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Article

Iridium-Catalyzed Anti-Markovnikov Hydrosilylation of Vinylbenzenes with a Bis-Silane-Capped Double-Decker Silsesquioxane

Sean P. Walsh, Andre Lee,* and Robert E. Maleczka, Jr*

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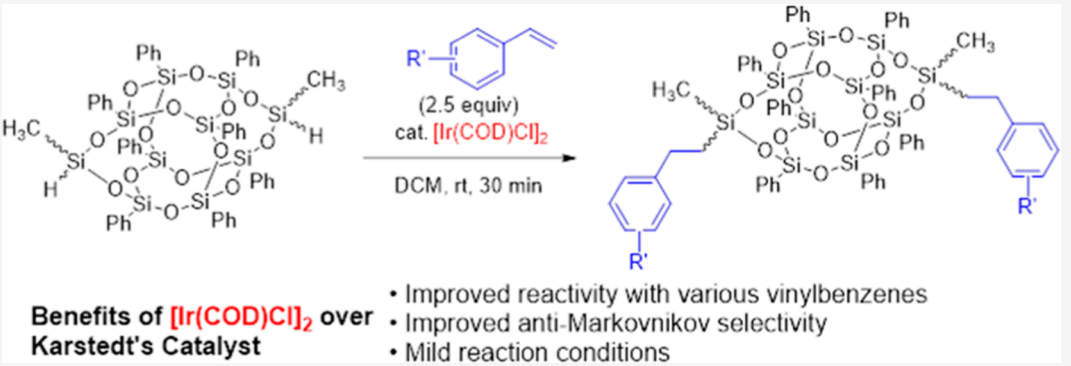


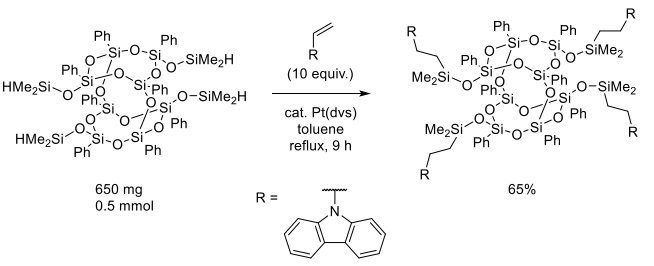
ABSTRACT: Hydrosilylation of double-decker silsesquioxanes is an efficient approach for preparing hybrid materials, especially polymeric materials. Karstedt's catalyst, Pt(dvs), is widely used for this purpose due to its commercial availability, high yields, and good hydrosilylation selectivity. Despite this, vinylbenzenes have been shown to produce multiple hydrosilylated products. This study employs a method involving an iridium catalyst that was significantly more selective for the anti-Markovnikov hydrosilylation product with vinylbenzenes and bis-silane-capped double-decker silsesquioxanes. Obtaining higher purity of hydrosilylated products will allow for the development of the fundamental structure−property relationship of hybrid materials.

1. INTRODUCTION

Capping double-decker silsesquioxanes (DDSQ) with chlorosilanes is an effective method to introduce new functionality. However, the arduous preparation of chlorosilanes in addition to a narrow number of commercially available substrates limits the diversification of DDSQ through this method. Therefore, postfunctionalization of capped DDSQ plays an important role in the synthesis of more elaborated DDSQ. Among such postfunctionalization methods, the utility of hydrosilylation reactions has been reported in copious publications (Scheme 1).[1−7]

In many cases, hydrosilylation is not the final step of the synthetic protocol. For instance, DDSQ hydrosilylation products have been further modified resulting in AB-like hybrid polymers, where the silicon core is incorporated into a polymer backbone.[2−4,7] This posthydrosilylation modification therefore demands that the hydrosilylation tolerates a variety of functional groups. Karstedt's catalyst [Pt(dvs)] is commonly employed in silane-capped DDSQ hydrosilylations because it is commercially available and offers high yields with many olefins.[1−7] Despite many claims to the contrary, Pt(dvs)-catalyzed hydrosilylations have produced a complex mixture of products.[6,8−10] For example, Strassner et al. have demonstrated

Scheme 1. Silane-Capped DDSQ Functionalized via Hydrosilylation[5]



that various platinum catalysts, including Karstedt's catalyst, fail to provide good selectivity for the anti-Markovnikov product of styrene with dimethoxymethylsilane. They

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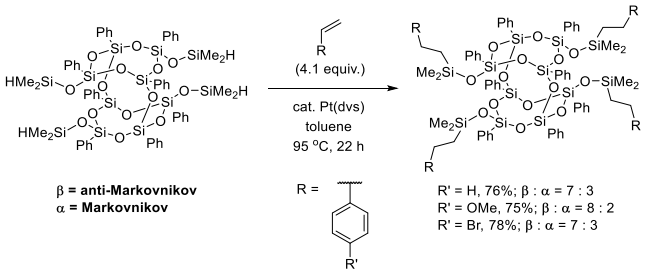
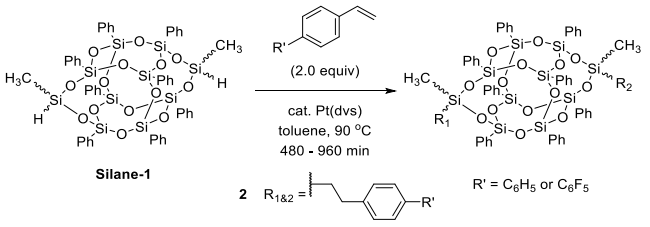
evaluated Karstedt's catalyst with various stir times and temperatures; yet the best selectivity at 100% conversion was 85:15 anti-Markovnikov: Markovnikov.[9] With respect to DDSQ, in 2019, Dudziec et al. have reported the modest regioselectivity for the Pt(dvs)-catalyzed hydrosilylation of vinylbenzene derivatives and tetra-silane-capped DDSQ (Scheme 2).[6]

Scheme 2. Catalytic Screening for the Hydrosilylation of Tetra-Silane-Capped DDSQ[6]



Despite this precedent, multiple papers have reported exclusive anti-Markovnikov products for the Pt(dvs)-catalyzed DDSQ hydrosilylation of vinylbenzenes.[1,4,6] The ^{1}H NMR assignments of the β and α products can be complicated due to the proximity of the signals and the presence of impurities such as water. As an example, in 2017 Dudziec, Marciniec et al. claimed (Scheme 3) "no side products," for their Pt(dvs)

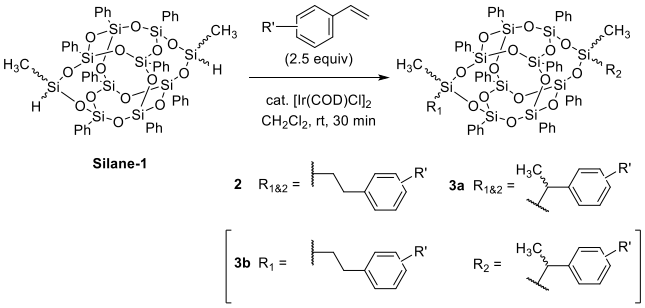
Scheme 3. Literature Report of Karstedt's-Catalyzed Hydrosilylation with Vinylbenzene Yielding Only anti-Markovnikov Products[1]



catalyzed hydrosilylation of **Silane-1** with various vinylbenzenes.[1] Again, in a 2019 publication, they explained "in the case of hydrosilylation of vinylarenes with dihydrosubstituted DDSQ, the process was regioselective toward exclusive formation of β-isomers, which may also prove the importance of Si−H chemical surrounding (Si order) and its electronic and steric effect."[6]

