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C_2-Symmetric Fluorous Diamino-Dialkoxide Complexes of Early Transition Metals

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Coordination of the new fluorous diamino-dialkoxy tetradentate ligands $[OC(CF_3)_2CH_2N(Me)(CH_2)_nN(Me)C(CF_3)_2O]^{2-}$ ($n = 2$, $[ON^2NO]^{2-}$; $n = 3$, $[ON^3NO]^{2-}$) onto group 3 and group 4 metals has been studied. The diamino-diols $[ON^nNO]H_2$ ($n = 2$, **1a**; $n = 3$, **1b**), prepared by ring-opening of $(CF_3)_2\overline{COC}H_2$ with the corresponding secondary diamine, react cleanly with $Ti(OiPr)_4$ to yield quantitatively the dialkoxy complexes $[ON^nNO]Ti(OiPr)_2$ ($n = 2$, **2a**; $n = 3$, **2b**). The chloride displacement reaction between $TiCl_4$ and **1a** in the presence of NEt_3 leads to the dichlorotitanium complex $[ON^2NO]TiCl_2$ (**3**). Alkane elimination and amine elimination reactions provide efficient routes to the zirconium and yttrium complexes $[ON^2NO]Zr(CH_2Ph)_2$ (**4**), $[ON^2NO]Y(N(SiHMe_2)_2)(THF)$ (**5**), and $[ON^2NO]Y(CH_2SiMe_3)(THF)$ (**6**). X-ray crystallographic analyses show that in the solid state **3** and **4** adopt a distorted octahedral structure with a *trans*-O, *cis*-N, *cis*-X ligand (X = Cl, CH_2Ph). Solution NMR data for **2**−**4** are consistent with this C_2-symmetric structure. Variable-temperature NMR studies establish that **4** undergoes inversion of metal configuration (i.e., Λ/Δ isomerization, racemization) on the NMR time scale at elevated temperatures ($\Delta G^{\ddagger}$(racemization) = 17.0(1) kcal/mol). An X-ray crystallographic analysis reveals that **6** adopts in the solid state a seven-coordinate, distorted structure due to Y···F coordination to one of the four CF_3 substituents (Y−F = 2.806(2) Å). In contrast, NMR studies show that **6** adopts a C_2-symmetric structure in solution analogous to those of **2**−**4**, while **5** features a C_1-symmetric structure.

Introduction

Investigation into the use of alkoxide/aryloxide ancillary ligands to replace the ubiquitous cyclopentadienyl-type ligands in modern coordination chemistry of early transition metals (groups 3−5) has become very popular in recent years. This is largely related to the permanent search for new-generation catalysts, in particular for the polymerization of olefins and polar monomers.[1] Hard, electronegative π-donor ligands such as alkoxides/aryloxides are attractive because they offer strong metal−oxygen bonds that are expected to stabilize complexes of these electropositive metals.[2,3] Also, the great variety of these ligands conveniently obtained from alcohols allows considerable variation in steric and electronic features. Most successful developments in terms of synthetic organometallic chemistry and catalysis have appeared using chelating bis(*aryloxide*) ligands, in particular with tridentate and tetradentate ligands having (an) additional coordinating heteroatom(s) (*N*, *O*, *S*).[4,5] The synthetic chemistry of *alkoxide*-based complexes proved much more complicated; this is inherent to the high tendency of the relatively more basic alkoxide ligands (compared to aryloxides) to act as bridging ligands, eventually resulting in (highly) agglomerated structures. This difficulty can be partly overcome by increasing the steric bulk of the −OR moieties or tailoring the alkoxide ligand with additional donor functionalities.[2] Another possible approach con-

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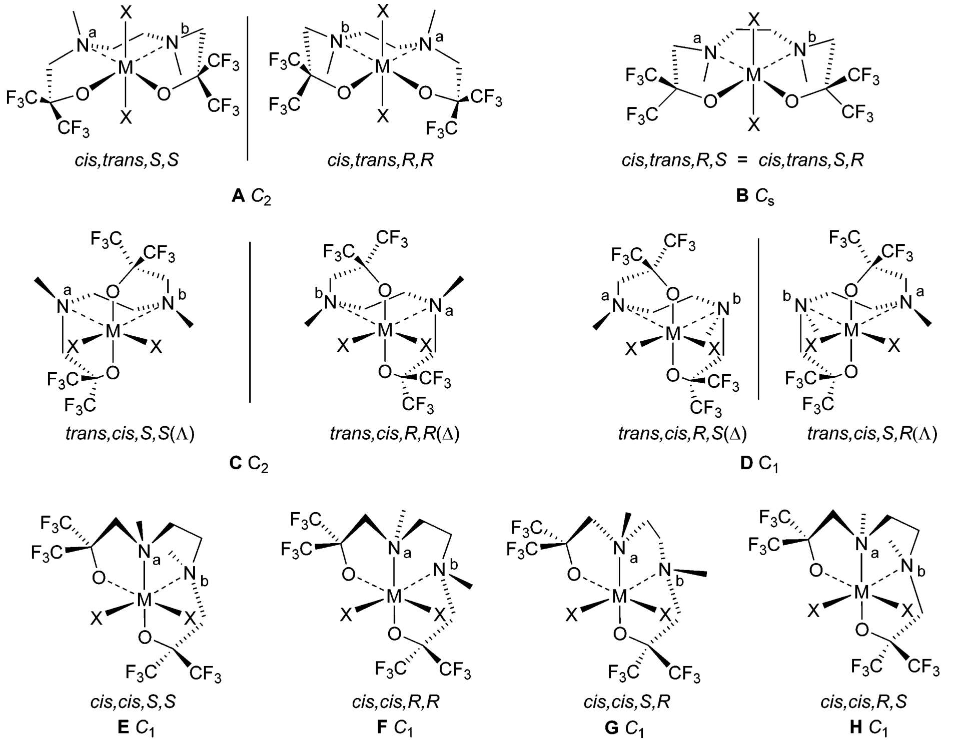
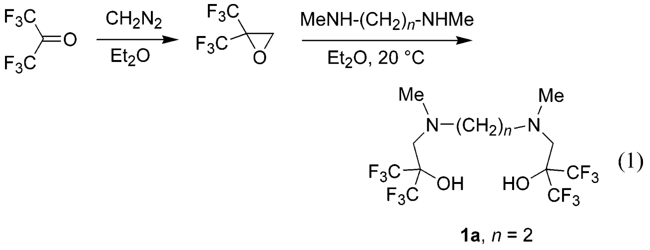


Figure 1. Possible isomers for octahedral $[ON^2NO]MX_2$ complexes. The four entries in the descriptor (e.g., *cis*, *trans*, *S*, *S*) refer to the arrangement of alkoxide ligands, the arrangement of X ligands, the configuration of N^a, and the configuration of N^b, respectively. Note that the amine ligands must be *cis*. For isomers **C** and **D**, the descriptor in parentheses (Λ, Δ) refers to the absolute configuration of the metal.[11]

sists of the use of highly stable fluorinated tertiary alcohol ligands. The exchange of α-CH_3 groups in alkoxides by significantly enlarged and electron-withdrawing CF_3 groups generates increased intra- and intermolecular repulsions and a less basic alkoxide O atom, and as a result, a less distinct bridging tendency is observed.[2] This approach remains largely undeveloped, likely because of synthetic difficulties encountered in the preparation of fluorous systems.[6] On the basis of the above principles, we have designed and synthesized potentially tetradentate $[ON^nNO]^{2-}$ ligand systems that have a diamine bridge flanked by two fluorinated tertiary alkoxides.

