Homogeneous Catalysis Hot Paper

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Methoxide-Enabled Zirconium-Catalyzed Migratory Alkene Hydrosilylation

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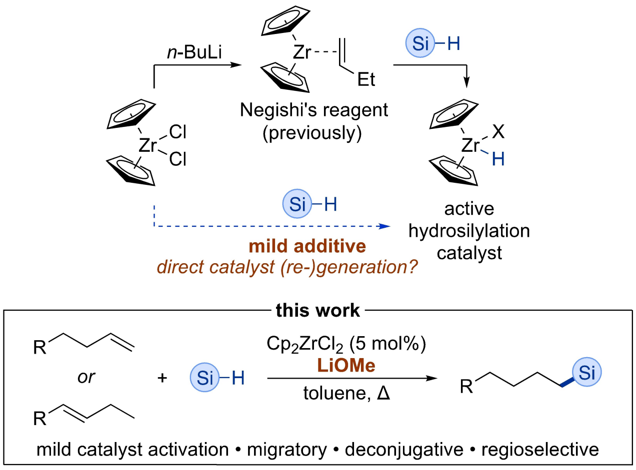
Abstract: A zirconocene dichloride-catalyzed alkene hydrosilylation is reported that can be applied to non-activated and conjugated terminal and internal alkenes. It involves a catalytic Zr-walk process and leads to a selective conversion to the linear product. Lithium methoxide serves as mild catalyst activating agent, which significantly increases the applicability and operational simplicity in comparison to earlier zirconium(II)-based protocols. Supported by additional experiments and calculations, a mechanism via zirconium(IV) intermediates is proposed. Due to the benign nature and ready-availability of the zirconium catalyst, the reaction is an attractive alternative to established alkene hydrosilylation methods.



Scheme 1. Concept of a zirconium-catalyzed migratory hydrosilylation under mild activating conditions.

The transition metal-catalyzed hydrosilylation of alkenes is an atom-economic reaction that is of industrial importance for the production of surfactants, silicones, adhesives, and fine chemicals.[1] Traditional hydrosilylation catalysts are based on precious late transition metals like Pt, Rh, Ru, and Ir that are expensive and toxic but at the same time highly reactive. Over the past decades, catalysts based on first row, earth abundant transition metals such as iron, nickel, cobalt, and manganese as well as rare earth metals have been developed that show a high performance and regioselectivity control, but usually require the synthesis of sophisticated ligands.[2–4] Alkene hydrosilylation catalysts based on "earlier" group IV transition metals are less investigated. In the 1990s, it has been shown that in particular Cp_2Zr(1-butene), Negishi's reagent, is a competent alkene hydrosilylation precatalyst.[5] However, the requirement of highly reactive reagents such as *n*-butyllithium or ethylmagnesium bromide to form the zirconium(II) alkene reagent in situ significantly impacted the applicability (Scheme 1). We now report a broadly applicable and operationally simple zirconium-catalyzed olefin hydrosilylation that addresses this issue through the in situ formation of an alkoxide zirconocene catalyst from readily-available Cp_2ZrCl_2. The reaction can be applied to terminal and internal alkenes and is suggested to proceed via a zirconium(IV) mechanism.

One striking feature of zirconocene hydride species is their ability to migrate internal olefins along an alkyl chain towards a terminal position by a so-called Zr-walk.[6] While migratory hydrosilylations via such a metal walk have been reported for certain late transition metal catalysts,[1,3b–d,7] it is basically only linear alkene isomers that have been shown to undergo a terminal-selective hydrosilylation with Negishi's reagent as precatalyst.[5] As part of our ongoing research on zirconium hydride catalysis,[8] we have recently reported a catalytic remote defunctionalization of ethers, amines, and thioethers that is based on a catalytic Zr-walk reaction.[8b] While this reaction still required $LiAlH_4$ as terminal reducing agent, it was reported in parallel that the addition of LiOMe facilitates the formation of the active Zr–H catalyst in a migratory alkene diboration reaction.[9] Moreover, it has been shown for titanium-catalyzed hydrosilylations of carbonyls, dienes, and vinyl silanes that catalysts with different X-type ligands, for example Cp_2TiF_2 and $Cp_2Ti(OPh)_2$, do not require additional activators but directly form titanium(III) hydride species in presence of a silane.[10,11] We therefore envisioned that in situ formation of a zirconocene alkoxide would facilitate the generation of the zirconium hydride catalyst and enable the desired migratory alkene hydrosilylation. This was further encouraged by

