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Zirconium Amide, Halide, and Alkyl Complexes Supported by Tripodal Amido Ligands Derived from *cis,cis*-1,3,5-Triaminocyclohexane

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Zirconium complexes containing the chelating triamido ligands [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]^{3-}$ and {*cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3N]_3C_6H_9\}^{3-}$ are reported. The dimethylamido complexes [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrNMe_2(NHMe_2)$ (**3**) and {*cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3N]_3C_6H_9\}ZrNMe_2(NHMe_2)$ (**4**) were prepared from $Zr(NMe_2)_4$ and *cis,cis*-1,3,5-$(C_6F_5NH)_3C_6H_9$ (**1**) or *cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3NH]_3C_6H_9$ (**2**), respectively. As determined by X-ray crystallography, an *ortho* fluorine atom in the triamido ligand of complex **3** is coordinated to the zirconium center. The zirconium chloride complexes [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrCl$ (**5**) and {*cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3N]_3C_6H_9\}ZrCl(THF)_2$ (**6**) were prepared from Np_3ZrCl and **1** or **2**, respectively. Compound **5** reacts with MeMgBr, $LiCH(SiMe_3)_2$, $LiCH_2SiMe_3$, and $PhCH_2MgCl$ to give the corresponding alkyl derivatives [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrMe(Et_2O)$ (**7**), [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrCH(SiMe_3)_2$ (**8**), [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrCH_2SiMe_3$ (**9**), and [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrCH_2Ph$ (**10**). An X-ray crystallographic study of **8** reveals the presence of an α-agostic interaction, as well as the coordination of two *ortho* fluorines to the metal center. These interactions persist in solution, as indicated by NMR studies. Compound **6** reacts with MeMgCl and $LiCH(SiMe_3)_2$ to give the corresponding alkyl derivatives {*cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3N]_3C_6H_9\}ZrMe(THF)_2$ (**11**) and {*cis,cis*-1,3,5-$[3,5\text{-}(CF_3)_2C_6H_3N]_3C_6H_9\}ZrCH(SiMe_3)_2(THF)$ (**12**). The methyl derivative **7** reacts with 3 equiv of xylyl isocyanide to yield $[cis,cis\text{-}1,3,5\text{-}(C_6F_5N)_3C_6H_9]\overline{Zr\{N(2,6\text{-}Me_2C_6H_3){=}CMeC[{=}C{=}N(2,6\text{-}Me_2C_6H_3)]N}(2,6\text{-}Me_2C_6H_3)\}$ (**15**), which was structurally characterized. Complex **15** features three molecules of xylyl isocyanide that have been coupled to give a diazazirconacycle with an exocyclic ketenimine group. The alkyl derivatives **7**−**12** react with hydrogen at elevated temperatures to yield ZrF species derived from the activation of the fluorinated substituents on the triamido ligands, presumably via reactive hydride intermediates.

Introduction

Early-transition-metal complexes containing multidentate amido ligands have been the focus of considerable research in recent years, as these ligands have proven to be versatile alternatives to the ubiquitous cyclopentadienyl-derived systems.[1,2] The ability of amido ligands to function as effective σ- and π-donors enables electronic stabilization of highly electrophilic d^0 metal centers, which have found applications in the catalysis of processes such as olefin polymerization,[3−6] hydrogenation,[7−9] dehydropolymerization,[10−12] and hydrosilylation.[13−16] Additionally, multidentate amido ligands functionalized with sterically encumbering substituents can potentially shield a large sector of the coordination sphere of transition-metal complexes, thus enforcing coordinative unsaturation and providing a mechanism for tuning the steric environment at the reactive site.

With the goal of developing reactive metal fragments for applications in catalysis, we have been interested in delineating electronic and steric factors that control the course of reactions involving d^0 metal centers. In this context, research efforts in our laboratories have been directed toward developing multidentate amido ligands for use as ancillary ligands for d^0 transition metals.[17−21] Here we report the synthesis and initial

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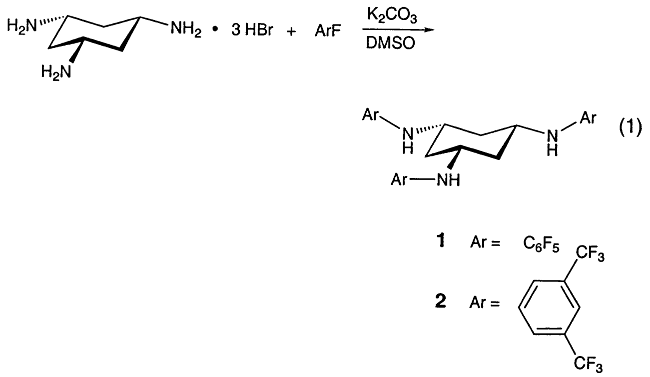
studies of a series of zirconium complexes containing a novel chelating triamido ligand derived from *cis,cis*-1,3,5-triaminocyclohexane (tach).[22−25] Main-group and late-transition-metal complexes containing neutral derivatives of this triamine have been thoroughly investigated for potential applications in the fields of radiopharmaceuticals and bioinorganic chemistry.[22−28] To our knowledge, however, there have been no reports on tripodal transition-metal amido complexes based on a cyclohexane framework.

A relatively small number of multidentate triamido ligand systems for transition metals have been examined previously. Tetradentate triamidoamine ligands[29−42] have featured prominently in the isolation of a number of unusual transition-metal species such as terminal phosphido and arsenido complexes[43] and terminal tantalum phosphinidene,[44] selenide, and telluride complexes.[45] Additionally, titanium and zirconium complexes containing tridentate triamido ligands derived from a neopentane, trisilylmethane, or trisilylsilane backbone have been studied by Gade[2,46−57] and Jia.[58]

The studies presented here are founded on the premise that a triamido ligand based on a cyclohexane framework might support particularly reactive early-transition-metal complexes, due in part to the rigidity of the constrained cyclohexane backbone and small bite angle, which should enforce a relatively "open" coordination sphere and electrophilicity at the metal center. Parkin and co-workers have observed such an effect in their comparison of zirconocene and *ansa*-zirconocene dihydride complexes.[59] On the basis of this study, it was concluded that the *ansa* ligands enhance the electrophilicity of the zirconium center, partly by imposing less steric demand on the reactive site. In developing triamido ligands based on a cyclohexane framework, we sought to employ sterically demanding aryl substituents that might suppress dimerization of the metal complexes while leaving the electrophilic metal center accessible to small-molecule reactants. Electron-withdrawing, fluorinated aryl groups have been used in this study, as they are expected to provide highly electrophilic, reactive metal centers. In addition, fluorinated aryl groups are readily introduced as substituents at nitrogen via nucleophilic aromatic substitution chemistry.

Results and Discussion

Ligand Synthesis. Nucleophilic attack on electron-deficient arenes by *cis,cis*-1,3,5-triaminocyclohexane (tach) provided a readily accessible synthetic route to aryl-functionalized tach ligands on a multigram scale (eq 1). Schrock and co-workers have used a similar methodology to prepare derivatives of triaminotriethylamine.[30] The reaction between *cis,cis*-1,3,5-triaminocyclohexane·3HBr and hexafluorobenzene in the presence of potassium carbonate gave *cis,cis*-1,3,5-tris[(pentafluorophenyl)amino]cyclohexane (**1**) in 83% yield. Similarly,



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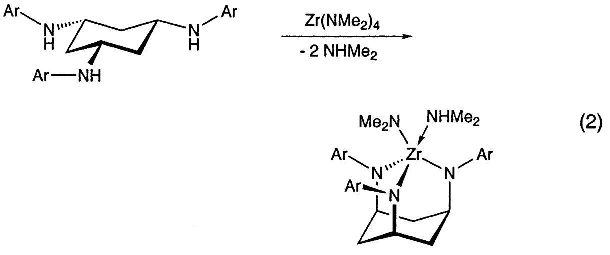
the analogous reaction of 3,5-bis(trifluoromethyl)fluorobenzene provided *cis,cis*-1,3,5-tris{[3,5-bis(trifluoromethyl)phenyl]amino}cyclohexane (**2**) in good yield. Both tach derivatives were isolated as analytically pure solids upon extraction into chloroform and subsequent aqueous workup. They are highly soluble in aromatic and donor solvents such as diethyl ether and THF but exhibit poor solubility in aliphatic hydrocarbon solvents.

Triamido Zirconium Complexes. The reaction between *cis,cis*-1,3,5-tris[(pentafluorophenyl)amino]cyclohexane (**1**) and Zr(NMe$_2$)$_4$ in toluene proceeded at room temperature to afford yellow, crystalline [*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrNMe$_2$(NHMe$_2$) (**3**) in 93% yield with loss of only 2 equiv of dimethylamine (eq 2). The coordination of 1 equiv of dimethylamine is evident by ^{1}H NMR spectroscopy (benzene-d_6), which reveals independent resonances for the dimethylamido (s, 2.39 ppm) and dimethylamine (d, 1.52 ppm, $^3J_{HH} = 4.5$ Hz) ligands. The N−H ^{1}H NMR resonance is observed as a broad multiplet at 1.25 ppm, and the N−H stretch for the dimethylamine ligand of **3** appears at 3326 cm^{-1}.



3 Ar = C$_6$F$_5$
4 Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$

The room-temperature ^{19}F NMR spectrum (benzene-d_6) of **3** is consistent with 3-fold symmetry, exhibiting three resonances at −152.9, −164.9, and −170.9 ppm, corresponding to the *ortho*, *meta*, and *para* fluorines, respectively, of rapidly rotating C$_6$F$_5$ substituents. However, upon cooling of a toluene-d_8 solution of **3** to −70 °C, each of the three ^{19}F resonances was resolved into a set of two resonances in a 2:1 ratio, consistent with C_s symmetry. These observations suggest rapid (NMR time scale) dissociation of the datively bound NHMe$_2$ ligand at room temperature, leading to effective 3-fold symmetry. A $\Delta G^{\ddagger}$ value of approximately 12(1) kcal mol^{-1} was calculated for this process.[60]

The reaction between *cis,cis*-1,3,5-tris{[3,5-bis(trifluoromethyl)phenyl]amino}cyclohexane (**2**) and Zr(NMe$_2$)$_4$ in toluene proceeded similarly at room temperature to afford yellow, crystalline {*cis,cis*-1,3,5-[3,5-(CF$_3$)$_2$C$_6$H$_3$N]$_3$C$_6$H$_9$}ZrNMe$_2$(NHMe$_2$) (**4**) in 93% yield with loss of only 2 equiv of dimethylamine (eq 2). The presence of dimethylamido and dimethylamine ligands is indicated by independent ^{1}H NMR resonances at 2.58 (s) and 1.71 (d, $^3J_{HH} = 6.4$ Hz) ppm, respectively (benzene-d_6 solution). The N−H stretch for the dimethylamine ligand is observed in the IR spectrum of **4** as a peak of weak intensity at 3382 cm^{-1}. The room-temperature ^{19}F NMR spectrum of **4** exhibits a single resonance at −63 ppm, consistent with 3-fold symmetry. This resonance simply broadened upon cooling to −80 °C (toluene-d_8).

