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Notes

Synthesis and Characterization of (2,6-^{i}PrNCN)HfCl$_2^-$ and (3,5-MeNCN)$_2$Hf^{2-} (where NCN = 2,6-bis[phenylazanidyl]methylphenyl): New Trianionic Pincer Ligands

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*Summary: The synthesis, isolation, and metalation of the trianionic NCN-pincer ligand [2,6-^{i}PrNCNLi$_3$]$_2$ (**2**) is described. The terdentate coordination ability of **2** is demonstrated in the synthesis of the hafnium dichloride anion [2,6-^{i}PrNCNHfCl$_2$][Li(DME)$_3$] (**3-DME**). Complex **3-DME** is distorted square pyramidal in the solid state, but NMR evidence indicates the complex is fluxional and trigonal bypyramidal in solution. Straightforward ligand modification provides the additional trianionic pincer ligand [3,5-MeNCNLi$_2$]$_2$[Li$_2$(DME)$_6$] (**5**). This sterically smaller ligand leads to the hafnium pincerate dianion complex [(3,5-MeNCN)$_2$Hf][Li$_2$(DME)$_2$] (**6**), which contains two trianionic pincer ligands. The new compounds are characterized by elemental analysis, multinuclear NMR, and X-ray diffraction crystallography.*

Introduction

Shaw described the synthesis of the first pincer ligand, 1,3-bis[(di-*tert*-butylphosphino)methyl]benzene, in 1976 and its coordination to Rh(III), Ir(III), and group X(II) ions.[1] Since then, both the pendant arms and backbone architecture of the parent PCP model pincer ligand have been systematically modified.[2] These modifications enable exquisite control over the electronic[3] and steric environment imparted to the metal ion of interest and have yielded a rich and diverse chemistry[4] including some chiral variants.[5] Pincer ligands are typically monoanionic[6] and are most often used as ancillary ligands for late transitions metals.[7] The soft−hard−soft (SHS-pincer) arrangement of donor atoms is a common pincer attribute, best suited for soft metals, and can result in remarkably stable complexes.[2,4] To alter the pincer architecture so that it matches an early transition metal, we sought a hard−hard−hard (3H-pincer) combination. As such, we began synthesizing ligands that can chelate via amido−arylide−amido linkages. Herein we report the synthesis and isolation of the two trianionic pincer ligand precursors, [2,6-^{i}PrNCNLi$_3$]$_2$ (**2**) and [3,5-MeNCNLi$_2$]$_2$[Li$_2$(DME)$_6$] (**5**), and their hafnium pincerate complexes.

Results and Discussion

While double N−H deprotonation of **1** is straightforward and has been previously demonstrated,[8] the Ar−H proton proved difficult to remove. Access to the trilithio salt [2,6-^{i}PrNCNLi$_3$]$_2$ (**2**) was eventually accomplished by refluxing the parent derivative *N,N′*-[1,3-phenylenebis(methylene)]bis-2,6-diisopropylaniline (2,6-^{i}PrNCNH$_3$) (**1**) in toluene with MeLi (eq 1). The solid-state structure of **2** was determined by X-ray diffraction, which revealed the C_2-symmetric dimer presented in Figure 1. Two aryl-Li atoms (Li1 and Li1A) sit within a 16-membered twisted macrocycle similar to that previously described for the dilithio derivative [2,6-^{i}PrNCNHLi$_2$]$_2$.[8] One LiC$_{ipso}$LiC$_{ipso}$ and two LiNLiN rhombi comprise the hexalithio core. The central rhombus contains two lithium atoms that bridge the C$_{ipso}$ pincer backbone with an average Li−C$_{ipso}$ distance of 2.219(12) Å.[9] Additional close contacts to adjacent nitrogen atoms range from 2.161(9) to 2.243(9) Å, thus rendering Li1 and Li1A four coordinate. The remaining lithium cations are also four coordinate, including close interactions with the central aryl C$_{ipso}$ observed for each (Li2−C1A = 2.229(10), Li2A−C1 = 2.222(10), Li3−C1A = 2.284(10), and Li3A−C1 = 2.362(10) Å).