Results and Discussion

Ligand Design and Synthesis. The fluorous diamino-diols $HOC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)C(CF_3)_2OH$ ($[ON^2NO]H_2$, **1a**) and $HOC(CF_3)_2CH_2N(Me)(CH_2)_3N(Me)C(CF_3)_2OH$ ($[ON^3NO]H_2$, **1b**), which have respectively an ethylene and a propylene bridge, are modeled after related diamine-diamido[7] and diamine-bis(aryloxide)[4a,8] ligands that we and others have reported previously. They were designed considering the following features: (i) they are readily prepared by the ring-opening of 2 equiv of the fluorinated oxirane $(CF_3)_2\overline{COC}H_2$, in situ generated from hexafluoroacetone and diazomethane,[9] with 1 equiv of the corresponding secondary diamine (eq 1).[10] This one-pot procedure leads to **1a** and **1b** in 31% and 43% (unoptimized) yields, respectively, after



(1)

1a, $n = 2$
1b, $n = 3$

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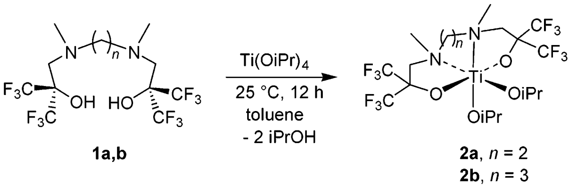
workup. (ii) The $[ON^nNO]^{2-}$ ligand framework is flexible and therefore should be able to coordinate strongly to a variety of early transition metals; and (iii) the diamino-diols have C_2-symmetry, which may lead to C_2-symmetric structures for $[ON^nNO]MX_2$ complexes of group 4 metals[4] of potential interest for stereoselective catalysis. Assuming an ideal octahedral arrangement, eight $[ON^nNO]MX_2$ isomeric structures are possible (**A**–**H**, Figure 1), of which two have C_2-symmetry and one C_s-symmetry. These structures differ in the arrangement (*cis* vs *trans*) of the pairs of alkoxide and X ligands and in the configuration of the amine nitrogens, which become stereogenic centers as binding to the metal center occurs. (iv) The diamino-dialkoxy $[ON^nNO]^{2-}$ are isoelectronic to tetradentate diamino-diamido[7] and diamino-bis(aryloxide)[4,8] systems that have been used successfully in group 4 metal chemistry, which allows comparison of structures and reactivities of complexes.

Synthesis of Titanium and Zirconium Complexes of Diamino-diols 1a,b. The synthesis of the isopropoxy titanium complexes of diamino-diols **1a** and **1b** proceeded in high yield (eq 2), as is common of simple exchange reactions between titanium alkoxide complexes and alcohols.[2] Addition of diamino-diols **1a**,**b** to titanium tetraisopropoxide dissolved in toluene gave colorless solutions, from which $[ON^nNO]Ti(O\textit{i}Pr)_2$ (n = 2, **2a**; n = 3, **2b**) are isolated in quantitative yields as white solids after removal of volatile materials. The synthesis of the dichloro titanium complex of ethylenediamino-diol **1a** proved more difficult. Attempts to achieve 2-propanol elimination from **1a** and $Ti(O\textit{i}Pr)_2Cl_2$ in toluene[12] or comproportionation of $TiCl_4$ with "$Ti[ON^2NO]_2$" (prepared in situ from the reaction of $Ti(O\textit{i}Pr)_4$ and 2 equiv of **1a**)[13] gave complex mixtures of products that could not be separated. Careful addition of **1a** to $TiCl_4$ in toluene in the presence of triethylamine as a base,[14] filtration to remove the salt formed, and evaporation of the clear solution gave a white solid, of which NMR indicated the presence of $[ON^2NO]TiCl_2$ (**3**) as the major product, together with residual $NEt_3{\cdot}HCl$ and other unidentified materials (although unlikely to be isomers of **3**) (eq 3). Complex **3** was obtained in pure form in 35% yield by recrystallization of the crude product from benzene at room temperature. Finally, the reaction of ethylenediamino-diol **1a** with $Zr(CH_2Ph)_4$ in toluene or benzene solutions results in clean toluene elimination and yields pure $[ON^2NO]Zr(CH_2Ph)_2$ (**4**) in quantitative yield after removal of volatiles (eq 4). The hexafluoro derivatives **2**–**4** are all highly soluble in aromatic and chlorinated solvents.



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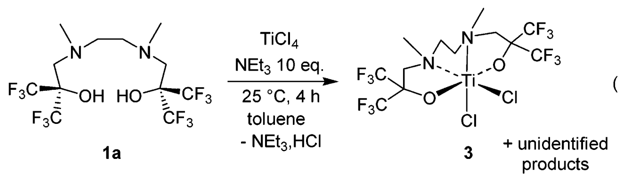

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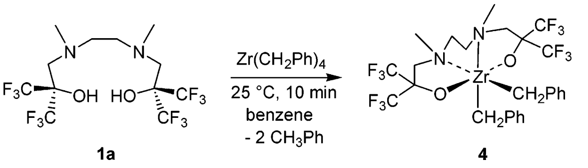

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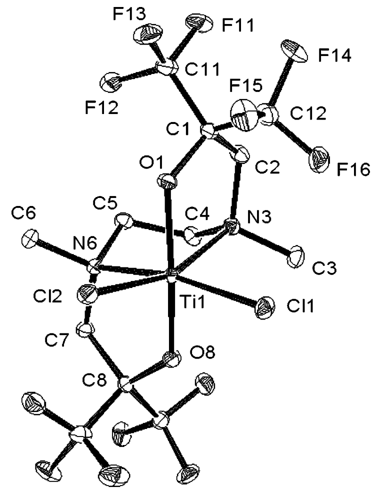

Figure 2. ORTEP view of $[ON^2NO]TiCl_2$ (**3**), depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

Solid State Structures of 3 and 4. X-ray diffraction studies were performed on **3** and **4** to determine the metal and ligand geometries and the structure of the benzyl groups in the latter case. Single crystals of **3** were obtained from a benzene solution at room temperature, and crystals of **4** were obtained from a toluene solution at −35 °C. ORTEP views are shown in Figures 2 and 3, and crystallographic details and key bond distances and angles are listed in Tables 1–3. Both complexes **3** and **4** are monomeric in the solid state and adopt a distorted octahedral geometry in which the oxygens of the alkoxide ligand are *trans* and the amine and X ligands (X = Cl, CH_2Ph, respectively) are *cis*, with an approximate (noncrystallographic) C_2-symmetry axis, i.e., a type **C** structure (Figure 1). The *trans* O–M–O angles for **3** and **4** are 163.77(6)° and 142.70(3)°, respectively. The *cis* L–M–L angles associated with the chelated amino-

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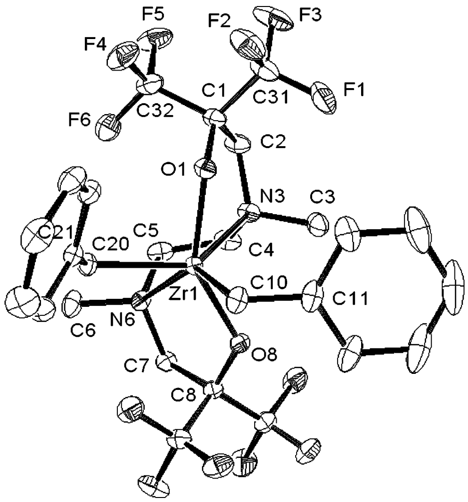

Figure 3. ORTEP view of $[ON^2NO]Zr(CH_2Ph)_2$ (**4**), depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

Table 1. Crystal Data and Structure Refinement

	3	**4**	**6**
formula	$C_{12}H_{14}Cl_2F_{12}N_2O_2Ti$	$C_{26}H_{28}F_{12}N_2O_2Zr$	$C_{20}H_{33}F_{12}N_2O_3SiY$
cryst size, mm	0.08 × 0.08 × 0.06	0.35 × 0.27 × 0.24	0.24 × 0.12 × 0.08
M, g mol^{-1}	565.05	719.72	694.48
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	7.3661(2)	16.5131(2)	10.2291(2)
b, Å	10.8162(4)	11.63810(10)	16.7352(4)
c, Å	12.8858(5)	17.0637(2)	16.8838(4)
α, deg	71.9240(10)	90	90
β, deg	83.218(2)	117.97	97.594(2)
γ, deg	80.626(2)	90	90
V, Å^3	960.45(6)	2896.17(5)	2864.92(11)
Z	2	4	4
D_{calc}, Mg/m^3	1.954	1.651	1.610
T, K	100(2)	100(2)	120(2)
θ range, deg	6.86−31.04	2.21−33.19	2.35−27.49
μ, mm^{-1}	0.851	0.485	2.180
no. of measd reflns	12 709	69 238	38 671
no. of indep reflns	6052	11 007	6556
no. of reflns with $I > 2\sigma(I)$	4733	9759	5164
no. of params	282	390	441
goodness of fit	1.085	1.019	0.980
R [$I > 2\sigma(I)$]	0.0397	0.0307	0.0360
$R_w{}^2$	0.0917	0.0733	0.0883
lgst diff, e Å^{-3}	0.885	0.894	0.60