Although the 2017 work stated that the reaction conditions formed no side products, several of the ^{1}H NMR spectra presented in their Supporting Information featured doublets at approximately 1.5 ppm that the authors attributed to water (see ref 1, Supporting Information pages S-9, S-12, S-15, and S-18). We questioned if in fact their reported doublet corresponded to the Markovnikov product. Admittedly, identifying Markovnikov products in complex mixtures can be challenging. For example, as illustrated in Table 1, while the anti-Markovnikov product (**2**) lacks a stereocenter, the Markovnikov (**3a**) and mixed-Markovnikov (**3b**) hydrosilylation products feature stereocenters, thereby allowing for the generation of a complex mixture of diastereomers. Thus, for bis- or tetrahydrosilylations of DDSQ, a method that is truly selective for the anti-Markovnikov product would be

Table 1. Iridium-Catalyzed Hydrosilylation of Silane-1 with Various Vinylbenzene Derivatives[a]



entry	product	R'[b]	yield[c] (%)	2:3a + 3b[d]
1	2A	H	99	>99:1
2	2B	*p*-OCH_3	99	>99:1
3	2C	*m*-CF_3	98	>99:1
4	2D	*p*-CH_3	92	>99:1
5	2E	*p*-Ph	85	>99:1
6	2F	*m*-Cl	66	>99:1
7[e]	2G	*p*-COOMe	32[f]	>99:1
8	2H	*p*-Br	58	99:1
9	2I	*p*-Cl	79	98:2
10	2J	*o*-Cl	83	93:7
11	2K	*p*-Bpin	60	87:13
12	2L	*p*-C_6F_5	88	85:15

[a]Standard reaction conditions: **Silane-1** (0.75 mmol, 1.0 equiv), $[Ir(COD)Cl]_2$ (1.0 mol %), vinylbenzene derivative (2.5 equiv), 3.0 mL dichloromethane, room temperature, 30 min. [b]All vinylbenzene derivatives were monosubstituted in either the *m*-(meta), *o*-(ortho), or *p*-(para) position. [c]Isolated yield. [d]Measured by ^{1}H NMR of the crude reaction mixture. [e]Deviation from standard reaction conditions. See experimental section for details. [f]98% conversion was observed, but most of the material was not isolated. See Supporting Information for details.

valuable. Furthermore, discounting the presence of minor Markovnikov products may result in the inaccurate characterization of material properties because these two products could exhibit distinct physical properties.[1,4,6]

When compared to Pt(dvs), chloro(1,5-cyclooctadiene)-iridium(I) dimer ($[Ir(COD)Cl]_2$) is an attractive catalyst because it is commercially available and it was demonstrated by Ding et al. to be highly selective for anti-Markovnikov hydrosilylations of unactivated alkenes.[11] $[Ir(COD)Cl]_2$ catalyzed hydrosilylations are known to proceed under mild reaction conditions and in the presence of a variety of functional groups.[11,12]

2. RESULTS AND DISCUSSION

We sought to study $[Ir(COD)Cl]_2$ catalyzed hydrosilylations on **Silane-1**. The vinylbenzenes employed were chosen for their distinct functionality and their potential for posthydrosilylation functionalization (Table 1). Unless otherwise stated, the ratios of **2A-L** to **3A-L** were measured using ^{1}H NMR by comparing the signal integration for the Si−CH_3 peak relative to the doublet or quartet peaks observed for the Markovnikov products.

The ^{1}H NMR spectra of crude iridium-catalyzed reaction mixtures indicated anti-Markovnikov selectivities >8:2 and for entries 1−7, > 99:1. Moreover, the crude reaction mixtures were highly pure relative to those of the corresponding platinum-catalyzed reaction mixtures vide infra (Figure 1 and

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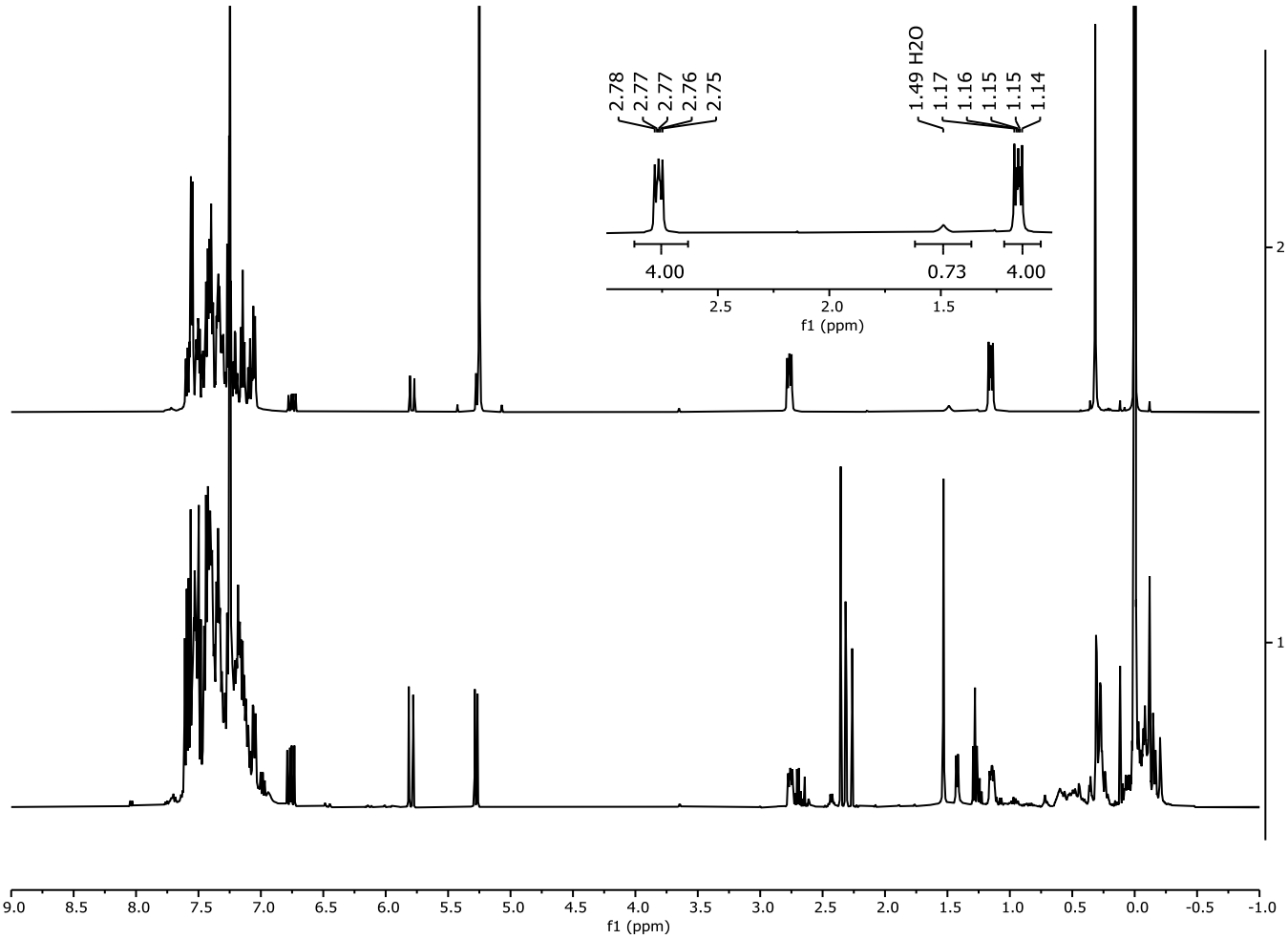

Figure 1. Stacked ^{1}H NMR spectra of the crude reaction mixture for **2E** prepared via $[Ir(COD)Cl]_2$-catalyzed hydrosilylation (top) and Pt(dvs)-catalyzed hydrosilylation (bottom). See experimental section for details.

