highly active SiH₄ and high pressure, which result in multiple hydrosilylation.^[7] The only representative catalysts from the main-group elements are the Lewis acids AlCl₃ and $B(C_6F_5)_3$.^[8]

As organometallic complexes of the heavier alkalineearth metals (Ca, Sr, and Ba) show similarities with organolanthanides^[9] and are increasingly used in catalysis,^[10–12] they could be potential candidates for early main-group metal hydrosilylation catalysts. A possible catalytic cycle could be analogous to that established for the hydrosilylation with lanthanide catalysts (Scheme 1). This mechanism poses two



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Hydrosilylation of Alkenes with Early Main-Group Metal Catalysts**

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The catalytical hydrosilylation of alkenes is of great importance in the production of silicon compounds.^[1] There are numerous methods to initiate this highly atom-efficient key transformation. Classical thermal and radical-initiated reactions often lead to oligomers, especially when readily polymerizable alkenes (e.g., styrenes) are used.^[2] The discovery of the Speier hydrosilylation catalyst [H2PtCl6]·6H2O/ *i*PrOH represented a major breakthrough in silicon chemistry.^[3] This catalyst was later replaced by the more active and selective Karstedt catalyst.^[4] Nevertheless, in some cases poor regiocontrol and side reactions, such as alkene isomerization and hydrogenation, are still an issue.^[5] The last decade has seen the development of lanthanide-based catalysts.^[6] Although these catalysts show poor regioselectivity in some cases, they certainly feature several advantages, such as 1) tunability of the regiochemistry by metal size and ligand choice and 2) enantioselective hydrosilylation. Hydrosilylation catalyzed by LiAlH₄ has been described but requires

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Scheme 1. Established catalytic cycle for hydrosilylation with lanthanide catalysts.

tentative problems: the proposed catalytically active species, a heteroleptic metal hydride complex, is currently unknown for the heavier alkaline-earth metals. Our previous attempts to isolate well-defined soluble heteroleptic Ca hydrides resulted in the precipitation of insoluble CaH₂.^[13] A highly reactive, short-lived Ca hydride complex as an intermediate in a catalytic cycle, however, remains feasible. The second problem is that early main-group metal alkyl complexes, and possibly also hydrides, only add to conjugated alkenes (e.g., styrene and butadiene), which also readily polymerize under these conditions.

Calcium-mediated hydrosilylation was first attempted with 1,1-diphenylethylene (DPE), a substrate which does not polymerize. Addition of 5 mol % of the heteroleptic catalyst **1** to a mixture of DPE and PhSiH₃ at 50 °C resulted in



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Scheme 2. Initiation and possible catalytic cycles for hydrosilylation with early main-group metal catalysts.

complete conversion of the α -Me₃Si-2-(Me₂N)-benzyl (DMAT) ligand into **5** (Scheme 2). The intense red color of the reaction mixture suggests addition of the resulting hydride to DPE and formation of MePh₂C⁻, an intermediate in catalytic cycle A. However, an overnight reaction gave only 10% conversion into hydrosilylation product **6** (R¹ = R² = Ph; Table 1, entry 1).

As homoleptic 2 generally shows higher reactivity than heteroleptic 1, this compound was also tested as a potential



catalyst (Table 1, entries 2 and 3). Despite the possible formation of insoluble CaH_2 in the initiation step, a clean and complete conversion of DPE and PhSiH₃ into the expected silane **6** was observed overnight (catalyst loading: 2.5 mol%; no traces of the other regioisomer could be found). An increase in the catalyst loading to 10 mol% gave full conversion within 2 h. The more reactive Sr analogue **3** gave similar results with a catalyst loading of 2.5 mol% (Table 1, entry 4).