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3 and 4

3		**4**	
Ti(1)−O(1)	1.8710(13)	Zr(1)−O(1)	2.0214(8)
Ti(1)−O(8)	1.8975(13)	Zr(1)−O(8)	2.0471(8)
Ti(1)−N(3)	2.3117(16)	Zr(1)−N(3)	2.4473(10)
Ti(1)−N(6)	2.3163(16)	Zr(1)−N(6)	2.5488(9)
Ti(1)−C(l1)	2.2493(5)	Zr(1)−C(10)	2.2657(12)
Ti(1)−C(l2)	2.2562(5)	Zr(1)−C(20)	2.2714(11)
N(3)−Ti(1)−N(6)	79.09(6)	N(3)−Zr(1)−N(6)	74.29(3)
Cl(1)−Ti(1)−C(l2)	97.77(2)	C(10)−Zr(1)−C(20)	93.35(4)
Cl(1)−Ti(1)−N(3)	95.01(4)	C(10)−Zr(1)−N(3)	127.51(4)
Cl(2)−Ti(1)−N(6)	92.01(4)	C(20)−Zr(1)−N(6)	82.26(4)
O(1)−Ti(1)−N(3)	74.82(6)	O(1)−Zr(1)−N(3)	69.80(3)
O(8)−Ti(1)−N(6)	74.75(6)	O(8)−Zr(1)−N(6)	69.04(3)
O(1)−Ti(1)−O(8)	163.77(6)	O(1)−Zr(1)−O(8)	142.70(3)
O(1)−Ti(1)−Cl(1)	101.41(5)	O(1)−Zr(1)−C(10)	93.04(4)
O(8)−Ti(1)−Cl(1)	90.13(4)	O(8)−Zr(1)−C(20)	125.78(4)
O(1)−Ti(1)−Cl(2)	89.27(4)	O(1)−Zr(1)−C(20)	91.49(4)
C(4)−N(3)−Ti(1)	105.51(11)	C(4)−N(3)−Zr(1)	109.05(7)
C(5)−N(6)−Ti(1)	105.12(11)	C(5)−N(6)−Zr(1)	102.75(7)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Y(1)−O(1)	2.1624(17)	O(2)−Y(1)−O(1)	109.02(8)
Y(1)−O(2)	2.149(2)	O(1)−Y(1)−N(1)	68.89(7)
Y(1)−N(1)	2.501(2)	O(2)−Y(1)−N(2)	67.30(8)
Y(1)−N(2)	2.704(2)	O(1)−Y(1)−C(20)	112.60(8)
Y(1)−O(3)	2.349(2)	O(2)−Y(1)−C(20)	137.41(9)
Y(1)−C(20)	2.421(3)	O(3)−Y(1)−C(20)	92.04(9)
Y(1)−F(9A)	2.811(3)	C(3)−N(1)−Y(1)	112.74(15)
N(1)−Y(1)−N(2)	69.50(7)	C(4)−N(2)−Y(1)	107.74(15)

alkoxide ligands are acute (74.75(6)° and 74.82(6)° for **3**; 69.04(3)° and 69.80(3)° for **4**), while several *cis* angles involving the X ligands are obtuse; this is especially marked for the benzyl complex **4** (O(8)−Zr(1)−C(20), 125.78(4)°; C(10)−Zr(1)−N(3), 127.51(4)°). These effects can be ascribed to the constraints imposed by the chelation and to benzyl/amino-alkoxide steric interactions. The gross structural features of **3** and **4** are reminiscent of titanium and zirconium complexes of tetrahydrosalen and 1,4-dithiabutanedienyl-bis(phenol) ligands.[4a−h] These compounds are also C_2-symmetric with *trans* aryloxide oxygens.

The Zr−O distances in **4** (2.0214(8), 2.0471(8) Å) are in the range (ca. 1.95−2.08 Å) observed for $Cp_2Zr(OR)_2$ and $Cp_2Zr(OAr)_2$ complexes[15] and compare well with the distances (1.995(3), 2.004(3) Å) observed in the pyridine-alcohol complex $(6\text{-pyCMe}_2O)_2Zr(CH_2Ph)_2$.[6d] The corresponding Ti−O distances in **3** are logically shorter (1.871(1), 1.898(1) Å), reflecting the ca. 10% decrease in the ionic radii of the metal centers.[16] In both structures, the M−O−C units are bent (Ti−O−C angles: 129.77(12)°, 129.42(12)°; Zr−O−C angles: 127.58(7)°, 130.75(7)°). It is reasonable to describe the oxygens in **3** and **4** as sp^2-hybridized and to regard the alkoxides as four-electron (σ, π) donors. The five-membered chelate rings are rather flat and appear not to be significantly strained. The Ti−N bond distances (2.312(2), 2.316(2) Å) in **3** and the Zr−N bond distances (2.447(1), 2.549(9) Å) in **4** are similar to those observed in the parent tetrahydrosalen complexes.[4a−d] Both the benzyl ligands of **4** have a normal structure (Zr(1)−C(10)−C(11) 106.75(8)°, Zr(1)−C(20)−C(21) 116.91(7)°; Zr(1)−C(11) 3.041(6) Å, Zr(1)−C(21) 3.234(6) Å), indicative of no significant Zr···Ph interaction. This was rather unexpected considering that a weak Zr···Ph interaction (i.e., η^2-benzyl) has been observed in the related bis(pyridine-alkoxide) dibenzyl zirconium complex $(pyCMe_2O)_2Zr(CH_2Ph)_2$,[6d] which may be assumed to have a less electron-deficient metal center than in the fluorinated amino-alkoxide complex **4**. Overall, **3** and **4** are best described as 16-electron species (counting the alkoxides as four-electron donors).

Solution Structures of 2−4 and Dynamics of 4. All NMR spectroscopic data of the complexes **2a**, **2b**, **3**, and **4** at room temperature in aromatic hydrocarbons (benzene, toluene) indicate in each case the presence of a single species with molecular C_2-symmetry. The ^1H NMR spectra of the complexes bearing the ethylene-bridged ligand **1a**, namely, **2a**, **3**, and **4**, exhibit two

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[16] Effective ionic radii for six-coordinate metal centers: Ti^{4+}, 0.605 Å; Zr^{4+}, 0.72 Å, Y^{3+}, 0.90 Å. Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

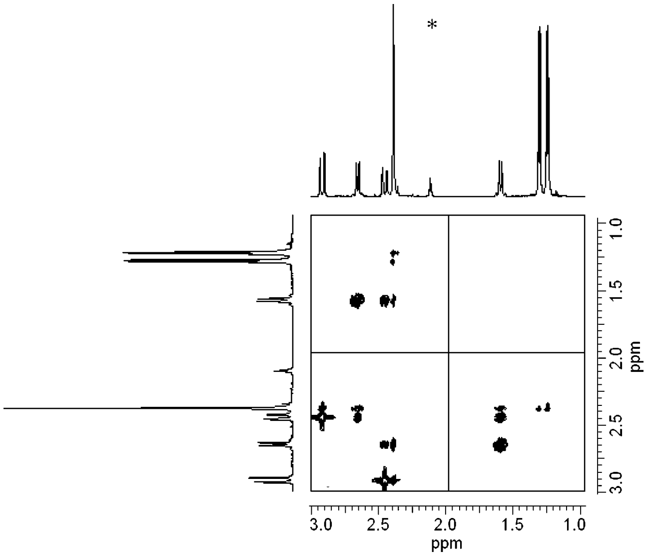
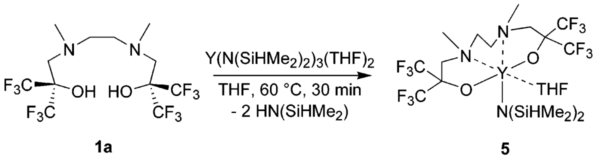