2). For the iridium-catalyzed reactions, the crude reaction impurities observed were solvent, excess vinylbenzene, and in some cases **3** (Table 1 entries 8−12). While all substrates highly favored the anti-Markovnikov products, reactions to form **2K** and **2L** were slightly less selective. When compared against the other substrates in Table 1, no clear selectivity trends emerge that would explain this observation. Additionally, minor impurities were observed, but the abundance of those impurities relative to **3** were low and therefore those products were not characterized. With some indication by ^{1}H NMR, but not definitive proof, dehydrogenative hydrosilylation was possibly occurring alongside the mixture of Markovnikov and anti-Markovnikov products with <1% yield. The second order splitting observed for products **2A-L** follows the AA'XX' spin system, and the shape of the signal likely arises from a strong preference for the *anti*-conformers.[13]

Due to the DDSQ framework, **2** has a higher degree of polarity than the styrene reactants, thus the final products were easily purified via column chromatography and crystallization. Predictably, the first fractions gave the excess styrene, and the column could then be flushed with 4:1 hexanes: ethyl acetate to give the product. Alternatively, a low bowling point styrene was able to be evaporated off, which eliminated the need for a column after the plug. However, the purification procedure was complicated when certain vinylbenzenes were evaporated. One example of such complication was the *p*-phenyl vinylbenzene, which appeared to polymerize under thermal conditions.

Although the α- and β-isomer mixtures were not completely separated or separately characterized in this study, it is likely that the physical properties of these two products vary. Cis and trans silsesquioxanes have been reported to have distinct physical properties such as polarity, solubility, and physical appearance.[14] Therefore, the melting points reported for these mixtures should be considered as solid to liquid transitions. Additionally, the ratio of the *cis*-to *trans*-isomers in a previous study was shown to impact solubility and melting point, and thus, the α- and β-isomer ratios would also likely impact the melting point experiments performed in this work.[14] The physical distinctions of the *cis*- and *trans*-hydrosilylation isomers were beneficial as the cis/trans mixtures of **2J** were readily separated via fractional crystallization (Figure 3). The cis and trans crystals for **2J** were visually distinct and therefore easily isolated using forceps. The crystal data for **2J**, and other experiments, are reported in the Supporting Information. This technique is advantageous to the isolation of DDSQ geometric isomers because the cis/trans mixture of **Silane-1** was not easily separated.

We wished to exploit the ability to easily enrich the geometric DDSQ isomers in this way. Therefore, we performed a Suzuki−Miyaura cross-coupling reaction of c.a. 70% trans **2K** with 1-bromo-2,3,4,5,6-pentafluorobenzene,

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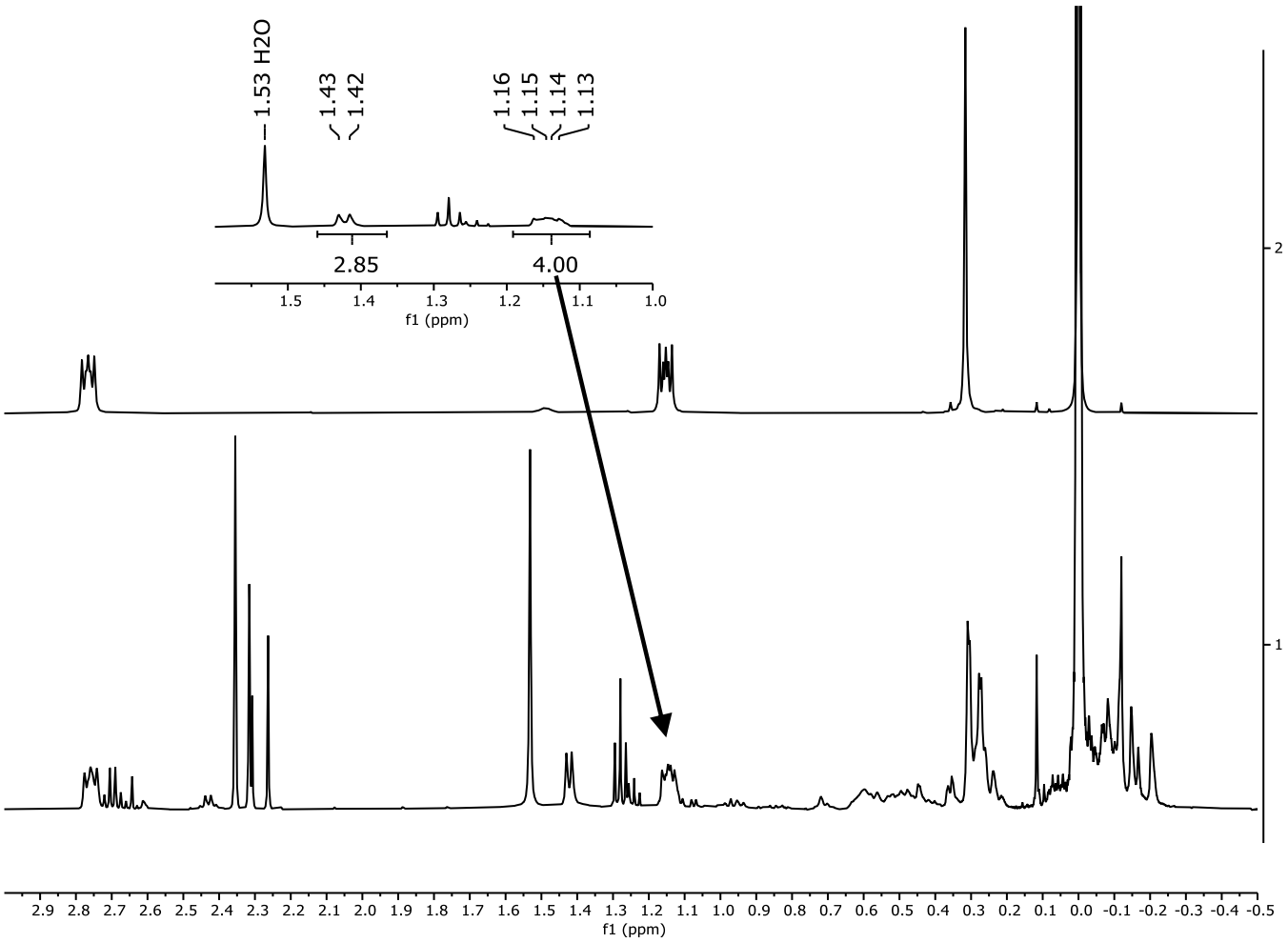

Figure 2. Magnified aliphatic region of Figure 1 for stacked ^{1}H NMR spectra of the crude reaction mixture for **2E** prepared via $[Ir(COD)Cl]_2$-catalyzed hydrosilylation (top) and Pt(dvs)-catalyzed hydrosilylation (bottom). The ratio of **2**: **3** was measured via the normalized integration of the 1.13−1.16 ppm multiplet (Si−C**H**$_2$; 4) versus the 1.43 ppm doublet (CH−C**H**$_3$; 6).

Figure 3. Visually distinct *cis*-enriched crystal (left) and *trans*-enriched crystal (right) of **2J**.

which afforded **2L** in 90% yield (see Supporting Information Scheme SI1). The ability to geometrically enrich **2L** and other hydrosilylation products allowed us to make tentative cis and trans assignments in the corresponding NMR spectra.