Dimer **2** is readily soluble in tetrahydrofuran (THF), toluene, and 1,2-dimethoxyethane (DME), but only sparingly soluble in diethyl ether (Et$_2$O), benzene, and aliphatic hydrocarbons. Group

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(1) (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) Shaw, B. L.; Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Goodfellow, R. J. *J. Chem. Soc., Chem. Commun.* **1979**, 498. (c) Shaw, B. L.; Errington, R. J.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2312. (d) Errington, R. J.; Shaw, B. L. *J. Organomet. Chem.* **1982**, *238* (3), 319. (e) Crocker, C.; Empsall, H.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, *7*, 1217.

(2) For recent reviews see: (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (b) Slagt, M. Q.; van Zwieten, D. A. P.; Moerkerk, A.; Gebbink, R.; van Koten, G. *Coord. Chem. Rev.* **2004**, *248, 2275*.

(3) For a specific discussion of *para*-substitution effects see: Slagt, M. Q.; Rodríguez, G.; Grutters, M. M. P.; Gebbink, R. J. M. K.; Klopper, W.; Jenneskens, L. W.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem.−Eur. J.* **2004**, *10*, 1331.

(4) Pincer-catalysts applied to organic synthesis have recently been reviewed: Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

(5) For some examples of chiral pincer ligands and enantioselective catalysis see: Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624* (1−2), 271.

(6) For a recent report describing a trianionic OCO-pincer ligand see: Agapie, T.; Bercaw, J. E. *Organometallics* **2007**, *26*, 2957.

(7) Trianionic N,N,N pincer-type ligands have been reported: (a) Schrock, R. R.; Lee, J.; Liang, L. C.; Davis, W. M. *Inorg. Chim. Acta* **1998**, *270*, 353. Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643. (b) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 2777.

(8) The synthesis of the parent ^{i}PrNCNH$_3$ ligand has been reported: Daniele, S.; Hitchcock, P. B.; Lappert, M. F.; Nile, T. A.; Zdanski, C. M. *J. Chem. Soc., Dalton Trans.* **2002**, 3980.

10.1021/om700597u CCC: $37.00

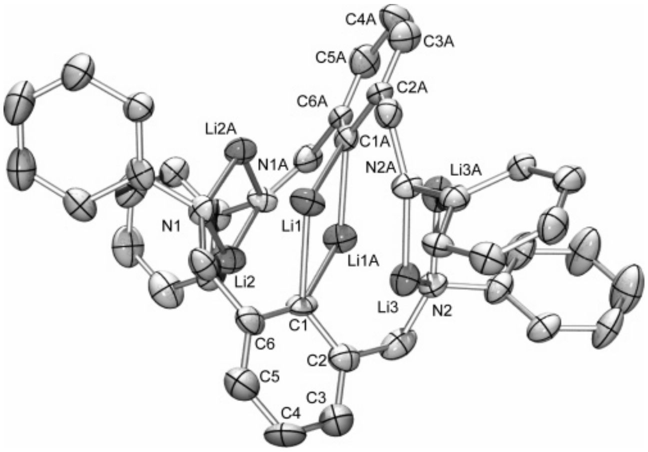
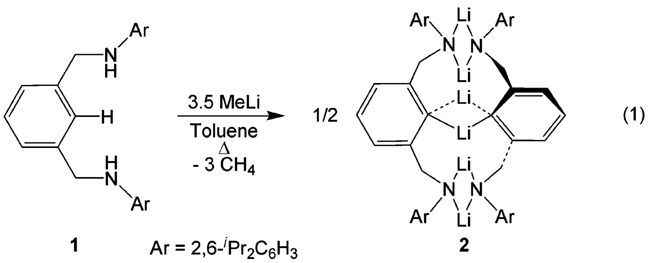
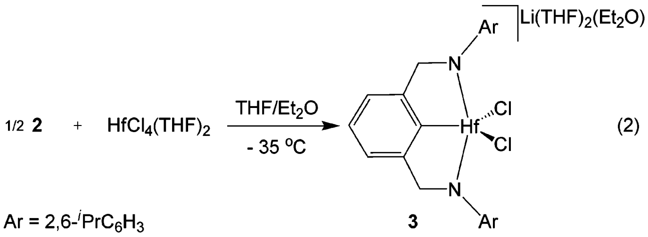