Figure 4. Details of the NOESY NMR spectrum of **2a** (toluene-d_8, 298 K, 500 MHz) (* denotes resonances for PhC*H*D$_2$ at δ 2.15).

doublets of an AB spin pattern for the CH$_2$ units in the bridge and two doublets for the CH$_2$ unit adjacent to C(CF$_3$)$_2$. Zirconium dibenzyl complex **4** shows an additional AB pattern for the CH$_2$ groups of the two *cis*-benzyl ligands. Also, the ^{19}F NMR spectra of **2a**, **3**, and **4** show two sharp quartets ($^4J_{F-F}$) of equal intensity for the two C(CF$_3$)$_2$ groups (for **4**, one quartet is broadened due to dynamics; vide infra). These data suggest that **2**−**4** adopt structures in solution at room temperature similar to those observed in the solid state. A C_2-symmetric type **C** structure (Figure 1) was clearly preferred over a C_2-symmetric type **A** structure in the case of the di-isopropoxy titanium complex **2a** on the basis of a NOESY experiment. Key features include the presence of cross-peaks between each of the hydrogens of the ethylene bridge (δ 1.61 and 2.65) and only one of the C(CF$_3$)$_2$C*HH* hydrogens (δ 2.45) (Figure 4); also, no cross-peak was observed between the hydrogens of the ethylene bridge and the hydrogens of the isopropoxy groups, while these are expected for a type **A** structure.

As noted above, the room-temperature ^{1}H NMR spectra of **2a**, **3**, and **4** all exhibit AB patterns for the diastereotopic CH$_2$ hydrogens, which implies that inversion of configuration at the metal (i.e., interconversion of Λ and Δ stereoisomers, racemization) is slow on the NMR time scale under these conditions.[17] To probe this issue and elucidate the dynamic properties of these complexes, we investigated in more detail the variable-temperature ^{19}F and ^{1}H NMR spectra of dibenzyl complex **4**; both series of spectra are shown in Figure 5. The ^{19}F NMR spectrum of **4** at 204 K contains two sets of signals in a 10:10:52:52 ratio attributed to two isomers. Upon heating, those signals coalesce (265 K) and give at 295 K a sharp quartet and a broadened quartet in a 1:1 ratio, which further coalesce into a broad singlet at 366 K. The ^{1}H NMR spectra at temperatures below 265 K are complicated due to significant overlapping, except for the N−CH$_3$ resonances. At 204 K, two (broadened) singlets in a 10:52 ratio are observed, which rapidly coalesce (220 K) into a sharp singlet above ca. 265 K. Between this temperature and 316 K, three well-resolved AB spin systems are observed for the (CF$_3$)$_2$C*HH* hydrogens (δ(290 K): 2.51 and 2.35, 2 d, J = 15.5 Hz), the benzyl hydrogens (δ 2.29 and 2.23, 2d, J = 10.1 Hz), and the hydrogens of the ethylene bridge (δ 1.93 and 1.58, J = 10.6 Hz). Upon heating, each of these pairs of doublets coalesce, and the ^{1}H NMR spectrum of **4** at 366 K contains only singlet-like resonances. All those dynamic phenomena are reversible upon lowering the temperature and are best explained as follows: (i) at low temperature, two C_2-symmetric isomers, i.e., **A** (minor) and **C** (major), coexist;[18] (ii) around room temperature, these isomers exchange fast on the NMR time scale; (iii) at high temperature, racemization at the metal center, which results in the interconversion between the diastereotopic hydrogens as well as between the diastereotopic CF$_3$ groups, is fast on the NMR time scale. The racemization barrier determined from the line shape changes of the C(CF$_3$)$_2$C*HH*, ZrC*HH*Ph, and NC*HH* in the ^{1}H NMR spectra is 17.0(1) kcal/mol,[19] a value comparable to those determined for related dibenzyl zirconium bis(amino-phenoxide) complexes.[17h]

Synthesis of Yttrium Complexes of Diamino-diol 1a. Yttrium complexes of the ethylene-bridged diamino-diol **1a** were also prepared via σ-bond metathesis routes. The amine elimination reaction between the tris(amido)-yttrium precursor Y(N(SiHMe$_2$)$_2$)$_3$(THF)$_2$ and **1a** in THF at 60 °C cleanly afforded the corresponding monoamido complex **5** with concomitant release of 2 equiv of bis(dimethylsilyl)amine (eq 5). Compound **5** is almost insoluble in aromatic hydrocarbons (toluene, benzene), limiting meaningful NMR data in these solvents. The ^{1}H NMR spectrum of **5** in THF-d_8 at room temperature features broad signals indicative of a fluxional behavior under these conditions. Upon heating to 360 K, those signals coalesce into singlets, but the latter are still



(5)

1a

5
(single, undefined C_1-isomer)

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(18) Unselective coordination of tetradentate ligands to give mixtures of complexes is frequent; see, for example, precedent with related titanium complexes of 1,5-dithiapentadiyl-bridged bis(phenol)s.[4h]

(19) (a) Racemization barriers $\Delta G^{\ddagger}$(racemization) were determined from the coalesence of the CH$_2$ AB patterns using the following equations: $\Delta G^{\ddagger}(\text{racemization}) = 4.576T_c[10.319 + \log(T_c/k_c)]$, where T_c is the coalesence temperature and k_c is the exchange rate constant at coalesence, which is given by $k_c = \pi[(\Delta\nu_{AB}{}^2 + 6J_{AB}{}^2]^{1/2}/2^{1/2}$. For C(CF$_3$)$_2$C*HH*: $\Delta\nu_{AB} = 82$ Hz, $J_{AB} = 15.5$ Hz, $T_c = 335$ K. For ZrC*HH*Ph, $\Delta\nu_{AB} = 32$ Hz, $J_{AB} = 10.1$ Hz, $T_c = 325$ K. For NC*HH*, $\Delta\nu_{AB} = 185$ Hz, $J_{AB} = 10.6$ Hz, $T_c = 350$ K. See: (b) Alexander, S. *J. Chem. Phys.* **1962**, *37*, 971. (c) Kurland, R. J.; Rubin, M. B.; Wise, W. B. *J. Chem. Phys.* **1964**, *40*, 2426. (d) Kost, D.; Zeichner, A. *Tetrahedron Lett.* **1974**, 4533

