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N-Heterocyclic carbene-based ruthenium-hydride catalysts for the synthesis of unsymmetrically functionalized double-decker silsesquioxanes†

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Ruthenium–N-heterocyclic carbene complexes with the generic formula [RuHCl(CO)(NHC)(PCy₃)] exhibit a high catalytic activity toward the (*E*)-selective silylative coupling of divinyl-substituted double-decker silsesquioxanes with two distinctly substituted styrenes. This process leads to a novel class of unsymmetrically functionalized silsesquioxane derivatives.

Polyhedral oligomeric silsesquioxanes (POSS) are a broad family of compounds that feature cage-like structures with Si–O–Si linkages and tetrahedral Si vertices.¹ Derivatives with a cubic T₈ cage have been most widely investigated so far,² but a double-decker silsesquioxane (DDSQ) core unit first synthesized in Japan just over a decade ago³ has also attracted much attention.⁴ It features open (M₄T₈) or closed (D₂T₈) frameworks with either four or two reactive moieties.

The physicochemical properties of silsesquioxanes, which determine their applications, are chiefly governed by the nature of their silicate rigid core and by the number and type of functional groups attached to it. Suitable functional groups (FG) allow binding silsesquioxanes to a polymer matrix or to react them with an organic monomer to obtain inorganic–organic hybrid materials with enhanced thermal, mechanical, or dielectric properties.⁵ Difunctional DDSQ compounds are particularly attractive in this respect, because they allow the synthesis of oligo- and polymeric networks.⁶

Two methods are available to introduce a desired FG onto a DDSQ core. They are based either on a hydrolytic condensation

of alkoxy silanes or on modifications of preformed DDSQ frameworks *via* Si–H, Si–OH, or Si–CH=CH₂ units, for instance.⁷ The latter category includes dehydrocoupling polycondensation, hydrosilylation, cross-metathesis, silylative coupling, and *O*-silylation reactions.^{8,9} These catalytic processes are often selective and efficient, but they are usually restricted to the introduction of one type of FG. Only a few reports describe the grafting of different types of FG onto a silsesquioxane core. They concern the hydrosilylation of octahydro-spherosilicate with a mixture of two olefins in various proportions.¹⁰ The Heck reaction was also applied to modify octavinyl- or octa(*p*-bromostyryl)silsesquioxanes with two different olefins.¹¹ The authors assumed that spatial vicinity effects between the functional groups in the cubic T₈ structures affected their statistical substitution, despite the use of a 1 : 1 stoichiometric mixture of olefins.

Herein, we disclose that ruthenium-hydride complexes bearing N-heterocyclic carbene (NHC) ligands are efficient catalysts for a model silylative coupling reaction. We also investigated a new synthetic pathway for obtaining unsymmetrically functionalized silsesquioxane derivatives by silylative coupling of divinyl–DDSQ precursors with a series of 4-substituted styrene derivatives.

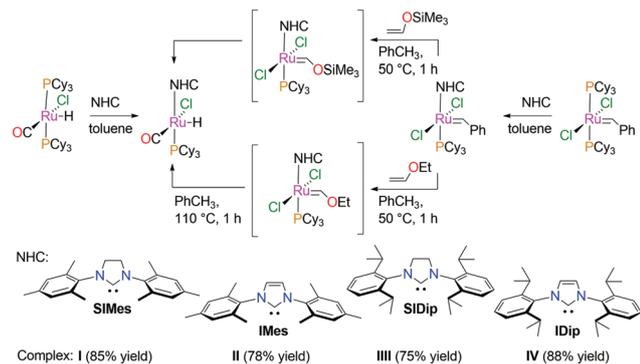
We began our research with the synthesis of four ruthenium-hydride complexes bearing common NHC ligands according to published procedures (Scheme 1).¹² Thus, [RuHCl(CO)(NHC)(PCy₃)] complexes **I–IV** were obtained either by exchanging one of the tricyclohexylphosphine (PCy₃) from [RuHCl(CO)(PCy₃)₂] with an NHC ligand or by converting Grubbs' second-generation ruthenium–benzylidene catalysts [RuCl₂(=CHPh)(NHC)(PCy₃)] into ruthenium-hydride species *via* the intermediacy of Fischer carbenes. Both approaches led to similar high yields. The one-step exchange procedure is more straightforward than the multi-step path, but relies on a highly air- and moisture-sensitive precursor that needs to be handled under strictly inert conditions, whereas ruthenium–alkylidene starting materials are more stable and commercially available. Compounds **I–IV** were isolated as air-sensitive yellow solids and characterized using spectroscopic methods. The data were consistent with those reported in the literature.¹³