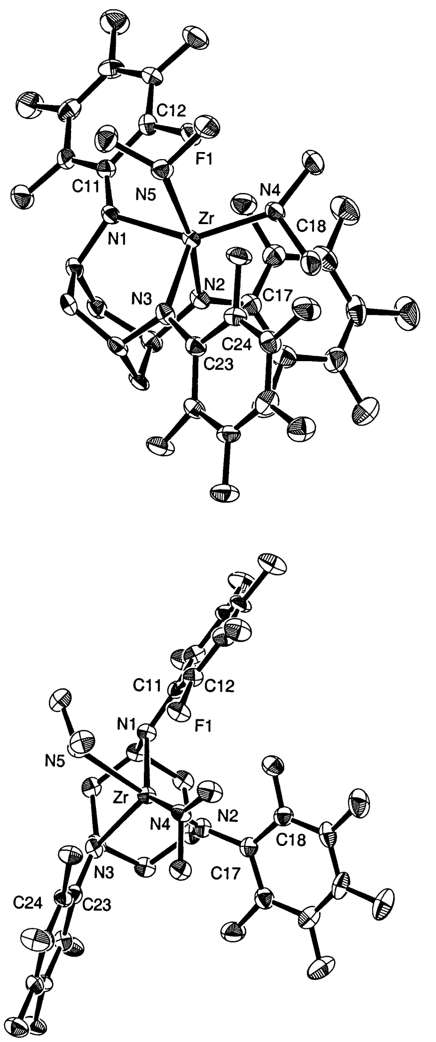


Figure 1. Two views of the crystallographically determined structure of **3**, depicted with 50% thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrNMe$_2$(NHMe$_2$) (3)

Bond Lengths (Å)			
Zr−N1	2.158(3)	Zr−N4	2.003(3)
Zr−N2	2.113(3)	Zr−N5	2.481(3)
Zr−N3	2.165(3)	Zr−F1	2.513(2)
Bond Angles (deg)			
N1−Zr−N2	84.4(1)	N3−Zr−N4	120.0(1)
N1−Zr−N3	102.1(1)	N3−Zr−N5	90.2(1)
N2−Zr−N(3)	87.7(1)	N4−Zr−N5	93.7(1)
N2−Zr−N5	169.9(1)		
Dihedral Angles (deg)			
Zr−N1−C11−C12	−23.0(5)		
Zr−N3−C23−C24	37.3(5)		
Zr−N2−C17−C18	−57.8(5)		

The solid-state structure of **3** was determined by X-ray crystallography, and two views of the molecule are shown in Figure 1. Selected bond distances and angles are summarized in Table 1. The structure consists of the expected Zr−N$_5$ core comprised of the three arms of the tach ligand, as well as dimethylamido and dimethylamine ligands. The geometry about the Zr center is approximately trigonal bipyramidal, with the dimethylamine ligand in one of the axial positions and the dimethylamido ligand in an equatorial site. The

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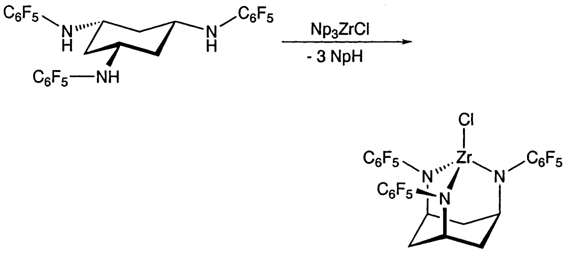
[60] Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: New York, 1993.

arms of the tach ligand take up the remaining axial and two equatorial sites. The chelate ligand bite angles (N1−Zr−N2 = 84.4(1)°, N2−Zr−N3 = 87.7(1)°, and N1−Zr−N3 = 102.1(1)°) are significantly compressed, indicating the constrained nature of the tach chelating framework. The Zr atom is located 1.20 Å out of the plane of the three tach nitrogen atoms, and the average Zr−N distance for the three tach nitrogens is 2.15 Å. One of the C_6F_5 rings (corresponding to C_{ortho} = C18) is oriented approximately perpendicular to the Zr−N−C_{ipso} plane, while the remaining two are approximately parallel to their respective planes, resulting in Zr−N−C_{ipso}−C_{ortho} dihedral angle values of −23.0(5)° for C12, −57.8(5)° for C18, and 37.3(5)° for C24. This orientation is likely encouraged by weak Zr−F_{ortho} interactions, as evidenced by a close Zr−F1 contact of 2.513(2) Å for one of the aryl rings oriented parallel to the Zr−N−C_{ipso}−C_{ortho} plane (corresponding to C_{ortho} = C12). Similar dative Zr−F interactions exhibiting comparable Zr−F distances have been reported previously.[61]

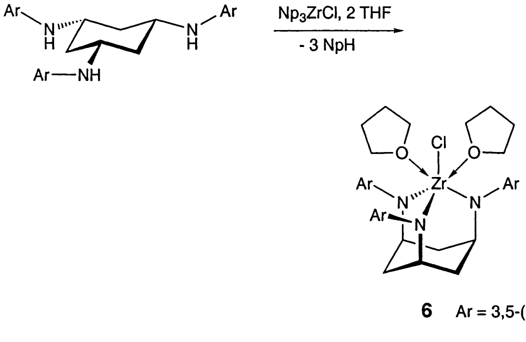
Attempts to convert either **3** or **4** to the corresponding zirconium halide complex via reaction with trimethylchlorosilane or methyl iodide under various reaction conditions proved unsuccessful. We were also unable to observe clean reactivity of the triamine derivatives **1** and **2** with $Zr(CH_2Ph)_4$ or $Zr(CH_2SiMe_3)_4$ in noncoordinating solvents such as benzene and toluene. However, the reaction of **1** with Np_3ZrCl[62] (Np = CH_2CMe_3) in toluene proceeded over the course of 3 days at room temperature to afford crystalline, yellow [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]ZrCl (**5**) in 88% yield upon loss of 3 equiv of neopentane (eq 3).



(3)

5

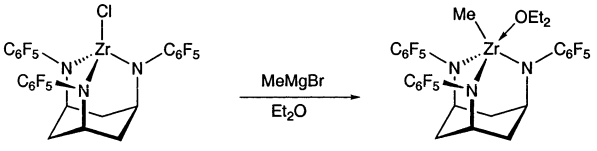
In contrast, **2** was found to be unreactive toward Np_3ZrCl at room temperature over the course of several days, and at elevated temperatures (up to 90 °C) Np_3ZrCl was observed to decompose without reacting with **2**. However, in the presence of 2 equiv of THF, **2** reacted cleanly with Np_3ZrCl at 65 °C over the course of 1 day to afford {*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9$}ZrCl$(THF)_2$ (**6**) in 92% yield (eq 4). Both **5** and **6** were isolated as yellow crystalline solids which exhibit limited solubility in toluene and benzene. The room-temperature ^{19}F NMR spectra of both complexes are consistent with 3-fold symmetry. However, the room-temperature ^1H NMR spectrum of **6** contains a broad peak in the aryl region which is resolved into two singlets (7.33 and 7.27 ppm, corresponding to the *ortho* and *para* protons, respectively, of 3,5-$(CF_3)_2C_6H_3$) at temperatures above 70 °C in toluene-d_8 solution. This phenomenon is likely due to hindered rotation of the aryl substituents on the tach ligand.



(4)

6 Ar = 3,5-$(CF_3)_2C_6H_3$

Synthesis of Zirconium Alkyl Complexes. Both **5** and **6** were readily alkylated by a variety of Grignard and alkyllithium reagents. Reaction of **5** with 1 equiv of MeMgBr in diethyl ether solution led to formation of the corresponding zirconium methyl complex **7**, which was isolated as a diethyl ether adduct in 80% yield (eq 5). Preliminary results have indicated that the diethyl ether ligand is labile and is readily displaced by stronger donors such as THF and PMe_3. The zirconium methyl protons of **7** are observed as a broad septet (0.65 ppm, $^3J_{HF}$ = 4.5 Hz, benzene-d_6) in the ^1H NMR spectrum, consistent with coupling to six *ortho* fluorines on the three C_6F_5 groups. Similar coupling has been reported previously for triamidozirconium and triamidotitanium methyl complexes in which the amido ligands bear aryl substituents with *ortho* fluorines, and this phenomenon has been interpreted as indirect evidence for coordination of the *ortho* fluorines to the metal center.[2,36,46,53] The room-temperature ^{19}F NMR spectrum of **7** (benzene-d_6) is consistent with 3-fold symmetry, in that it contains three resonances (−153.3, −164.5, and −170.5 ppm) for the rapidly rotating C_6F_5 substituents. However, at −80 °C (toluene-d_8), each of these ^{19}F resonances is resolved into a set of two resonances in a 2:1 ratio. These observations are consistent with rapid (NMR time scale) dissociation of the datively bound Et_2O ligand at room temperature, leading to apparent 3-fold symmetry. A $\Delta G^\ddagger$ value of approximately 13(1) kcal mol^{-1} was calculated for this process.[60] Attempts to generate a donor-free zirconium methyl complex by the reaction of **5** with methylating agents such as trimethylaluminum or dimethylzinc in toluene were not successful, as no reactivity with either reagent was observed up to 90 °C.



