Organometallic Syntheses of Hexa- and Nonanitrile Ligands and Their Ruthenium Complexes

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Hexa- and nonanitrile ligands were synthesized by the known CpFe$^+$-induced hexaallylation of hexamethylbenzene in [FeCp(η^6-C$_6$Me$_6$)][PF$_6$] and nonaallylation of mesitylene in [FeCp(η^6-1,3,5-C$_6$H$_3$Me$_3$)][PF$_6$], respectively, followed by Pt-catalyzed regioselective hydrosilylation of the iron-free polyolefins using (chloromethyl)dimethylsilane and sodium iodide catalyzed Williamson coupling with *p*-hydroxybenzonitrile. The hexanitrile star was coordinated to the piano-stool ruthenium complex [RuCp(PPh$_3$)$_2$Cl] by substitution of the six ruthenium-bound chlorides with nitriles using TlPF$_6$ to give the hexacationic hexaruthenium star complex, whereas the analogous metalation reaction partly failed, due to bulk constraint with the nonanitrile ligand. The strategy that involved lengthening of the tethers of the latter, however, successfully provided a nonacationic nonaruthenium complex.

Introduction

Some of the most promising aspects of metallodendrimer chemistry[1−3] are its applications to regenerable metallodendritic catalysts[4−6] and nanoscale molecular materials[7] with unusual physical properties such as nonlinear optics.[8] It has been pointed out that the design of star-shaped catalysts might overcome the steric problem at the dendrimer periphery encountered by metallodendritic catalysts, whose rate-limiting step involves coordination of a substrate onto the metal center.[9] Since ruthenium is one of the most active metals in homogeneous catalysis,[10] we have engaged a research program aimed at the synthesis of star-shaped hexanuclear ruthenium complexes[11] and relatively small dendritic nonanuclear analogues and report here our results along this line. In addition, we have also chosen the rigid (*p*-alkoxybenzonitrile)ruthenium segments in hexacationic and nonacationic complexes for their possible applications in materials science, including nonlinear optics. Our strategies to synthesize star-shaped and dendritic organic and organometallic molecules involves the known CpFe$^+$-induced hexaallylation of hexamethylbenzene in the complex [FeCp(η^6-C$_6$Me$_6$)-[PF$_6$][12] and the CpFe$^+$-induced nonaallylation of mesitylene in the complex [FeCp(η^6-1,3,5-C$_6$H$_3$Me$_3$)][PF$_6$][13] followed by photolytic decomplexation using visible light, Pt-catalyzed hydrosilylation, and subsequent functionalization and metalation. This note presents the straightforward results obtained in the star series and the steric problems encountered in the nonabranched dendrimer core series and how they could be solved.

Results and Discussion

The CpFe$^+$-induced hexaallylation of hexamethylbenzene in the complex [FeCp(η^6-C$_6$Me$_6$)][PF$_6$] (**1**), possible given the lowering by 14 units of the pK_a of this arene after complexation with CpFe$^+$,[12] is a straightforward route to the complex [FeCp{η^6-C$_6$(CH$_2$CH$_2$CH=CH$_2$)$_6$}]-[PF$_6$] (**2**). This compound can then either be directly hydrosilylated or first decomplexed before further functionalization. We favored the latter solution because of possible partial loss of iron in the subsequent steps. We

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applied our classic photolytic procedure using visible light in acetonitrile in the presence of 1 equiv of triphenylphosphine,[14] leading to the stable purple cationic complex [FeCp(NCMe)$_2$(PPh$_3$)][PF$_6$] (**3**), which is easily separated using selective extraction of the aromatic compound C$_6$(CH$_2$CH$_2$CH=CH$_2$)$_6$ (**4**) with ether. The hydrosilylation of double bonds is a well-known, efficient means for their functionalization,[15] and the hydrosilylation of **4** has already been carried out using ferrocenyldimethylsilane to give a hexasilylferrocene star.[16] To provide the possibility for further functionalization to air-stable star molecules, we have selected (chloromethyl)dimethylsilane, which has already been used by the Seyferth group[17] and by our group[18] for the synthesis of dendrimers with cores different from that of **4**. Thus, hydrosilylation of the hexaolefin **4** catalyzed by the Karsted catalyst was carried out at room temperature and gave the hexasilane C$_6$\{(CH$_2$)$_4$Si(Me)$_2$CH$_2$-Cl)\}$_6$ (**5**). We find that chloromethyl termini are indeed an excellent functional groups for coupling with para-substituted phenols in DMF at 80 °C in the presence of NaI as a catalyst to give air-stable stars containing para-substituted aryloxy termini. The most important side reaction in nucleophilic substitution of alkyl halides by various nucleophiles is the β-dehydrohalogenation. This reaction can be minimized but never completely avoided when hydrogen atoms are present in the β-position.[19] The presence of the SiMe$_2$ group in the β-position slightly reduces the nucleophilic reactivity for steric reasons, but it completely removes this side reaction. For instance, the nucleophilic substitution reaction has been carried out with **5** and *p*-hydroxybenzonitrile to give the colorless hexanitrile star C$_6$\{(CH$_2$)$_4$Si(Me)$_2$CH$_2$O-*p*-C$_6$H$_4$CN\}$_6$ (**6**) in 41% yield (Scheme 1). Finally, the hexanitrile star **6** has been shown to react with the ruthenium precursor [RuCp(PPh$_3$)$_2$Cl] (**7**) to give the light yellow, heat- and air-stable hexaruthenium star [C$_6$\{(CH$_2$)$_4$Si(Me)$_2$CH$_2$O-*p*-C$_6$H$_4$CNRuCp(PPh$_3$)$_2$\}$_6$]-[PF$_6$]$_6$ (**8**) in 40% yield, which was characterized by elemental analysis and ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy.