Figure 1. Molecular structure of **2** with ellipsoids drawn at the 50% probability level. Isopropyl groups and hydrogen atoms are removed for clarity.



IV metalation reactions were attempted in various solvents, but THF provided the best result. The hafnium complex [2,6-^{i}-PrNCNHfCl$_2$][Li(THF)$_2$(Et$_2$O)] (**3**) was obtained as a colorless crystalline solid by treating **2** with HfCl$_4$(THF)$_2$ at −35 °C in THF (eq 2).



The identity of **3** and its assignment as a pincerate complex was confirmed by X-ray crystallography and NMR spectroscopy. Numerous attempts to isolate single crystals of the THF/Et$_2$O-solvated species were unsuccessful. Suitable crystals for X-ray analysis could be obtained only from the synthesis of **3** in THF followed by recrystallization from DME layered with diethyl ether (Figure 2). The solid-state structure of **3-DME** indicates that exactly three DME molecules encapsulate the lithium ion. As a result, the lithium is well separated (10.8 Å) from the Hf atom and provides an opportunity to analyze the influence of the trianionic pincer ligand on the metal core geometry (Figure 2).

The coordination sphere of the hafnium ion in **3-DME** is considerably distorted from trigonal bypyramidal and more closely resembles a square pyramid with C_s symmetry. The Cl1−N1−C1−N2 atoms occupy basal positions, and the sum of their angles is nearly 360° (345° observed). The Hf center sits above the plane described by N1−C1−N2 by 0.4 Å, and the bite angle created by the pincer ligand is small (N2−Hf−N1 = 141.0(3)°). The Hf−C1 bond length of 2.217(8) Å is reasonable, and a $^{13}C\{^1H\}$ NMR spectrum of **3** revealed a broad resonance at 201.55 ppm, appropriate for C_{sp^2}-Hf.

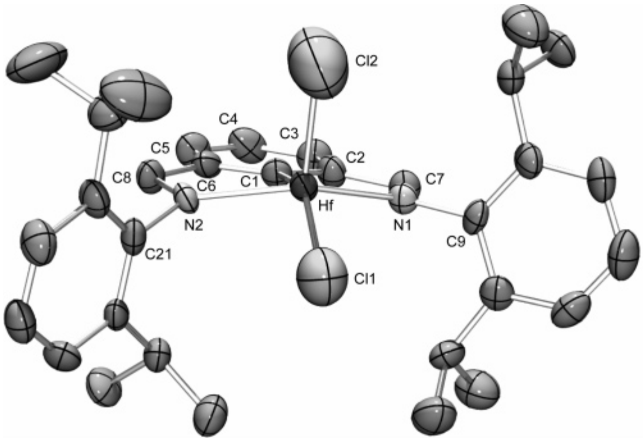
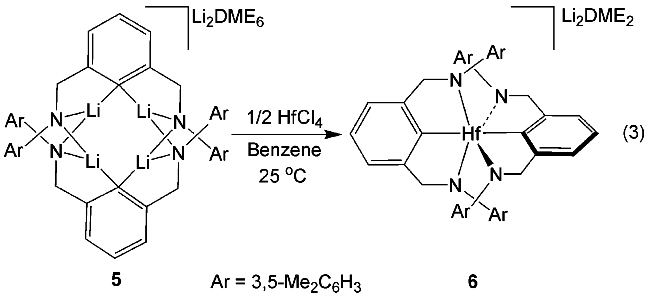


Figure 2. Molecular structure of **3-DME** with ellipsoids drawn at the 50% probability level. Hydrogen atoms and lithium counterions are removed for clarity.