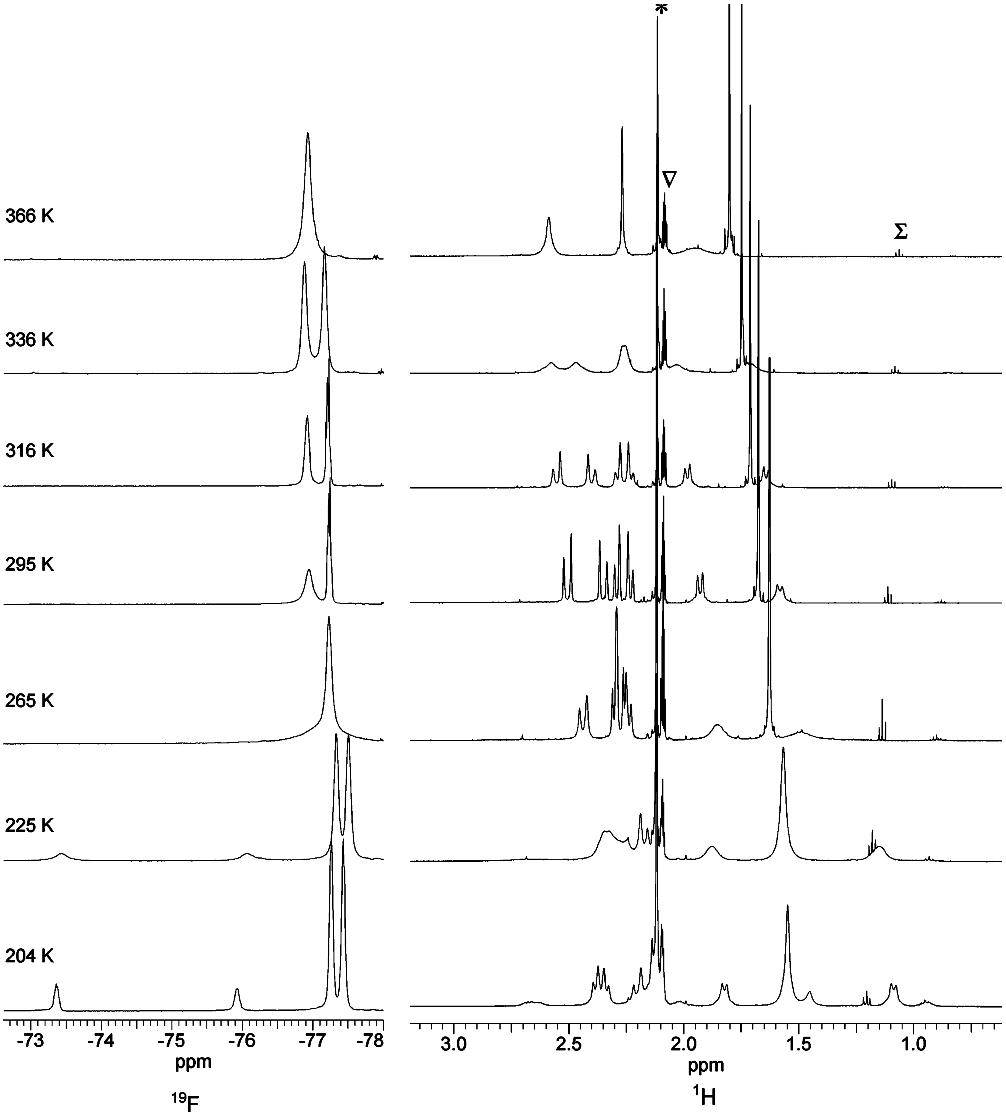
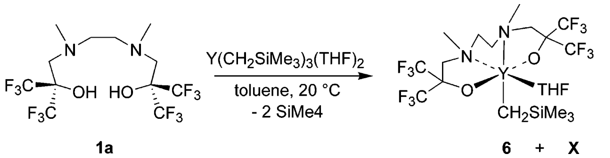


Figure 5. Variable-temperature ^{19}F (left, 470 MHz) and ^{1}H (right, 500 MHz) NMR spectra of dibenzyl complex [ON^{2}NO]Zr(CH$_2$Ph)$_2$ (**4**) (toluene-d_8) (*, ∇, and Σ denote resonances for PhCH_3, PhCHD$_2$, and residual Et$_2$O from ligand recrystallization, respectively).

broad, indicating that the fast exchange regime is not yet reached at this temperature. At low temperature (256 K), those signals decoalesce into a set of resonances that includes, in particular, two singlets for the two N−CH$_3$, four signals for the four hydrogens of the ethylene bridge, and two multiplets for the two Si−H; complex **5** features therefore C_1-symmetry in solution. Unfortunately, repeated attempts to grow X-ray quality crystals of **5** were unsuccessful, and the exact structure of **5** has not been established so far.

The parent hydrocarbyl complex [ON^{2}NO]Y(CH$_2$SiMe$_3$)(THF) (**6**) was prepared similarly by protonolysis of the tris(carbyl) precursor Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 1 equiv of **1a** in toluene (eq 6). The room-temperature ^{1}H NMR spectrum in toluene-d_8 of the solid material recovered from the above reaction exhibits sharp, well-resolved resonances. Whatever the reaction conditions used, a mixture of two products reproducibly forms in a 1:3 ratio based on the SiMe$_3$ resonances. The major product is a C_2-symmetric steroisomer of **6**, which features an AB pattern for the diastereotopic CH$_2$ hydrogens of the ligand, the expected high-field doublet for the Y−CH$_2$ moiety (δ −0.95, $^2J_{\text{Y-H}}$ = 3.1 Hz), and resonances for a coordinated THF molecule. The second product is characterized by a sharp doublet of doublets for the Y−CH$_2$ moiety (δ −0.59, $^2J_{\text{H-H}}$ = 10.1 Hz, $^2J_{\text{H-Y}}$ = 3.1 Hz) and very broad resonances for the ligand hydrogens. Noteworthy, all those signals are not modified (nor sharpened for the minor species) in the temperature range from 220 to 333 K, indicating that no exchange takes place between **6** and the other species. The same conclusions are derived from the ^{19}F NMR spectrum, which displays two sharp quartets of equal intensity for **6** and broad signals that emerge from the baseline and that are attributed to the minor unidentified species. Complex **6** was obtained in pure form by slow recrystallization of the crude material from



1a **6** + **X** (6)

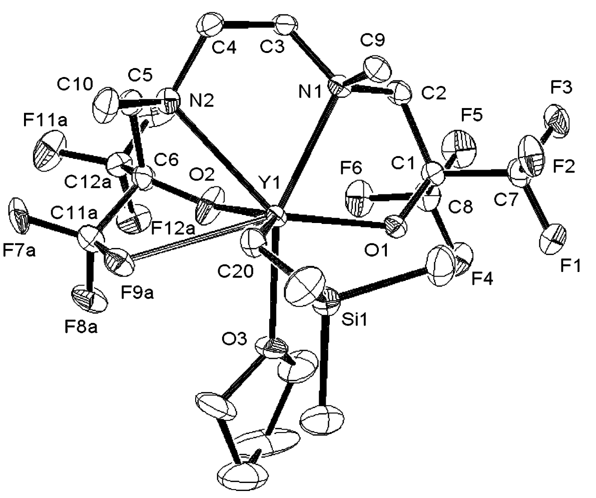


Figure 6. ORTEP view of $[ON^2NO]Y(CH_2SiMe_3)(THF)$ (**6**), depicted with 30% thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

toluene at −35 °C, and its structure was confirmed by an X-ray diffraction study.

Complex **6** is seven-coordinate in the solid state due to Y···F coordination to one of the four CF_3 substituents, with a bond distance of 2.806(2) Å as shown in Figure 6. This value is comparable with other weak Y···F interactions observed in some yttrium complexes bearing fluorinated groups, e.g., the phenoxy-imine complex $Y\{N(SiMe_3)_2\}[(2\text{-}C_6F_5N{=}CH)(6\text{-}Bu^t)C_6H_3O]_2$ (Y−F, 2.806(2) Å)[20] and the anilido-amine complex $Y(C_6F_5)_2(THF)[2,6\text{-}iPr_2C_6H_3N{-}C_6H_4CH_2N{=}(2,6\text{-}iPr_2C_6H_3)]$ (Y−F, 2.756(2) Å).[21] It is, however, significantly longer than that observed in more electron-deficient species, e.g., $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Y(OEt_2)$, in which the three fluorine atoms are coordinated to the yttrium center (Y−F, 2.438(6)−2.517(6) Å),[22] and $[(C_5H_4SiMe_3)_2Y]^+[MeB(C_6F_5)_3]^-$, in which the anion is coordinated in a chelating fashion via one *ortho*-fluorine atom (Y−F, 2.366(3) Å).[23] In agreement with the long Y···F distance, these yttrium−fluorine interactions are weak: the ^{19}F NMR chemical shifts of **6** are essentially identical to the spectrum of **2a** and **4** and give no indication for persistent Y···F coordination in solution. Apart from this feature that induces distortion in the octahedral coordination of the $[ON^2NO]$ ligand in the solid state, compound **6** is in other ways structurally similar to the titanium and zirconium complexes **3** and **4**. The distances Y−O (2.149(2)−2.162(2) Å) and Y−N (2.501(2)−2.704(2) Å) associated with the chelated amino-alkoxide ligand are longer than those in the Ti complex **3** and the Zr complex **4**, reflecting the larger ionic radius of yttrium.[16] This results also in smaller *cis* and *trans* L−Y−L bond angles, a phenomenon obviously magnified by the presence of a fluorine atom as the seventh ligand in the coordination sphere. The Y−O bond distances in **6** are only slightly longer than those observed in the nonchelated bis(trifluoromethyl)alkoxide yttrium complexes $Y\{OCMe(CF_3)_2\}_3(THF)_3$ (2.077−2.125 Å) and $[Y\{OCMe(CF_3)_2\}_3(diglyme)]$ (2.059−2.084 Å).[24]