To establish regiochemical outcomes for comparison purposes, we decided to hydrosilylate our chosen vinylbenzenes under platinum-catalyzed conditions. Hydrosilylations with Pt(dvs) were performed (Table 2); however, low conversions were observed (entries 1 and 3) under similar conditions to those reported by the 2017 work by Dudziec, Marciniec et al. Therefore, further experiments with increased catalyst loading were conducted with vinylbenzenes, which were tested by Walczak et al. (Table 2, entries 2 and 4) and similar selectivities were observed. In accordance with prior reports,[6,8,9] we observed a variety of hydrosilylation products by ^{1}H NMR for entries 1−4. For **2E**, we observed water as a singlet at 1.5 ppm and a doublet at 1.4 ppm corresponding to the Markovnikov product by 2D NMR. This result lends support to our earlier claim that the doublets appearing in spectra reported by Dudziec, Marciniec et al. likely corresponded to the Markovnikov product and not water.[1]

To expand on the preparation of **2L**, the vinylbenzene used in the corresponding hydrosilylations of **Silane-1** was made by a modified literature method involving the Suzuki−Miyaura coupling of 4-Bpin-styrene and C_6BrF_5 to make 4-(C_6F_5)-styrene.[15] That procedure also called for and described the generation of $(Cy_3P)_2Pd(dba)$. In our hands, the described method afforded two distinct and separable products. Though neither gave NMR data that exactly matched those previously reported,[15−17] the products were tentatively assigned as $(Cy_3P)Pd(dba)$ (**4a**) and $(Cy_3P)_2Pd(dba)$ (**4b**). In pilot studies, **4a** and **4b** were equally effective in generating 4-(C_6F_5)-styrene. Since **4a** was major and appeared cleaner by ^{31}P NMR, it was used to prepare 4-(C_6F_5)-styrene on c.a. one gram scale. Lastly, we further confirmed the assignments of the Markovnikov and anti- Markovnikov hydrosilylation products

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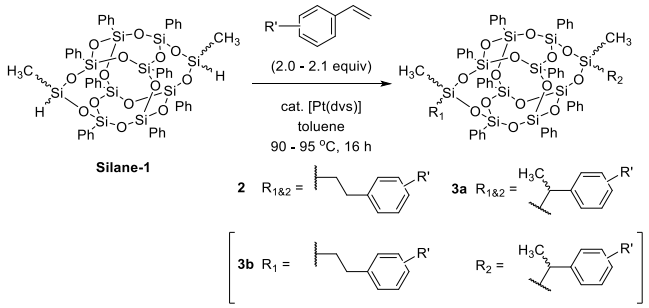
Table 2. Platinum-Catalyzed Hydrosilylation of Silane-1 with Various Vinylbenzene Derivatives



entry	product	conversion (%)[c]	2:3[c]
1[a]	2C	57	77:23
2[b]	2E	100	68:32
3[a]	2F	91	74:26
4[b]	2L	100	64:36

[a]Reaction conditions: **Silane-1** (0.75 mmol, 1.0 equiv), vinylbenzene derivative (2.1 equiv), Pt(dvs) (3.6×10^{-4} mmolof Pt), toluene (8.6 mL), 95 °C, 16 h. The reaction temperature tested by Dudziec, Marciniec et al. was 90 °C.[1] See experimental section for details. [b]Reaction conditions: **Silane-1** (0.75 mmol, 1.0 equiv), vinylbenzene derivative (2.0 equiv), Pt(dvs) (8.98×10^{-3} mmol of Pt), toluene (2.0 mL), 90 °C. See experimental section for details. [c]Measured by ^{1}H NMR of the crude reaction mixture.

by independently synthesizing **2L** through the Suzuki–Miyaura coupling of **2K** with pentafluorobromobenzene (See Supporting Information for further details).

We have not established a mechanistic reason for the improved anti-Markovnikov selectivity observed under iridium catalysis. However, mechanistic insights via a combination of experimental and computational results were presented by Zhang, Wu, Sun et al. Their data suggested an energy difference of 3.3 kcal/mol between the two regioisomers stemming from the iridium-catalyzed hydrosilylation of internal alkynes, which was said to be driven by the polarity of the triple bond during the hydrometalation of the substrate with the iridium hydride.[18,19] This mechanistic study was extrapolated to a variety of alkenes explored by Ding et al. in subsequent work.[11] Our work is complementary to the simple silanes used by Ding et al. in that the presence of DDSQ did not influence selectivity. Likely, the source of selectivity for this method arises from the differences between the mechanism proposed by Ding et al. versus the modified Chalk-Harrod mechanism. Although low yields were obtained for some substrates in this work, the reaction conditions were not optimized because the initial conditions gave excellent results for several substrates.

3. CONCLUSIONS

In conclusion, this work successfully demonstrated a more selective method for the preparation of DDSQ bis-silane-capped anti-Markovnikov hydrosilylation products from vinylbenzenes using $[Ir(COD)Cl]_2$. The subsequent isolation of the iridium-catalyzed products was straightforward compared to those reactions catalyzed by Pt(dvs) because the separation of the anti-Markovnikov product from the Markovnikov product was not necessary for many experiments. The implementation of this method in future works may enhance the accuracy of material property analyses. Additionally, the higher purity hydrosilylation products, compared to those prepared with Karstedt's catalyst, could offer higher purity polymers and other practical materials that incorporate DDSQ.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All chemicals were used as received unless otherwise stated. Column chromatography was performed with 230–400 mesh silica gel. Undenatured ethanol (100% - 200 proof) was sparged with N_2 before use. Toluene and triethylamine were distilled over CaH_2 under a N_2 atmosphere. Tetrahydrofuran was passed through a silica gel packed dry column, and then, it was refluxed over a sodium/benzophenone ketyl and distilled under a N_2 atmosphere. Dichloromethane was passed through a silica gel packed dry column. The dichloromethylsilane was distilled over CaH_2 under a N_2 atmosphere. Uncorrected melting points are reported.

4.2. Preparation of 9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19 Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (Silane-1). **Silane-1** was prepared following a modified literature procedure.[20,21] An oven-dried 1000 mL three-neck round-bottom flask was equipped with a stir bar and a N_2 gas inlet and outlet. 1,3,5,7,9,11,14,17-octaphenyl-2,4,6,8,10,12,13,15,16,18-decaoxa-1,3,5,7,9,11,14,17-octasilatricyclo-[7.3.3.3^{3,7}]octadecane-5,11,14,17-tetraol (9254 mg, 8.65 mmol, 1.0 equiv) was transferred into the flask. The flask was evacuated and N_2 was introduced. This process was repeated two more times. A gentle N_2 flow was started and dry tetrahydrofuran (280 mL) was added. The solution was stirred at room temperature for 10 min. Once the solution was homogeneous, dichloromethylsilane (1.8 mL, 17.3 mmol, 2.0 equiv) was transferred into the solution in one shot via a syringe. After 3 min of stirring, freshly distilled triethylamine (4.8 mL, 34.6 mmol, 4.0 equiv) was slowly added over 5 min. The resultant mixture appeared as a heterogeneous white slurry. The mixture was stirred for 4 h and then passed through a coarse fritted funnel topped with a Celite pad to remove the white precipitate. The filtrate was concentrated with a rotary evaporator. The resulting off-white solid was then washed with methanol (3 × 100 mL) and filtered. Volatiles were removed from the cake by drying it under low vacuum in an electric vacuum oven (50 mbar at 75 °C). The resulting white powder (9505 mg, 8.24 mmol, 95% yield) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 282–283 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.56 (app. d, J = 7.2 Hz, 8H), 7.44–7.30 (m, 17H), 7.27–7.24 (m, 6H), 7.20–7.15 (m, 9H), 4.99 (s, 2H), 0.37 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 134.1, 134.04, 134.0, 133.9, 131.6, 130.8, 130.7, 130.66, 130.5, 130.42, 130.4, 130.38, 127.8, 127.7, 127.64, 127.6, 0.6. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −32.78, −32.8, −77.82, −77.83, −79.1 (cis), −79.3 (trans), −79.5 (cis). These data were consistent with those previously published.[20,21]