The cleanliness and speed of the reactions indicate that soluble heteroleptic R-M-H species play a role in the catalytic cycle. The attempted isolation of a heteroleptic [(DMAT)-CaH] complex was not successful, and there is evidence that hydride-rich clusters of [{(DMAT)_{<1}CaH_{>1}}_n] exist in solution.^[14] It is, however, not excluded that small amounts of CaH₂ precipitate in a very fine highly reactive form and, after a heterogeneous reaction, are reintroduced in the catalytic cycle (in some cases a fine precipitate was observed). Freshly ground, commercially available CaH₂ was found not to be active as a hydrosilylation catalyst (Table 1, entry 5).

The scope of hydrosilylation with polar early main-group catalysts was further investigated by probing different substrates. The hydrosilylation of α -Me-styrene with PhSiH₃ proceeded slowly with Ca catalyst **2**, but use of the Sr analogue **3** gave fast conversion (Table 1, entries 6 and 7). Runs with a bulkier secondary silane (Table 1, entry 8) also gave good conversion, albeit slower. As expected, no conversion was observed in the hydrosilylation of unactivated alkenes, such as allylbenzene and norbornene.

In contrast to our expectations, the hydrosilylation of styrene with $PhSiH_3$ did not give polystyrene by-products, but clean and very fast regioselective hydrosilylation was observed already at room temperature (Table 1, entries 9 and 10). A decrease in the catalyst loading to 0.5 mol% (Table 1, entry 11) and reaction with a secondary silane (Table 1, entry 12) both gave a good conversion; furthermore, the heteroleptic calcium catalyst 1 was found to be active (Table 1, entry 13). The hydrosilylation of styrene is apparently much faster than its polymerization.

The alkaline-earth-metal catalysts 2 and 3 also showed very high activity in the hydrosilylation of the conjugated double bond in hexadiene, thus exclusively yielding the

Table 1: Summary of results for the hydrosilylation of alkenes with various main-group metal catalysts.

Entry	Substrates	Product	Catalyst	[cat.]/[alkene] [%]	т [°С]	<i>t</i> [h]	Conver. [%]
1	DPE PhSiH₃	PhH ₂ Si Me	1	5	50	16	10
2	DPE PhSiH₃	PhH ₂ Si Me	2	2.5	50	16	>98
3	DPE PhSiH₃	PhH ₂ Si Me Ph	2	10	50	2	>98
4	DPE PhSiH₃	PhH ₂ Si Me	3	2.5	50	2	>98
5	DPE PhSiH₃	_	$CaH_2^{[a]}$	25	50	48	0
6	Ph(Me)C=CH ₂ PhSiH ₃	PhH ₂ Si Me	2	2.5	50	24	20
7	Ph(Me)C=CH ₂ PhSiH ₃	PhH ₂ Si Me	3	2.5	50	2.5	>98
8	Ph(Me)C=CH ₂ Ph(Me)SiH ₂	Ph(Me)HSi	3	2.5	50	24	>98
9	styrene PhSiH₃	PhH ₂ Si Me	2	2.5	20	< 0.1	>98
10	styrene PhSiH₃	PhH ₂ Si Me	3	2.5	20	< 0.1	>98
11	styrene PhSiH₃	PhH ₂ Si Me	2	0.5	50	1.5	>98
12	styrene Ph(Me)SiH ₂	Ph(Me)HSi Me Ph	2	2.5	20	< 0.1	>98
13	styrene PhSiH₃		1	5	50	20	>98
14	cyclohexadiene PhSiH₃	PhH ₂ Si	2	2.5	20	< 0.1	>98
15	cyclohexadiene PhSiH₃	PhH ₂ Si	3	2.5	20	< 0.1	>98
16	DPE PhSiH₃	Ph Ph PhH ₂ Si H	4	5	50	2	>98
17	DPE PhSiH₃	Ph Ph PhH ₂ Si	KH ^[c]	25	50	4 ^[d]	>98
18	Ph	PhH ₂ Si Ph	4	5	50	16	>98
	PhSiH₃	H ₃ Si Ph 10%					
19 ^[e]	DPE PhSiH₃	Ph Ph PhH ₂ Si	2	2.5	50	3	>98
20 ^[e]	DPE PhSiH₃	Ph Ph PhH ₂ Si H	3	2.5	50	2	>98
21 ^[e]	DPE PhSiH₃	Ph Ph PhH ₂ Si	4	5	20	< 0.1	>98

monosilylated product with a Si atom in the allylic position (Table 1, entries 14 and 15).