Stereoselectivity of $[ON^nNO]^{2-}$ Coordination. An interesting aspect of this study is the stereoselectivity of coordination of $[ON^nNO]^{2-}$ to group 4 metal centers. It is remarkable that for the four $[ON^nNO]MX_2$ compounds described here (**2a**, **2b**, **3**, and **4**) only a single C_2-symmetric isomer is formed at room temperature, out of the eight possible isomers (Figure 1). Only for $[ON^2NO]Zr(CH_2Ph)_2$ (**4**) has a mixture of two single C_2-symmetric isomers been evidenced at low temperature. These structural trends appear to reflect more the conformational preferences of the $[ON^nNO]^{2-}$ ligand than the donor properties of the X ligands. On the basis of the latter properties, structure **A** would be expected to be generally favored since the electron-deficient bis(trifluoromethyl)alkoxide ligands are *trans* to the strong σ-donor amino X groups. Conversely, structure **C** has the X ligands *trans* to the strong donor amino group, which is expected to be favorable only for weak donor X ligands, e.g., X = Cl. In fact, as noted above, X-ray structural data and NOESY data establish that **3** and **4**, and **2a** adopt structure **C** in the solid state and in solution, respectively. Additionally, the ^{13}C NMR data for the $[ON^2NO]^{2-}$ ligand of $[ON^2NO]Zr(CH_2Ph)_2$ (**4**) and $[ON^2NO]Y(CH_2SiMe_3)(THF)_2$ (**6**) are very similar to those of C_2-**2a**, which suggests that those species may also have a type **C** structure in solution.

In conclusion, alcohol, alkane, and amine elimination reactions of the new achiral fluorinated diamino-diol $[ON^nNO]H_2$ with $Ti(OiPr)_4$, $Zr(CH_2Ph)_4$, $Y(CH_2SiMe_3)_3(THF)_2$, and $Y(N(SiHMe_2)_2)_3(THF)_2$ provide efficient access to $[ON^nNO]MX_2$ (M = Ti, Zr; X = O*i*Pr, CH_2Ph) and $[ON^nNO]YX(THF)_n$ (X = CH_2SiMe_3, $N(SiHMe_2)_2$) complexes. The coordination of the $[ON^nNO]^{2-}$ ligand to group 4 metals is highly stereoselective. For each $[ON^nNO]MX_2$ compound prepared, only a single C_2-symmetric isomer (**2a**, **2b**, **3**) or a mixture of two single C_2-symmetric isomers (**4**) is formed, out of the eight possible isomers. It appears that the structure of $[ON^nNO]MX_2$ complexes is controlled by the conformational preferences of the $[ON^nNO]^{2-}$ ligand. The potential of these species for polymerization of olefins and polar monomers is currently under investigation in our group.

Experimental Section

General Considerations. All manipulations were performed under a purified argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. Solvents (toluene, pentane, THF) were freshly distilled from Na/K alloy under nitrogen and degassed thoroughly by freeze−thaw−vacuum cycles prior to use. Deuterated solvents (>99.5% D, Eurisotop) were freshly distilled from sodium/potassium amalgam under argon and degassed prior to use. Anhydrous hexafluoroacetone was purchased from SynQuest Fluorochemicals and used as received. Zirconium and yttrium precursors $Zr(CH_2Ph)_4$,[25] $Y(CH_2SiMe_3)_3(THF)_2$,[26] and $Y[N(SiHMe_2)_2]_3(THF)_2$[27] were prepared following literature procedures. NMR spectra

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were recorded on Bruker AC-300 and AM-500 spectrometers in Teflon-valve NMR tubes at ambient probe temperature (23 °C) unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported in ppm vs $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was made from $^1H-^1H$ COSY, $^1H-^{13}C$ HMQC, and HMBC NMR experiments. ^{19}F NMR spectra were referenced externally to neat $BF_3\cdot Et_2O$. All coupling constants are given in hertz. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. IR spectra were recorded on a Nicolet 510 FTIR spectrophotometer in KBr pellets and are expressed by wavenumber (cm^{-1}). Melting and decomposition points are uncorrected.

[$HOC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)C(CF_3)_2OH$] ([ON^{2}NO]-H$_2$, 1a). To a reaction flask equipped with a dry ice condenser was slowly added anhydrous hexafluoroacetone (2.80 g, 16.6 mmol) into a diethyl ether solution of diazomethane prepared from Diazald (0.70 g, 16.6 mmol) and using a homemade Diazald apparatus. The reaction was stopped after the color of solution had changed from light yellow to colorless, and the resulting mixture was stirred for 2 h to allow the complete formation of the CF_3-substituted oxirane $(CF_3)_2\overline{COC}H_2$. After then, *N*,*N*′-dimethylethylenediamine (0.70 g, 8.3 mmol) was added dropwise into this solution over a period of 15 min, and the reaction mixture was stirred at room temperature for 24 h. Finally, the reaction was quenched by addition of water and washed with a saturated $NaHCO_3$ solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, the diethyl ether solvent evaporated in vacuo, and the resultant oily material taken into a minimum amount of warm hexane. Crystalline material of ligand **1a** (1.20 g, 2.60 mmol, 31%) was obtained upon keeping the hexane solution at room temperature overnight. Selected spectral data: MS (EI, 70 eV) observed (actual) [assignment]: *m/z* 379 (379) [M − CF_3], 281 (281) [M − $(CF_3)_2C(OH)$], 238 (238) [M − $(CF_3)_2C(OH)CH_2$-NMe], 224 (224) [$(CF_3)_2C(OH)CH_2N(Me)_2$]. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.21 (br, OH, 2H) 2.96 (s, CH_2, 4H), 2.72 (s, CH_2, 4H), 2.46 (s, NCH_3, 6H). ^{1}H NMR (toluene-d_8, 500 MHz): δ 6.42 (br, 2H, OH), 2.54 (s, 4H, $NCH_2C(CF_3)_2$), 2.02 (s, 4H, CH_2CH_2), 1.94 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 123.1 (q, CF_3, $^1J_{CF}$ = 286.0 Hz), 72.8 (sept, $C(CF_3)_2$, $^2J_{CF}$ = 30.0 Hz), 56.6 (s, $NCH_2C(CF_3)_2$), 55.0 (s, CH_2) 44.5 (s, NCH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125 MHz): δ 123.6 (q, $^1J_{C-F}$ = 284 Hz, CF_3), 73.1 (sept, $^2J_{C-F}$ = 28.0 Hz, $C(CF_3)_2$), 55.7 ($NCH_2C(CF_3)_2$), 54.4 (CH_2CH_2), 43.1 (CH_3N). ^{19}F NMR (470 MHz, $CDCl_3$, 295 K): δ −78.02 (6F). IR (KBr): ν 2984 (w), 2866 (w), 2839 (w), 1470 (m), 1282 (s), 1203 (vs), 1146 (s), 1018 (m), 698 (s) cm^{-1}. Mp: 77−78 °C. Anal. Calcd for $C_{12}H_{16}F_{12}N_2O_2$: C, 32.15; H, 3.60; N, 6.25. Found: C, 31.63; H, 3.82; N, 6.11.