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, analytical data, and NMR spectra of all the products isolated. See DOI: 10.1039/c8cc01316k



Scheme 1 Synthesis of $[\text{RuHCl}(\text{CO})(\text{NHC})(\text{PCy}_3)]$ complexes **I–IV**.

Complexes **I–IV** were first tested as precatalysts in a model silylative coupling reaction. For these exploratory runs, we followed the experimental procedure previously defined in our laboratory when working with $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$.⁸ Thus, styrene and tris(trimethylsilyloxy)vinylsilane $[\text{ViSi}(\text{OSiMe}_3)_3]$ were chosen as substrates because they led to straightforward GC or GC/MS analyses of the reaction mixtures. Moreover, the steric and electronic properties of $\text{ViSi}(\text{OSiMe}_3)_3$ mimic the chemical surroundings of the ViSi functional group in the silsesquioxanes, and styrene is a highly reactive olefin that does not isomerize or polymerize under the reaction conditions adopted.¹⁴ Copper(I) chloride was added to the reaction media to ease the dissociation of tricyclohexylphosphine and to speed up the formation of active catalytic species.¹⁵

The addition of 1 mol% of a $[\text{RuHCl}(\text{CO})(\text{NHC})(\text{PCy}_3)]$ complex and 5 mol% of CuCl to a 1 : 1 mixture of styrene and $\text{ViSi}(\text{OSiMe}_3)_3$ in CH_2Cl_2 at 45 °C led to the clean formation of the expected styrylsilane product, as revealed by GC/MS analysis (Table 1). The $^3J_{\text{H,H}}$ coupling constant of 19 Hz observed between the olefinic protons of this compound on ^1H NMR spectroscopy indicated that the (*E*)-isomer was obtained exclusively. Control experiments performed in the absence of CuCl (entries 2, 4, and 6) confirmed the beneficial influence of this additive on the reaction course.

Table 1 Silylative coupling of styrene and tris(trimethylsilyloxy)vinylsilane catalyzed by $[\text{RuHCl}(\text{CO})(\text{NHC})(\text{PCy}_3)]$ complexes **I–IV**^a

Entry	Catalyst	Time (h)	CuCl	Conversion of $\text{ViSi}(\text{OSiMe}_3)_3$ ^b (%)	(<i>E</i>)-Selectivity ^c (%)
1	I	8	Yes	> 99	100
2	I	24	No	85	100
3	II	24	Yes	84	100
4	II	24	No	80	100
5	III	5	Yes	> 99	100
6	III	24	No	88	100
7	IV	24	Yes	90	100

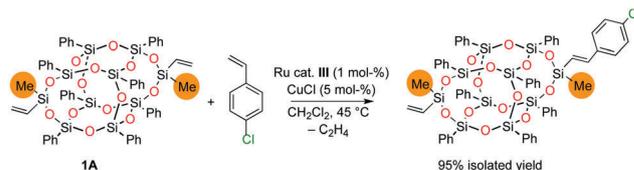
^a Experimental conditions: styrene (86.2 μmol), $\text{ViSi}(\text{OSiMe}_3)_3$ (86.2 μmol), Ru cat. (0.862 μmol), CuCl (4.31 μmol), CH_2Cl_2 (2 mL), 45 °C, argon.