In principle, nonabranched derivatives are also accessible using the known CpFe$^+$-induced nonaallylation of mesitylene in the robust complex [FeCp(η^6-1,3,5-C$_6$H$_3$-Me$_3$)][PF$_6$] (**9**). This reaction benefits from a favorable steric situation that allows us, using KOH and allyl bromide in THF at room temperature, to synthesize [FeCp\{η^6-1,3,5-C$_6$H$_3$C(CH$_2$CH$_2$CH=CH$_2$)$_3$\}$_3$][PF$_6$] (**10**) (Scheme 2).[20] The known photolytic decomplexation of **10** in MeCN and 1 equiv of PPh$_3$ leads to the free arene 1,3,5-C$_6$H$_3$C(CH$_2$CH$_2$CH=CH$_2$)$_3$\}$_3$ (**11**). The Pt-catalyzed hydrosilylation of **11** with (chloromethyl)dimethylsilane, similar to that carried out with the hexastar derivative **3** above, provides the nonabranched derivative 1,3,5-

C$_6$H$_3$\{C[(CH$_2$)$_3$Si(Me)$_2$CH$_2$Cl]$_3$\}$_3$ (**12**). Reaction of **12** with *p*-hydroxybenzonitrile at 80 °C in DMF in the presence of NaI and K$_2$CO$_3$ gives the nonanitrile compound 1,3,5-C$_6$H$_3$\{C[(CH$_2$)$_3$Si(Me)$_2$CH$_2$O*p*-C$_6$H$_4$CN]$_3$\}$_3$ (**13**), but repeated reactions of **13** with [RuCp(PPh$_3$)$_2$-Cl] give only partial metalation. It is reasonable to assume that bulk problems encountered at the periphery of **13** severely inhibit full metalation, due to the large size of the ruthenium fragment. At this point, we believed that a strategy that involved a lengthening of the nine tethers was necessary in order to organize more space between these organometallic fragments at the periphery of the dendritic core. It is known from calculations that, in dendrimers with large molecular termini, these termini have less tendency to fold back toward the dendritic center than when the termini are not bulky.[21] This principle clearly leads to an enhanced possibility for dendrimers with long tethers to contain large termini without dramatic steric constraint compared to analogous dendrimers with short tethers. Therefore, we allowed **12** to react with *p*-hydroxyphenyl undecen-1-yl ether (**14**), which gave the nonaolefin **15** having long tethers. The catalyzed hydrosilylation of **15** with (chloromethyl)dimethylsilane provided the nonasilane **16**, whose reaction with *p*-hydroxybenzonitrile at 80 °C in DMF gave the nonanitrile derivative **17**. At this time, nonametalation of **17** using [RuCp(PPh$_3$)$_2$Cl] (**7**) gave the light yellow nonacationic nonaruthenium complex **18**, as shown by the considerable decrease of the free nitrile band at 2225 cm^{-1} in the infrared spectrum of **18** by comparison to that present in the infrared spectrum of **17**.

Conclusion

Hexa- and nonanitrile ligands and their polycationic piano-stool ruthenium cyclopentadienyl bis(triphenylphosphine) complexes have been synthesized with star- or dendritic-core shapes. The route involves an application of the CpFe$^+$-induced polybranching of allyl groups onto hexamethylbenzene and mesitylene followed by Pt-catalyzed hydrosilylation of the double bonds using (chloromethyl)dimethylsilane and nucleophilic substitution of the chloride by *p*-hydroxybenzonitrile. The latter reaction has the key advantage of not being marred by the classic side dehydrohalogenation of alkyl halides bearing β-hydrogens. Complexation of the polynitrile ligands to ruthenium worked in the case of the hexanuclear star, yielding a star-shaped hexaruthenium complex, but not in the nonabranched series, due to steric constraints. Lengthening of the nine tethers provided a solution for the introduction of nine bulky organometallic fragments at the periphery of the nonabranched dendritic core. This method is promising for the functionalization of larger dendrimers with a suitable relatively large fragment at the dendrimer periphery.