(5)

5 **7**

Donor-free triamido alkyl complexes of zirconium were prepared by reaction of an alkyllithium reagent with **5** in toluene (eq 6). In this way [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]$ZrCH(SiMe_3)_2$ (**8**) and [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]$ZrCH_2SiMe_3$ (**9**) were obtained in good yields by reaction of **5** with $LiCH(SiMe_3)_2$ and $LiCH_2SiMe_3$, respectively. In the case of **8**, the zirconium-bound methine protons are observed as a broad septet at 0.49 ppm ($^3J_{HF}$ = 4.5 Hz, benzene-d_6) in the ^1H NMR

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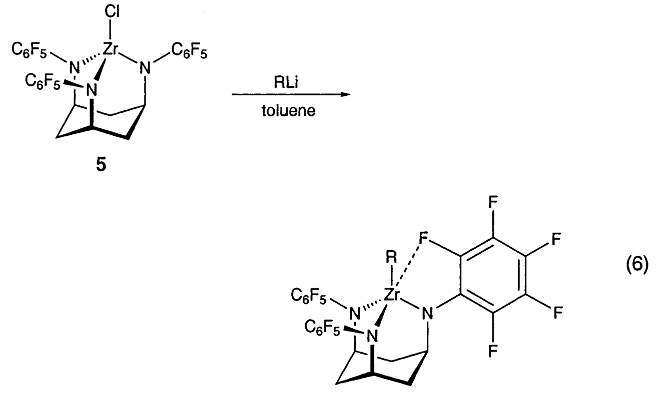


5

8 R = CH(SiMe$_3$)$_2$
9 R = CH$_2$SiMe$_3$

spectrum, while for **9**, the zirconium-bound methylene protons are observed as a broad septet at 0.85 ppm ($^3J_{HF}$ = 4.0 Hz, benzene-d_6), suggesting coupling of these protons to the six *ortho* fluorines on the three C_6F_5 groups of the tach-derived ligand. The ^{19}F NMR spectra of both **8** and **9** are consistent with 3-fold symmetry at temperatures down to −80 °C (toluene-d_8).

The solid-state structure of **8** was determined by a single-crystal X-ray diffraction experiment and is shown in Figure 2. Selected bond distances and angles are summarized in Table 2. The Zr atom is located 1.14 Å out of the plane of the three ligand nitrogen atoms, and the average Zr−N distance is 2.08 Å. The Zr−C bond length is 2.235(3) Å, which is comparable to other reported values for triamidozirconium alkyl complexes.[63-66] Two of the C_6F_5 rings are approximately parallel to the Zr−N−C_{ipso} plane, while the third (involving C27) is approximately perpendicular to this plane. The corresponding Zr−N−C_{ipso}−C_{ortho} dihedral angles for C_{ortho} = C15, C21, C27 are 9.6(3), 17.1(4), and 61.1(3)°, respectively. As in the case of **3**, this orientation is likely determined by weak Zr−F interactions, which give rise to close Zr−F contacts of 2.516(2) Å (Zr−F1, corresponding to C_{ortho} = C15) and 2.601(2) Å (Zr−F6, corresponding to C_{ortho} = C21). These distances are within the range expected for Zr−F dative bonds (2.24−2.70 Å).[61] The methine hydrogen atom of the CH(SiMe$_3$)$_2$ ligand (H1) was located in the difference Fourier map, and its position was refined. The angles about C7 are significantly distorted, especially the Zr−C7−H1 angle (88(2)°), which is significantly compressed. This distortion suggests the presence of an α-agostic interaction in the solid state.[67] The small C−H coupling constant for the α-CH bond in **8** ($^1J_{CH}$ = 70 Hz) is consistent with the presence of such an α-agostic interaction in solution (benzene-d_6).[20,67] The presence of Zr−F dative interactions, as well as an α-agostic CH bond, suggest that the rigid framework and constrained bite angle of the tach ligand leave the zirconium center coordinatively and electronically unsaturated.

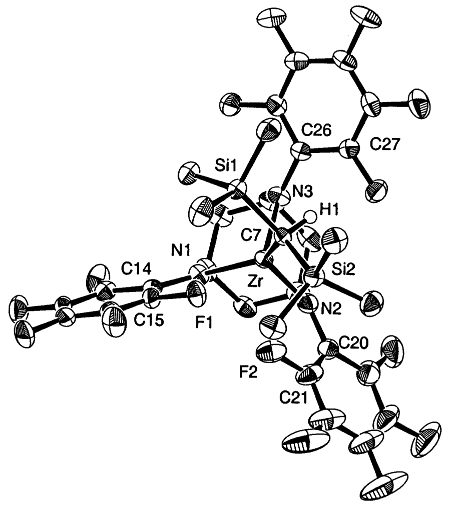
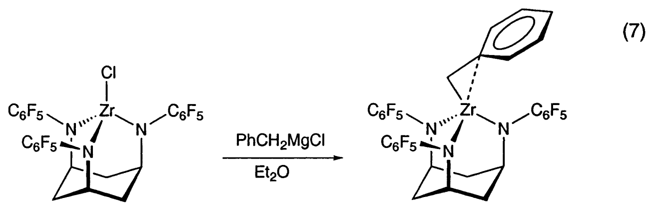


Figure 2. Crystallographically determined structure of **8**, depicted with 50% thermal ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-1,3,5-(C_6F_5N)$_3C_6H_9$]ZrCH(SiMe$_3$)$_2$ (8)

	Bond Lengths (Å)		
Zr−N1	2.119(2)	Zr−C7	2.233(2)
Zr−N2	2.091(2)	Zr−F1	2.515(1)
Zr−N3	2.037(2)	Zr−F2	2.602(1)
	Bond Angles (deg)		
N1−Zr−N2	92.98(7)	N3−Zr−C7	103.01(8)
N1−Zr−N3	93.49(7)	Si1−C7−Si2	117.4(1)
N2−Zr−N3	91.36(8)	Zr−C7−Si1	109.3(1)
N1−Zr−C7	136.46(8)	Zr−C7−Si2	126.3(1)
N2−Zr−C7	126.00(8)	Zr−C7−H1	88(2)
	Dihedral Angles (deg)		
Zr−N1−C14−C15			−9.7(3)
Zr−N3−C26−C27			61.1(3)
Zr−N2−C20−C21			16.9(3)

Further attempts to obtain a donor-free triamido zirconium alkyl complex targeted the introduction of a benzyl ligand, which can bind in an η^2 or η^3 manner to occupy more than one coordination site. Indeed, the reaction of **6** with PhCH$_2$MgCl in diethyl ether solution produced yellow, microcrystalline [*cis,cis*-1,3,5-(C_6F_5N)$_3$-C_6H_9]ZrCH$_2$Ph (**10**) in 89% yield (eq 7). The zirconium-bound methylene protons are observed as a broad singlet at 2.41 ppm in the ^{1}H NMR spectrum of **10** (benzene-d_6), with no additional coupling to fluorine as observed for **7**−**9**. The ^{13}C NMR spectrum of **10** does, however, indicate ^{19}F coupling to the benzyl C_α, which appears as a septet ($^2J_{CF}$ = 7 Hz) at 73.92 ppm. The room-temperature ^{19}F NMR spectrum of **10** (benzene-d_6) is consistent with 3-fold symmetry. In solution, the benzyl ligand likely adopts a predominantly η^2 config-



5　**10**

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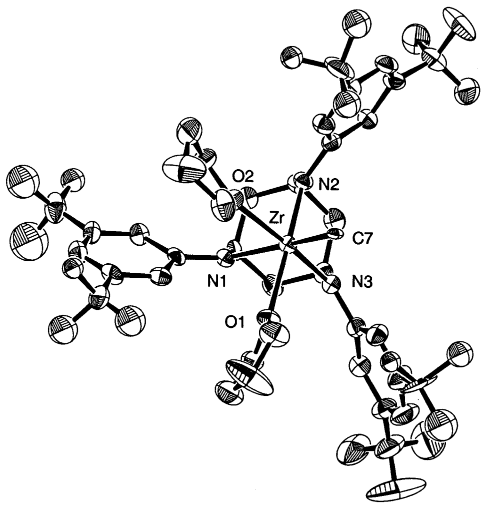


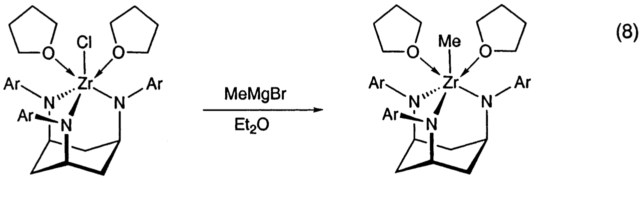
Figure 3. Crystallographically determined structure of **11**, depicted with 50% thermal ellipsoids.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for {*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9$}ZrMe$(THF)_2$ (11)

Bond Lengths (Å)			
Zr−O1	2.371(5)	Zr−O2	2.372(6)
Zr−N1	2.159(7)	Zr−N2	2.093(7)
Zr−N3	2.122(7)	Zr−C7	2.316(7)
Bond Angles (deg)			
O1−Zr−O2	92.3(2)	O1−Zr−N2	175.9(2)
O2−Zr−N2	89.3(2)	O2−Zr−N3	172.8(2)
N1−Zr−N2	92.1(3)	N1−Zr−N3	91.5(3)
N1−Zr−C7	158.8(2)	N2−Zr−N3	89.6(3)
N2−Zr−C7	100.6(3)	N3−Zr−C7	105.4(3)
Dihedral Angles (deg)			
Zr−N1−C16−C17			135.7(7)
Zr−N3−C28−C29			140.6(8)
Zr−N2−C22−C23			−47(1)

uration, as shown by the upfield ^{1}H NMR shift of the ortho protons (6.49 ppm), the relatively high $^1J_{CH}$ value of 132 Hz for the Zr*CH₂* group, and the upfield ipso carbon resonance (137.41 ppm).[68−70]

Reaction of **6** with MeMgCl in THF solution led to isolation of {*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9$}ZrMe$(THF)_2$ (**11**) in 67% yield (eq 8). The zirconium methyl resonance is observed as a singlet at 0.69 ppm in the ^{1}H NMR spectrum of **11** (benzene-d_6). The ^{19}F NMR spectrum of **11** exhibits of a single resonance at −62.96 ppm, consistent with 3-fold symmetry. A single-crystal X-ray diffraction experiment revealed the solid-state structure of **11**, as shown in Figure 3. The expected connectivity is observed in the structure, with a distorted-octahedral geometry about the six-coordinate zirconium center (Table 3).