C_s symmetry is not maintained in solution. Instead, the basal and apical chlorides are averaged over two positions providing overall C_{2v} symmetry. The ^{1}H NMR spectrum of **3** indicated the methine (4.00 ppm) and methylene protons (5.56 ppm) are equivalent, and only two unique doublets are observed for the ^{i}Pr methyls at 1.49 and 1.25 ppm ($J = 6.0$ Hz). Broad resonances for the coordinated solvent molecules are observed and complement the solid-state structure findings.[10]

The synthesis of **3** cannot be achieved above milligram quantities due to separation complications from the presence of LiCl. To improve the solubility and yield of these new pincerate complexes, we altered the N-aryl substituent and synthesized a trilithio salt bearing 3,5-CH$_3$ groups. We also anticipated the 3,5-substitution pattern would minimize steric congestion around the metal core. When yellow **5**[11] is treated with HfCl$_4$ in benzene, the solution becomes colorless and a white precipitate forms (eq 3), which is removed by filtration. After all volatiles are removed a ^{1}H NMR spectrum of the crude material revealed a symmetric complex with a broad singlet at 5.56 ppm that is typical of pincer arm methylene protons of at least C_{2v} symmetry.



A single-crystal X-ray crystallography experiment identified the pseudo−D_{2d} symmetric dianionic hafnium pincerate complex **6**, which features two trianionic pincer ligands and is displayed

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(9) Similar bridging Ar−Li interactions are observed for the monolithiated {(2,6-CH$_2$NMe$_2$)C$_6$H$_2$]Li NCN pincer: Steenwinkel, P.; James, S. L.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Chem.−Eur. J.* **1996**, *13*, 1440.

(10) Similar ^{1}H NMR resonances are observed for the ligand protons regardless of the solvent coordinated to Li.

(11) Compound **5** is obtained by treating the *ipso*-Br derivative 3,5-MeNCNH$_2$Br (**4**) with 3.3 equiv of ^{n}BuLi. See Supporting Information for additional details pertaining to the synthesis of **4**.

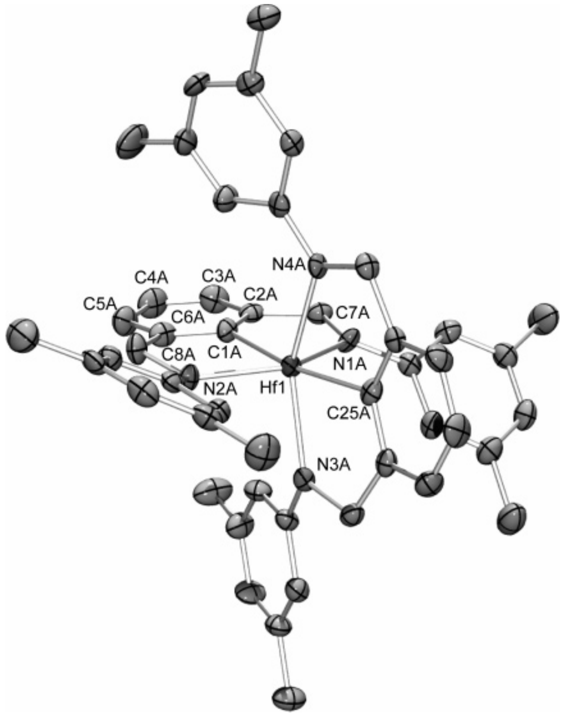

Figure 3. Molecular structure of **6** with ellipsoids drawn at the 50% probability level. Lithium counterions and solvent molecules are removed for clarity.