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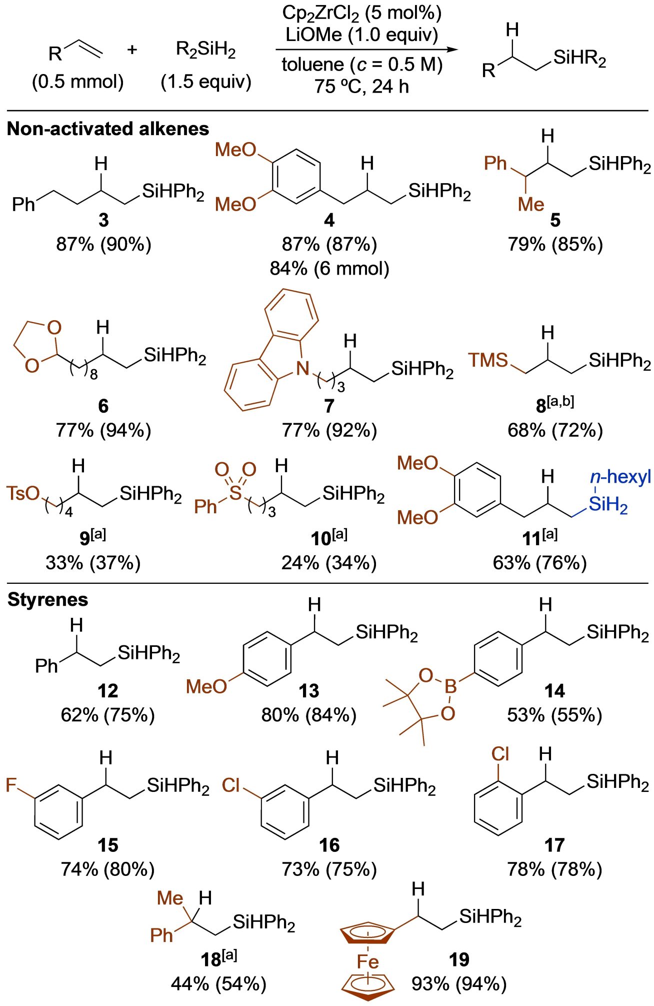
recent reports of complementary zirconium catalysis systems for reductions of carbonyls, esters, amides, and alkynes with silanes as reducing agents.[12] However, certain challenges that are frequently observed in alkene hydrosilylations such as suppressing competing alkene hydrogenation and achieving a high regioselectivity would have to be met.

We started investigating the hydrosilylation using 4-phenyl-1-butene (**1**) and Ph_2SiH_2 (**2**) as reaction partners, Cp_2ZrCl_2 as catalyst precursor, and LiOMe as catalyst-activating additive (Table 1). It was quickly found that the reaction proceeded well with only 5 mol % of catalyst and 1.5 equiv. of silane in 2-MeTHF, the solvent used in our earlier remote defunctionalization protocol,[8b] giving the linear hydrosilylation product **3** in 77 % yield as determined by ^{1}H NMR with an internal standard (entry 1). No reaction occurred in absence of catalyst or lithium methoxide.[13] Changing the solvent to toluene improved the result, showing quantitative conversion and 94 % NMR yield (entry 2). The hydrosilylation was found to be chemo- and regioselective, giving the desired linear product. A further reduction in catalyst loading to 3 mol % was possible (87 %), but lowering the reaction temperature to 50 °C led to a diminished yield of 55 % (entries 3, 4). Substituting LiOMe with LiBr or NaOMe showed that the methoxide anion was essential for the reaction to occur but the cation could be exchanged (entries 5, 6). Bulkier lithium alkoxides also drastically reduced the yield.[13]