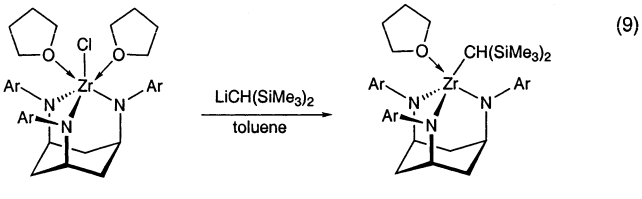


(8)

6

11 Ar = 3,5-$(CF_3)_2C_6H_3$

We considered that perhaps a more sterically demanding alkyl ligand would inhibit coordination of THF to the metal center, thus allowing access to a more coordinatively unsaturated zirconium complex. Indeed, reaction of **6** with $LiCH(SiMe_3)_2$ in toluene led to formation of the corresponding alkyl complex **12** in 44% yield with only one molecule of coordinated THF (eq 9).



(9)

6

12 Ar = 3,5-$(CF_3)_2C_6H_3$

The NMR properties of **12** are similar to those of **11**, with the zirconium-bound methine proton resonating at 0.77 ppm in the ^{1}H NMR spectrum and a single resonance observed in the ^{19}F NMR spectrum at −62.96 (benzene-d_6). The $^1J_{CH}$ value of 86 Hz for the methine CH of the $CH(SiMe_3)_2$ ligand is lower than expected for an sp^3-hybridized carbon atom, suggesting the possibility of an α-agostic interaction with the metal center.[20,67]

Reactivity of Zirconium Alkyl Complexes. We initially attempted to probe the activity of tach-containing zirconium alkyl complexes toward σ-bond metathesis processes involving hydrosilanes and H_2. In all cases, no reaction was observed between $PhSiH_3$ (up to 10 equiv) and zirconium alkyls containing either the [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9]^{3-}$ or the {*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9\}^{3-}$ ligand (benzene-d_6, up to 90 °C). Also, under a variety of conditions the hydrogenolysis of the Zr−C bonds is not facile, with no reactions observed at room temperature. For sterically congested [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]ZrCH$(SiMe_3)_2$ (**9**), no reactivity with hydrogen (1 atm) was observed, even at temperatures up to 100 °C. However, upon heating benzene-d_6 solutions of [*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]ZrR (R = Me(Et_2O), CH_2Ph, CH_2SiMe_3) at 80 °C for 3 days under an atmosphere of hydrogen, the alkane resulting from hydrogenolysis of the Zr−C bond was observed in solution (by ^{1}H NMR spectroscopy). The ^{1}H NMR spectra of these reaction mixtures do not, however, contain resonances that can be assigned to a zirconium hydride species. In addition, no methane was generated upon addition of methyl iodide to the product solution. However, the ^{19}F NMR spectra of the reaction mixtures indicate the quantitative formation of a new tach-containing product (**13**), as shown by the appearance of a new set of resonances corresponding to the C_6F_5 rings. Additionally, a new resonance is observed at −28.9 ppm, significantly downfield shifted with respect to organic fluorides, thus suggesting the formation of a Zr−F-bonded species.[71,72]

These results are consistent with C−F bond activation[71,73−75] of the C_6F_5 substituents on the amido

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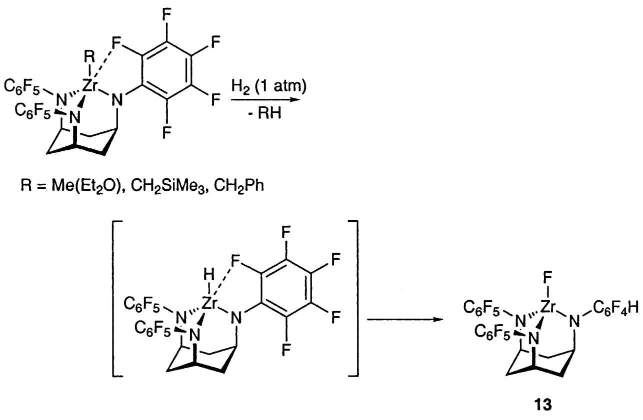
Scheme 1



nitrogens, presumably via a transiently generated, highly reactive zirconium hydride intermediate (Scheme 1) to yield the zirconium fluoride complex **13**. It has previously been shown that transition-metal hydrides, such as $[Cp_2ZrH_2]_2$ and Cp_3ZrH, react readily with perfluorobenzene to form C−F bond activation products.[76−78] The major driving force of this reaction is the formation of a strong Zr−F bond.[71,73,76−78] Mechanistic studies carried out by Jones and co-workers[76−78] on zirconocene hydride mediated aromatic C−F bond activation processes indicate that this reactivity likely involves coordination of fluorine to zirconium, which we have observed both in the solid state and in solution for complexes containing the C_6F_5-substituted tach ligand. It has been proposed that such fluorocarbon coordination to a Lewis acidic metal center results in weakening of the C−F bond, leading to subsequent C−F activation.[61,78−79] Attempts to trap the intermediate hydride species by generating it in the presence of unsaturated hydrocarbons (e.g., 1-hexene, diphenylacetylene, and 4,4-dimethyl-2-pentyne) led to complicated reaction mixtures.

On a preparative scale, a solution of [*cis*,*cis*-1,3,5-$(C_6F_5N)_3C_6H_9]ZrCH_2SiMe_3$ (**9**) in benzene was heated at 80 °C under an atmosphere of hydrogen for 3 days, over the course of which **13** crystallizes out of the reaction mixture. The isolated off-white solid exhibited little solubility in aromatic hydrocarbon solvents; however, addition of several drops of diethyl ether to a toluene slurry of this solid resulted in clean formation of the more soluble diethyl ether adduct (**13·OEt$_2$**). The ^{19}F NMR spectrum of the diethyl ether adduct contains a slightly shifted (relative to **13**) Zr−F resonance at −35.5 ppm.

Similar results were obtained in attempts to generate a hydride complex containing the {*cis*,*cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9\}^{3-}$ ligand. For example, reaction of {*cis*,*cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N]_3C_6H_9\}ZrCH(SiMe_3)_2$(THF) (**12**) with an atmosphere of hydrogen in benzene solution proceeded at 80 °C over the course of 2 days, with loss of $CH_2(SiMe_3)_2$ and clean formation of a new tach-containing product (**14**). Upon removal of the volatile reaction components under reduced pressure, **14** was isolated as an off-white solid exhibiting poor solubility in aromatic hydrocarbon solvents. The room-temperature ^{19}F NMR spectrum of **14** consists of a resonance at −62.99 ppm corresponding to the CF_3 groups of the tach-derived ligand as well as a significantly downfield shifted resonance at 103.89 ppm, consistent with the presence of a zirconium-bound fluorine.[71,72] The ^{1}H NMR spectrum of this isolated product indicates coordination of two molecules of THF to the Zr center and does not contain a resonance that can be assigned to a Zr−H moiety. Additionally, **14** did not react with 1-hexene or methyl iodide, further suggesting that the targeted Zr−H complex was not isolated. Rather, these results are again consistent with C−F bond activation of the tach-derived ligand. On the basis of this preliminary evidence, we formulate the final product of this reaction as {*cis*,*cis*-1,3,5-[3-(CF_2H)-5-$(CF_3)C_6H_3N][3,5$-$(CF_3)_2C_6H_3N]_2C_6H_9\}ZrF(THF)_2$ (**14**), resulting from activation of a ligand CF_3 group by a transient Zr−H species. We tentatively assign a resonance at −62.83 ppm in the ^{19}F NMR spectrum of **14** to the CF_2H moiety; however, we did not observe the expected HF coupling in the proton-coupled ^{19}F NMR spectrum. This may be due to overlap with the adjacent CF_3 peak at −62.99 ppm. Alternatively, the product of this bond activation may be formulated as a diamido−amine complex, featuring a ligand CF_2 group covalently bound to a Zr−F moiety.[80] However, due to the unfavorable strain associated with such an intramolecular reaction pathway, as well as the ^{1}H NMR evidence of a highly symmetric cyclohexane ligand backbone for **14**, we favor the structure in which the tach ligand remains bound to Zr in a trianionic fashion.[81]

The apparent difference in chemical shifts for the Zr−F groups of **13** and **14** is puzzling but may perhaps be attributed to the varying nature of the donor ligands bound to zirconium. Both shifts are observed downfield of organic fluorides and fall well within the wide range of reported shifts for Zr−F species.[71] We found only two other examples of zirconium fluoride complexes supported by amido ligands, $[2,6\text{-}^{i}Pr_2C_6H_3N(SiMe_3)]_2ZrF_2$ and $\{(C_5Me_5)[2,6\text{-}^{i}Pr_2C_6H_3N(SiMe_3)]\}ZrF_2$, and in both cases the ^{19}F NMR resonances are observed at downfield shifts, relative to organic fluorides.[72] In the former compound, the Zr−F NMR shift is observed at 109.6 ppm, while in the latter compound the observed shift is 78.2 ppm (both in benzene-d_6, downfield of $CFCl_3$). By comparison, the ^{19}F NMR shift for Cp_3ZrF is reported as −37.04 ppm (THF-d_8, corrected for $CFCl_3$ reference at δ 0.00), indicating the wide range of chemical shifts possible for such species.[76]

To investigate the reactivity of tach-containing Zr alkyl complexes toward the insertion of unsaturated

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(80) We thank a reviewer for bringing this alternative structural formulation to our attention.

(81) We have independently prepared Zr complexes containing tach ligands bound in a dianionic fashion as "diamido−amine" species. These types of complexes feature inequivalent environments for each proton in the ligand cyclohexane backbone and exhibit ^{1}H NMR spectral features that are significantly more complicated than examples where the tach ligand coordinates in a trianionic fashion.