Experimental Section

General Methods. Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium-benzophenone anion under argon im-

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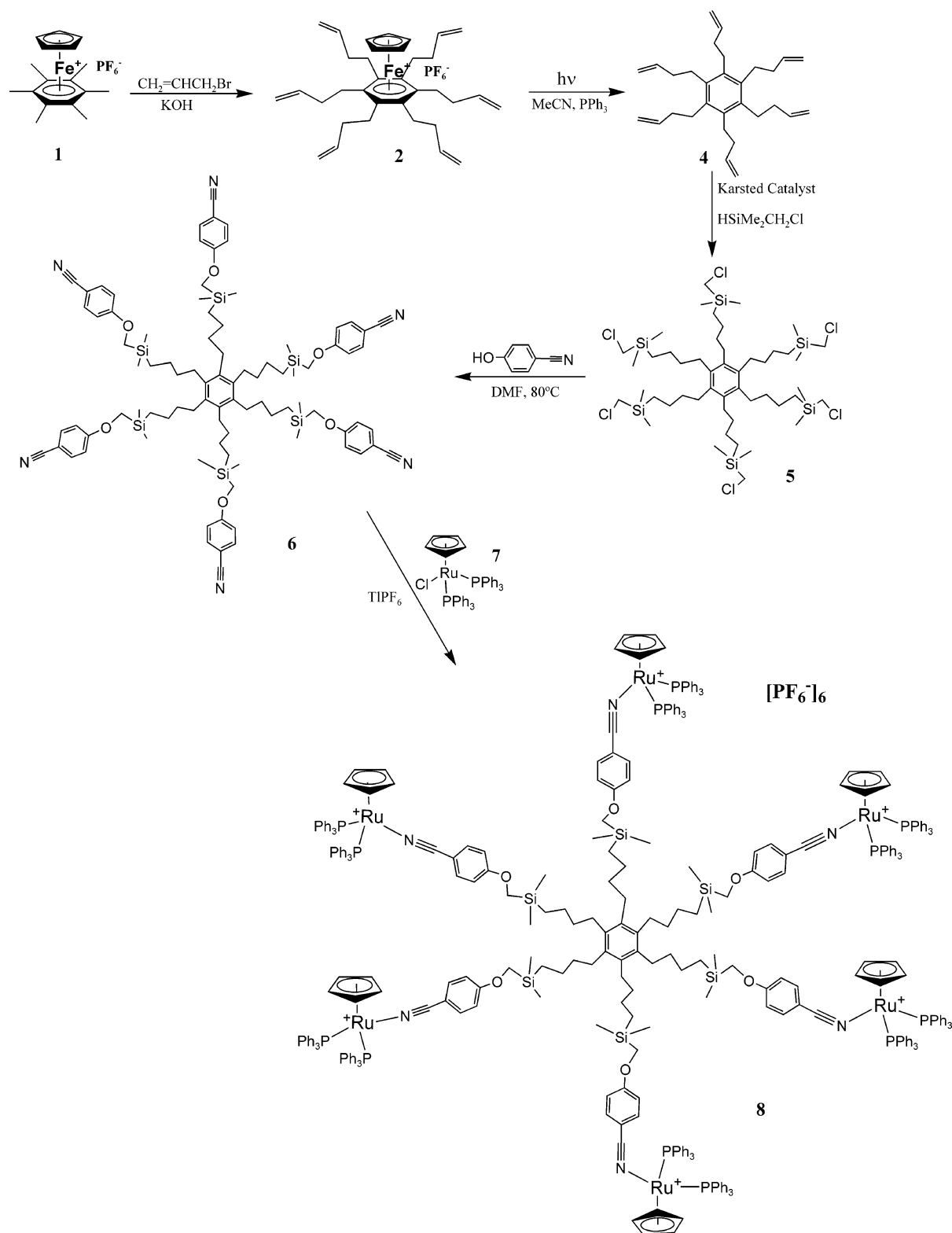(17) Ksda, S. W.; Syferth, D. *J. Am. Chem. Soc.* **1998**, *120*, 3604.
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Scheme 1

mediately prior to use. Acetonitrile (CH₃CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH₂Cl₂) was distilled from calcium hydride just before use. All other chemicals were used as received. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres Dri-Lab. ¹H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ¹³C NMR spectra were obtained in the pulsed FT mode at 62.91 MHz with a Bruker AC 300 spectrometer. All chemical

shifts are reported in parts per million (δ, ppm) with reference to Me₄Si (TMS). Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne, France.

