New Early Transition Metal Porphyrins: A New Route to Diorgano Complexes of Zirconium and Hafnium and the Preparation of Cationic Derivatives

Holger Brand, Joseph A. Capriotti, and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720

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The group 4 metal dialkyl chlorides $(Me_3SiCH_2)_2MCl_2(Et_2O)_2$ (M = Zr, Hf) are prepared from stoichiometric amounts of alkyllithium and metal chlorides. Reaction with dilithium porphyrinates affords $(P)M(CH_2SiMe_3)_2$ derivatives [P = dianion of *p*-tetratolylporphyrin (TTP), dianion of octaethylporphyrin (OEP)] in good yields. *Cis*-ligation in these out-of-plane derivatives can be inferred from ^1H NMR and ^{13}C NMR data. Protonolysis of the OEP derivatives with 1 equiv of $[HNMe_2Ph][BPh_4]$ generates the cationic species $[(OEP)M(CH_2SiMe_3)][BPh_4]$, whereas the TTP analogs remain unreactive under similar conditions. Preliminary reactivity studies show that these novel cationic compounds are unreactive toward ethylene.

Introduction

The recent interest in early transition metal porphyrins has in part been sparked by the realization that the out-of-plane nature of these derivatives induces *cis*-ligation of the attendant ligands, with resulting reactivities quite unlike those of the later transition metal porphyrins.[1,2] Entry into organometallic derivatives is usually found by alkylating the corresponding metalloporphyrin halides. However, recently we reported a facile, one-pot synthesis of a highly functionalized organometallic porphyrin compound by reacting Me_3TaCl_2[3] with $Li_2(OEP)(THF)_n$ to afford $(OEP)TaMe_3$ in excellent yield.[4] Since the zirconium alkyl halides $(Me_3CCH_2)_2ZrCl_2(Et_2O)_2$[5] and $(Me_3SiCH_2)_2ZrCl_2$[6] and others[7] are known we extended this methodology to group 4 porphyrin compounds. Here we report the preparation of $(P)M(CH_2SiMe_3)_2$ derivatives [P = dianion of *p*-tetratolylporphyrin (TTP), dianion of octaethylporphyrin (OEP)]. Furthermore, we describe the generation of some cationic porphyrin species and attempted reactions with alkenes.

Results and Discussion

Reaction of $(Me_3CCH_2)_2ZrCl_2(Et_2O)_2$ with $Li_2(OEP)(THF)_n$ does not afford $(OEP)Zr(CH_2CMe_3)_2$, nor does the interaction of $LiCH_2CMe_3$ or $Mg(CH_2CMe_3)_2$ with $(OEP)ZrCl_2$[2b,d] yield the desired dialkyl. Since $(OEP)Zr(CH_2CMe_3)_2$ might be inherently unstable we decided to investigate a new entry into the known $(OEP)Zr(CH_2SiMe_3)_2$.[2b,d]

$(Me_3SiCH_2)_2ZrCl_2$[6] had been generated in situ from the stoichiometric interaction of $(Me_3SiCH_2)_4Zr$ and $ZrCl_4$. In order to isolate this compound we use the methodology reported by Schrock for the preparation of $(Me_3CCH_2)_2ZrCl_2(Et_2O)_2$ (eq 1).[5]

$$ZrCl_4 + \underset{n=1,2}{n\,LiCH_2SiMe_3} \xrightarrow{Et_2O/pentane} (Me_3SiCH_2)_nZrCl_{4-n}(Et_2O)_2 \quad (1)$$