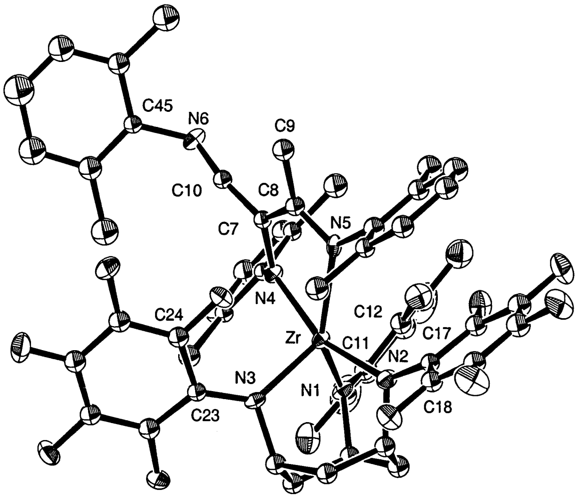
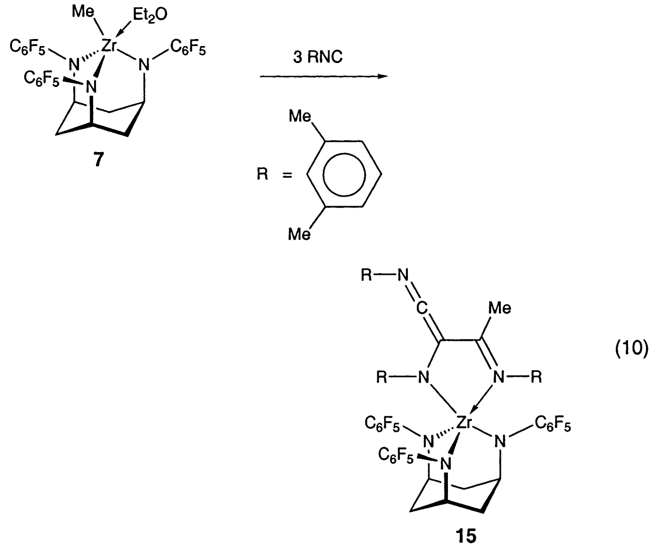


Figure 4. Crystallographically determined structure of **15**, depicted with 50% thermal ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-1,3,5-(C_6F_5N)$_3$$C_6H_9$]Zr{(2,6-$Me_2C_6H_3$)N=CMeC[=C=N(2,6-$Me_2C_6H_3$)]N(2,6-$Me_2C_6H_3$)} (15)

Bond Lengths (Å)			
Zr−N1	2.069(8)	Zr−N3	2.119(8)
Zr−N2	2.152(8)	Zr−N4	2.177(8)
Zr−N5	2.379(8)		
Bond Angles (deg)			
N1−Zr−N2	93.2(3)	N1−Zr−N3	91.5(3)
N2−Zr−N3	94.8(3)	N1−Zr−N5	144.2(3)
N2−Zr−N4	160.5(3)	N2−Zr−N5	91.6(3)
C10−N6−C45	133(1)	N6−C10−C7	170(1)
Dihedral Angles (deg)			
Zr−N1−C11−C12	35(1)		
Zr−N3−C23−C24	−32(1)		
N4−C7−C8−C9	−178.2(9)		
C7−N4−C29−C34	68(1)		
C8−N5−C37−C38	−76(1)		
Zr−N2−C17−C18	−60(1)		
N4−C7−C8−N5	1(1)		
N5−C8−C7−C10	−179(1)		
C7−C10−N6−C45	−178(5)		

substrates, reactions with small molecules such as ethylene, carbon monoxide, and xylyl isocyanide were examined. None of the alkyl complexes reacted cleanly with CO (1 atm, benzene-d_6), and only insignificant amounts of polyethylene were formed upon reaction of **7-12** with C_2H_4 (1 atm, benzene-d_6). Complex **7** did, however, react with xylyl isocyanide to initially give a mixture of products, which over the course of 2 days at room temperature converted to a single tach-containing species (**15**). The ^{1}H NMR spectrum of the isolated complex reveals three different sets of xylyl methyl protons, suggesting formation of a species more complicated than the η^2-iminoacyl that would result from a single insertion of the isocyanide into the Zr−Me bond.



(10)

The structure of **15**, determined by X-ray crystallography (Figure 4, Table 4), corresponds to the incorporation of 3 equiv of the isocyanide to yield a diazazirconacycle with an exocyclic ketenimine group (eq 10). The metrical parameters are consistent with a 2,5-diazazirconacyclopent-2-ene ring, as shown in eq 10. The Zr−N(5) distance of 2.379(8) Å is considerably longer than the Zr−N(4) distance of 2.177(8) Å. The former distance is comparable to the Zr−$NHMe_2$ dative bond distance of 2.482(3) for **3**, while the latter is more similar to distances of amido groups bound to zirconium. This structure is closely related to a Ta analogue previously reported by Rothwell and co-workers, (2,6-^{i}Pr_2-C_6H_3O)$_2$$Cl_2$Ta(N(^{t}Bu)=CHC(=C=N^{t}Bu)N^{t}Bu}, in which three *tert*-butyl isocyanide molecules are coupled via insertion into a Ta−H functional group to yield a similar diazametallacycle.[82] Additionally, the oxa−aza metallacyclic analogue Cp*$_2$ClTh{OC(CH_2^{t}Bu)C(=C=NR)NR} and the dioxa derivative Cp*$_2$ClTh{OC(SiR_3)C(=C=NR)O} have been reported.[83,84]

Concluding Remarks

In this contribution, new triamido ligands derived from *cis,cis*-1,3,5-triaminocyclohexane (tach) and containing fluorinated aromatic substituents on the donor nitrogen atoms are introduced. Zirconium amide, halide, and alkyl complexes containing such ligands can be readily prepared. The alkyl derivatives appear to be reactive, as indicated by the oligomerization of 3 equiv of xylyl isocyanide by the triamidozirconium methyl complex **7**. However, attempts to produce triamidozirconium hydride complexes via hydrogenation of these alkyl complexes led to the isolation of ZrF species derived from activation of the fluorinated ligand substituents, presumably via transiently generated, highly reactive zirconium hydride intermediates. This reactivity is likely enabled by the strong fluorophilicity of the electrophilic zirconium center, as well as by, in some cases, association of the ligand fluorines to the electron-deficient metal center, as indicated by both NMR and solid-state evidence. We are continuing to investigate the chemistry of transition-metal complexes containing tach-derived ligands, including studies of ligands containing nonfluorinated aromatic substituents as well as studies aimed at extending the chemistry of these tach derivatives to group V and VI metals.

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Experimental Section

General Considerations. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Dry, oxygen-free solvents were distilled from sodium/benzophenone ketyl, with the exception of toluene, which was distilled from molten sodium, and DMSO, which was degassed and distilled from CaH_2. Deuterated NMR solvents were degassed and stored over 4 Å molecular sieves. All NMR data were recorded at room temperature, unless otherwise noted, using a Bruker AMX, AM, or DRX spectrometer. ^{1}H NMR spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. ^{13}C NMR spectra were referenced internally by the ^{13}C signal of the NMR solvent relative to tetramethylsilane. ^{19}F NMR spectra were referenced using an external standard of α,α,α-trifluorotoluene (−64 ppm relative to $CFCl_3$), with downfield shifts taken to be positive. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. The compounds *cis,cis*-1,3,5-triaminocyclohexane·3HBr,[23] 3,5-$(CF_3)_2C_6H_3F$,[30] $Zr(NMe_2)_4$,[85] $(Me_3CH_2)_3ZrCl$,[62] $LiCH_2(SiMe_3)$,[86] and $LiCH(SiMe_3)_2$[87] were prepared according to literature procedures.

***cis,cis*-1,3,5-$(C_6F_5NH)_3C_6H_9$ (1).** Dimethyl sulfoxide (100 mL) was added to solid *cis,cis*-1,3,5-triaminocyclohexane·3HBr (7.0 g, 18.8 mmol) and potassium carbonate (26.85 g, 188 mmol). The resulting slurry was stirred vigorously and heated to 90 °C over the course of 1 h, allowing for the evolution of CO_2. The reaction mixture was then cooled to room temperature, and an excess of hexafluorobenzene (42 g, 226 mmol) was added. The mixture was stirred and heated at 90−100 °C for 3 days, over the course of which the solution darkened in color. The crude suspension was then poured into water (700 mL) and extracted into chloroform (3 × 250 mL). The chloroform layers were combined and washed with water (5 × 250 mL). The organic fraction was then dried over anhydrous magnesium sulfate, and the volatiles were removed under reduced pressure to afford **1** (9.8 g, 83% yield) as a pale peach-colored solid. IR (cm^{-1}): 3401 (NH). ^{1}H NMR (benzene-d_6, 300 MHz): δ 3.096 (m, 3 H, CH), 2.767 (br m, 3 H, NH), 1.944 (m, 3 H, CH_2), 0.040 (m, 3 H, CH_2). ^{13}C{^{1}H} NMR (chloroform-d, 100.6 MHz): δ 139.72 (br m, C_6F_5), 137.30 (br m, C_6F_5), 135.75 (br m, C_6F_5), 133.30 (br m, C_6F_5), 122.04 (br m, C_6F_5), 51.60 (CH), 42.04 (CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −159.6 (d, 6 F, $^3J_{FF}$ = 21 Hz, *o*-F), −164.0 (t, 6 F, $^3J_{FF}$ = 22 Hz, *m*-F), −170.2 (t, 3 F, $^3J_{FF}$ = 22 Hz, *p*-F). Mp: 143.5−146 °C. Anal. Calcd for $C_{24}H_{12}N_3F_{15}$: C, 45.95; H, 1.93; N, 6.70. Found: C, 45.56; H, 1.76; N, 6.50.

***cis,cis*-1,3,5-$(3,5\text{-}(CF_3)_2C_6H_3NH)_3C_6H_9$ (2).** This ligand was prepared in a manner similar to that used to prepare **1**, starting from *cis,cis*-1,3,5-triaminocyclohexane·3HBr (3.60 g, 9.66 mmol) and 3,5-bis(trifluoromethyl)fluorobenzene (13.45 g, 57.9 mmol). The reaction mixture was stirred and heated at 90−100 °C for 4 days. Following extraction of the crude suspension into chloroform and aqueous workup, **2** (3.5 g, 47% yield) was obtained as an off-white crystalline solid. IR (cm^{-1}): 3457 (NH). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.282 (s, 3 H, *p*-H_{Ar}), 6.624 (s, 6 H, *o*-H_{Ar}), 2.951 (m, 3 H, NH), 2.613 (br m, 3 H, CH), 1.887 (m, 3 H, CH_2), 0.200 (m, 3 H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6, 100.6 MHz): δ 147.73 (CNH), 133.51 (CCF_3, $^2J_{CF}$ = 33 Hz), 124.56 (CF_3, $^1J_{CF}$ = 273 Hz), 112.67 (*o*-C_{Ar}), 111.13 (*p*-C_{Ar}), 47.96 (CH), 38.72 (CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −63.32 (CF_3). Mp: 182−184 °C. Anal. Calcd for $C_{30}H_{21}N_3F_{18}$: C, 47.06; H, 2.76; N, 5.49. Found: C, 46.73; H, 2.96; N, 5.51.