4.3. General Iridium-Catalyzed Hydrosilylation Procedure. **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial equipped with a magnetic spin vane. The vial was sealed with a rubber septum and the vial was evacuated and N_2 was introduced. This process was repeated two more times. A N_2 filled balloon fitted with a needle was inserted into the rubber septum. Then, a syringe was used to transfer a vinylbenzene derivative (1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). With stirring, a clean syringe was used to dropwise transfer a solution of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.74×10^{-3} mmol, 1.0 mol %) in dichloromethane (1.5 mL) into the vial over 2 min. The solution was stirred at room temperature for 30 min. To determine the anti-Markovnikov: Markovnikov ratio, a sample of the crude reaction mixture (0.1 mL) was analyzed by ^{1}H NMR. Then, the reaction mixture was transferred onto a silica gel plug (15 g) and eluted with dichloromethane. The eluate was concentrated with a rotary evaporator. The excess vinylbenzene derivative was removed in one of three ways, or in a combination thereof. In most cases, the postplug mixture was dissolved into a minimal amount of dichloromethane and transferred onto a hexanes-packed silica gel column (50 g), which was then flushed with hexanes. In cases where the product

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coeluted with the vinylbenzene, the vinylbenzene could be removed by heating the mixture in an electric vacuum oven (50 mbar and 110 °C), or by recrystallization. For some vinylbenzene mixtures, heating the product in the vacuum oven would polymerize the vinylbenzene. Therefore, recrystallization, followed by column chromatography, followed by heating in an electric vacuum oven, was the most efficient technique for removing most starting vinylbenzene derivatives. The resulting solid was analyzed by NMR spectroscopy. For recrystallization, the solid product was dissolved into a minimal amount of dichloromethane (c.a. 4 mL), and hexanes (c.a. 15 mL) were carefully layered on top of the dichloromethane solution in a 20 mL scintillation vial. The scintillation vial was uncapped and left overnight at room temperature. The remaining solution was decanted into a separate scintillation vial, and the loose crystals were removed from the crystallization vial. Some of the recrystallized mixtures were not a 1:1 cis: trans mixture due to the different solubilities of the cis and trans products.[14]

*4.3.1. 9,19-Dimethyl-9,19-Diphenethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane (**2A**).* Following the general hydrosilylation procedure, **Silane-1** (866 mg, 0.751 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer styrene (196 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.74 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexane packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (1021 mg, 0.749 mmol, 99%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 214−215 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54 (app. d, J = 7.0 Hz, 8H), 7.45−7.18 (m, 26H), 7.16−7.06 (m, 12H), 6.99 (app. d, J = 7.1 Hz, 4H), 2.74−2.70 (m, 4H), 1.13−1.10 (m, 4H), 0.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 144.34, 144.33, 134.07 (cis), 134.05 (trans), 134.04 (cis), 133.9, 131.9, 131.0 (cis), 130.9 (trans), 130.8 (cis), 130.4, 130.3, 128.2, 127.8, 127.76, 127.7, 125.4, 28.8, 18.8, −1.0. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.2, −78.6, −79.4 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) calcd m/z for $C_{66}H_{65}O_{14}Si_{10}$ (M + H$^+$) 1361.2067, found 1361.2128.

*4.3.2. 9,19-Bis(4-Methoxyphenethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2B**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-methoxy-4-vinylbenzene (251 mg, 1.87 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)-iridium(I) dimer (5 mg, 7.74 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 35 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (1055 mg, 0.742 mmol, 99%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 182−183 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54−7.53 (m, 8H), 7.46−7.30 (m, 16H), 7.27−7.24 (m, 7H), 7.22−7.09 (m, 9H), 6.90 (app. d, J = 8.6 Hz, 4H), 6.67−6.63 (m, 4H), 3.70−3.698 (overlapping s [cis and trans CH_3−O], 6H), 2.69−2.65 (m, 4H), 1.10−1.07 (m, 4H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 157.4, 136.5, 134.08 (cis), 134.06 (trans), 134.04 (cis), 133.9, 132.0, 131.0 (cis), 130.9 (trans), 130.8 (cis), 130.4, 130.3, 128.6, 127.7, 127.66, 127.65, 113.6, 55.2, 27.9, 19.0, −0.9. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.1, −78.6, −79.5 (cis), −79.55 (trans), −79.6 (cis). HRMS (APCI) calcd m/z for $C_{68}H_{69}O_{16}Si_{10}$ (M + H$^+$) 1421.2278, found 1421.2172. (We acknowledge that the mass defect is 2 ppm outside of the 5 ppm limit. Given the quality of the corresponding ^{1}H, ^{13}C, and ^{29}Si NMR spectra, we are confident in the structure assignment.)

*4.3.3. 9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-9,19-Bis(3-(Trifluoromethyl)Phenethyl)-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2C**).* Following the general hydrosilylation procedure, **Silane-1** (866 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-(trifluoromethyl)-3-vinylbenzene (323 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.59 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The amber-red solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (1103 mg, 0.736 mmol, 98%) was analyzed by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR. mp 189−190 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54 (app. d, J = 7.2 Hz, 8H), 7.45−7.29 (m, 18H), 7.29−7.08 (m, 22H), 2.77−2.74 (m, 4H), 1.11−1.08 (m, 4H), 0.30 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 145.15, 145.14, 134.0 (cis), 133.98 (trans), 133.94 (cis), 133.9, 131.8, 131.22, 131.21, 130.9 (cis), 130.8 (trans), 130.7 (cis), 130.5, 130.47, 130.43, 130.3, 130.0, 128.6, 127.9, 127.72 (cis), 127.71 (trans), 127.7 (cis), 125.3, 124.4 (q, J = 3.7 Hz), 123.2, 122.4 (q, J = 3.8 Hz), 121.0, 28.6, 18.5, −0.9. ^{19}F NMR (470 MHz, $CDCl_3$ with 1% v/v TMS and 1 drop of C_6F_6) δ −65.6. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.68, −18.69, −78.5, −79.4 (cis), −79.46 (trans), −79.5 (cis). HRMS (APCI) calcd m/z for $C_{68}H_{63}F_6O_{14}Si_{10}$ (M + H$^+$) 1497.1815, found 1497.1808.

*4.3.4. 9,19-Dimethyl-9,19-Bis(4-Methylphenethyl)-1,3,5,7,11,13,15,17-Oct-Phenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2D**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-methyl-4-vinylbenzene (222 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.74 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (962 mg, 0.692 mmol, 92%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 189−190 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54−7.52 (m, 8H), 7.45−7.30 (m, 16H), 7.26−7.09 (m, 16H), 6.94−6.92 (m, 4H), 6.90−6.88 (m, 4H), 2.70−2.67 (m, 4H), 2.24 (s, 6H), 1.11−1.07 (m, 4H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 141.3, 134.8, 134.1 (cis), 134.06 (trans), 134.0 (cis), 133.9, 132.0, 131.0 (cis), 130.9 (trans), 130.8 (cis), 130.4, 130.34, 130.33, 130.31, 128.9, 127.8, 127.7, 28.3, 20.9, 18.9, −0.9. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.1, −78.6, −79.47 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) calcd m/z for $C_{68}H_{69}O_{14}Si_{10}$ (M + H$^+$) 1389.2380, found 1389.2433.

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*4.3.5. 9,19-Bis(2-([1,1′-Biphenyl]-4 Yl)Ethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2E**).* Following the general hydrosilylation procedure **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 4-vinyl-1,1′-biphenyl (339 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)-iridium(I) dimer (5 mg, 7.59 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (964 mg, 0.636 mmol, 85%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. The reported spectra are the 3:2 cis: trans mixture. mp 219−220 °C. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.56−7.54 (m, 8H), 7.52−7.49 (m, 4H), 7.46−7.19 (m, 37H), 7.16−7.13 (m, 3H), 7.10−7.04 (m, 6H), 2.78−2.74 (m, 4H), 1.17−1.13 (m, 4H), 0.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 143.5, 141.2, 138.4, 134.08 (cis), 134.07 (trans), 134.06 (cis), 133.9, 131.9, 131.0 (cis), 130.9 (trans), 130.8 (cis), 130.4, 130.39, 130.38, 130.37, 128.7, 128.2, 127.8, 127.7 (cis), 127.68 (trans), 127.67 (cis), 127.0, 126.9, 126.88, 28.4, 18.7, −0.9. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) −18.2, −78.5, −79.4 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) calcd m/z for $C_{78}H_{73}O_{14}Si_{10}$ (M + H^+) 1513.2693, found 1513.2627.