$(Me_3SiCH_2)_2ZrCl_2(Et_2O)_2$ and $(Me_3SiCH_2)ZrCl_3(Et_2O)_2$ are isolated as slightly yellow, viscous oils in good yields. Attempts to prepare crystalline derivatives by addition of THF, DME, PMe_3, PMe_2Ph, or TMEDA were unsuccessful. The ^1H NMR spectrum for $(Me_3SiCH_2)_2ZrCl_2(Et_2O)_2$ displays broad signals at 3.22, 2.25, 0.96, and 0.32 ppm with the relative intensities 8:4:12:18. By analogy to $(Me_3CCH_2)_2ZrCl_2(Et_2O)_2$, the first and third signals are assigned to the diethyl ether hydrogens and the remaining two to the silylmethylene and -methyl hydrogens, respectively. Protonolysis with MeOH affords Et_2O and $SiMe_4$ in a ratio of 1:1. A similar spectrum is obtained for $(Me_3SiCH_2)ZrCl_3(Et_2O)_2$; however, the silylmethylene signals are shifted significantly downfield, as expected when considering the more electropositive character of the central metal in $(Me_3SiCH_2)ZrCl_3(Et_2O)_2$ vs $(Me_3SiCH_2)_2ZrCl_2(Et_2O)_2$. A similar downfield shift for the $SiCH_2$ resonance has been observed for $(Me_3SiCH_2)TiCl_3$ vs $(Me_3SiCH_2)_2TiCl_2$.[8] A ratio of 1:2 for the silyl and diethyl ether moieties was observed by integration of the corresponding signals before and after protonolysis with methanol.

Reaction of $(Me_3SiCH_2)_2ZrCl_2(Et_2O)_2$ with 1 equiv of $Li_2(OEP)(THF)_n$ affords $(OEP)Zr(CH_2SiMe_3)_2$ in excel-

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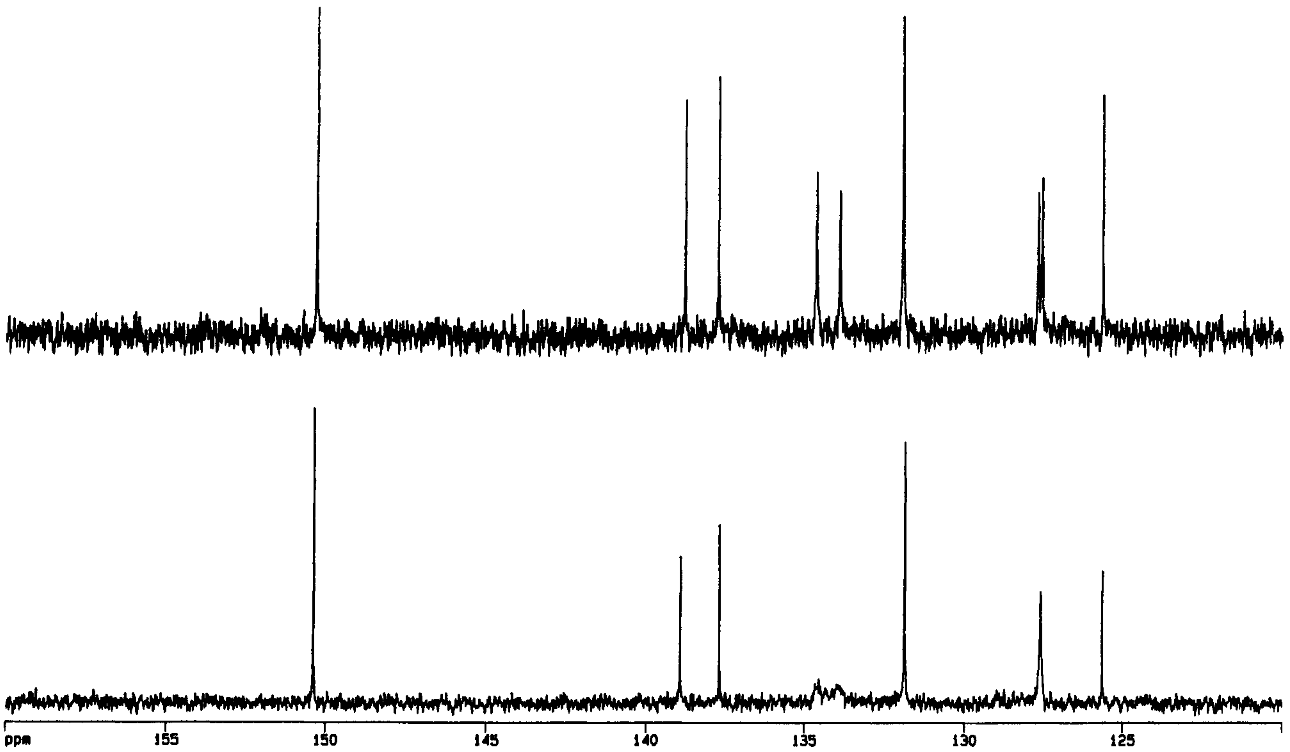