[*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]$ZrNMe_2(NHMe_2)$ (3). Solid $Zr(NMe_2)_4$ (0.085 g, 0.319 mmol) was added to a toluene (5 mL) solution of **1** (0.20 g, 0.319 mmol) at room temperature. The resulting pale yellow solution was allowed to stand for 14 h at room temperature. The reaction mixture was concentrated to 2 mL under reduced pressure and cooled to −30 °C to give **3** (0.24 g, 93% yield) as a yellow microcrystalline solid. IR (cm^{-1}): 3326 (NH). ^{1}H NMR (benzene-d_6, 500 MHz): δ 3.839 (br m, 3 H, CH), 2.392 (s, 6 H, NMe_2), 1.912 (m, 3 H, CH_2), 1.591 (m, 3 H, CH_2), 1.517 (d, 6 H, $NHMe_2$), 1.084 (br m, 1 H, $NHMe_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 142.5−136.8 (br, C_6F_5), 55.99 (CH), 39.10 (NMe_2), 38.73 ($NHMe_2$), 36.77 (CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −152.9 (d, 6 F, $^3J_{FF}$ = 21 Hz, *o*-F), −164.9 (t, 6 F, $^3J_{FF}$ = 22 Hz, *m*-F), −170.9 (m, 3 F, *p*-F). Anal. Calcd for $C_{28}H_{22}N_5F_{15}Zr$: C, 41.79; H, 2.76; N, 8.70. Found: C, 42.13; H, 3.05; N, 8.49.

{*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N$]$_3C_6H_9$}$ZrNMe_2(NHMe_2)$ (4). Solid $Zr(NMe_2)_4$ (0.070 g, 0.261 mmol) was added to a toluene (5 mL) solution of **2** (0.20 g, 0.261 mmol) at room temperature. The resulting yellow solution was allowed to stand for 14 h at room temperature. The reaction mixture was concentrated to 2 mL under reduced pressure and cooled to −30 °C to give **4** (0.23 g, 93% yield) as a yellow microcrystalline solid. IR (cm^{-1}): 3382 (NH). ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.234 (s, 3 H, *p*-H_{Ar}), 6.849 (s, 6 H, *o*-H_{Ar}), 3.643 (br m, 3 H, CH), 2.577 (s, 6 H, NMe_2), 1.726 (br d, 6 H, $NHMe_2$), 1.263 (br m, 7 H, CH_2 and $NHMe_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 153.99 (CNH), 132.99 (CCF_3, $^2J_{CF}$ = 33 Hz), 124.31 (CF_3, $^1J_{CF}$ = 273 Hz), 115.14 (*o*-C_{Ar}), 110.91 (*p*-C_{Ar}), 52.89 (CH), 39.91 ($NHMe_2$), 39.29 (NMe_2), 33.45 (CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −63.09 (CF_3). Anal. Calcd for $C_{34}H_{31}N_5F_{18}Zr$: C, 43.31; H, 3.31; N, 7.43. Found: C, 43.19; H, 3.56; N, 7.82.

[*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]ZrCl (5). Solid $(Me_3CH_2)_3ZrCl$ (0.32 g, 0.94 mmol) was added to a room-temperature toluene (10 mL) solution of **2** (0.59 g, 0.94 mmol). The resulting clear orange reaction mixture was allowed to stand at room temperature in the dark for 3 days. The solution was then concentrated under reduced pressure to ca. 3 mL in volume and cooled to −30 °C to afford **5** (0.62 g, 88% yield) as a yellow-orange crystalline solid. ^{1}H NMR (benzene-d_6, 400 MHz): δ 3.782 (br m, 3 H, CH), 1.680 (m, 3 H, CH_2), 1.361 (m, 3 H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 142.02−137.45 (br m, C_6F_5), 57.96 (CH), 34.84 (CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −150.6 (br d, 6 F, $^3J_{FF}$ = 18 Hz, *o*-F), −163.1 (br t, 6 F, $^3J_{FF}$ = 18 Hz, *m*-F), −165.5 (br m, 3 F, *p*-F). Anal. Calcd for $C_{24}H_9N_3ClF_{15}Zr\cdot 0.5C_7H_8$: C, 41.44; H, 1.64; N, 5.27. Found: C, 41.53; H, 1.91; N, 5.12.

{*cis,cis*-1,3,5-[3,5-$(CF_3)_2C_6H_3N$]$_3C_6H_9$}ZrCl(THF)$_2$ (6). Solid $(Me_3CH_2)_3ZrCl$ (0.50 g, 1.47 mmol) was added to a room-temperature toluene (30 mL) solution of **2** (1.12 g, 1.47 mmol). THF (0.24 mL, 3 mmol) was added to the reaction mixture. The resulting clear orange solution was heated at 65−70 °C for 14 h. Solvent was removed under reduced pressure, and the remaining residue was dissolved in ca. 5 mL of toluene and the solution cooled to −30 °C to give **6** (1.40 g, 92% yield) as a yellow-orange crystalline solid. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.55−7.26 (br, 9 H, H_{Ar}), 3.701 (br m, 3 H, CH), 3.421 (br m, 8 H, OCH_2), 1.335 (br m, 6 H, CH_2), 1.003 (br m, 8 H, OCH_2CH_2). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 155.18 ($CNZr$), 131.93 (CCF_3, $^2J_{CF}$ = 33 Hz), 124.51 (CF_3, $^1J_{CF}$ = 273 Hz), 117.79 (*o*-C_{Ar}), 111.24 (*p*-C_{Ar}), 72.76 (OCH_2), 54.14 (CH), 34.23 (CH_2), 24.97 (OCH_2CH_2). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −62.90 (CF_3). Anal. Calcd for $C_{38}H_{34}N_3F_{18}O_2ClZr$: C, 44.17; H, 3.32; N, 4.07. Found: C, 43.92; H, 3.59; N, 4.35.

[*cis,cis*-1,3,5-$(C_6F_5N)_3C_6H_9$]ZrMe(Et_2O) (7). MeMgBr (0.22 mL, 3.0 M in Et_2O, 0.67 mmol) was added to a solution of **5** (0.5 g, 0.67 mmol) in diethyl ether (5 mL) at −30 °C. The

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orange reaction mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure, and the resulting solid was extracted into ca. 5 mL of toluene. The toluene extracts were filtered through Celite, and the filtrate was concentrated to 2 mL under reduced pressure and refrigerated at −30 °C to give **7** (0.43 g, 80% yield) as a pale yellow microcrystalline solid. ^{1}H NMR (benzene-d_6, 500 MHz): δ 3.950 (br m, 3 H, C*H*), 3.103 (br m, 4 H, OC*H*$_2$), 1.692 (m, 3 H, C*H*$_2$), 1.490 (m, 3 H, C*H*$_2$), 0.646 (br sep, 3 H, $^3J_{HF}$ = 4.5 Hz, ZrC*H*$_3$), 0.332 (br m, 6 H, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 141.60−135.32 (br m, *C*$_6$F$_5$), 66.10 (O*C*H$_2$), 54.27 (*C*H), 48.56 (Zr*C*H$_3$), 35.99 (*C*H$_2$), 12.61 (OCH$_2$*C*H$_3$). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −153.3 (br d, 6 F, $^3J_{FF}$ = 21 Hz, *o*-F), −164.5 (t, 6 F, $^3J_{FF}$ = 22 Hz, *m*-F), −170.5 (br m, 3 F, *p*-F). Anal. Calcd for $C_{29}H_{22}N_3F_{15}OZr$: C, 43.28; H, 2.76; N, 5.22. Found: C, 43.49; H, 2.75; N, 5.15.

[*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrCH(SiMe$_3$)$_2$ (8). Solid LiCH(SiMe$_3$)$_2$ (0.055 g, 0.33 mmol) was added to a solution of **5** (0.25 g, 0.33 mmol) in toluene (5 mL) at −30 °C. The pale orange solution was stirred at room temperature for 12 h. The reaction mixture was filtered through Celite, and the toluene was removed under reduced pressure. The remaining residue was extracted into ca. 20 mL of pentane. The pentane extracts were filtered through Celite and cooled to −30 °C to give **8** (0.23 g, 80% yield) as an off-white crystalline solid. ^{1}H NMR (benzene-d_6, 400 MHz): δ 3.88 (br m, 3 H, C*H*), 1.60 (m, 3 H, C*H*$_2$), 1.39 (m, 3 H, C*H*$_2$), 0.49 (br sep, 1 H, $^3J_{HF}$ = 4.5 Hz, ZrC*H*), −0.07 (s, 18 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 142.4−136.5 (br m, *C*$_6$F$_5$), 82.56 (Zr*C*H), 55.60 (*C*H), 36.17 (*C*H$_2$), 2.64 (Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 125.7 MHz): δ 82.56 (d, Zr*C*H, $^1J_{CH}$ = 70 Hz). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −151.3 (d, 6 F, $^3J_{FF}$ = 21 Hz, *o*-F), −163.1 (t, 6 F, $^3J_{FF}$ = 21 Hz, *m*-F), −167.9 (t, 3 F, $^3J_{FF}$ = 22 Hz, *p*-F). Anal. Calcd for $C_{31}H_{28}N_3F_{15}Si_2Zr$: C, 42.55; H, 3.23; N, 4.80. Found: C, 42.81; H, 3.00; N, 4.58.