The "in situ" generation of highly reactive alkaline-earthmetal hydrides drew our attention to the use of organopotassium compounds as potential catalysts in alkene hydrosilylation. The reaction of 5 mol% of K(DMAT) 4 with DPE and PhSiH₃ immediately produced the initiation product 5, and complete conversion of the substrates was reached within 2 h (Table 1, entry 16). Analysis, however, showed exclusive formation of the other regioisomer 7. Interestingly, similar results were obtained with commercially available KH; however, a 90-min induction period was observed (Table 1, entry 17). Hydrosilylation of other alkenes with the potassium catalyst 4 either resulted in no reaction (allylbenzene, norbornene), a sluggish reaction (cyclohexadiene), or partial alkene polymerization (styrene and α -Me-styrene).

It is unlikely that regioisomer 7 is formed by the hydride cycle (cycle A) through a 1,2-insertion which produces the resonanceunstabilized Ph₂CHCH₂⁻ ion. The fast and exclusive formation of hydrosilylation product 7 (no traces of 6 could be detected) indicates that the potassium-mediated hydrosilvlation might operate through a different mechanism. A possible route could be the silanide pathway (cycle B), a mechanism that has been rejected for lanthanide-catalyzed hydrosilylation^[6a] but has been proposed in transition-metal-catalyzed hydrosilylation.^[15] The first step is well established: KH reacts with PhSiH₃ to hypervalent $PhSiH_4^-K^+$, form which yields PhSiH₂⁻K⁺ after the loss of H₂.^[16] Addition of the silanide to DPE (cycle B) gives the resonance-stabilized intermediate PhSiH₂CH₂CPh₂K⁺, which gives 7 after o-bond metathesis with PhSiH₃.

A recently reported crystal structure of $Ph_3SiH_2^-K^{+[17]}$ raises the possibility that potassiummediated hydrosilylation could

[a] Commercially obtained CaH₂ was freshly ground under nitrogen. [b] Both diastereomers were obtained in an approximate ratio of 1:1. [c] KH was isolated from a commercially available suspension in paraffin oil. [d] A 90-min induction period was observed. [e] Reaction in THF.

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proceed through a concerted insertion reaction of the alkene with the pentavalent $PhSiH_4^-$ intermediate (Scheme 2, cycle C). Steric interactions between the Ph rings in DPE and the silanide anion would result in the exclusive formation of regioisomer **7**. This mechanism is analogous to the well-established mechanism for the KF-catalyzed hydrosilylation of ketones (Scheme 3).^[18]



Scheme 3. Mechanism for the KF-catalyzed hydrosilylation of ketones.

Hydrosilylation of a cyclic alkene gave strong support for a silanide mechanism: overnight reaction of 1-Ph-cyclohexene with PhSiH₃ using potassium catalyst 4 (Table 1, entry 18) resulted in the formation of 1-Ph-2-PhSiH₂-cyclohexane exclusively as a cis diastereomer, from which a trans addition of the silane can be concluded. This result essentially rules out a concerted addition as in cycle C, but is in agreement with the two-step silanide mechanism in cycle B. Exclusive formation of the cis isomer can be explained by σ -bond metathesis in which PhSiH₃ approaches from the least-hindered side. This preferred stereochemistry is opposite to that in the hydroboration and therefore allows access to the complementary alcohols after a Tamao-Fleming oxidation. The additional formation of approximately 10% of cis-1-Ph-2-SiH₃-cyclohexane and even larger amounts of Ph₂SiH₂ also points to a concomitant disproportionation of the silane substrate during the overnight reaction (2PhSiH₃ \rightarrow Ph₂SiH₂+SiH₄, etc.) and formation of KSiH₃. This base-catalyzed disproportionation,^[19] which is proposed to proceed through a hypervalent intermediate,^[16] could be reproduced by reaction of **4** with excess PhSiH₃ in the absence of an alkene.^[20] The formation of KSiH₃ is in agreement with the recent finding that prolonged reaction of KH with PhSiH₃ yields KSiH₃.^[21]