Hexachloro Ligand 5. The hexaolefin $C_6(CH_2CH_2CH=CH_2)_6$ (**4**; 0.121 g, 0.300 mmol) was dried and introduced into a Schlenk flask, and then dry ether (15 mL) was added. Under nitrogen, (chloromethyl)dimethylsilane (0.388 g, 3.60 mmol) and 10 drops of a commercial xylene solution (2%) of the Karsted catalyst was added. The reaction mixture was mag-

Scheme 2
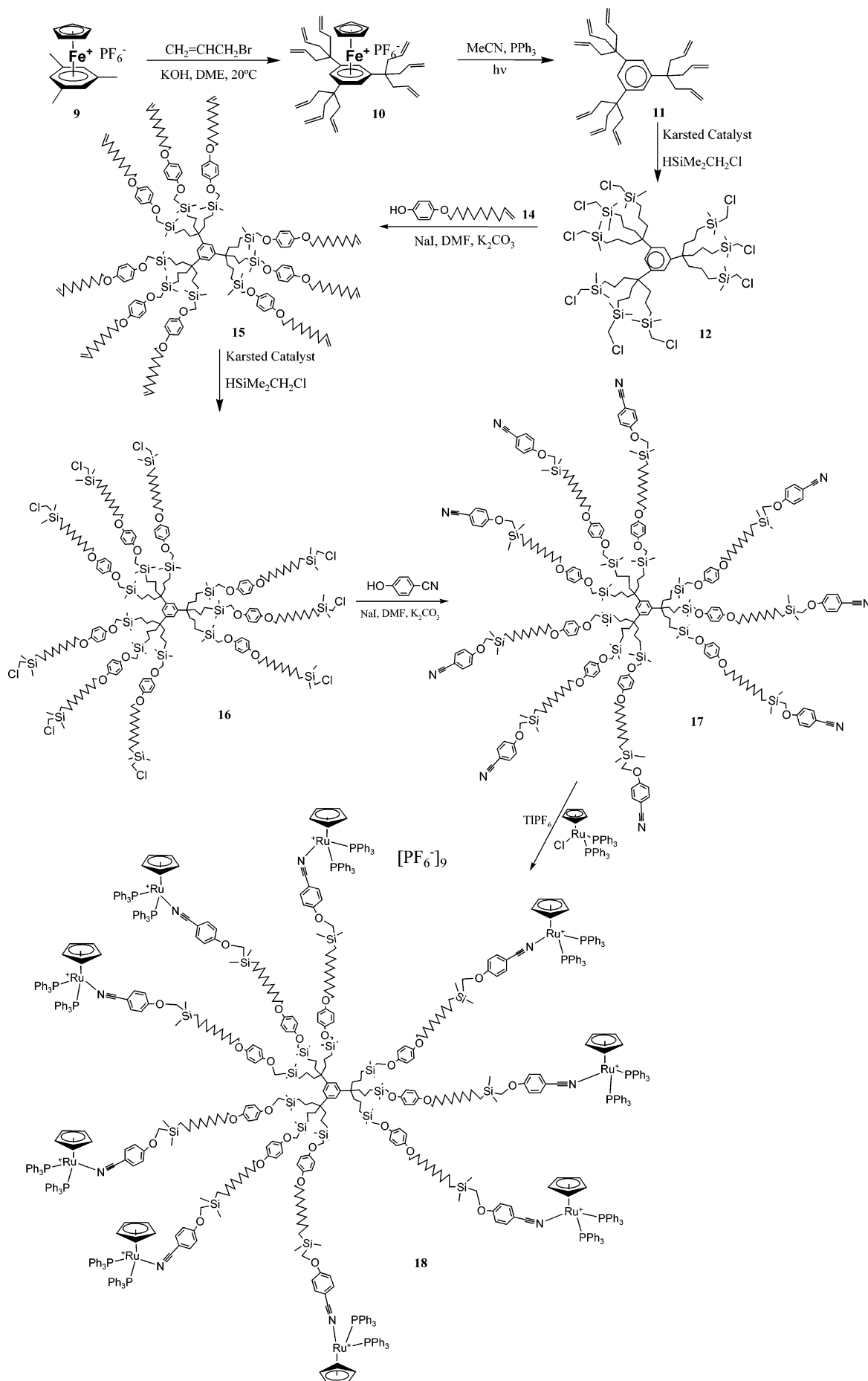
netically stirred at room temperature for 2 days. After removing the solvent under vacuum, the product was purified by flash chromatography (silica column with CH_2Cl_2), to remove the catalyst. After drying under vacuum, 0.337 g (94% yield) of product was obtained as a colorless oil.

^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm): 2.7 (s, 12H SiCH_2Cl), 2.50 (m, 12H, CH_2CH$_2$CH$_2$CH$_2$Si), 1.52 (s, 12H, CH$_2$CH_2CH_2-CH$_2$Si), 0.72 (s, 12H, CH$_2$CH$_2$CH_2Si), 0.14 (s, 54H, Si(CH_3)$_2$).