[*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrCH$_2$SiMe$_3$ (9). Solid LiCH$_2$(SiMe$_3$) (0.025 g, 0.27 mmol) was added to a solution of **5** (0.20 g, 0.27 mmol) in toluene (5 mL) at −30 °C. The pale orange solution was stirred at room temperature for 12 h. The reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. The remaining residue was extracted into ca. 20 mL of pentane. The pentane extracts were filtered through Celite and cooled to −30 °C to give **9** (0.15 g, 69% yield) as a pale yellow crystalline solid. ^{1}H NMR (benzene-d_6, 300 MHz): δ 4.09 (br m, 3 H, C*H*), 1.45 (m, 6 H, C*H*$_2$), 0.85 (br sep, 2 H, $^3J_{HF}$ = 4.0 Hz, ZrC*H*$_2$), 0.03 (s, 9 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 141.2−137.8 (br m, *C*$_6$F$_5$), 68.42 (Zr*C*H$_2$), 52.87 (*C*H), 35.85 (*C*H$_2$), 1.61 (Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 125.7 MHz): δ 68.42 (t, Zr*C*H$_2$, $^1J_{CH}$ = 104 Hz). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −154.3 (d, 6 F, $^3J_{FF}$ = 21 Hz, *o*-F), −162.8 (t, 6 F, $^3J_{FF}$ = 22 Hz, *m*-F), −169.7 (t, 3 F, $^3J_{FF}$ = 24 Hz, *p*-F). Anal. Calcd for $C_{28}H_{20}N_3F_{15}SiZr$: C, 41.89; H, 2.51; N, 5.23. Found: C, 41.92; H, 2.37; N, 5.23.

[*cis,cis*-1,3,5-(C$_6$F$_5$N)$_3$C$_6$H$_9$]ZrCH$_2$Ph (10). PhCH$_2$MgCl (0.28 mL, 1.0 M in Et$_2$O, 0.28 mmol) was added to a solution of **5** (0.21 g, 0.28 mmol) in toluene (5 mL) at −30 °C. The orange reaction mixture was stirred at room temperature for 14 h. Solvent was removed under reduced pressure, and the resulting solid was extracted into ca. 5 mL of toluene. The toluene extracts were filtered through Celite, and the filtrate was concentrated to 2 mL under reduced pressure and refrigerated at −30 °C to give **10** (0.20 g, 89% yield) as a bright yellow-orange microcrystalline solid. ^{1}H NMR (benzene-d_6, 300 MHz): δ 6.627−6.426 (m, 5 H, H$_{Ar}$), 4.001 (br m, 3 H, C*H*), 2.412 (br s, 2 H, ZrC*H*$_2$), 1.409 (m, 6 H, C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 141.6−139.3 (br m, *C*$_6$F$_5$), 137.41 (C$_{Ar}$), 129.65 (C$_{Ar}$), 127.33 (C$_{Ar}$), 125.02 (C$_{Ar}$), 73.92 (sep, $^2J_{CF}$ = 7.04 Hz, Zr*C*H$_2$), 53.45 (*C*H), 35.67 (*C*H$_2$). ^{13}C NMR (benzene-d_6, 125.7 MHz): δ 73.92 (t, Zr*C*H$_2$, $^1J_{CH}$ = 132 Hz). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −155.1 (d, 6 F, $^3J_{FF}$ = 22 Hz, *o*-F), −163.4 (t, 6 F, $^3J_{FF}$ = 22 Hz, *m*-F), −170.6 (t, 3 F, $^3J_{FF}$ = 21 Hz, *p*-F). Anal. Calcd for $C_{31}H_{16}N_3F_{15}Zr$: C, 46.16; H, 2.00; N, 5.21. Found: C, 46.11; H, 2.18; N, 5.00.

{*cis,cis*-1,3,5-[3,5-(CF$_3$)$_2$C$_6$H$_3$N]$_3$C$_6$H$_9$}ZrMe(THF)$_2$ (11). MeMgCl (0.048 mL, 3.0 M in THF, 0.145 mmol) was added to a −30 °C diethyl ether (5 mL) solution of **6** (0.15 g, 0.145 mmol). The orange reaction mixture was warmed to room temperature over the course of 20 min, during which a precipitate formed. Solvent was removed under reduced pressure, and the remaining residue was extracted into toluene. The toluene extracts were filtered through Celite, and the solvent was removed under reduced pressure, affording **11** (0.098 g, 67% yield) as an analytically pure yellow-orange microcrystalline solid. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.247 (s, 3 H, *p*-H$_{Ar}$), 7.075 (s, 6 H, *o*-H$_{Ar}$), 3.663 (br m, 3 H, C*H*), 3.453 (br m, 8 H, OC*H*$_2$), 1.324 (br m, 6 H, C*H*$_2$), 1.171 (br m, 8 H, OCH$_2$C*H*$_2$), 0.686 (s, 3 H, Zr*Me*). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 155.23 (*C*NZr), 132.66 (*C*CF$_3$, $^2J_{CF}$ = 33 Hz), 124.97 (*C*F$_3$, $^1J_{CF}$ = 273 Hz), 116.74 (*o*-C$_{Ar}$), 110.80 (*p*-C$_{Ar}$), 70.30 (O*C*H$_2$), 53.41 (*C*H), 53.23 (Zr*Me*), 34.77 (*C*H$_2$), 25.41 (OCH$_2$*C*H$_2$). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −62.96 (C*F*$_3$). Anal. Calcd for $C_{39}H_{37}N_3F_{18}O_2Zr$: C, 46.24; H, 3.68; N, 4.15. Found: C, 45.90; H, 3.89; N, 3.88.

{*cis,cis*-1,3,5-[3,5-(CF$_3$)$_2$-C$_6$H$_3$N]$_3$C$_6$H$_9$}ZrCH(SiMe$_3$)$_2$(THF) (12). Solid LiCH(SiMe$_3$)$_2$ (0.040 g, 0.24 mmol) was added to a solution of **6** (0.25 g, 0.24 mmol) in diethyl ether (5 mL) at −30 °C. The pale orange solution was warmed to room temperature over the course of 2 h. Solvent was removed under reduced pressure, and the remaining residue was extracted into ca. 5 mL of toluene. The toluene extracts were filtered through Celite, and the solvent was removed under reduced pressure. The remaining residue was extracted into ca. 20 mL of pentane. The pentane extracts were filtered through Celite and cooled to −30 °C to give **12** (0.12 g, 44% yield) as a yellow-orange microcrystalline solid. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.45 (s, 3 H, *p*-H$_{Ar}$), 7.19 (s, 6 H, *o*-H$_{Ar}$), 3.53 (br m, 4 H, OC*H*$_2$), 3.42 (br m, 3 H, C*H*), 1.32 (m, 3 H, C*H*$_2$), 1.21 (br m, 4 H, OCH$_2$C*H*$_2$), 1.07 (m, 3 H, C*H*$_2$), 0.77 (s, 1 H, ZrC*H*), −0.14 (s, 18 H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 154.96 (*C*NZr), 133.06 (*C*CF$_3$, $^2J_{CF}$ = 33 Hz), 124.06 (*C*F$_3$, $^1J_{CF}$ = 273 Hz), 120.58 (*o*-C$_{Ar}$), 114.39 (*p*-C$_{Ar}$), 79.54 (Zr*C*H), 70.92 (O*C*H$_2$), 57.61 (*C*H), 34.08 (*C*H$_2$), 25.15 (OCH$_2$*C*H$_2$), 3.94 (Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 125.7 MHz): δ 79.54 (d, Zr*C*H, $^1J_{CH}$ = 86 Hz). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −62.96 (C*F*$_3$). Anal. Calcd for $C_{41}H_{45}N_3F_{18}OSi_2Zr$: C, 45.38; H, 4.18; N, 3.87. Found: C, 45.22; H, 4.44; N, 4.00.

[*cis,cis*-1,3,5-(C$_6$F$_5$N)$_2$(C$_6$F$_4$H)C$_6$H$_9$]ZrF (13). A thick-walled glass vessel was charged with **9** (0.20 g, 0.25 mmol) and C$_6$H$_6$ (2 mL). The solution was degassed via three freeze−pump−thaw cycles, and upon warming to room temperature, 1 atm of H$_2$ was admitted into the reaction vessel. The resulting solution was heated to 80 °C for 3 days, over the course of which an off-white crystalline precipitate formed. The reaction mixture was then cooled to room temperature, the supernatant solution was decanted off, and the crystalline residue was dried under vacuum, affording **13** as an off-white solid (0.098 g, 55% yield). Due to the limited solubility of isolated **13** in aromatic hydrocarbon solvents, a diethyl ether adduct was prepared by adding several drops of Et$_2$O to a toluene slurry of **13** (0.07 g, 0.098 mmol), affording **13·OEt$_2$** (0.073 g, 95% yield) as an off-white solid upon removal of the volatiles under vacuum. ^{1}H NMR (**13·OEt$_2$**, benzene-d_6, 500 MHz): δ 3.835 (br m, 3 H, CH), 2.875 (br q, 4 H, $^3J_{HH}$ = 7.5 Hz, OC*H*$_2$), 1.677 (br m, 3 H, C*H*$_2$), 1.454 (br m, 3 H, C*H*$_2$), 0.707 (br t, 6 H, $^3J_{HH}$ = 7.5 Hz, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (**13·OEt$_2$**, benzene-d_6, 125.7 MHz): δ 141.91−137.51 (br m, *C*$_6$F$_5$), 65.94 (O*C*H$_2$) 55.94 (*C*H), 35.97 (*C*H$_2$), 13.79 (OCH$_2$*C*H$_3$). ^{19}F NMR (**13·OEt$_2$**, benzene-d_6, 376.5 MHz): δ −35.5 (s, 1 F, Zr*F*), −153.1 (br s, 4 F, *o*-F), −164.7 (t, 4 F, *p*-F), −170.0 (t, 2 F, *p*-F); resonances corresponding to the unsymmetrically substituted C$_6$F$_4$H ring are observed as broad, highly coupled