^b Determined by GC analysis. ^c Determined by ^1H NMR analysis of the crude reaction mixture.

Although all the precatalysts **I–IV** were remarkably efficient in the test reaction under scrutiny, the exact nature of the carbene ligand significantly influenced its outcome. Indeed, ruthenium complexes **I** and **III** containing NHCs with a saturated backbone (SIMes or SIDip) led to higher conversions within shorter periods of time than their counterparts **II** and **IV** bearing the aromatic imidazolylidene derivatives IMes and IDip (Table 1, entries 1 and 5 vs. 3 and 7). This dichotomy suggests that saturated NHCs facilitate the formation of catalytically active 14-electron species, such as $[\text{RuCl}(\text{SiR}_3)(\text{CO})(\text{NHC})]$. The lower efficacy of the complexes containing unsaturated NHCs in the silylative coupling of styrene and $\text{ViSi}(\text{OSiMe}_3)_3$ is consistent with similar tendencies observed with ruthenium-hydride complexes **I–IV** in the hydro-silylation of terminal alkynes¹³ and with second-generation Grubbs catalysts in olefin metathesis,¹⁶ *i.e.*, processes for which the dissociation of a phosphine ligand is the rate-determining step.¹⁷

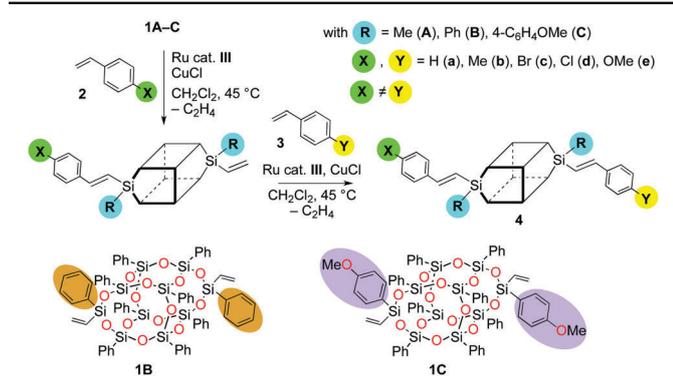
Having identified $[\text{RuHCl}(\text{CO})(\text{SIDip})(\text{PCy}_3)]$ (**III**) as the most promising catalyst precursor for the silylative coupling of $\text{ViSi}(\text{OSiMe}_3)_3$ among the four complexes tested, we turned our attention to the functionalization of a dimethyldivinyl-substituted double-decker silsesquioxane (Scheme 2). This substrate noted DDSQ-2SiViMe (**1A**) was obtained by the hydrolytic condensation of incompletely condensed silsesquioxane tetrasilanol $(\text{Ph}_8\text{O}_8\text{Si}_8)(\text{OH})_4$ (DDSQ-4OH) with dichloro(methyl)vinylsilane according to a previously described methodology.^{8a} Gratifyingly, an efficient coupling with the evolution of ethylene occurred upon treatment of DDSQ-2SiViMe (**1A**) with one equivalent of *p*-chlorostyrene in the presence of ruthenium catalyst **III** and copper(I) chloride in refluxing dichloromethane. We were not able to monitor the reaction course by GC because of the high molecular weight and low volatility of the silsesquioxyl product, but a ^1H NMR analysis of the reaction mixture performed after 8 h showed a complete conversion of both substrates and the selective formation of the expected silylative coupling product in an almost quantitative yield.