in Figure 3. The asymmetric unit consists of two crystallographically independent molecules. The lithium atoms (not shown) bridge a pair of nitrogen atoms from opposed ligands and are each coordinated by a molecule of DME. The two trianionic pincer ligands are coordinated in a meridional fashion and form a distorted octahedral coordination sphere about the hafnium metal center. Small bite angles are again observed for both the NCN ligands (N1A−Hf1−N2A = 142.80(12)° and N3A−Hf1−N4A = 144.07(12)°), and the Hf1−C1A and Hf1−C25A bond distances are both 2.277(4) Å, which is 0.06 Å longer than in **3**. The major difference between **3** and **6** is the orientation of the N-aryl groups. In **3** the N-aryl rings are perpendicular to the $-CH_2-N-Hf-$ plane, whereas in **6** they are nearly coplanar with an average dihedral angle of ∼16°. Clearly by locating the smaller methyl substituents in the 3,5-positions, the N-aryl groups are able to rotate and allow a second ligand to approach and bind to the hafnium ion.

This report establishes the synthesis of two new trianionic NCN-pincer ligands and their coordination to Hf(IV). The trilithio salts $[2,6\text{-}{}^{i}PrNCNLi_3]_2$ (**2**) and $[3,5\text{-}MeNCNLi_2]_2[Li_2(DME)_6]$ (**5**) are dimers in both the solid and solution state and can be synthesized in good yields. Complex **3** can be made in only milligram quantities but offers the first opportunity to examine the influence of a trianionic NCN-pincer ligand on early transition metal coordination geometry. The results from X-ray crystallography indicate a rare square-pyramidal Hf(IV) core in the solid state for **3**.[12,13] By altering the ligand sterics the hafniumate dianion (**6**) containing two pincer ligands can be synthesized in moderate yield (54%). Three important findings are established: (1) trilithio salts with classic pincer architecture can be synthesized and are viable ligand precursors for early transition metals, (2) the trianionic pincer ligand is capable of coordinating in a meridional terdentate fashion analogous to common monoanionic pincer ligands, and (3) choice of N-aryl group sterics determines the metal complex composition and geometry.

Experimental Section

General Procedures. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Pentane, hexanes, toluene, diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane were dried using a GlassContour drying column. C_6D_6 (Cambridge Isotopes) was dried over sodium−benzophenone ketyl, distilled or vacuum transferred, and stored over 4 Å molecular sieves. Sublimed $HfCl_4$ was purchased from Strem Chemicals and used without further purification. MeLi, 1.6 M in diethyl ether, was purchased from Acros. NMR spectra were obtained on Gemini (300 MHz), VXR (300 MHz), or Mercury (300 MHz) spectrometers. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual protio solvent peak was referenced as an internal reference. GC/MS spectra were recorded on an Agilent 6210 TOF-MS instrument. Elemental analyses were determined by Robertson Microlit Laboratories Inc. and Complete Analysis Laboratories Inc.

Synthesis of $[2,6\text{-}{}^{i}PrNCNLi_3]_2$ (2). To a solution of **1** (10.0 g, 21.1 mmol) in 250 mL of toluene was added 46.1 mL of MeLi solution (1.6 M, 73.8 mmol) via syringe at −35 °C. The solution was allowed to warm to room temperature and then refluxed for 45 min. All volatiles were removed in vacuo, and the remaining solid was suspended in diethyl ether, filtered, and washed with liberal amounts of diethyl ether followed by pentane to yield **2** as a white powder. The product can be recrystallized from hot toluene as colorless crystals; yield 7.28 g (15.3 mmol, 70%). ^1H NMR (300 MHz, C_6D_6, δ): 7.22−6.91 (m, 10H, Ar Hs), 5.25 (d, $J = 15$ Hz, 4H, $-CH_2-$), 4.35 (d, $J = 15$ Hz, 4H, $-CH_2-$), 3.39 (sept, $J = 6$ Hz, 2H, $-CH(CH_3)_2$), 2.39 (sept, $J = 6$ Hz, 2H, $-CH(CH_3)_2$), 1.30 (d, $J = 6$ Hz, 6H, $-CH(CH_3)_2$), 1.23 (d, $J = 6$ Hz, 6H, $-CH(CH_3)_2$), 0.61 (d, $J = 6$ Hz, 6H, $-CH(CH_3)_2$), 0.16 (d, $J = 6$ Hz, 6H, $-CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.36 Hz, C_6D_6, δ): 23.60 ($-CH(CH_3)_2$), 24.30 ($-CH(CH_3)_2$), 25.87 ($-CH(CH_3)_2$), 27.61 ($-CH(CH_3)_2$), 29.16 ($-CH(CH_3)_2$), 30.36 ($-CH(CH_3)_2$), 67.29 ($-CH_2-$), 122.96 (s, *C*H, aromatic), 124.50 (s, *C*H, aromatic), 125.04 (s, *C*H, aromatic), 126.43 (s, *C*H, aromatic), 131.26 (s, *C*H, aromatic), 143.09 (s, *C*H, aromatic), 148.19 (s, *C*H, aromatic), 153.62 (s, *C*H, aromatic), 156.45 (s, N−*C*, aromatic), 164.25 (br s, *C*−Li, aromatic). Anal. Calcd for $C_{64}H_{82}Li_6N_4$: C, 81.00; H, 8.71; N, 5.90. Found: C, 80.72; H, 8.44; N, 5.64.