Figure 1. ^{13}C NMR spectra of $(TTP)Zr(CH_2SiMe_3)_2$ in $CDCl_3$ at 25 °C (bottom) and −10 °C (top).

lent yield after workup. Following the reaction in CD_2Cl_2 by ^1H NMR spectroscopy showed product formation within 10 min at room temperature and no generation of side products. For the following large scale reactions, $(Me_3SiCH_2)_2MCl_2(Et_2O)_2$ (M = Zr, Hf) was generated in situ from 2 equiv of $LiCH_2SiMe_3$ and MCl_4 as described above or from equimolar amounts of $M(CH_2SiMe_3)_4$ and MCl_4 as reported by Wilkinson.[6] In general, $Li_2(OEP)(THF)_n$ or $Li_2(TTP)(Et_2O)_2$ was stirred with 1.2 equiv of $(Me_3SiCH_2)_2MCl_2(Et_2O)_2$ in solvents such as methylene chloride, toluene, or diethyl ether, and the pure product was isolated by crystallization (eq 2).

$$Li_2(P)(solv)_n + (Me_3SiCH_2)_2MCl_2(Et_2O)_2 \rightarrow (P)M(CH_2SiMe_3)_2 \quad (2)$$

$$P = OEP,\ solv = THF;\ P = TTP,\ solv = Et_2O;\ M = Zr, Hf$$

All the compounds were isolated in good to excellent yields and were fully characterized by ^1H NMR, ^{13}C NMR, UV/vis spectroscopy, mass spectrometry, and elemental analysis. The out-of-plane nature of these derivatives is easily detected by inspecting their ^1H NMR spectra. A complicated multiplet is seen for the diastereotopic octaethylporphyrin methylene hydrogens,[9] and four signals are observed for the TTP-tolyl *ortho*- and *meta*-hydrogens indicating inequivalence of the two porphyrin sides.[10] The ^{13}C NMR spectra of the $(TTP)M(CH_2SiMe_3)_2$ derivatives shows only broad resonances for the *ortho*- and *meso*-carbons at room temperature. Similar results were reported for metal porphyrin compounds with two different *trans*-ligands.[11] The signals, however, resolve to two doublets upon cooling to −10 °C (Figure 1). An upfield shift of about 0.6 ppm is observed in the ^1H NMR spectrum of the Hf derivatives relative to the Zr compounds. The same magnitude of upfield shifts is observed for group 4 metallocene as well as for homoleptic (trimethylsilyl)methyl derivatives upon substituting Hf vs Zr and is no doubt due to the lower electronegativity of Hf.[12,13]

In attempts to use a similar methodology in order to prepare $(P)M(CH_2SiMe_3)Cl$ derivatives, reaction of $Li_2(OEP)(THF)_n$ with 1 equiv of $(Me_3SiCH_2)ZrCl_3(Et_2O)_2$ gave only the dialkyl compound. Monitoring this reaction by ^1H NMR spectroscopy in CD_2Cl_2 shows formation of $(OEP)Zr(CH_2SiMe_3)_2$ and an unidentified porphyrin product, but no $(OEP)Zr(CH_2SiMe_3)Cl$.

Due to their significance in alkene polymerization processes, cationic d^0 transition metal compounds have been subject to intense research efforts.[14] Recently, Jordan and co-workers isolated a number of cationic derivatives of zirconium and hafnium tetraazamacrocycles and showed them to undergo insertion of alkynes into the M−C bonds.[15] We have reported insertion of small molecules such as CO, CO_2, and acetone into Zr−C[2d] and insertion of alkenes into Zr−H bonds[2b] of OEP dialkyl derivatives. Furthermore, in the case of orga-