A number of non-activated terminal alkenes was then submitted to the optimized conditions on a 0.5 mmol scale at which alkene **1** and methyl eugenol both gave 87 % isolated yield (Scheme 2). The reaction with the latter was repeated on a 6 mmol scale to demonstrate scalability (84 %). Likewise, 3-phenylbutyl product **5** was isolated in good yield (79 %). Substrates bearing acetal and carbazole groups were converted into **6** and **7**, respectively (77 % each), and a trimethylsilyl group was tolerated (**8**).[14] We then tested less common, potentially labile functional groups and, to our surprise, an alkenyl tosylate and an alkenyl sulfone were tolerated to some extent, giving products **9** and **10** in 33 % and 24 % yield, respectively, after chromatography. In the case of **9**, undefined decomposition of the remaining

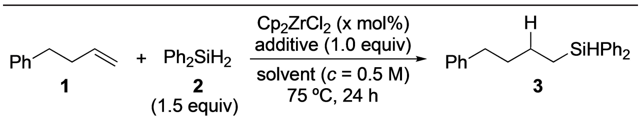


Scheme 2. Scope of non-activated terminal alkene and styrene substrates. Yields of isolated product. Brackets show ^{1}H NMR yields determined with mesitylene as internal standard. [a] Reaction at 125 °C. [b] Yield calculated from the mixture with coeluting Ph_2SiH_2.

material occurred while in the case of **10**, a complex mixture was received from which *n*-pentyl phenyl sulfone was isolated as a byproduct (17 %). We further found that *n*-hexylsilane was also a potent coupling partner.[13] It should be noted that the best yield for products **8**–**11** was achieved at 125 °C reaction temperature. The scope evaluation then continued on various styrene substrates, all of which selectively gave the linear product. Phenylethyl silane **12** was received in 62 % isolated yield (*vs* 75 % NMR yield) due to difficult purification whereas the more polar *para*-methoxy derivative **13** was conveniently isolated in 80 % yield. Interestingly, a pinacol boronate was tolerated and the corresponding silane **14** was obtained in 53 % yield. Fluoride and chloride substituents were unproblematic (**15**–**17**, 73–78 % yield) and α-methylstyrene, representing a 1,1-disubstituted alkene, gave silane **18** in 44 % yield (54 % NMR yield) at 125 °C. Finally, vinyl ferrocene proved to be an excellent substrate, giving silane **19** in 93 % yield.

Afterwards, the migratory hydrosilylation of internal alkenes was investigated, which required an efficient Zr-

Table 1: Reaction optimization.[a]



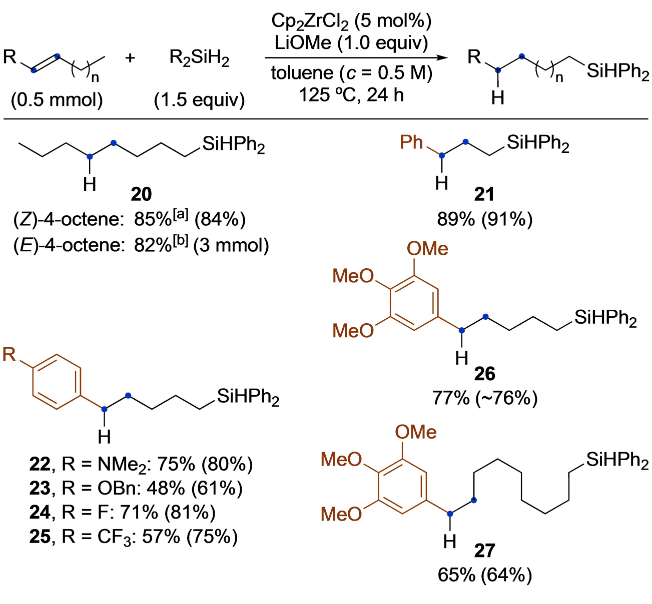
Entry	x	Additive	Solvent	Yield (%)[b]
1	5	LiOMe	2-MeTHF	77
2	**5**	**LiOMe**	**Toluene**	**94**
3	3	LiOMe	Toluene	87
4	5	LiOMe	Toluene	55[c]
5	5	LiBr	Toluene	0
6	5	NaOMe	Toluene	88

[a] Reactions on a 0.2 mmol scale at 75 °C run for 24 h, unless noted otherwise. [b] Yields determined by ^{1}H NMR analysis of the crude mixture using mesitylene as internal standard. [c] Reaction carried out at 50 °C.