[$HOC(CF_3)_2CH_2N(Me)(CH_2)_3N(Me)C(CF_3)_2OH$] ([ON^{3}NO]-H$_2$, 1b). The procedure was identical to that of **1a**, using diazomethane (0.20 g, 6.0 mmol), anhydrous hexafluoroacetone (ca. 1.0 g, 6.0 mmol), and *N*,*N*′-dimethylpropylenediamine (0.30 g, 3.0 mmol). After removal of solvent and quenching the reaction mixture with excess water, recrystallization from warm hexane gave **1b** as a colorless crystalline compound (0.60 g, 43% yield). Selected spectral data: MS (EI, 70 eV) observed (actual) [assignment]: *m/z* 462 (462) [M], 393 (393) [M − CF_3] 295 (295) [M − $(CF_3)_2C(OH)$], 251 (251) [M − $(CF_3)_2C(OH)CH_2$-NMe], 224 (224) [$(CF_3)_2C(OH)CH_2N(Me)_2$]. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 6.52 (br, OH, 2H), 2.91 (s, CH_2, 4H), 2.65 (t, NCH_2, $^3J_{HH}$ = 7.5 Hz, 4H), 2.45 (s, NCH_3, 6H), 1.72 (m, CH_2, $^3J_{HH}$ = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 123.3 (q, CF_3, $^1J_{CF}$ = 285.6 Hz), 71.3 (sept, $C(CF_3)_2$, $^2J_{CF}$ = 30.0 Hz), 56.3 (s, $NCH_2C(CF_3)_2$), 54.4 (s, $CH_2CH_2CH_2$) 43.1 (s, NCH_3), 25.1 (s, $CH_2CH_2CH_2$). ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ −78.55 (s). IR (KBr): ν 2968 (w), 2875 (w), 2828(w), 1471 (m), 1281 (s), 1205 (vs), 1155 (s), 1015 (m), 597 (w) cm^{-1}. Mp: 43 °C. Anal. Calcd for $C_{13}H_{18}F_{12}N_2O_2$: C, 33.78; H, 3.92; N, 6.06. Found: C, 33.69; H, 4.10; N, 6.05.

[$OC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)C(CF_3)_2O$]Ti(O*i*Pr)$_2$-([ON$_2$NO]Ti(O*i*Pr)$_2$, 2a). A solution of diamino-diol **1a** (0.068 g, 0.154 mmol) in toluene (2 mL), cooled at −30 °C, was added dropwise over 5 min, under vigorous stirring, to a solution of Ti(OiPr)$_4$ (0.043 g, 0.154 mmol) in toluene (2 mL) cooled at −30 °C. The clear mixture was slowly warmed to room temperature over 12 h under magnetic stirring. Volatiles were removed under vacuum, and the solid residue was washed with pentane and dried in vacuo to give **2a** as a white solid (0.094 g, 100%). ^{1}H NMR (toluene-d_8, 500 MHz): δ 4.83 (sept, $^2J_{H-H}$ = 6.1, 2H, CH O*i*Pr), 2.91 (d, $^2J_{H-H}$ = 15.4, 2H, $NCH_2C(CF_3)_2$), 2.65 (d, $^2J_{H-H}$ = 10.6, 2H, CH_2CH_2), 2.45 (d, $^2J_{H-H}$ = 15.4, 2H, $NCH_2C(CF_3)_2$), 2.39 (s, 6H, NCH_3), 1.61 (d, $^2J_{H-H}$ = 10.6, 2H, CH_2CH_2), 1.33 (d, $^2J_{H-H}$ = 6.1, 6H, CH_3 O*i*Pr), 1.27 (d, $^2J_{H-H}$ = 6.1, 6H, CH_3 O*i*Pr). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125 MHz): δ 124.7 (q, $^1J_{C-F}$ = 285, CF_3), 84.8 (sept, $^2J_{C-F}$ = 28, $C(CF_3)_2$), 79.5 (s, CH O*i*Pr), 61.3 (s, $NCH_2C(CF_3)_2$), 59.4 (s, CH_2CH_2), 49.2 (s, CH_3N), 25.0 (s, CH_3 O*i*Pr), 24.6 (s, CH_3 O*i*Pr). ^{19}F NMR (toluene-d_8): δ −74.5 (q, $^4J_{F-F}$ = 10.7, 6F), −76.6 (q, $^4J_{F-F}$ = 10.7, 6F). Anal. Calcd for $C_{18}H_{28}F_{12}N_2O_4Ti$: C, 35.31; H, 4.61; N, 4.58. Found: C, 35.12; H, 4.96; N, 4.78.

[$OC(CF_3)_2CH_2N(Me)(CH_2)_3N(Me)C(CF_3)_2O$]Ti(O*i*Pr)$_2$-([ON^{3}NO]Ti(O*i*Pr)$_2$, 2b). Complex **2b** was prepared in a manner analogous to that for complex **2b**, starting from diamino-diol **1b** (0.050 g, 0.108 mmol) and Ti(O*i*Pr)$_4$ (0.030 g, 0.108 mmol). White powder (0.067 g, 100%). ^{1}H NMR (toluene-d_8, 500 MHz): δ 4.89 (sept, $^2J_{H-H}$ = 6.2, 2H, CH O*i*Pr), 2.80 (m, 4H, $NCH_2C(CF_3)_2$), 2.36 (s, 6H, NCH_3), 2.29 (m, 4H, CH_2-CH_2CH_2), 1.26 (m, 2H, $CH_2CH_2CH_2$), 1.26 (d, $^2J_{H-H}$ = 6.2, 12H, CH_3 O*i*Pr). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125 MHz): δ 125.2 (q, $^1J_{C-F}$ = 286, CF_3), 85.1 (sept, $^2J_{C-F}$ = 28, $C(CF_3)_2$), 80.3 (s, CH OiPr), 60.1 (s br, $NCH_2C(CF_3)_2$), 59.8 (s, $CH_2CH_2CH_2$), 49.6 (s, CH_3N), 24.6 (s, CH_3 OiPr), 23.4 (s, $CH_2CH_2CH_2$). Anal. Calcd for $C_{19}H_{30}F_{12}N_2O_4Ti$: C, 36.44; H, 4.83; N, 4.47. Found: C, 36.24; H, 4.98; N, 4.67.

[$OC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)C(CF_3)_2O$]$TiCl_2$([ON^2-NO]$TiCl_2$, 3). A solution of diamino-diol **1a** (0.094 g, 0.210 mmol) in toluene (2 mL), cooled at −30 °C, was introduced dropwise over 2 min, under vigorous stirring, onto a solution of $TiCl_4$ (0.040 g, 0.210 mmol) in toluene (2 mL) cooled at −30 °C. A fine precipitate progressively formed over the addition course. Triethylamine (0.213 g, 2.10 mmol), cooled at −30 °C, was added dropwise to the mixture by cannula, resulting in the immediate formation of a precipitate. The reaction mixture was slowly warmed to room temperature over 4 h under magnetic stirring. The mixture was filtered, and the filtrate was concentrated under vacuum, leaving a white solid, which was washed with pentane and dried under vacuum (0.101 g, 85%). ^{1}H NMR (THF-d_8, 300 MHz): δ 3.88 (d, ^2J = 15.8, 2H, $NCH_2C(CF_3)_2$), 3.70 (d, ^2J = 15.8, 2H, $NCH_2C(CF_3)_2$), 2.32 (d, ^2J = 9.5, 2H, CH_2CH_2), 2.99 (d, ^2J = 9.5, 2H, CH_2CH_2), 2.93 (s, 6H, NCH_3). Anal. Calcd for $C_{12}H_{14}Cl_2F_{12}N_2O_2Ti$: C, 25.51; H, 2.50 N, 4.96. Found: C, 25.12; H, 2.96; N, 4.78.