Hexanitrile Ligand 6. The hexachloro derivative **5** (0.307 g, 0.292 mmol), 4-cyanophenol (0.417 g, 3.50 mmol), NaI (0.525 g, 3.5 mmol), and K$_2$CO$_3$ (0.525 g, 3.5 mmol) were dried and introduced into a Schlenk flask; then dry DMF (20 mL) was added and the reaction mixture was heated at 80 °C for 2 days with magnetic stirring. After the solvent was removed in vacuo, CH$_2$Cl$_2$ (20 mL) was added, and the mixture was filtered on Celite to remove K$_2$CO$_3$. The solvent was removed in vacuo, and the residue was washed with methanol (2 × 10 mL) to remove any remaining 4-cyanophenol. After drying in vacuo, 0.192 g (41% yield) of **6** was obtained as a colorless oil.

^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm): 7.55 and 6.98 (d, 12H, CH arom), 3.63 (s, 12H, SiCH_2O), 2.50 (s, 12H, CH_2CH$_2$CH$_2$-CH$_2$Si), 1.52 (s, 12H, CH$_2$CH_2CH$_2$CH$_2$Si), 0.75 (s, 12H, CH$_2$-CH$_2$CH_2Si), 0.15 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 164.7 (Cq, Ar), 136.46 (CqO, arom), 133.8 (C$_q$CN), 119.33 (CN), 114.8 (CH, Ar), 60.8 (SiCH$_2$O), 35.1 (CH$_2$CH$_2$CH$_2$-CH$_2$Si), 29.48 (CH$_2$CH$_2$CH$_2$CH$_2$Si), 24.7 (CH$_2$CH$_2$CH$_2$CH$_2$Si), 13.36 (CH$_2$CH$_2$CH$_2$CH$_2$Si), −4.79 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz; δ, ppm): 1.06 (SiCH$_2$O). Infrared: ν_{CN} 2224 cm^{-1} (strong). MS (MALDI-TOF; m/z): calcd for C$_{90}$H$_{120}$N$_6$NaO$_6$Si$_6$, 1571.78; found, 1571.89. Anal. Calcd for C$_{90}$H$_{120}$N$_6$O$_6$Si$_6$: C, 69.72; H, 7.80. Found: C, 69.48; H, 8.05.

Hexaruthenium Complex 8. [RuCp(PPh$_3$)$_2$Cl] **7** (0.650 g, 0.896 mmol) was introduced under nitrogen into a flame-dried Schlenk flask, and then CH$_3$OH (10 mL) and CH$_2$Cl$_2$ (10 mL) were added, solubilizing **7**; then TlPF$_6$ (0.352 g, 1.010 mmol) was added. After 30 min, the mixture was filtered under nitrogen into a CH$_2$Cl$_2$ solution (10 mL) of **5** (0.180 g, 0.112 mmol), the reaction mixture was stirred for 15 h and then filtered under nitrogen using a cannula, and the solvent was removed in vacuo. The solid residue was dissolved in 10 mL of CH$_2$Cl$_2$, and then 30 mL ether was added in order to precipitate **8**, which was obtained as a light yellow powder after filtration (0.332 g; 40% yield). This complex is of modest thermal stability, and it is air sensitive in solution.

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 7.2−6.08 (m, PPh$_3$), 6.85 (d, 12H, CH arom), 4.55 (s, Cp), 3.63 (s, 12H, SiCH_2O), 2.41 (s, 12H, CH_2CH$_2$CH$_2$Si), 1.43 (s, 12H, CH$_2$CH_2CH_2CH$_2$-Si), 0.64 (s, 18H, CH$_2$CH$_2$CH_2Si), 0.0006 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 165.72 (Cq, Ar), 136−128 (PPh$_3$), 115.35 (CH, Ar), 83.75 (C$_5$H$_5$), 60.59 (SiCH$_2$O), 23.02 (CH$_2$), 15.25 (CH$_2$), 13.27 (CH$_2$), −4.78 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz; δ, ppm): 1.04 (SiCH$_2$O). ^{31}P NMR (CDCl$_3$, 81 MHz; δ, ppm): 41.86 (PPh$_3$), −144 (PF$_6$). Infrared: ν_{CN} 2223 cm^{-1}. Anal. Calcd for C$_{336}$H$_{330}$F$_{36}$N$_6$O$_6$Si$_6$: C, 61.47; H, 5.06. Found: C, 61.33; H, 5.98.