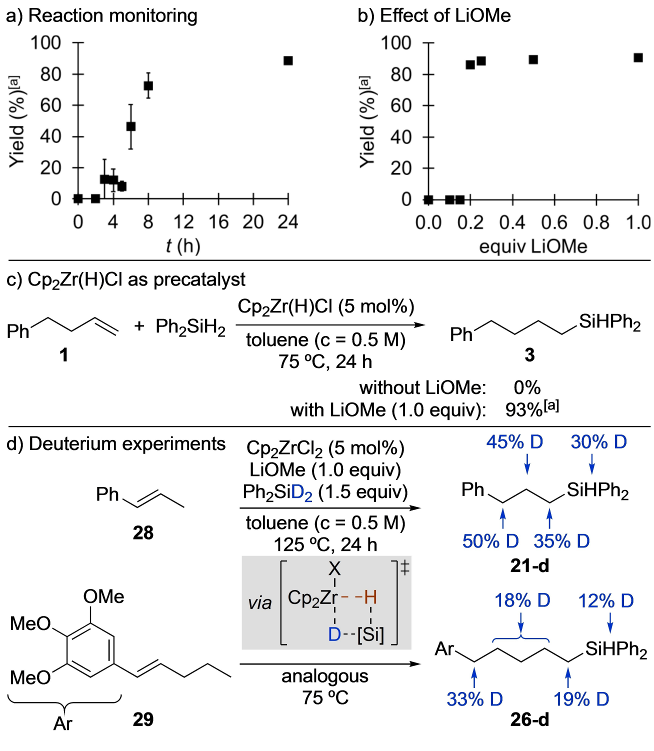
walk along the alkyl chain towards the terminal position (Scheme 3). Gratifyingly, submitting (*E*)- or (*Z*)-4-octene to the hydrosilylation conditions resulted in the regioselective formation of *n*-octylsilane **20** with NMR yields in the range 79–93 % (*E*) and 73 % (*Z*).[14] At 125 °C, however, we found that yields were more reliable and improved for (*Z*)-4-octene to 85 %. We could further demonstrate on the example of (*E*)-4-octene that if the reaction is carried out on a larger scale, the coeluting diphenylsilane can be removed by distillation (82 % yield). β-Methyl styrene and related substrates with longer alkyl chains that required a deconjugation of the alkene and a walk over at least three carbons were particularly challenging substrates. To our knowledge, examples of such deconjugative migratory hydrosilylations are scarce.[5a,15] At 75 °C, significant amounts of propyl benzene, originating from a formal alkene hydrogenation, and $(Ph_2SiH)_2$ were obtained as byproducts together with the desired product **21**. In general, both side reactions, alkane and disilane formation, are known from hydrosilylations with Negishi's catalyst and independent reports of zirconium-catalyzed silane oligomerizations.[5,16] They have been observed as minor side reactions for all scope entries and were reduced at 125 °C. At that temperature, a smooth terminal-selective silylation to **21** took place (89 % isolated yield). Likewise, particularly electron-rich and electron-poor arylalkenes underwent the reaction to give **22**–**26** in 48–77 % yield (61–81 % NMR yield), showing no strong electronic influence of the aryl substituent. Lastly, the migrative hydrosilylation was successful even on a C_9 carbon chain (**27**), demonstrating an efficient Zr-walk.

We then turned our attention to the reaction mechanism in order to understand the differences between the current hydrosilylation and the earlier reactions with Cp_2Zr(1-butene). The hydrozirconation mechanism with the latter as catalyst has been discussed over the past decades. The original proposal involving a Chalk–Harrod-like mechanism via oxidative addition, hydrozirconation and Si–C reductive elimination has been expanded with alternative suggestions, including alkene silazirconation and σ-bond metathesis steps.[5,17] A computational study of the hydrosilylation of ethylene with SiH_4 then concluded a hydrozirconation via C–Si coupling followed by ethylene-assisted C–H reductive elimination as most feasible scenario, but also that hydrozirconation followed by silylation through σ-metathesis was likely at high silane-alkene ratios.[18]