Table 5. Crystallographic Data for Compounds 3, 8, 11, and 15

	3	**8**	**11**	**15**
empirical formula	$ZrN_5C_{28}F_{15}H_{22}$	$ZrN_3C_{31}F_{15}H_{28}Si_2$	$ZrN_3O_2C_{53}F_{18}H_{53}$	$ZrN_6C_{59}F_{15}H_{47}$
fw	804.71	874.95	1197.21	1216.26
cryst color, habit	yellow block	yellow block	yellow block	yellow block
cryst size (mm)	0.20 × 0.25 × 0.06	0.39 × 0.21 × 0.14	0.25 × 0.20 × 0.04	0.26 × 0.12 × 0.04
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.8384(7)	9.9266(3)	12.6254(3)	11.500(1)
b (Å)	10.3156(7)	21.1450(6)	13.7279(3)	14.455(1)
c (Å)	15.616(1)	16.9786(4)	19.91180(10)	17.658(2)
α (deg)	92.599(1)	90	90.564(1)	105.317(1)
β (deg)	97.500(1)	98.229(1)	100.091(1)	99.796(1)
γ (deg)	111.710(1)	90	115.028(1)	108.666(1)
V (Å^3)	1452.3(2)	3527.1(1)	3065.02(10)	2576.0(4)
no. of orientation rflns (2θ range (deg))	3222 (3.5−45)	8192 (3.5−45)	5138 (3.5−45)	3642 (3.5−45)
Z	2	4	2	2
D_{calcd} (g/cm^3)	1.840	1.648	1.297	1.568
F_{000}	800.00	1752.00	1220.00	1236.00
μ(Mo Kα) (cm^{-1})	5.06	4.87	2.71	3.16
diffractometer	SMART			
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromated			
temp (°C)	−114.0	−115.0	−105.0	−124.0
scan type (deg/frame)	ω (0.3)			
scan rate (s/frame)	10.0	10.0	20.0	20.0
$2\theta_{max}$ (deg)	52.0	49.4	46.5	46.5
no. of rflns measd				
total	8049	15 697	14 128	11 882
unique	4957	5963	8602	7218
R_{int}	0.026	0.016	0.026	0.077
transmission factors				
T_{max}	1.00	0.97	0.98	1.00
T_{min}	0.83	0.80	0.82	0.86
structure soln	direct methods (SIR92)			
no. of observns ($I > 3.00\sigma(I)$)	3263	4370	5456	3963
no. of variables	442	472	676	435
rfln/param ratio	7.38	9.26	8.07	9.11
residuals: R; R_w; R_{all}	0.034; 0.035; 0.062	0.023; 0.029; 0.034	0.080; 0.090; 0.120	0.056; 0.079; 0.108
goodness of fit	1.11	1.20	2.78	1.98
max shift/error in final cycle	0.01	0.00	0.02	0.00
max, min peaks in final diff map (e/Å^3)	0.44; −0.56	0.28; −0.24	1.15; −0.76	0.63; −0.70

multiplets in the region between −150 and −170 ppm. Anal. Calcd for $C_{24}H_{10}N_3F_{15}Zr$: C, 40.23; H, 1.41; N, 5.86. Found: C, 38.77; H, 1.64; N, 5.37. Combustion elemental analysis results for **13** were found to consistently show percentages of carbon slightly lower than those calculated, while giving accurate results for hydrogen and nitrogen, suggesting incomplete combustion due to zirconium carbide formation.

{*cis,cis*-1,3,5-[3-(CF_2H)-5-(CF_3)C_6H_3N][3,5-(CF_3)$_2C_6H_3N$]$_2$-C_6H_9}ZrF(THF)$_2$ (14). A thick-walled glass vessel was charged with **12** (0.20 g, 0.18 mmol) and C_6H_6 (2 mL). The solution was degassed via three freeze−pump−thaw cycles, and upon warming to room temperature, 1 atm of H_2 was admitted into the reaction vessel and the solution was heated to 80 °C for 2 days. The reaction mixture was then cooled to room temperature, and the solvent was removed under reduced pressure. The residue obtained was extracted into toluene (3 × 3 mL), and the toluene extracts were filtered through Celite. The solvent was removed under reduced pressure to give **14** (0.081 g, 45% yield) as an analytically pure off-white solid. ^{1}H NMR (benzene-d_6, 500 MHz): δ 7.21−7.01 (br, 9 H, H_{Ar}), 3.756 (br m, 3 H, C*H*), 3.386 (br m, 8 H, OCH_2), 1.373 (m, 6 H, CH_2), 0.973 (br m, 8 H, OCH$_2$CH_2). ^{13}C{^{1}H} NMR (THF-d_8, 125.7 MHz): δ 155.34 (*C*NZr), 132.72 (*C*CF$_3$, $^2J_{CF}$ = 33 Hz), 125.04 (*C*F$_3$, $^1J_{CF}$ = 272 Hz), 116.43 (*o*-C_{Ar}), 110.40 (*p*-C_{Ar}), 53.27 (*C*H), 35.72 (*C*H$_2$); resonances for the unsymmetrically substituted $C_6H_4F_5$ ring could not be assigned due to low intensity. ^{19}F NMR (benzene-d_6, 376.5 MHz): δ 103.89 (s, 1 F, Zr*F*), −62.99 (s, 15 F, CF_3), −62.83 (s, 2 F, CF_2H). Anal. Calcd for $C_{38}H_{35}N_3F_{18}O_2Zr$: C, 45.69; H, 3.53; N, 4.21. Found: C, 45.66; H, 3.53; N, 4.04.

[*cis,cis*-1,3,5-(C_6F_5N)$_3C_6H_9$]Zr{N(2,6-$Me_2C_6H_3$)=CMeC-[=C=N(2,6-$Me_2C_6H_3$)]N(2,6-$Me_2C_6H_3$)} (15). Xylyl isocyanide (0.098 g, 0.75 mmol) was added to a solution of **7** (0.20 g, 0.25 mmol) in C_6H_6 (10 mL), and the reaction mixture was allowed to stand at room temperature. After 2 days, the solvent was removed under reduced pressure, and the residue was extracted into Et_2O (3 × 4 mL). The Et_2O extracts were filtered through Celite and concentrated under reduced pressure to ca. 5 mL. The concentrated solution was cooled at −30 °C to afford **15** (0.18 g, 60% yield) as yellow-orange crystals. IR (cm^{-1}): 2020 (C=N). ^{1}H NMR (benzene-d_6, 500 MHz): δ 6.723−6.522 (m, 9 H, H_{Ar}), 3.724 (br m, 3 H, C*H*), 2.200 (s, 6 H, CCH_3), 2.030 (br m, 3 H, CH_2), 2.004 (s, 6 H, CCH_3), 1.776 (s, 6 H, CCH_3), 1.623 (br m, 3 H, CH_2), 1.457 (s, 3 H, NCCH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 125.7 MHz): δ 177.84, 175.02, 146.66, 146.31, 142.49−136.00 (br m, C_6F_5), 134.12, 133.45, 132.57, 131.72, 129.09, 128.66, 125.81, 124.53, 101.71, 58.22 (*C*H), 36.68 (*C*H$_2$), 19.64 (C*C*H$_3$), 18.82 (C*C*H$_3$), 18.38 (C*C*H$_3$), 17.50 (NC*C*H$_3$). ^{19}F NMR (benzene-d_6, 376.5 MHz): δ −150.6 (br s, 6 F, *o*-F), −165.8 (br s, 6 F, *m*-F), −170.6 (br s, 3 F, *p*-F). Anal. Calcd for $C_{54}H_{44}N_6F_{15}Zr \cdot OC_2H_5$: C, 56.13; H, 4.12; N, 7.01. Found: C, 55.82; H, 4.15; N, 6.81.

X-ray Structure Determinations. General Considerations. X-ray diffraction measurements were made on a Siemens SMART diffractometer equipped with a CCD area detector, using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation. The crystal was mounted on a quartz fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $3.5 < 2\theta < 45°$. The frame data were integrated using the program SAINT.[88] An empirical absorption correction based on measurements of multiply redundant data was performed using the programs XPREP (part of the SHELXTL Crystal Structure Determination Package[89]) or SADABS.[90] Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of Molecular Structure Corp., using direct methods, and expanded with Fourier techniques. Apart from noted exceptions, non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p factor to downweight the intense reflections. Crystallographic data are summarized in Table 5.

Crystal Data for 3. Crystals suitable for X-ray diffraction were obtained from a toluene solution at −30 °C. Hydrogen atoms were refined isotropically in geometrically calculated positions.

Crystal Data for 8. Crystals suitable for X-ray diffrraction were obtained from a pentane solution at −30 °C. All hydrogen atoms were refined isotropically in geometrically calculated positions, with the exception of H1, which was located in the difference Fourier map; its positional coordinates were refined.

Crystal Data for 11. Crystals suitable for X-ray diffraction were obtained from a toluene solution at −30 °C. The structure was solved using direct methods and was found to contain one molecule of the title zirconium complex as well as 3.5 molecules of toluene per asymmetric unit. Of the six CF_3 groups in the title complex, four exhibited significant rotational disorder. The disordered fluorines (F1−F18 and F22−F27) were observed in two orientations approximately 60° apart and were refined isotropically with occupancies in the ratio of 7:3. The remaining two CF_3 groups, comprised of F19, F20, F21, F28, F29, and F30, were refined anisotropically at full occupancy. All other non-hydrogen atoms in the zirconium complex were refined anisotropically. The asymmetric unit contains two full toluene molecules, for which the carbon atoms were refined anisotropically. Additionally, three toluene molecules were found to crystallize about inversion centers. Thus, the toluene molecule containing C47, C48, C49, and C50 was found to crystallize about the inversion center at (1, 0, 1). The toluene methyl carbon (C50) is disordered over two positions and was refined with 50% occupancy, while the remaining toluene carbon atoms were refined with full occupancies. The toluene molecule containing C58, C59, C60, C61, C62, and C63 crystallized about the inversion center at (1, 0, $^1/_2$) and is disordered such that the methyl carbon (C59) of one disordered component occupies the same position as the para carbon of the other half of the disordered molecule. The fifth toluene molecule, containing C64, C65, C66, C67, C68, and C69, crystallized about the inversion center at ($^1/_2$, 0, $^1/_2$) and is similarly disordered such that the methyl carbon of one disordered component occupies the same position as the para carbon of the other half of the disordered molecule. Additionally, the methyl carbon is disordered over the positions occupied by C64 and C68. C58−C68 were refined with 50% occupancies, while C69 was refined at full occupancy. The carbon atoms for these three disordered toluene molecules were refined isotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions.

Crystal Data for 15. Crystals suitable for X-ray diffraction were obtained from an Et_2O/toluene solution at −30 °C. All hydrogen atoms were refined isotropically in geometrically calculated positions. Due to weak intensity data, all carbon atoms were refined isotropically. All other non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: Tables giving summaries of crystallographic data, bond distances and angles, atomic coordinates, and anisotropic displacement parameters for **3**, **8**, **11**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(88) SAX Area-Detector Integration Program, version 4.024; Siemens Industrial Automation, Inc., Madison, WI, 1995.

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