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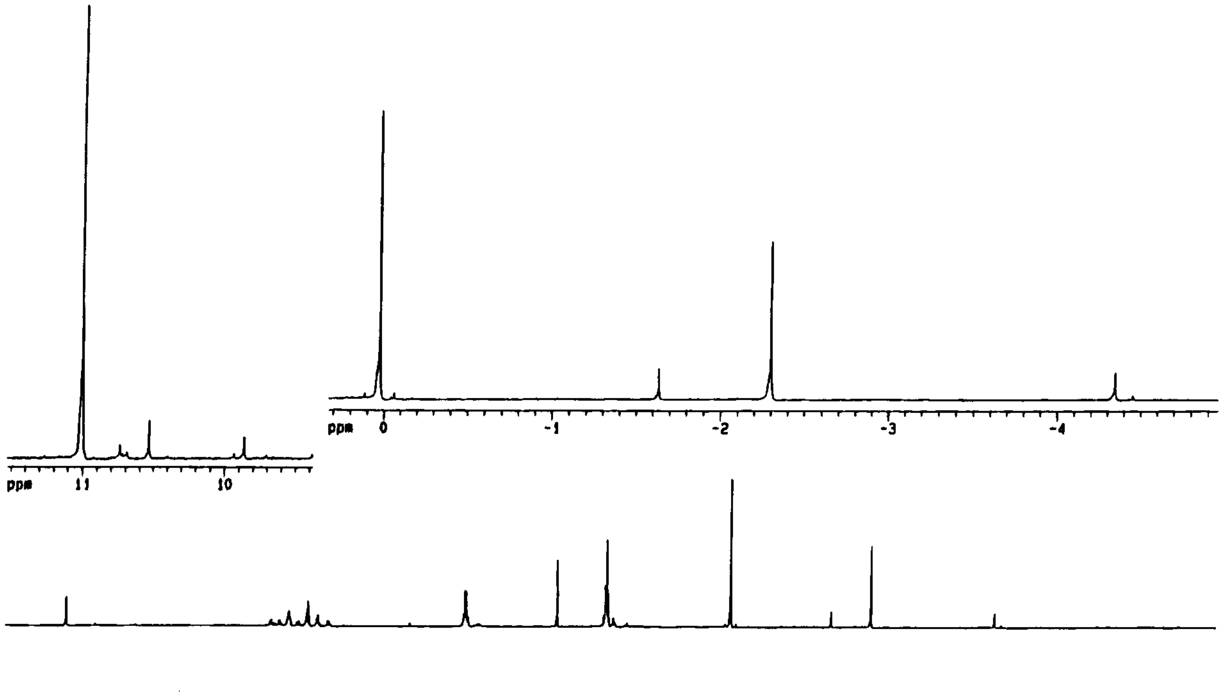

Figure 2. ^{1}H NMR spectrum of [(OEP)Zr(CH$_2$SiMe$_3$)][BPh$_4$] generated in situ in CD$_2$Cl$_2$. A small amount of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ is still present.

nometallic (OEP)Ta compounds, protonolysis routes allowed the formation of the cationic derivatives [(OEP)TaMe$_2$][BPh$_4$] and [(OEP)Ta(Me)(O^{t}Bu)][BPh$_4$].[4] These studies prompted us to find entry into cationic group 4 porphyrin derivatives and to investigate their reactivities toward alkenes.

Reaction of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ with 1 equiv of [HNMe$_2$Ph][BPh$_4$][16] or [HNEt$_2$CH$_2$Ph][BPh$_4$][16] in CH$_2$Cl$_2$ results in a slight color change to dark red. Attempts to generate crystalline material from a variety of solvents, however, failed. An oil, which turns into a foamy solid upon long exposure to vacuum, was isolated and identified as [(OEP)Zr(CH$_2$SiMe$_3$)][BPh$_4$] by ^{1}H NMR spectroscopy (eq 3).

$$\text{(OEP)M(CH}_2\text{SiMe}_3)_2 + [\text{HNMe}_2\text{Ph}][\text{BPh}_4] \rightarrow [\text{(OEP)Zr(CH}_2\text{SiMe}_3)][\text{BPh}_4] + \text{SiMe}_4 + \text{NMe}_2\text{Ph} \qquad (3)$$