The hydrosilylation yield of **1** was determined for varied reaction times, which revealed a 2–5 h initiation time followed by rapid product formation (Scheme 4a).[13] We further discovered that 20 mol % of LiOMe (4 catalyst equivalents) already gave a decent NMR yield (86 %) while less resulted in no reaction (Scheme 4b). We could exclude that LiOMe increased the reactivity of the silane through the formation of a pentacoordinate silicon ate complex, as previously reported for mixtures of $PhSiH_3$ and alkali alkoxides in THF.[19] In toluene, no reaction occurred between Ph_2SiH_2 or $PhSiH_3$ and LiOMe, and no disproportionation of the silane was observed.[13] Monitoring the reaction of Cp_2ZrCl_2 with varying amounts of LiOMe at 75 °C by NMR over 2 h, in analogy to the earlier report by Wang et al.,[9] showed the formation of $Cp_2Zr(OMe)_2$.[13]

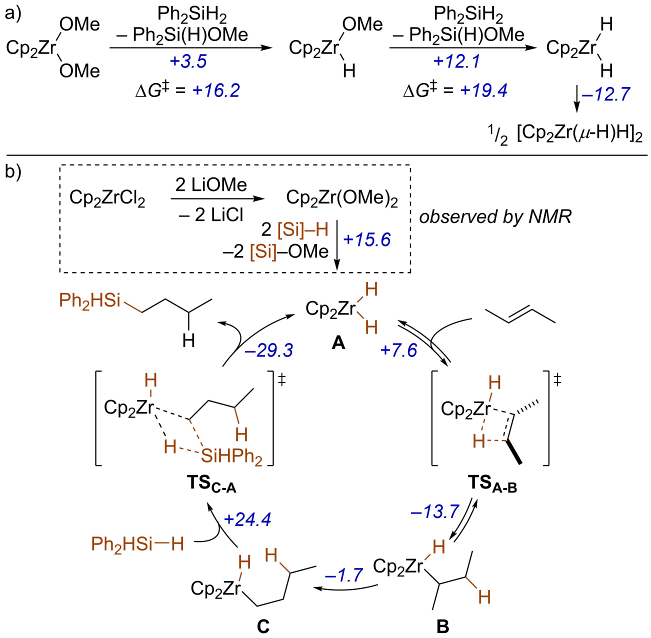


Scheme 3. Migratory and deconjugative hydrosilylation of internal alkenes including styrenes. Yields of isolated product. Brackets show ^{1}H NMR yields determined with mesitylene as internal standard. [a] Yield calculated from the mixture with coeluting Ph_2SiH_2. [b] After removal of residual Ph_2SiH_2 under high vacuum at 80 °C.



Scheme 4. Mechanistic experiments. a) Time-dependent product formation showing an initiation time. b) Plot of reaction yield *vs* equiv. of LiOMe. c) Reactions with $Cp_2Zr(H)Cl$ as precatalyst. d) Deuterium experiments with Ph_2SiD_2 and proposed σ-metathesis mechanism (grey inset). [a] ^{1}H NMR yield determined with mesitylene as internal standard.