*4.3.6. 9,19-Bis(3-Chlorophenethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2F**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-chloro-3-vinylbenzene (259 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)-iridium(I) dimer (5 mg, 7.44 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting beige-white solid (712 mg, 0.500 mmol, 66%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. The reported spectra are the 1:2 cis: trans mixture.mp 198−201 °C; 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54 (app. d, J = 7.1 Hz, 8H), 7.45−7.31 (m, 14H), 7.28−7.10 (m, 18H), 7.06−7.04 (m, 2H), 7.02−6.98 (m, 4H), 6.83−6.81 (app. d, J = 7.5 Hz, 2H), 2.70−2.66 (m, 4H), 1.09−1.06 (m, 4H), 0.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 146.35, 146.34, 134.03 (cis), 134.0 (trans), 133.98 (cis), 133.9, 131.8, 130.9 (cis), 130.8 (trans), 130.6 (cis), 130.5, 130.47, 130.45, 130.4, 129.4, 127.9, 127.8, 127.76 (cis), 127.7 (trans), 127.68 (cis), 126.0, 125.7, 28.5, 18.4, −0.9. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.6, −78.5, −79.4 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) calcd m/z for $C_{66}H_{63}Cl_2O_{14}Si_{10}$ (M + H^+) 1429.1288, found 1429.1304.

*4.3.7. Dimethyl 4,4′-((9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane-9,19-Diyl)Bis(Ethane-2,1-Diyl))Dibenzoate (**2G**).* The general hydrosilylation procedure was modified for this experiment. Methyl 4-vinylbenzoate was purchased from A2B Chem, and it was found to be partially polymerized. The partially polymerized methyl 4-vinylbenzoate mixture (360 mg, 18% methyl 4-vinylbenzoate by ^{1}H NMR) was partially dissolved in DCM (10 mL), and the solution was decanted into a 25 mL pear-shaped flask. The solution was concentrated using a rotary evaporator at 45 °C for 2 h. A sample of the white solid was analyzed by ^{1}H NMR, and it was determined that the solid contained 19% of the desired methyl 4-vinylbenzoate (187 mg mixture, 36 mg calculated of methyl 4-vinylbenzoate, 0.219 mmol, 2.5 equiv). **Silane-1** (101 mg, 0.0875 mmol, 1.0 equiv) was transferred into the flask along with a magnetic stir bar. The flask was sealed with a rubber septum, the flask was evacuated, and N_2 was introduced. This process was repeated two more times. A N_2-filled balloon fitted with a needle was inserted into the rubber septum. Then, a syringe was used to transfer dichloromethane (1.5 mL) and the solution was stirred for 3 min. Next, a clean syringe was used to transfer a solution (0.35 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (1 mg, 8.75 × 10^{-4} mmol, 1.0 mol %) dropwise into the vial over 2 min. The amber-red transparent solution was stirred at room temperature for 30 min. Then, the reaction mixture was transferred onto a silica gel column (50 g) and eluted with dichloromethane. The eluate was concentrated, and then dichloromethane (c.a. ten mL) was used to transfer the product into a 20 mL scintillation vial. The solution was concentrated with a rotary evaporator. The resulting white solid was dissolved into a minimal amount of dichloromethane (4 mL), and hexane (15 mL) was carefully layered on top of the solution. The solution was left uncapped overnight at room temperature, and colorless transparent needles had grown on top of an opaque white resin. The remaining solution (5 mL) was decanted into a separate scintillation vial, and the loose crystals were removed from the scintillation vial. The loose crystals, sticky resin, and solution were concentrated on a rotary evaporator, and then they were further dried in an electric vacuum oven (50 mbar and 75 °C) overnight. The white loose crystals, white sticky resin, and white mother liquor (41 mg, 79 mg, and 9 mg, respectively) were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. While the sticky resin and mother liquor contained some of the desired product mixed with various impurities, the colorless loose crystals were determined to be the isolated desired product with almost no impurities (41 mg, 0.0277 mmol, 32%). The structure of the trans product was characterized by X-ray crystallography. The reported spectra are the 2:3 cis: trans mixture. mp 177−178 °C; 32% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.79−7.77 (m, 4H), 7.54−7.52 (m, 8H), 7.44−7.32 (m, 16H), 7.26 (app. t, J = 7.6 Hz, 8H), 7.20 (app. t, J = 7.7 Hz, 2H), 7.15 (app. t, J = 7.6 Hz, 4H), 7.10 (app. t, J = 7.7 Hz, 2H), 7.00 (app. d, J = 8.3 Hz, 4H), 3.88 (s, 6H), 2.76−2.73 (m, 4H), 1.11−1.08 (m, 4H), 0.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 167.2, 149.89 (trans), 149.87 (cis), 134.03 (cis), 134.01 (trans), 134.0 (cis), 133.9, 131.8, 130.9 (cis), 130.8 (trans), 130.7 (cis), 130.52, 130.48, 130.4, 129.6, 127.9, 127.8, 127.74, 127.7, 127.68, 127.4, 51.9, 28.9, 18.4, −1.0. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.55 (cis), −18.56 (trans), −78.5, −79.4 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) analysis failed to afford a discernible calcd m/z for $C_{70}H_{69}O_{18}Si_{10}$ (M + H^+) 1477.2177. However, all other data, including single crystal X-ray analysis data, were consistent with the proposed structure.

*4.3.8. 9,19-Bis(4-Bromophenethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2H**).* Following the general hydrosilylation procedure, **Silane-1** (866 mg, 0.751 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-bromo-4-vinylbenzene (344 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.44 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 37 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid (664

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mg, 0.437 mmol, 58%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 172−175 °C; 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.53−7.51 (m, 8H), 7.44−7.33 (m, 16H), 7.27−7.24 (m, 7H), 7.22−7.10 (m, 13H), 6.80 (app. d, J = 8.3 Hz, 4H), 2.66−2.63 (m, 4H), 1.08−1.04 (m, 4H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 143.24, 143.23, 134.0, 133.9, 131.8, 131.1, 130.9 (cis), 130.8 (trans), 130.7 (cis), 130.5, 130.46, 130.4, 129.5, 127.9, 127.8 (cis), 127.7 (trans), 127.67 (cis), 119.1, 28.2, 18.63, 18.62, −1.0. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) −18.45, −18.46, −78.5, −79.48 (cis), −79.52 (trans), −79.6 (cis).

*4.3.9. 9,19-Bis(4-Chlorophenethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2I**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-chloro-4-vinylbenzene (260 mg, 1.875 mmol, 2.50 equiv) into the vial along with dichloromethane (1.5 mL). Next, chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.59 × 10^{-3} mmol, 1.0 mol %) and dichloromethane (1.5 mL) were transferred dropwise into the vial over 2 min. The amber-red solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and recrystallized. The mother liquor was concentrated on a rotary evaporator and then redissolved into a minimal amount of dichloromethane. The mother liquor solution was loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C) along with the recrystallized product. The resulting beige-white solid and crystals (845 mg, 0.590 mmol, 79%) were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. The reported spectra are the 1:9 cis: trans crystals. Beige-white solid; mp 218−220 °C; 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.53−7.51 (m, 8H), 7.44−7.33 (m, 17H), 7.27−7.10 (m, 15H), 7.05−7.02 (m, 4H), 6.86−6.84 (m, 4H), 2.68−2.65 (m, 4H), 1.08−1.04 (m, 4H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 142.7, 134.0, 133.9, 131.8, 131.0, 130.8, 130.46, 130.45, 129.1, 128.2, 127.9, 127.73, 127.7, 127.67, 28.2, 18.7, −1.0. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.4, −78.5, −79.5 (trans). HRMS (APCI) calcd m/z for $C_{66}H_{63}Cl_2O_{14}Si_{10}$ ($M + H^+$) 1429.1288, found 1429.1271.