Nonakis(benzonitrile) Ligand 13. The nonachloro derivative **12** (0.320 g, 0.219 mmol), 4-cyanophenol (0.471 g, 3.95 mmol), and K$_2$CO$_3$ (2.76 g, 19.7 mmol) were dried in a Schlenk flask, and dry DMF (20 mL) was added. The reaction mixture was stirred at 80 °C for 2 days, and the DMF was removed. A 20 mL portion of CH$_2$Cl$_2$ was added, and the solution was filtered on Celite to remove K$_2$CO$_3$. The solvent was removed in vacuo, and the product was washed with methanol in order to remove any excess of starting material. A 0.428 g amount (89% yield) of **13** was obtained.

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 7.52 (d, 18H, arom), 6.99 (s, 3H, arom core), 6.92 (d, 18H, arom), 3.53 (s, 18H, SiCH_2O), 1.62 (s, 18H, CH_2CH$_2$CH$_2$Si), 1.12 (s, 18H, CH$_2$CH_2CH$_2$Si), 0.57 (s, 18H, CH$_2$CH$_2$CH_2Si), 0.038 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 163.3 (Cq, Ar core), 144.6 (CH, Ar core), 132.6 and 113.0 (CH, Ar), 120.2 and 102.4 (Cq,

Ar), 59.7 (SiCH$_2$O), 42.7 (CqCH$_2$), 16.54 (CH$_2$CH$_2$CH$_2$Si), 14.00 (CH$_2$CH$_2$CH$_2$), 13.30 (CH$_2$CH$_2$CH$_2$Si), −5.87 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz; δ, ppm): 0.69 (SiCH$_2$O). Infrared: ν_{CN} 2224 cm^{-1}. MS (MALDI-TOF; m/z): calcd for C$_{126}$H$_{165}$N$_9$NaO$_9$-Si$_9$, 2223.05; found, 2223.11. Anal. Calcd for C$_{126}$H$_{165}$N$_9$O$_9$Si$_9$: C, 68.71; H, 7.55. Found: C, 68.61; H, 7.28.

Reaction between 13 and 7. The ruthenium complex **7** (0.373 g, 0.500 mmol) was introduced under nitrogen into a flame-dried Schlenk flask, CH$_3$OH (10 mL) and CH$_2$Cl$_2$ (10 mL) were added, solubilizing the complex, and then TlPF$_6$ (0.209 g, 0.600 mmol) was added. After 30 min, the mixture was filtered under nitrogen into a CH$_2$Cl$_2$ solution of **13** (0.104 g, 0.048 mmol), and the mixture reaction was stirred for 15 h and then filtered under nitrogen using a small filter. The solvent was removed in vacuo. The product was dissolved with CH$_2$Cl$_2$ (10 mL) and precipitated with ethyl ether (50 mL), giving a yellow-green powder (0.156 g). The analysis of the integration of signals of the ^{1}H NMR spectrum showed a 2/3 ratio of Cp of ruthenium to nitrile ligand.

^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm): 7.4−6.08 (m, CH arom of PPh$_3$, and CH arom of core), 4.55 (s, 30H Cp), 3.50 (s, 18H, SiCH_2O), 1.55 (s, 18H, CH_2CH$_2$CH$_2$Si), 1.12 (s, 18H, CH$_2$CH_2-CH$_2$Si), 0.64 (s, 18H, CH$_2$CH$_2$CH_2Si), 0.038 (s, 54H, Si(CH_3)$_2$).

***p*-Hydroxyphenyl Undecen-1-yl Ether (14).** Hydroquinone (5.06 g, 46 mmol), 11-bromo-1-undecene (2 mL, 9.20 mmol), and K$_2$CO$_3$ (6.44 g, 46 mmol) were introduced into a Schlenk flask and dried. A 20 mL portion of dry DMF was added, the reaction mixture was stirred at 80 °C for 2 days, DMF was removed under vacuum, and then 20 mL of CH$_2$Cl$_2$ was added to the residue. The mixture was stirred for a few minutes and filtered to remove K$_2$CO$_3$, the solid residue was washed with 10 mL of CH$_2$Cl$_2$, and the solvent was then removed under vacuum. The solid residue was dissolved in CH$_2$Cl$_2$ and submitted to silica gel column chromatography using CH$_2$Cl$_2$ as eluent, which provided 1.635 g (68%) of **14** as a white powder.

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 6.76 (d, 4H, arom), 5.79 (m, 1H, HC=CH$_2$), 4.99 (m, 2H, HC=CH_2), 4.47 (s, 1H, OH), 3.88 (t, 2H, OCH_2), 2.07 (m, 2H, OCH$_2$CH_2), 1.59 (m, 2H, CH_2-HC=CH$_2$), 1.29 (s, 12H, (CH_2)$_6$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 153.2 (COH), 149,5 (Cq, Ar), 139.2 (HC=CH$_2$), 116.0 (HC=CH$_2$), 114.1 (CH, Ar), 68.8 (OCH$_2$), 33.8 (OCH$_2$CH$_2$), 29.3 ((CH$_2$)$_6$ and CH$_2$HC=CH$_2$). Anal. Calcd for C$_{17}$H$_{26}$O$_2$: C, 77.82; H, 9.99. Found: C, 77.83; H, 9.91.