After 2 h, equilibration was not yet complete and three equivalents of LiOMe were required to form significant amounts of $Cp_2Zr(OMe)_2$. With 20 equivalents LiOMe, a 1:2.8 ratio Cp_2ZrCl_2 *vs* $Cp_2Zr(OMe)_2$ was achieved. $Cp_2Zr(H)OMe$ was not observed and previously proposed to disproportionate into Cp_2ZrH_2 and $Cp_2Zr(OMe)_2$ (in THF).[20] Subsequent addition of Ph_2SiH_2 led to the release of $Ph_2SiH(OMe)$, which was then the only visible methoxy species. The nature of the Zr species formed could not be established, but Cp_2ZrH_2 is known to form the in toluene poorly soluble $[Cp_2Zr(\mu\text{-H})H]_2$ and to undergo alkene hydrozirconation.[20,21] However, preformation of $Cp_2Zr(OMe)_2$ or pre-stirring the catalyst, LiOMe, and the silane did not lead to a shortened induction time, which indicated that the presence of the alkene was required to overcome the induction period. Using Schwartz's reagent, $Cp_2Zr(H)Cl$, as precatalyst would only result in product formation if LiOMe was present (93 % NMR yield) and, hence, substitution of the remaining chloride was necessary to form the active catalyst (Scheme 4c). Deuterium labeling experiments with Ph_2SiD_2 and Zr-walk substrates **28** and **29** showed D-incorporation along the alkyl chain and with the highest amount in the benzylic position (Scheme 4d). We could confirm for product **21-d** that deuteration occurred at all alkyl positions. This was in agreement with a reversible hydrozirconation via a zirconium(IV) hydride species and in disagreement with an isomerization via a 1,3-hydrogen shift.[22] This further rendered a hydrozirconation mechanism via alkene silazirconation unlikely. Moreover, as reported earlier for reactions with Negishi's reagent, D–H exchange at the silicon center was observed, which supported a σ-bond metathesis exchange mechanism.[5b, 16–18] A scrambling via dimer formation was discarded, because $[Cp_2Zr(\mu\text{-H})(SiHPh_2)]_2$ (**31**) was reported to be catalytically inactive.[5a] Supporting DFT calculations on the RIJCOSX-PW6B95-D4-CPCM/def2-QZVP//r^{2}SCAN-3c-CPCM level using ORCA 5.0.4 showed that the stepwise conversion of $Cp_2Zr(OMe)_2$ into Cp_2ZrH_2 through reaction with Ph_2SiH_2 proceeded via reasonable energy barriers (Scheme 5a).[13,23] As expected, dimerization to $[Cp_2Zr(\mu\text{-H})H]_2$ was then favored.[5,21] Under our conditions, these species would be in equilibrium and monomeric Cp_2ZrH_2 could be accessible for undergoing hydrozirconation. An exemplary catalytic cycle for the migratory hydrosilylation of (*E*)-2-butene was then evaluated (Scheme 5b).[13] The reaction starts with the formation of Cp_2ZrH_2 (**A**) through double chloride-methoxide exchange and then double hydride transfer from Ph_2SiH_2. Reversible 1,2-hydrozirconation via $\mathbf{TS_{A\text{-}B}}$ then leads to intermediate **B** and accounts for the observed alkene isomerization as is supported by the obtained low activation barriers in either direction (7.6 and 13.7 kcal mol^{-1}). Isomerization to the linear alkylzirconium intermediate **C** is favored by 1.7 kcal mol^{-1}. The final step is then a presumably rate-determining σ-metathesis via $\mathbf{TS_{C\text{-}A}}$ with a barrier of +24.4 kcal mol^{-1} to release the product and regenerate **A**. The whole cycle releases $\Delta G_{\text{cycle}} = -12.8$ kcal mol^{-1}. It was further found that the formation of $Cp_2Zr[(E)\text{-2-butene}]$ from **A** via the release of H_2 required more energy than reaching $\mathbf{TS_{A\text{-}B}}$ (+1.6 kcal mol^{-1}).[13] Like-



Scheme 5. a) Computed energies for the formation of zirconocene dihydride and its dimer. b) Proposed reaction mechanism via zirconium(IV) catalysis. Blue values are calculated Gibbs free energies in solution kcal mol^{-1}.

wise, the formation of $Cp_2Zr(H)(SiHPh_2)$ was endergonic (+4.0 kcal mol^{-1} *vs* Cp_2ZrH_2).[13] Thus, the relatively low hydrozirconation barrier was in agreement with the earlier computational study,[18] but an involvement of Cp_2Zr^{II}-(alkene) or $Cp_2Zr(H)(SiHR_2)$ seemed less likely. We therefore propose the mechanism in Scheme 5 as a realistic scenario.

In conclusion, a catalytic alkene hydrozirconation based on Cp_2ZrCl_2 as readily available catalyst and LiOMe as mild additive has been developed. It can be applied to a broad range of terminal and internal alkenes to give linear alkyl silanes, which renders it an attractive alternative to late transition metal catalyzed hydrosilylations as well as to the earlier zirconium(II)-based protocol. A mechanism proceeding via zirconium(IV) species is proposed that will be further investigated in following works.

Supporting Information

The authors have cited additional references within the Supporting Information (Ref. [24–57]).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Experimental procedures, characterization data, computational details and coordinates, and reproductions of NMR spectra are available free of charge in the Supporting Information. The original NMR spectra as well as the input and output files of the calculations are available on Zenodo at https://doi.org/10.5281/zenodo.12733307.

Keywords: alkene · catalysis · hydrosilylation · metal walk · zirconium

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