴

The dehydrogenative coupling of hydrosilanes to polysilanes provides a route to poly- and oligosilanes having a number of potential applications as advanced materials. Harrod was the first who used Cp_2ZrMe_2 and Cp_2TiMe_2 as catalysts for the polycondensation of PhSiH_3 .⁵ Since then, other transition-metal catalysts have been found, but the group 4 metallocene complexes provide the most active of the dehydrocoupling catalysts.⁶

We report here that crystalline and well defined titanocene and zirconocene alkyne complexes are effective catalysts in the dehydrocoupling of hydrosilanes like PhMeSiH_2 , Ph_2SiH_2 and PhSiH_3 .



Precatalysts:



The results of the catalyzed reactions of PhMeSiH_2 with our catalysts are in good agreement with the results of those carried out by Corey.¹¹ Only the unbridged titanocene alkyne complexes are more active compared to the analogous zirconocene examples.

Table 1. Oligomerization of PhMeSiH_2 with various metallocene alkyne complexes

catalysts	PhMeSiH_2 (%)	$\text{H(PhMeSi)}_2\text{H}$ (%)	$\text{H(PhMeSi)}_3\text{H}$ (%)	$\text{H(PhMeSi)}_n\text{H}$ (%)
1	46	23	28	3
2	47	22	27	4
3	40	22	27	9
4	69	21	9	1
5	34	50	16	-
6	59	34	7	-
7	89	11	-	-
8	68	30	2	-

Determined by gas chromatography; general conditions: silane/cat.: 40; 80°C; 72h; toluene

Dehydrocoupling of Ph_2SiH_2 leads to moderate yield which could be explained by the steric bulk of the phenyl substituents compared to the methyl groups.

Table 2. Oligomerization of Ph_2SiH_2 with various metallocene alkyne complexes

catalysts	Ph_2SiH_2 (%)	$\text{H(Ph}_2\text{Si)}_2\text{H}$ (%)
2	65	35
3	58	42
5	69	31
9	82	18
10	85	15

Conditions like PhMeSiH_2

With the primary silane PhSiH_3 only the unbridged metallocene complexes are active, and no monosilane was detected after treatment. Byproducts in this reaction are cyclic oligosilanes, which were not observed in the catalysis without solvent using complex 2.

Table 3. Polymerization of PhSiH_3 with various metallocene alkyne complexes

catalysts	polymers (%)	M_n	M_w
1 ^a	90	910	1446
2 ^b	93	3253	19460
2 ^c	92	958	4840
3 ^b	84	1041	1760
6 ^c	87	502	802
7 ^c	77	404	591

GPC against polystyrene (eluent: toluene); general conditions: silane/cat.: 100; 72h; r.t.;

^a) in THF (silane/THF: 1); ^b) neat; ^c) in toluene (silane/toluene: 1)

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