The successful catalytic silylative coupling between DDSQ-2SiViMe (**1A**) and *p*-chlorostyrene to yield a monostyryl-substituted DDSQ derivative prompted us to carry out two successive reactions with separate olefins to probe the feasibility of a one-pot procedure leading to a novel class of unsymmetrically functionalized silsesquioxane derivatives. Hence, we performed reactions between divinyl-DDSQ cages with pendant methyl, phenyl, or *p*-anisyl groups (**1A–C**) and two different styrene derivatives, either unsubstituted or bearing a *para*-halogen or methoxy group (**2** and **3**). The catalytic system relied on a mixture of $[\text{RuHCl}(\text{CO})(\text{SIDip})(\text{PCy}_3)]$ (**III**) and CuCl in refluxing dichloromethane. ^1H NMR analyses of the reaction mixtures after 24 h indicated a complete conversion of the substrates



Scheme 2 Silylative coupling of *p*-chlorostyrene and DDSQ-2SiViMe (**1A**) catalyzed by $[\text{RuHCl}(\text{CO})(\text{SIDip})(\text{PCy}_3)]$ (**III**).

Table 2 Silylative coupling of divinyl-substituted silsesquioxanes DDSQ-2ViSi (**1A–C**) with two different styrenes (**2** and **3**) catalyzed by [RuHCl(CO)-(SIDip)(PCy₃)] (**III**)^a



Entry	DDSQ-2SiVi (1)	Styrene (2)	Styrene (3)	Product (4)	Isolated yield (%)
1	1A	2a	3c	4A-a-c	95
2	1A	2a	3e	4A-a-e	91
3	1A	2b	3e	4A-b-e	90
4	1A	2c	3e	4A-c-e	93
5	1A	2d	3e	4A-d-e	96
6	1B	2a	3b	4B-a-b	92
7	1B	2a	3e	4B-a-e	94
8	1B	2c	3e	4B-c-e	95
9	1B	2d	3e	4B-d-e	92
10	1C	2a	3b	4C-a-b	94
11	1C	2a	3c	4C-a-c	95
12	1C	2a	3d	4C-a-d	95
13	1C	2a	3e	4C-a-e	97
14	1C	2b	3c	4C-b-c	94

^a Experimental conditions: DDSQ-2ViSi **1** (290 μmol), styrene **2** (290 μmol) then styrene **3** (290 μmol), [RuHCl(CO)(SIDip)(PCy₃)] **III** (2.9 μmol), CuCl (14.5 μmol), CH₂Cl₂ (6 mL), 45 °C, 24 h, argon.

and the formation of unsymmetrically difunctionalized products (**4**) with a DDSQ core (Table 2). After solvent evaporation, the remaining crude solids were purified using column chromatography followed by a precipitation from methanol, acetone, or *n*-hexane, depending on the polarity of their substituents. Further spectroscopic characterization of the pure products confirmed their identity and purity (see the ESI† for detailed experimental procedures and analytical data).

In all cases, we observed the complete functionalization of the two terminal vinyl groups of substrates **1A–C** and the formation of unsymmetrical products **4** with an exclusive (*E*)-stereochemistry around the newly formed Si–CH=CH–Ar double bonds. A competitive polymerization of the styrene monomers was never observed. Such a remarkable selectivity and efficiency of the coupling process, together with the absence of by-products, could be achieved thanks to the highly active [RuHCl(CO)(NHC)(PCy₃)]/CuCl catalytic system that was operative under very mild reaction conditions (45 °C). The intrinsic structure of the DDSQ scaffold separates the two vinyl groups through space and bonding, and enables them to react independently from each other. It should be pointed out, however, that symmetrically difunctionalized DDSQ derivatives with only one type of styryl groups may also be obtained, based on statistical considerations. The formation of these undesired by-products could be avoided, not only by using an appropriate catalytic system,

but also by lowering the concentration of the reagents in the reaction mixture.