$$\text{M} = \text{Zr, Hf}$$

Monitoring the protonolysis of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ by ^{1}H NMR spectroscopy in CD$_2$Cl$_2$ shows quantitative formation of [(OEP)Zr(CH$_2$SiMe$_3$)][BPh$_4$], 1 equiv of SiMe$_4$, and free NMe$_2$Ph. The resonances for the methine hydrogens are shifted downfield from 10.54 to 11.01 ppm, in accordance with the presence of a positive charge. The methylene and methyl resonances of the alkyl ligands are shifted from −4.44 and −1.62 to −4.32 and −2.30 ppm (Figure 2). Two effects, acting in opposite directions, are responsible for these shifts. The alkyl ligand in the five-coordinate cationic derivative, being closer to center of the porphyrin ring, experiences increased ring anisotropy resulting in an upfield shift.[17] The positive charge of the central metal induces a downfield shift, however, which should be strongest for the methylene resonances. Addition of a slight excess of pyridine moves the resonances to 10.73, −2.25, and −4.84 ppm. However, we were not able to isolate crystalline base adducts with bases such as THF, pyridine, *tert*-butylpyridine, or PMe$_3$. Treatment of [(OEP)Zr(CH$_2$SiMe$_3$)][BPh$_4$] with a slight excess of LiCH$_2$SiMe$_3$ in C$_6$D$_6$ regenerates the dialkyl precursor, therefore confirming our assignment. [(OEP)Hf(CH$_2$SiMe$_3$)][BPh$_4$] can be formed similarly, but both TTP dialkyl derivatives are unreactive under these conditions. The cationic compounds are stable for days in CD$_2$Cl$_2$, and surprisingly even in CDCl$_3$.

[(OEP)Zr(CH$_2$SiMe$_3$)][BPh$_4$] is unreactive toward ethylene (2−3 atm) in CD$_2$Cl$_2$ nor does any reaction occur when the cationic species are generated in situ in CD$_2$Cl$_2$ or C$_7$D$_8$. Attempted larger scale reactions of the cationic compound with ethylene were also unsuccessful.

Summary and Conclusions

Organometallic group 4 porphyrins can be prepared directly from dilithium porphyrinates and dialkyl metal halides in a one-pot synthesis in good yields. NMR studies show that the Zr is displaced out of the porphyrin plane with attendant ligands cis to each other. Cationic octaethylporphyrin derivatives are accessible via protonolysis routes; however, isolation of the products in crystalline form has proven difficult so far. From preliminary reactivity studies it is apparent that, unlike their metallocene analogs, cationic group 4 porphyrins are unreactive toward ethylene insertion. This contrasts with the facile insertion of small molecules into the Zr−C and Zr−H bonds of *cis*-ligated zirconium porphyrins. We have noted previously elongation of Zr−C bonds in these *cis*-dialkyl derivatives relative to their metallocene counterparts, which we ascribed to the steric demand imposed by the bulky porphyrin ring. In

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the absence of structural data we can only speculate that the relief in steric strain by going from a six-coordinate to a five-coordinate metalloporphyrin renders the Zr−C bonds less reactive in comparison to the metallocene analogs. On the other hand, back donation from the porphyrin ring to the transition metal might also be responsible for the decreased reactivity. Work toward the isolation of crystalline cationic octaethylporphyrin derivatives is in progress.

Experimental Section

General Considerations. Inert atmosphere glovebox and Schlenk-line techniques were used throughout the preparative procedures.[18] NMR tube experiments were performed either in flame-sealed or Teflon-stoppered NMR tubes, unless stated otherwise. Diethyl ether, hexanes, benzene, pentane, and toluene were all predried over 4 Å moleculer sieves and, with the exception of toluene, were all distilled from purple sodium/benzophenone under N_2. Toluene was distilled from sodium under N_2. Dichloromethane was predried over 4 Å moleculer sieves, degassed by three freeze, pump, and thaw cycles, and distilled from calcium hydride under N_2. All NMR solvents were dried like their undeuterated counterparts, but were purified by vacuum transfer, then passed through activated alumina.

$ZrCl_4$ and $HfCl_4$ were obtained from commercial sources and were sublimed before use. $Li_2OEP(THF)_n$,[19] $Li_2TTP(Et_2O)_2$,[20] $LiCH_2SiMe_3$,[21] $Zr(CH_2SiMe_3)_4$,[12] and $Hf(CH_2SiMe_3)_4$[12] were prepared according to the literature procedures. All other reagents were obtained from commercial sources and were used as received.

Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. UV/vis spectra were recorded in 0.2 cm quartz cells and are reported in the form λ_{max} in nm (log ϵ). Elemental analyses and mass spectra (EI, 70 eV) were performed within the College of Chemistry, University of California, Berkeley. ^1H and $^{13}C\{^1H\}$ spectra were recorded at ambient temperatures. Chemical shifts (δ) for ^1H NMR spectra are reported relative to residual protons in the deuterated solvents and for ^{13}C NMR spectra relative to carbons in the deuterated solvent.