Synthesis of $[(2,6\text{-}{}^{i}PrNCN)HfCl_2][Li(THF)_2(Et_2O)]$ (3). A suspension of $HfCl_4(THF)_2$ (150 mg, 323 μmol) in 5 mL of THF was cooled to −35 °C and added dropwise to a solution of **2** (153 mg, 161 μmol) in 5 mL of THF at −35 °C. The solution was allowed to warm to room temperature and stirred for an additional 60 min. The solvent was removed in vacuo, and the remaining solid was extracted with diethyl ether (2 × 5 mL). The organic layers were combined, filtered, concentrated, and then recrystallized at −35 °C. The product **3** was filtered off as an off-white crystalline powder; crude yield 51 mg (48 μmol, 16%). To obtain analytically pure samples, the crude product can be recrystallized multiple times from a saturated diethyl ether solution at −35 °C. After multiple recrystallizations THF solvent molecules were replaced with diethyl ether. ^1H NMR (300 MHz, C_6D_6, δ): 7.22−6.91 (m, 10H, Ar Hs), 5.56 (s, 4H, −CH2−), 4.00 (sept, $J = 6$ Hz, 4H, $-CH(CH_3)_2$), 3.10, (q, $J = 6$ Hz, 4H, $Et_2O/-OCH_2-$) 3.07 (br s, 8H, THF/$-OCH_2-$), 1.49 (d, $J = 6$ Hz, 12H, $-CH(CH_3)_2$), 1.25 (d, $J = 6$ Hz, 12H, $-CH(CH_3)_2$), 1.24 (br s, 8H, THF/$-CH_2-$), 0.96 (t, $J = 6$ Hz, 6H, Et2O/$-CH_3$). $^{13}C\{^1H\}$ NMR (75.36 MHz, C_6D_6, δ):

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[12] (a) Aizenberg, M.; Turculet, L.; Davis, W. M; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795. (b) Liang, L. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **2000**, *19*, 2526. (c) Schrock, R. R.; Adamchuck, J.; Ruhland, K.; Lopez, L. P. H.; *Organometallics* **2000**, *24*, 857.

[13] Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 1769.