To highlight the differences in spectroscopic features of unsymmetrically and symmetrically functionalized DDSQ derivatives, we compared the ¹H NMR spectrum of mixed compound **4A-a-e** with those recorded for the symmetrical products with two phenyl moieties [DDSQ-2(Si–CH=CH–Ph), **4A-a-a**] or two *p*-anisyl groups [DDSQ-2(Si–CH=CH–C₆H₄OMe), **4A-e-e**] (Fig. 1). The resonances for the alkenyl protons close to the silicon atom in **4A-a-a** and **4A-e-e** (Si–CH=CH–Ar) were doublets located at 6.44 and 6.27 ppm with ³J_{H,H} coupling constants of 19.4 and 19.1 Hz, respectively, in line with the shielding effect exerted by the *p*-methoxy substituent and an (*E*)-configuration of the double bonds. Additionally, the two methoxy groups of **4A-e-e** gave rise to a signal integrated for 6 H at 3.80 ppm. In full agreement with an unsymmetrical formulation, ¹H NMR analysis of compound **4A-a-e** nicely revealed the presence of two doublets at 6.44 and 6.27 ppm with ³J_{H,H} coupling constants of 19.4 and 19.1 Hz, respectively, integrated for one proton each, and a methoxy signal at 3.82 ppm corresponding to 3 H. In all three compounds, resonances for the alkenyl protons in the vicinity of the aryl rings (Si–CH=CH–Ar) were shifted to a lower field and merged into the aromatic region, thereby precluding their identification. Analogous tendencies were observed for ¹³C and ²⁹Si NMR spectra (see the ESI† for further information).

In summary, we have demonstrated that ruthenium-hydride complexes with the generic formula [RuHCl(CO)(NHC)(PCy₃)] were efficient catalyst precursors for the (*E*)-selective silylative coupling of styrene and tris(trimethylsiloxy)vinylsilane when used in conjunction with copper(i) chloride. NHCs with a saturated backbone, and more specifically 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIDip), were particularly suitable ancillary ligands for this process. Indeed, the high catalytic activity displayed by [RuHCl(CO)(SIDip)(PCy₃)] (**III**) under mild experimental conditions allowed us to achieve the one-pot difunctionalization of three divinyl-substituted DDSQ cage compounds (**1A–C**) with a wide range of styrene derivatives

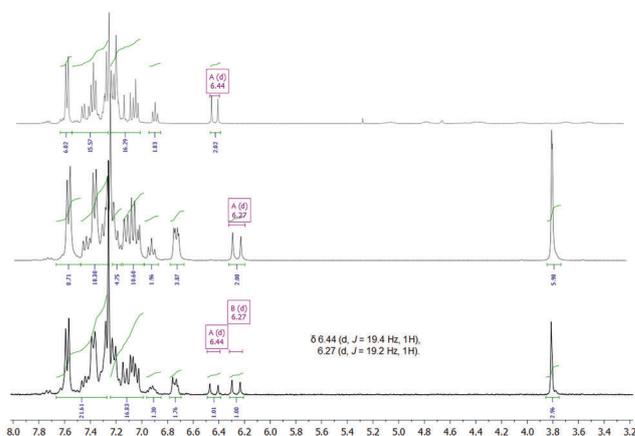


Fig. 1 Stacked ¹H NMR spectra of symmetrically functionalized DDSQ-2(Si–CH=CH–Ph) (**4A-a-a**) (top), DDSQ-2(Si–CH=CH–C₆H₄OMe) (**4A-e-e**) (middle), and unsymmetrically functionalized DDSQ **4A-a-e** (bottom).

(2a–e and 3a–e) in a seamless way, thereby leading to a novel class of unsymmetrically functionalized silsesquioxane derivatives. Fourteen new products were obtained in high yields using this straightforward pathway. They were fully characterized using various analytical techniques.

In light of the results described above, the silylative coupling reaction should now be regarded as a promising catalytic tool for grafting two distinct styryl groups onto a DDSQ scaffold. It therefore nicely complements previous strategies based on hydrosilylation and Heck reactions for the unsymmetrical functionalization of cubic T₈ structures.^{10,11} Because the compounds obtained in this study may be subjected to further independent transformations on both ends, the method has great potential for fine-tuning the physicochemical properties of advanced materials based on DDSQ core units and for expanding their application field.

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Conflicts of interest

There are no conflicts to declare.

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