$Zr(CH_2SiMe_3)_2Cl_2(OEt_2)_2$. $LiCH_2SiMe_3$ (1.21 g, 12.9 mmol) in 20 mL of Et_2O was slowly added to a stirred suspension of $ZrCl_4$ (1.50 g, 6.44 mmol) in 40 mL of Et_2O. The $ZrCl_4$ dissolved slowly, and a fine white precipitate formed. The solvent was removed in vacuo, and the crude product was extracted with 30 mL of an Et_2O/hexane (3:7) mixture. The solution was filtered, and the solvent was removed to yield 2.90 g (93%) of a viscous yellow oil, which was pure $Zr(CH_2SiMe_3)_2Cl_2(OEt_2)_2$ according to ^1H NMR spectroscopy. Attempts to obtain a crystalline material by recrystallization from a variety of solvents failed. Reaction of this compound with methanol in C_6D_6 afforded Et_2O and Me_4Si in the ratio 1:1. ^1H NMR (C_6D_6): δ 3.22 (br s, 8 H, CH_2O), 2.25 (br s, 4 H, CH_2Si), 0.96 (br s, 12 H, CH_3CH_2), 0.32 (br s, 18 H, CH_3Si).

$Zr(CH_2SiMe_3)Cl_3(OEt_2)_2$. Et_2O (20 mL) was vacuum transferred onto $LiCH_2SiMe_3$ (0.80 g, 8.51 mmol) and $ZrCl_4$ (2.82 g, 12.1 mmol). The reaction mixture was stirred for 2 h after which the solvent was removed in vacuo. A hexane/Et_2O (1:1) mixture (20 mL) was added, and the mixture was cooled to −40 °C for 2 h in order to precipitate excess $ZrCl_4$ and LiCl. After filtration the solvent was removed in vacuo to give 3.21 g (87%) of a viscous yellow oil. Reaction of this compound with methanol in C_6D_6 afforded Et_2O and Me_4Si in the ratio 2:1. ^1H NMR (C_6D_6): δ 3.29 (br q, 8 H, CH_2O), 2.80 (br s, 4 H, CH_2Si), 0.97 (t, 12 H, CH_3CH_2), 0.34 (s, 18 H, CH_3Si).

Generation of $(OEP)Zr(CH_2SiMe_3)_2$. $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$ (15.0 mg, 30.5 μmol) in 0.2 mL of CD_2Cl_2 was added to $Li_2OEP(THF)_{1.5}$ (20.0 mg, 30.5 μmol) in 0.2 mL of CD_2Cl_2. The ^1H NMR spectrum showed that only $(OEP)Zr(CH_2SiMe_3)_2$ had been formed.

Attempted Generation of $(OEP)Zr(CH_2SiMe_3)Cl$. $Zr(CH_2SiMe_3)Cl_3(Et_2O)_2$ (13.0 mg, 30.5 μmol) in 0.5 mL of C_6D_6 was added to $Li_2OEP(THF)_{1.5}$ (20.0 mg, 30.5 μmol) in 0.5 mL of C_6D_6. Most of the $Li_2OEP(THF)_{1.5}$ dissolved, and a ^1H NMR spectrum showed that only $(OEP)Zr(CH_2SiMe_3)_2$ and some other OEP derivative was present, but no $(OEP)Zr(CH_2SiMe_3)Cl$.

$(OEP)Zr(CH_2SiMe_3)_2$. $Zr(CH_2SiMe_3)_4$ (0.223 g, 0.508 mmol) in 10 mL of Et_2O was added to $ZrCl_4$ (0.118 g, 0.508 mmol) in 10 mL of Et_2O at −10 °C. The reaction mixture was allowed to warm to room temperature and was then added to $Li_2OEP(THF)_{1.5}$ (0.633 g, 0.967 mmol) in 20 mL of CH_2Cl_2 at −78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for 2.5 h. The solvent was then removed in vacuo and the product extracted with 10 mL of CH_2Cl_2. The filtrate was concentrated to 5 mL, and then 20 mL of pentane was added. Red crystals (0.613 g, 71%) were collected by filtration after slowly cooling the solution to −40 °C over night and identified as $(OEP)Zr)CH_2SiMe_3)_2$ by ^1H NMR spectroscopy.[2d]