15.45 (s, Et$_2$O/−O*C*H$_3$), 24.74 (s, −*C*H(CH$_3$)$_2$), 25.82 (s, THF/−*C*H$_2$−), 28.32 (s, −CH(*C*H$_3$)$_2$), 28.7 (s, −CH(*C*H$_3$)$_2$), 66.09 (THF/−O*C*H$_2$), 69.33 (s, Et$_2$O/−O*C*H$_2$−), 73.74 (s, −*C*H$_2$−), 119.04 (s, *C*H, aromatic), 124.33 (s, C(^{i}Pr)*C*H, aromatic), 124.99 (s, *C*H, aromatic), 127.52 (s, C(^{i}Pr)CH*C*H, aromatic), 148.44 (s, C(CH$_2$)-*C*H, aromatic), 151.85 (s, C(CH$_2$)CH*C*H, aromatic), 156.07 (s, N−*C*, aromatic, 201.55 (s, Hf−*C*, aromatic). Anal. Calcd for C$_{44}$H$_{71}$Cl$_2$HfLiN$_2$O$_6$: C, 53.90; H, 7.30; N, 2.86. Found: C, 53.84; H, 6.63; N, 3.00.

Synthesis of 3,5-MeNCNH$_2$Br (4). To a solution of 3,5-dimethlyaniline (8.26 mL, 66 mmol) in 125 mL of THF was added 26.7 mL of ^{n}BuLi solution (2.5 M in hexanes, 66 mmol) via syringe at 0 °C. The solution was allowed to warm to room temperature, and then 2-bromo-1,3-bis(bromomethyl)benzene (11.4 g, 33 mmol) was added as a THF (30 mL) solution. The solution quickly turned dark brown and was refluxed for 20 h. After removing all volatiles the resulting brown oil was taken up in diethyl ether and washed with H$_2$O (2 × 10 mL). The organic layer was dried over MgSO$_4$, filtered, and then evaporated. The resulting light brown solid was recrystallized from hot hexanes to provide **3** as a tan microcrystalline solid; yield 7.31 g (17.3 mmol, 52%). ^{1}H NMR (300 MHz, C$_6$D$_6$, δ): 7.14 (d, $J = 6$ Hz, 2H, C*H*CHC*H*), 6.86 (t, $J = 6$ Hz, 1H, CHC*H*CH), 6.35 (s, 2H, C(CH$_3$)C*H*C(CH$_3$)), 6.14 (s, 4H, N−CC*H*), 4.25 (d, $J = 6$ Hz, 4H, −C*H*$_2$−), 3.52 (t, $J = 6$ Hz, N*H*), 2.10 (s, 12H, −C*H*$_3$). ^{13}C{^{1}H} NMR (75.36, C$_6$D$_6$, δ): 22.02 (s, *C*H$_3$), 49.28 (s, −*C*H$_2$−), 111.53 (s, *C*HC(CH$_3$)CHC(CH$_3$)*C*H, aromatic), 120.49 (s, CHC(CH$_3$)*C*HC(CH$_3$)CH, aromatic), 124.37 (s, *C*−Br, aromatic), 127.92 (s, CH*C*HCH, aromatic), 128.33 (s, *C*HCH*C*H, aromatic), 139.17 (s, CH*C*(CH3)CH*C*(CH$_3$)CH, aromatic), 139.94 (s, *C*CHCH, aromatic), 148.61 (s, N−*C*, aromatic). ESI-MS (*m*/*z*): [M + H]$^+$ calcd for C$_{24}$H$_{27}$BrN$_2$, 423.144; found, 423.142. Anal. Calcd for C$_{24}$H$_{27}$BrN$_2$: C, 68.08; H, 6.43; N, 6.62. Found: C, 67.92; H, 6.61; N, 6.62.