A Nonaolefin with Long Tethers: 15. The compounds **12** (0.252 g, 0.173 mmol), **14** (0.635 g, 2.42 mmol), K$_2$CO$_3$ (2.15 g, 15.6 mmol), and NaI (0.467 g, 3.11 mmol) were introduced into a Schlenk flask and dried. A 20 mL portion of DMF was added, and the mixture was stirred at 80 °C for 2 days. DMF was removed under vacuum, 20 mL of CH$_2$Cl$_2$ was added, and K$_2$CO$_3$ was removed by filtration. The product **15** was purified by silica gel column chromatography using CH$_2$Cl$_2$ as the eluent, giving 0.413 g of a colorless waxy product (65%).

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 7.01 (s, 3H, arom. core), 6.81 (d, 36H, arom), 5.81 (m, 9H, HC=CH$_2$), 4.99 (m, 18H, HC=CH_2), 3.85 (t, 18H, OCH_2CH$_2$), 3.46 (s, 18H, SiCH_2O), 2.06 (m, 18H, OCH$_2$CH_2), 1.73 (m, 18H, CH_2HC=CH$_2$), 1.62 (s, 18H, CH_2CH$_2$CH$_2$Si), 1.31 (s, 108H, (CH$_2$)$_6$), 1.14 (s, 18H, CH$_2$CH_2-CH$_2$Si), 0.59 (s, 18H, CH$_2$CH$_2$CH_2Si), 0.039 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 155.7 (Cq, Ar), 153.0 (Cq, Ar), 145.6 (CH, Ar core), 139.1 (HC=CH$_2$), 115.2 (HC=CH$_2$), 114.1 (CH, Ar), 68.7 (OCH$_2$), 60.9 (SiCH$_2$O), 43.93 (Cq CH$_2$), 42.0 (CH$_2$CH$_2$CH$_2$Si), 33.8 (OCH$_2$CH$_2$), 29.5 (CH$_2$HC=CH$_2$), 17.9 (CH$_2$CH$_2$CH$_2$), 14.64 (CH$_2$CH$_2$CH$_2$Si), −4.51 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz), δ_{ppm}: 0.30 (SiCH$_2$O). MS (MALDI-TOF; m/z): calcd for C$_{216}$H$_{354}$NaO$_{18}$Si$_9$, 3514.89; found, 3514.17. Anal. Calcd for C$_{216}$H$_{354}$O$_{18}$Si$_9$: C, 74.30; H, 10.21. Found: C, 74.28; H, 10.49.

A Nonachloro Derivative with Long Tethers: 16. A nonaolefin with long tethers, **15** (0.180 g, 0.052 mmol), was dried and introduced into a Schlenk flask, and then dry ether

(15 mL) was added. Under nitrogen, (chloromethyl)dimethyl-silane (0.189 g, 1.7 mmol) and 10 drops of Karsted catalyst were added, and the reaction mixture was magnetically stirred at room temperature for 2 days. After the solvent was removed under vacuum, the product was purified by flash chromatography (silica column with CH_2Cl_2). After drying under vacuum, 0.220 g (95% yield) of product **16** was obtained as a colorless oil.

^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm): 7.05 (s, 3H, arom core), 6.78 (d, 36H, arom), 3.84 (t, 18H, OCH_2CH$_2$), 3.43 (s, 18H, SiCH_2O), 2.6 (s, 18H, CH$_2$Cl), 1.66 (m, 18H, CH_2CH$_2$CH$_2$), 1.32 (s, 108H, (CH2)$_6$), 1.12 (s, 18H, CH$_2$), 0.65 (s, 18H, CH$_2$CH_2-CH$_2$Si), 0.10 and 0.039 (s, 108H, Si(CH_3)$_2$).

A Nonanitrile Derivative with Long Tethers: 17. The compounds **16** (0.220 g, 5.08 × 10^{-2} mmol), *p*-cyanophenol, K$_2$-CO$_3$ (0.630 g, 9.13 × 10^{-2} mmol), and NaI (0.137 g, 9.13 × 10^{-2} mmol) were introduced into a Schlenk flask and dried. A 20 mL portion of dry DMF was then added, and the reaction mixture was stirred for 2 days at 80 °C. After DMF was removed under vacuum, 20 mL of CH_2Cl_2 was added; this mixture was stirred for a few minutes and then filtered on Celite to remove K$_2$CO$_3$, and the solvent was removed under vacuum. The solid residue was washed with 3 × 10 mL of methanol to remove any remaining starting material, which gave **17** as a colorless oil (0.250 g, 4.88 mmol, 96% yield).