$(OEP)Hf(CH_2SiMe_3)_2$. $LiCH_2SiMe_3$ (0.088 g, 0.933 mmol) and $HfCl_4$ (0.150 g, 0.466 mmol) were stirred in 10 mL of Et_2O for 1 h. This mixture was then added to $Li_2OEP(THF)_{1.5}$ (0.255 g, 0.389 mmol) in 20 mL of CH_2Cl_2 at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was then removed under vacuum and the product extracted with 10 mL of toluene. The toluene was concentrated to 5 mL, and 15 mL of hexane was added. Red crystals (0.297 g, 82%) which contained 0.5 equiv of toluene were obtained after slow cooling to −40 °C. Mp: 125 °C dec. ^1H NMR (C_6D_6): δ 10.57 (s, 4 H, CH), 3.94 (m, 16 H, CH_2CH_3), 1.85 (t, 24 H, CH_2CH_3), −1.13 (s, 18 H, $SiCH_3$), −4.47 (s, 4 H, CH_2Si). ^{13}C NMR (C_6D_6): δ 147.9, 142.7, 102.5, 57.1, 20.2, 18.5, 2.8. UV/vis (CH_2Cl_2): 332 (4.27), 398 (5.47), 532 (4.11), 570 (4.42). EI/MS: 973 (M^+ + CH_2SiMe_3, 30), 886 (M^+, 45). Anal. Calcd for $C_{70}H_{47.5}N_4Si_2Hf$: C, 61.23; H, 7.57; N, 6.01. Found: C, 61.28; H, 6.92; N, 6.61.

$(TTP)Zr(CH_2SiMe_3)_2$. Et_2O (75 mL) was condensed onto $Li_2TTP(Et_2O)_2$ (1.05 g, 1.24 mmol), $LiCH_2SiMe_3$ (0.279 g, 2.967 mmol), and $ZrCl_4(THF)_2$ (0.560 g, 1.483 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Soon the color had changed from blue-green to orange. The solvent was then removed in vacuo, the product extracted with 20 mL of CH_2Cl_2, and the filtrate concentrated to 5 mL. Pentane (20 mL) was added and the solution slowly cooled to −40 °C to afford 1.05 g (89%) of blue microcrystals which contained 0.25 equiv of CH_2Cl_2. Mp: 130 °C dec. ^1H NMR (C_6D_6): δ 9.10 (s, 8 H, pyrrole-H), 8.65 (br s, 4 H, Ph-H), 7.76 (br s, 4 H, Ph-H), 7.35 (br s, 4 H, Ph-H), 7.24 (br s, 4 H, Ph-H), 2.40 (s, 12 H, tol-CH_3), −0.96 (s, 18 H, $SiCH_3$), −3.38 (s, 4 H, CH_2Si). ^{13}C NMR ($CDCl_3$, −10 °C) 150.3, 138.8, 137.8, 134.7, 134.0, 132.0, 127.8, 127.6, 125.7, 56.6, 21.7, 1.8. UV/vis (CH_2Cl_2): 414 (5.57), 513 (3.61), 547 (4.32), 580 (3.37). EI/MS: 847 (M^+ − CH_2SiMe_3, 60). Anal. Calcd for $C_{56.25}H_{58.5}Cl_{0.5}N_4Si_2Zr$: C, 70.69; H, 6.17; N, 5.86. Found: C, 70.19; H, 5.97; N, 6.12.

$(TTP)Hf(CH_2SiMe_3)_2$. $Hf(CH_2SiMe_3)_4$ (0.119 g, 0.226 mmol) and $HfCl_4$ (0.072 g, 0.226 mmol) were stirred in 20 mL of Et_2O for 1 h. This mixture was then added to $Li_2TTP(Et_2O)_2$ (0.320 g, 0.377 mmol) in 20 mL of Et_2O. Soon the color changed from blue-green to orange and the reaction mixture was allowed to stir for 12 h. The solvent was removed in vacuo and the crude product recrystallized from 15 mL of Et_2O at −40 °C to afford 0.299 g (79%) of blue crystals. Mp: 140 °C dec. ^1H NMR