Synthesis of [3,5-MeNCNLi$_2$]$_2$[Li$_2$(DME)$_6$] (5). To an orange DME (3 mL) solution of **4** (500 mg, 1.18 mmol) was added 3.3 equiv of ^{n}BuLi solution (1.56 mL, 2.5 M in hexanes, 3.89 mmol) via syringe at −35 °C. Upon warming to room temperature, a bright yellow precipitate formed. After stirring for 5 min the solution was filtered to provide a yellow solid that was washed with DME then dried in vacuo to provide **5** as a yellow microcrystalline solid; yield 366 mg (0.58 mmol, 50%. The yellow salt **5** can be further purified by recrystallization from hot benzene if necessary. ^{1}H NMR (300 MHz, C$_6$D$_6$, δ): 7.50 (s, 4H, C*H*CHC*H*), 7.50 (s, 2H, CHC*H*CH), 6.08 (br s, 4H, C(CH$_3$)C*H*C(CH$_3$)), 6.06 (s, 8H, N−CC*H*), 4.78 (s, 8H, −C*H*$_2$−), 2.90 (br s, 36H, DME/−OC*H*$_3$), 2.83 (br s, 24H, DME/−C*H*$_2$O), 2.19 (s, 24H, −C*H*$_3$). ^{13}C{^{1}H} NMR (75.36, toluene-*d*$_8$, δ): 22.14 (s, *C*H$_3$), 58.98 (s, DME/−O*C*H$_2$), 60.89 (s, −*C*H$_2$−), 70.95 (s, DME/−O*C*H$_3$), 111.92 (br s, *C*−Li, aromatic), 113.56 (s, *C*HCH*C*H, aromatic), 123.80 (s, CHC(CH$_3$)*C*HC(CH$_3$)-CH, aromatic), 126.18 (s, CH*C*HCH, aromatic), 138.05 (s, CH*C*(CH$_3$)CH*C*(CH$_3$)CH, aromatic), 142.43 (s, *C*HC(CH$_3$)CHC-(CH$_3$)*C*H, aromatic), 156.99 (s, *C*CHCH, aromatic), 160.54 (s, N−*C*, aromatic). Anal. Calcd for C$_{72}$H$_{110}$HfLi$_6$N$_4$O$_{12}$: C, 68.34; H, 8.76; N, 4.43. Found: C, 68.12; H, 8.49; N, 4.55.

Synthesis of [(3,5-MeNCN)$_2$Hf][Li$_2$(DME)$_2$] (6). Benzene solutions of **5** (300 mg, 0.24 mmol) and HfCl$_4$ (76 mg, 0.24 mmol) were combined at room temperature. The initial suspension quickly dissolved, and then a white precipitate formed which was removed by filtration. The product was precipitated as a white microcrystalline solid by addition of the filtrate (5 mL) to 100 mL of cold pentane; yield 7.31 g (0.13 mmol, 54%). ^{1}H NMR (300 MHz, C$_6$D$_6$, δ): 7.45 (s, 4H, C*H*CHC*H*), 7.45 (s, 2H, CHC*H*CH), 7.01 (s, 8H, N−CC*H*), 6.16 (s, 4H, C(CH$_3$)C*H*C(CH3), 5.56 (s, 8H, −C*H*$_2$−), 2.89 (br s, 12H, DME/−OC*H*$_3$), 2.78 (br s, 8H, DME/−C*H*2O), 2.00 (s, 24H, −C*H*$_3$). ^{13}C{^{1}H} NMR (75.36, C$_6$D$_6$, δ): 21.97 (s, *C*H$_3$), 59.28 (s, DME/−O*C*H$_2$), 69.26 (s, −*C*H$_2$−), 71.48 (s, DME/−O*C*H$_3$), 117.01 (s, CHC(CH$_3$)*C*HC(CH$_3$)CH, aromatic), 118.76 (s, *C*CHCH, aromatic), 119.68 (s, CH*C*(CH$_3$)CH*C*(CH$_3$)-CH, aromatic), 127.63 (s, N−*C*, aromatic), 137.66 (s, *C*HC(CH$_3$)-CH(CH$_3$)*C*H, aromatic), 154.83 (s, *C*HCH*C*H, aromatic), 156.94 (s, CH*C*HCH, aromatic), 204.28 (s, Hf−*C*, aromatic). Anal. Calcd for C$_{56}$H$_{70}$HfLi$_2$N$_4$O$_4$: C, 63.72; H, 6.68; N, 5.31. Found: C, 61.69; H, 6.52; N, 5.31.

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Supporting Information Available: Text describing experimental procedures, analytical, spectroscopic, and crystallographic data, tables of bond lengths and angles, and cif files for **2**, **3-DME**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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