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 7.58 and 7.01 (d, 18H, CH arom), 6.79 (d, 36H, CH arom), 3.84 (t, 18H, OCH_2CH$_2$), 3.61 and 3.44 (s, 18H, SiCH_2O), 1.68 (m, 18H, CH_2CH$_2$Si), 1.26 (s, 108H, (CH_2)$_6$), 1.15 (s, 18H, CH$_2$CH_2CH$_2$Si), 0.65 (s, 18H, CH$_2$CH$_2$CH_2Si), 0.13 and 0.027 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 155.7 and 153.0 (*C*q, Ar), 133.8 (*C*qCN), 114.8 (*C*H, Ar), 68.6 (O*C*H$_2$), 60.9 (Si*C*H$_2$O), 44.4 (*C*qCH$_2$), 42.0 (*C*H$_2$CH$_2$CH$_2$Si), 33.4 (O*C*H$_2$*C*H$_2$), 29.5 (*C*H$_2$)$_6$, 26.0 ((CH$_2$)$_6$*C*H$_2$CH$_2$Si), 23.6 ((CH$_2$)$_6$CH$_2$*C*H$_2$Si), 14.5 (CH$_2$*C*H$_2$-CH$_2$Si), 13.57 (CH$_2$CH$_2$*C*H$_2$Si), −4.57 et −4.82 (Si*Me*$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz; δ, ppm): 0.96 and 0.31 (*Si*CH$_2$O). Infrared: ν_{CN} 2225 cm^{-1}. MS (MALDI-TOF; *m*/*z*), calcd for

C$_{306}$H$_{471}$N$_9$NaO$_{27}$Si$_{18}$, 5213.6; found, 5212.8. Anal. Calcd for C$_{306}$H$_{471}$N$_9$O$_{27}$Si$_{18}$: C, 70.49; H, 9.11. Found: C, 70.44; H, 9.33.

A Nonaruthenium Derivative with Long Tethers: 18. In a flame-dried Schlenk flask was introduced under nitrogen the orange ruthenium complex **7** (0.428 g, 0.591 mmol), and it was dissolved in a 1/1 mixture of CH$_3$OH and CH_2Cl_2 (20 mL). A 0.223 g (0.64 mmol) portion of TlPF$_6$ was added with stirring. After the mixture was stirred for 15 min, 0.250 g (0.049 mmol) of **17** dissolved in CH_2Cl_2 (5 mL) was added. After this mixture was stirred for 15 h, a white precipitate appeared. The solution was filtered under nitrogen, and the solvent was removed under vacuum. The yellow product was dissolved in 10 mL of CH_2Cl_2 and precipitated with ether, the solution was filtered, and the yellow precipitate was washed twice with 10 mL of ether. The yellow powder was dried under vacuum. Yield: 0.250 g of a yellow powder of **18** (45%).

^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 7.4−7.14 (m, PPh$_3$), 7.01 (d, 18H, CH arom), 6.83 (d, 36H, CH arom), 4.55 (s, Cp), 3.88 (t, 18H, OCH$_2$CH$_2$), 3.66 and 3.51 (s, 18H, SiCH$_2$O), 1.73 (m, 18H, CH$_2$CH$_2$Si), 1.31 (s, 108H, (CH$_2$)$_6$), 1.25 (s, 18H, CH$_2$-CH$_2$CH$_2$Si), 0.65 (s, 18H, CH$_2$CH$_2$CH$_2$Si), 0.14 and 0.067 (s, 54H, Si(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 62 MHz; δ, ppm): 152.7 (*C*q, Ar), 135.8−129.1 (PPh$_3$), 127.3 (Cq CN), 114.8 (CH, Ar), 83.8 (*C*$_5$H$_5$), 68.6 (OCH$_2$), 60.9 (Si*C*H$_2$O), 33.4 (OCH$_2$CH$_2$), 29.5 (CH$_2$)$_6$, 26.0 ((CH$_2$)$_6$*C*H$_2$CH$_2$Si), 23.6 ((CH$_2$)$_6$CH$_2$*C*H$_2$Si), 14.5 (CH$_2$*C*H$_2$CH$_2$Si), 13.57 (CH$_2$CH$_2$*C*H$_2$Si), −4.57 and −4.85 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz; δ, ppm): 0.92 and 0.28 (*Si*CH$_2$O). ^{31}P NMR (CDCl$_3$, 81 MHz; δ, ppm): 41.91 (PPh$_3$), −144 (PF$_6$). Infrared: ν_{CN} 2220 cm^{-1}. Anal. Calcd for C$_{675}$H$_{786}$O$_{27}$-Si$_{18}$: C, 63.66; H, 6.22. Found: C, 62.07; H, 6.06.