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(C_6D_6): δ 9.12 (s, 8 H, pyrrole-*H*), 8.63 (br s, 4 H, Ph-*H*), 7.76 (br s, 4 H, Ph-*H*), 7.34 (br s, 4 H, Ph-*H*), 7.24 (br s, 4 H, Ph-*H*), 2.40 (s, 12 H, tol-C*H*$_3$), −0.96 (s, 18 H, SiC*H*$_3$), −4.06 (s, 4 H, C*H*$_2$Si). ^{13}C NMR ($CDCl_3$, −10 °C) δ 150.1, 138.6, 137.7, 134.6, 133.8, 132.0, 127.7, 127.5, 125.6, 58.0, 21.5, 2.3. UV/vis (CH_2Cl_2): 413 (5.48), 513 (3.57), 548 (4.21), 580 (3.23). EI/MS: 1110 (M^+ + CH_2SiMe_3, 45), 1024 (M^+). Anal. Calcd for $C_{56}H_{58}N_4Si_2Hf$: C, 65.83; H, 5.72; N, 5.48. Found: C, 65.47; H, 5.53; N, 5.62.

[(OEP)Zr(CH_2SiMe_3)][BPh_4]. CH_2Cl_2 (10 mL) was condensed onto (OEP)Zr(CH_2SiMe_3)$_2$ (0.153 g, 0.192 mmol) and [$HNMe_2Ph$][BPh_4] (0.080 g, 0.188 mmol). The reaction mixture was allowed to slowly warm to room temperature after which it was filtered. Toluene (15 mL) was added and the solution slowly cooled to −40 °C. An oily red substance precipitated at the side of the flask and was separated and dried in vacuo. The oily red residue of [(OEP)Zr(CH_2SiMe_3)][BPh_4] still contained some Me_2NPh (0.101 g, 51%). Reaction of stoichiometric amounts of [(OEP)Zr(CH_2SiMe_3)][BPh_4] and $LiCH_2SiMe_3$ in C_6D_6 afforded (OEP)Zr(CH_2SiMe_3)$_2$. ^{1}H NMR (CD_2Cl_2): δ 11.01 (s, 4 H, C*H*), 7.34 (br m, 8 H, ortho-*H*), 7.03 (t, 8 H, meta-*H*), 6.69 (t, 4 H, para-*H*), 4.26 (m, 16 H, C*H*$_2$CH$_3$), 1.98 (t, 24 H, CH$_2$C*H*$_3$), −2.30 (s, 9 H, SiC*H*$_3$), −4.32 (s, 2 H, C*H*$_2$Si).

[(OEP)Hf(CH_2SiMe_3)][BPh_4] was produced in a manner similar to [(OEP)Zr(CH_2SiMe_3)][BPh_4] and was isolated as a red, oily compound in 46% yield. ^{1}H NMR ($CDCl_3$): δ 10.93 (s, 4 H, C*H*), 7.27 (br m, 8 H, ortho-*H*), 6.99 (t, 8 H, meta-*H*), 6.83 (t, 4 H, para-*H*), 4.33 (m, 16 H, C*H*$_2$CH$_3$), 2.04 (t, 24 H, CH$_2$C*H*$_3$), −2.38 (s, 9 H, SiC*H*$_3$), −5.01 (s, 2 H, C*H*$_2$Si).

Generation of [(OEP)Zr(CH_2SiMe_3)][BPh_4] in Situ. (OEP)Zr(CH_2SiMe_3)$_2$ (10.5 mg, 12.5 μmol) and [$HNMe_2Ph$][BPh_4] (5.3 mg, 12.5 μmol) were reacted in CD_2Cl_2. ^{1}H NMR showed formation of [(OEP)Zr(CH_2SiMe_3)][BPh_4] (>90%), $SiMe_4$, and Me_2NPh as well as the presence of a small amount of (OEP)Zr(CH_2SiMe_3)$_2$.

Attempted Reaction of [(OEP)Zr(CH_2SiMe_3)][BPh_4] with Ethylene. [(OEP)Zr(CH_2SiMe_3)][BPh_4] (5.0 mg, 4.9 μmol) in CD_2Cl_2 was degassed by three freeze, pump, and thaw cycles, and ethylene gas (2−3 atm) was admitted. No reaction took place within 1 day as judged by ^{1}H NMR spectroscopy.

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