*4.3.10. 9,19-Bis(2-Chlorophenethyl)-9,19-Divmethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2J**).* Following the general hydrosilylation procedure, **Silane-1** (866 mg, 0.751 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 1-chloro-2-vinylbenzene (261 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)-iridium(I) dimer (5 mg, 7.89 × 10^{-3} mmol, 1.1 mol %) was transferred dropwise into the vial over 2 min. The solution turned from a white slurry to an amber-red homogeneous solution with the first drops of catalyst solution; this solution appeared to homogenize faster than most of the other hydrosilylation reactions. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and recrystallized. Some crystals were visually distinct, and forceps were used to separate these crystals. The mother liquor was concentrated on a rotary evaporator and then redissolved into a minimal amount of dichloromethane. The mother liquor solution was loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C) along with the recrystallized product. The resulting beige-white solid and crystals (896 mg, 0.626 mmol, 83%) were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR. mp 235−238 °C; 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.56 (app. d, J = 7.1 Hz, 8H), 7.46−7.19 (m, 28H), 7.14 (app. t, J = 7.5 Hz, 4H, trans), 7.08 (app. t, J = 7.5 Hz, 2H, cis), 7.03−6.93 (m, 6H), 2.84−2.80 (m, 4H), 1.12−1.08 (m, 4H), 0.333−0.331 (s, overlapped, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 141.8, 134.07 (cis), 134.06 (trans), 134.04 (cis), 133.9, 133.5, 131.9, 131.0 (cis), 130.9 (trans), 130.8 (cis), 130.4, 130.37 (cis), 130.34 (trans), 130.3 (cis), 129.6, 129.2, 127.8, 127.7 (cis), 127.63 (trans), 127.6 (cis), 126.9, 126.7, 26.9, 17.0, −1.0. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.43, −18.44, −78.5, −79.47 (cis), −79.5 (trans), −79.52 (cis). HRMS (APCI) calcd m/z for $C_{66}H_{63}Cl_2O_{14}Si_{10}$ ($M + H^+$) 1429.1288, found 1429.1169. (We acknowledge that the mass defect is 3 ppm outside of the 5 ppm limit. Given the crystal structures of the cis and trans isomers of **2J**, as well as the corresponding ^{1}H, ^{13}C, and ^{29}Si NMR spectra, we are confident in the structure assignment.)

*4.3.11. 9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-9,19-Bis(4-(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Phenethyl)-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane (**2K**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (432 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (1.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.44 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, the resulting solid was dissolved into a minimal amount of dichloromethane and recrystallized. Three crops were collected and dried in an electric vacuum oven (50 mbar and 110 °C). The resulting white solid and crystals (720 mg, 0.446 mmol, 60%) were analyzed using ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR. The reported spectra are the 1:9 cis: trans mixture. mp 244−246 °C; 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.62 (m, 4H), 7.55−7.53 (m, 8H), 7.45−7.29 (m, 16H), 7.26−7.09 (m, 16H), 7.01 (app. d, J = 8.0 Hz, 4H), 2.75−2.71 (m, 4H), 1.33 (s, 24H), 1.11−1.08 (m, 4H), 0.28 (s, 6H). ^{11}B NMR (160 MHz, $CDCl_3$ with 1% v/v TMS) 31.9 (broad s). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 148.0 (trans), 147.9 (cis), 134.8, 134.04 (cis), 134.01 (trans), 134.0 (cis), 133.9, 131.9, 131.0 (cis), 130.9 (trans), 130.7 (cis), 130.39, 130.37, 127.8, 127.7 (cis), 127.68 (trans), 127.65 (cis), 127.2, 83.6, 29.0, 24.8, 18.6, −0.9. ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.4, −78.5, −79.3 (cis), −79.5 (trans), −79.6 (cis). HRMS (APCI) analysis failed to afford a discernible m/z for $C_{78}H_{87}B_2O_{18}Si_{10}$ ($M + H^+$) 1613.3771. However, all other data, including single crystal X-ray analysis data, were consistent with the proposed structure. Furthermore, Suzuki−Miyaura reaction of **2K** to **2L** afforded spectra, including HRMS (APCI) consistent with the proposed structure.

*4.3.12. 9,19-Dimethyl-9,19-Bis(2-(2′,3′,4′,5′,6′-Pentafluoro-[1,1′-Biphenyl]-4 Yl)Ethyl)-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane (**2L**).* Following the general hydrosilylation procedure, **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial. Then, a syringe was used to transfer **5** (506 mg, 1.88 mmol, 2.5 equiv) into the vial along with dichloromethane (2.5 mL). Next, a dichloromethane solution (1.5 mL) of chloro(1,5-cyclooctadiene)iridium(I) dimer (5 mg, 7.74 × 10^{-3} mmol, 1.0 mol %) was transferred dropwise into the vial over 2 min. The solution turned from a white slurry to an amber-red homogeneous solution with the first drops of catalyst solution; this solution appeared to homogenize faster than most of the other hydrosilylation reactions. The solution was stirred at room temperature for 30 min. After the product was passed through a silica gel plug and concentrated, it was dissolved into a minimal amount of dichloromethane and loaded onto a hexanes-packed silica gel column (50 g). The column was flushed with hexanes followed by dichloromethane. The dichloromethane fractions were concentrated in a rotary evaporator and then dried in an electric vacuum oven (50 mbar and 110 °C). The resulting beige-white solid (1118 mg, 0.660

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mmol, 88%) was analyzed by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR. mp 202−204 °C; 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$ with 1% v/v TMS) δ 7.54 (app. d, J = 6.8 Hz, 8H), 7.46−7.20 (m, 26H), 7.16−7.13 (m, 8H), 7.08−7.05 (m, 6H), 2.79−2.75 (m, 4H), 1.16−1.12 (m, 4H), 0.32−0.31 (s, overlapped, 6H). ^{13}C NMR (125 MHz, $CDCl_3$ with 1% v/v TMS) δ 145.72, 145.71, 134.1, 133.9, 131.8, 130.9 (cis), 130.8 (trans), 130.7 (cis), 130.5, 130.4, 129.9, 128.2, 127.9, 127.7, 123.4, 28.7, 18.5, −1.0. ^{19}F NMR (470 MHz, $CDCl_3$ with 1% v/v TMS and 1 drop of C_6F_6) δ −146.6 (dt, J = 23.2, 7.5 Hz, 4F), −159.5 (t, J = 21.0 Hz, 2F), −165.7 − −165.8 (m, 4F). ^{29}Si NMR (99 MHz, $CDCl_3$ with 1% v/v TMS) δ −18.4, −78.5, −79.4 (cis), −79.5 (trans), −79.6 (cis).