The complete change in regioselectivity observed in switching from Ca (or Sr) catalysts to the corresponding K catalyst indicates that metal–carbon bond polarity could be a decisive factor. For this reason, we also studied the effect of the solvent on the regioselectivity. Whereas hydrosilylation of DPE with Ca catalyst 2 in benzene gave essentially similar results as the solvent-free runs (that is, sole formation of product 6), experiments in THF gave fast and exclusive formation of regioisomer 7 (Table 1, entry 19). The reaction in Et₂O produced a mixture of isomers 6 (75%) and 7 (25%), which shows that regioselectivity can be tuned by solvent polarity. The use of other styrenic substrates led to oligomeric products. A complete change in regioselectivity was also observed for the Sr catalyst **3** in THF (Table 1, entry 20). The reaction in Et_2O only gave regioisomer **7**, which is in agreement with the larger ionicity of the Sr–C bond. The addition of THF to the DPE/PhSiH₃/4 system gave essentially the same product as found in the THF-free system; however, the conversion was much faster (Table 1, entry 21). Phenylcyclohexane could not be hydrosilylated using catalysts **2** and **3** in THF (also not without solvent). This behavior indicates that the metal plays an important role in the catalytic species and rules out the ion-pair mechanism (cycle C).

It is hitherto unclear how bond polarity redirects the catalytic reaction from the hydride cycle to the silanide cycle. The reaction is initiated in all cases by formation of **5** and a metal hydride, which either reacts with the alkene or the silane. A reasonable explanation could be that large cations and polar solvents favor the formation of the intermediate ion pair $[M^+][PhSiH_4^-]$, which converts into a silanide.^[22]

In summary, the first hydrosilylation catalysts based on early main-group metals (Ca, Sr, and K) are very effective for the conversion of conjugated double bonds. The catalytic reactions are initiated in all cases by the formation of a highly reactive metal hydride, which either adds to an alkene or to the silane. The regiochemistry for the hydrosilylation of DPE can be completely controlled by either the polarity of the solvent or metal choice. Further research will be directed to the isolation of well-defined heteroleptic alkaline-earth-metal hydrides and other possible intermediates; therefore, better insight into the mechanisms involved may be gained. In addition, possible enantioselective hydrosilylation with these catalysts will be explored.

Experimental Section

All experiments were carried out using standard Schlenk techniques and freshly dried solvents. Alkene substrates were dried over CaH_2 and freshly distilled prior to use. The silanes PhSiH₃ (Fluka) and Ph(Me)SiH₂ (Aldrich) were used as received. The catalysts were prepared according to our previously reported methods: **1**,^[10b] **2**,^[10a] **3**,^[23] and **4**.^[23]

A typical hydrosilylation experiment: a dry Schlenk tube was charged with the alkene substrate (2.0 mmol) and the silane (2.0 mmol). After addition of the catalyst (generally 2.5 mol%) and heating of the solution to the required temperature (generally 50 °C), a color change to red was usually observed. In some cases, a fine material, presumably a metal hydride, was deposited. To follow the conversion, samples were taken at regular time intervals and analyzed by ¹H NMR spectroscopy and GC MS. In all cases (except entry 18 in Table 1), the crude reaction products consisted of essentially pure hydrosilylation product with traces of the product of initiation 5 and in some cases small amounts of one of the substrates. All hydrosilylation products and initiation products were isolated as pure compounds and completely characterized by ¹H, ¹³C, and 2D NMR spectroscopy and by GC MS (see the Supporting Information). In a typical larger scale experiment (20 mmol of styrene and PhSiH₃; Ca catalyst 2), product 6 ($R^1 = Ph$, $R^2 = H$) was obtained after isolation by column chromatography in 92% yield.

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