4.4. Platinum-Catalyzed Hydrosilylations. *4.4.1. 9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-9,19-Bis(3-(Trifluoromethyl)-Phenethyl)-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane (**2C**).* **Silane-1** (868 mg, 0.752 mmol, 1.0 equiv) was transferred into an oven-dried 20 mL scintillation vial equipped with a stir bar. The vial was sealed with a rubber septum, the vial was evacuated, and N_2 was introduced. This process was repeated two more times. Then, a syringe was used to transfer 1-(trifluoromethyl)-3-vinylbenzene (272 mg, 1.58 mmol, 2.1 equiv) into the vial along with toluene (8.6 mL). The vial was heated to 95 °C in a silicone oil bath and stirred for 10 min. Next, a 2% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene (3.5 mg, 3.6 × 10^{-4} mmol of Pt, 0.05 mol %) was transferred into the flask, and the solution was continued to stir at 95 °C. At 16 h, a sample was taken, concentrated, and analyzed by NMR spectroscopy. The anti-Markovnikov: Markovnikov ratio was determined based on the relative integration between the multiplet at 1.09 ppm and the doublet (J = 7.5 Hz, 6H) at 1.40 ppm. Additional 1-(trifluoromethyl)-3-vinylbenzene (171 mg, 1.00 mmol, 1.3 equiv) was added after 16 h. After a total of 40 h, the reaction was concentrated with a rotary evaporator. The off-white viscous oil (c.a. one g) was transferred onto a silica gel column (50 g) with a minimal amount of diethyl ether (4 mL). The column was packed as a slurry of silica gel and a hexane: diethyl ether (15:1) solution, and this solution was used as the eluent. The fractions containing UV-active compounds (Rf = 0.38) were combined and concentrated on a rotary evaporator. The white solid (604 mg, 0.403 mmol, 54%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR, and it was determined to be a mixture of hydrosilylation products.

*4.4.2. 9,19-Bis(2-([1,1′-Biphenyl]-4 Yl)Ethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2E**).* **Silane-1** (199 mg, 0.173 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial equipped with a magnetic spin vane. The vial was sealed with a rubber septum, the vial was evacuated, and N_2 was introduced. This process was repeated two more times. Then, the vial was transferred into a N_2-filled polyethylene glove bag, and 4-vinyl-1,1′-biphenyl (63 mg, 0.347 mmol, 2.0 equiv) was loaded into the vial along with toluene (2.0 mL). The vial was capped with a screw cap and removed from the glove bag. With stirring, the colorless transparent solution was heated to 90 °C. The cap was removed, and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (0.1 mL of 2% Pt in xylene, 8.98 × 10^{-3} mmol of Pt, 5.2 mol %) was quickly transferred into the vial, immediately followed by the replacement of the screw cap. The opaque brown solution was stirred for 14.5 h at 90 °C. Then, the screw cap was removed, and the crude reaction mixture (0.1 mL) was transferred into a scintillation vial. The solution in the scintillation vial was concentrated via a rotary evaporator at 40 °C for 1 h. This concentrated oil was dissolved into deuterated chloroform (0.7 mL with 1% v/v TMS) and analyzed by NMR spectroscopy. The anti-Markovnikov: Markovnikov ratio was determined based on the relative integration between the multiplet at 1.14 ppm and the doublet (J = 7.5 Hz, 6H) at 1.42 ppm. The remaining reaction solution was transferred onto a hexanes-packed silica gel column (50 g) and flushed with hexanes (500 mL), followed by hexanes: ethyl acetate (9:1, 500 mL) and dichloromethane (500 mL). A transparent, colorless oil (120 mg) was obtained from concentrating the hexanes eluate; a yellow-green off-white solid (92 mg) was obtained from concentrating the hexanes: ethyl acetate eluate, and a brown off-white solid (86 mg) was obtained from concentrating the dichloromethane eluate.

*4.4.3. 9,19-Bis(3-Chlorophenethyl)-9,19-Dimethyl-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]Tetracosane (**2F**).* **Silane-1** (865 mg, 0.750 mmol, 1.0 equiv) was transferred into an oven-dried 20 mL scintillation vial equipped with a stir bar. The vial was sealed with a rubber septum, the vial was evacuated, and N_2 was introduced. This process was repeated two more times. Then, 1-chloro-3-vinylbenzene (220 mg, 1.58 mmol, 2.1 equiv) was transferred into the vial along with toluene (8.6 mL). The vial was heated to 95 °C in a silicone oil bath and stirred for 10 min. Next, a 2% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene (3.5 mg, 3.6 × 10^{-4} mmol of Pt, 0.05 mol %) was transferred into the flask, and the solution was continued to stir at 95 °C. At 16 h, a sample was taken, concentrated, and analyzed by NMR spectroscopy. The anti-Markovnikov: Markovnikov ratio was determined based on the relative integration between the multiplet at 1.14 ppm and the doublet (J = 7.5 Hz, 6H) at 1.36 ppm. Additional 1-chloro-3-vinylbenzene (39 mg, 0.281 mmol, 0.37 equiv) was added at 16 h. After a total of 40 h, the reaction was concentrated with a rotary evaporator. The off-white viscous oil (c.a. one g) was transferred onto a silica gel column (50 g) with a minimal amount of diethyl ether (4 mL). The column was packed as a slurry of silica gel and a hexane: diethyl ether (15:1) solution, and this solution was used as the eluent. The fractions containing UV-active compounds (Rf = 0.38) were combined and concentrated on a rotary evaporator. The white solid (503 mg, 0.352 mmol, 47%) was analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR, and it was determined to be a mixture of hydrosilylation products.

*4.4.4. 9,19-Dimethyl-9,19-Bis(2-(2′,3′,4′,5′,6′-Pentafluoro-[1,1′-Biphenyl]-4 Yl)Ethyl)-1,3,5,7,11,13,15,17-Octaphenyl-2,4,6,8,10,12,14,16,18,20,21,22,23,24-Tetradecaoxa-1,3,5,7,9,11,13,15,17,19-Decasilapentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-Tetracosane (**2L**).* **Silane-1** (199 mg, 0.173 mmol, 1.0 equiv) was transferred into an oven-dried 5 mL conical vial equipped with a magnetic spin vane. The vial was sealed with a rubber septum, the vial was evacuated, and N_2 was introduced. This process was repeated two more times. Then, the vial was transferred into a N_2-filled polyethylene glove bag and 5 (95 mg, 0.352 mmol, 2.0 equiv) was loaded into the vial along with toluene (2.0 mL). The vial was capped with a screw cap and removed from the glove bag. With stirring, the colorless transparent solution was heated to 90 °C. The cap was removed, and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (0.1 mL of 2% Pt in xylene, 8.98 × 10^{-3} mmol, 5.2 mol %) was quickly transferred into the vial, immediately followed by the replacement of the screw cap. The opaque brown solution was stirred for 17.5 h at 90 °C. Then, the screw cap was removed, and the crude reaction mixture (0.1 mL) was transferred into an NMR tube with deuterated chloroform (0.7 mL with 1% v/v TMS) and analyzed by NMR spectroscopy. The anti-Markovnikov: Markovnikov ratio was determined based on the relative integration between the multiplet at 1.13 ppm and the doublet (J = 7.5 Hz, 6H) at 1.42 ppm. The remaining reaction solution (c.a. 1.9 mL) was transferred onto a hexanes-packed silica gel column (50 g) and flushed with hexanes (500 mL), followed by hexanes: ethyl acetate (9:1, 500 mL) and dichloromethane (500 mL). A white solid (72 mg) was obtained from concentrating the hexanes eluate, a dark brown solid (108 mg) was obtained from concentrating the hexanes: ethyl acetate eluate, and another dark brown solid (91 mg) was obtained from concentrating the dichloromethane eluate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00022.

Product spectra and crystal reports (PDF)

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CCDC 2124142, 2143195, 2239629, 2240545, 2243991, and 2244285 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Andre Lee − *Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824-1226, United States;* orcid.org/0000-0001-6921-7214; Email: leea@egr.msu.edu

Robert E. Maleczka, Jr − *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322, United States;* orcid.org/0000-0002-1119-5160; Email: maleczka@chemistry.msu.edu

Author

Sean P. Walsh − *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.4c00022

Notes

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