[$OC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)C(CF_3)_2O$]Zr($CH_2$-Ph)$_2$ ([ON^{2}NO]Zr(CH_2Ph)$_2$, 4). Diamino-diol **1a** (0.050 g, 0.111 mmol) and $Zr(CH_2Ph)_4$ (0.051 g, 0.111 mmol) were introduced in an NMR tube, and C_6D_6 was vacuum transferred in at −78 °C. The tube was vigorously shaken and gently warmed to room temperature over 10 min. ^{1}H NMR indicated complete conversion of the reagents to **4** and concomitant release of 2 equiv of toluene. Removal of volatiles under vacuum left **4** as a white powder (0.082 g, 100%). Anal. Calcd for $C_{26}H_{28}F_{12}N_2O_2Zr$: C, 43.39; H, 3.92; N, 3.89. Found: C, 42.89; H, 4.25; N, 3.88. IR (KBr): ν 3074 (w), 3018 (w), 2882 (w), 1594 (m), 1485 (m), 1463 (m), 1332 (w), 1303 (m), 1288 (s), 1201 (vs), 1148 (m), 1051 (s), 998 (s), 950 (m), 698 (s) cm^{-1}. Mp: 184 °C (dec at 205 °C). ^{1}H NMR (toluene-d_8, 500 MHz,

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366 K): δ 7.11 (d, ^3J = 7.5, 4H, *o*-H), 6.77 (t, 4H, ^3J = 7.0, *m*-H), 2.58 (s, 4H, $NCH_2C(CF_3)_2$), 2.26 (s, 4H, $ZrCH_2Ph$), 1.95 (br m, 4H, CH_2CH_2), 1.80 (s, 6H, NCH_3). ^{19}F NMR (toluene-d_8, 470 MHz, 366 K): δ −77.0 (br m, 12F). ^{1}H NMR (toluene-d_8, 500 MHz, 295 K): δ 7.21 (d, ^3J = 7.5, 4H, *o*-H), 7.11 (m, 2H, *p*-H), 6.83 (t, 4H, ^3J = 7.0, *m*-H), 2.51 (d, ^2J = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.35 (d, ^2J = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.29 (d, ^2J = 10.1, 2H, $ZrCH_2Ph$), 2.23 (d, ^2J = 10.1, 2H, $ZrCH_2Ph$), 1.93 (d, ^2J = 10.5, 2H, CH_2CH_2), 1.76 (s, 6H, NCH_3), 1.58 (d, ^2J = 10.6, 2H, CH_2CH_2). ^{19}F NMR (toluene-d_8, 470 MHz, 295 K): δ −77.0 (br m, 6F), −77.3 (q, $^4J_{F-F}$ = 9.6, 6F). ^{1}H NMR (C_6D_6, 300 MHz, 290 K): δ 7.41 (d, ^3J = 7.5, 4H, *o*-H), 7.24 (m, 2H, *p*-H), 6.97 (t, 4H, ^3J = 7.0, *m*-H), 2.61 (d, ^2J = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.47 (d, ^2J = 10.1, 2H, $ZrCH_2Ph$), 2.44 (d, ^2J = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.40 (d, ^2J = 10.1, 2H, $ZrCH_2Ph$), 1.97 (d, ^2J = 10.5, 2H, CH_2CH_2), 1.76 (s, 6H, NCH_3), 1.59 (d, ^2J = 10.6, 2H, CH_2CH_2). ^{13}C NMR (toluene-d_8, 75 MHz, 290 K): δ 144.8 (d, ^2J = 6, C_{ipso}), 128.8 (m, *o*-C, *m*-C), 126.1 (q, $^1J_{C-F}$ = 216 Hz, $\mathit{C}F_3$), 122.7 (d, $^1J_{C-H}$ = 6, *p*-C), 84.6 (m, $\mathit{C}(CF_3)_2$), 70.9 (t, $^1J_{C-H}$ = 125, $\mathit{C}H_2Ph$), 60.5 (t, $^1J_{C-H}$ = 138, $N\mathit{C}H_2C(CF_3)_2$), 58.0 (t, $^1J_{C-H}$ = 136.5, $CH_2\mathit{C}H_2$), 47.9 (q, $^1J_{C-H}$ = 140.5, CH_3N). At 206 K two sets of signals were recorded both in ^{19}F and ^{1}H NMR, consistent with the existence of two isomers of **4** in the ratio 10:52. **Major isomer**: ^{1}H NMR (toluene-d_8, 500 MHz, 205 K): δ 7.41 (d, ^3J = 7.5, 4H, *o*-H), 6.88 (t, 4H, ^3J = 7.0, *m*-H), 2.38 (d, ^2J = 10.0, 2H, $ZrCH_2Ph$), 2.33 (d, ^2J = 10.0, 2H, $ZrCH_2Ph$), 2.19 (d, ^2J = 15.6, 2H, $NCH_2C(CF_3)_2$), 2.01 (d, ^2J = 15.5, 2H, $NCH_2C(CF_3)_2$), 1.82 (d, ^2J = 10.0, 2H, CH_2CH_2), 1.54 (s, 6H, NCH_3), 1.08 (d, ^2J = 10.0, 2H, CH_2CH_2). ^{19}F NMR (toluene-d_8, 470 MHz, 205 K): δ −77.4 (br m, 6F), −77.6 (br m, 6F). **Minor isomer**: ^{1}H NMR (toluene-d_8, 500 MHz, 205 K): δ 7.37 (m br, 4H, *o*-H), 2.66 (m, 4H, $ZrCH_2Ph$), 2.02 (m, 2H, $NCH_2C(CF_3)_2$), 1.45 (s, 6H, NCH_3), 0.95 (m, 2H, CH_2CH_2). ^{19}F NMR (toluene-d_8, 470 MHz, 205 K): δ −73.5 (br m, 6F), −76.0 (br m, 6F).

[OC(CF$_3$)$_2$CH$_2$N(Me)(CH$_2$)$_2$N(Me)C(CF$_3$)$_2$O]Y(N(SiHMe$_2$)$_2$)(THF) ([ON^{2}NO]Y(N(SiHMe$_2$)$_2$)(THF), 5). An NMR tube was charged with diamino-diol **1a** (0.056 g, 0.089 mmol) and $Y(N(SiHMe_2)_2)_3(THF)_2$ (0.056 g, 0.089 mmol). THF was vacuum transferred in at −100 °C, and the tube was allowed to warm to room temperature. The tube was shaken vigorously, and the solution was heated for 30 min at 60 °C. After removing of volatiles under vacuum, THF-d_8 was vacuum transferred in at −100 °C and ^{1}H NMR spectra were recorded at variable temperatures. The spectrum at room temperature established that the starting materials were consumed and featured numerous and broadened resonances. ^{1}H NMR (THF-d_8, 256 K, 500 MHz): δ 4.74 (m, 1H, $Si\mathit{H}Me_2$), 4.67 (m, 1H, $Si\mathit{H}Me_2$), 3.29 (d, $^2J_{H-H}$ = 15.1, 2H, $NCH_2C(CF_3)_2$), 3.07 (d, $^2J_{H-H}$ = 15.1, 2H, $NCH_2C(CF_3)_2$), 3.05 (m, 1H, CH_2CH_2), 3.05 (m, 1H, CH_2CH_2), 2.93 (m, 1H, CH_2CH_2), 2.84 (d, $^2J_{H-H}$ = 9.4, 1H, CH_2CH_2), 2.78 (s, 3H, NCH_3), 2.71 (s, 3H, NCH_3), 0.14 (m, 12H, $NSiH\mathit{Me}_2$). ^{1}H NMR (THF-d_8, 360 K, 500 MHz): δ 4.74 (br, 2H, $N(Si\mathit{H}Me_2)_2$), 3.15 (s br, 4H, $NCH_2C(CF_3)_2$), 2.92 (s br, 4H, CH_2CH_2), 2.71 (s br, 6H, NCH_3), 0.15 (s br, 12H, $NSiH\mathit{Me}_2$). ^{13}C{^{1}H} NMR (THF-d_8, 360 K, 125 MHz): δ 124.9 (q, $^1J_{C-F}$ = 213, $C(\mathit{C}F_3)_2$), 84.8 (m, $\mathit{C}(CF_3)_2$), 60.9 (s, $N\mathit{C}H_2C(CF_3)_2$), 57.9 (s, $CH_2\mathit{C}H_2$), 45.8 (s, NCH_3), 2.51 (s, $NSiHMe_2$).

[OC(CF$_3$)$_2$CH$_2$N(Me)(CH$_2$)$_2$N(Me)C(CF$_3$)$_2$O]Y(CH$_2$SiMe$_3$)(THF) ([ON^{2}NO]Y(CH$_2$SiMe$_3$)(THF), 6). A solution of diamino-diol **1a** (0.047 g, 0.095 mmol) in toluene (3 mL), cooled at −30 °C, was introduced dropwise over 2 min, under vigorous stirring, onto a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.042 g, 0.095 mmol) in toluene cooled at −30 °C. The clear solution was slowly warmed to room temperature over 2 h under magnetic stirring. Removal of volatiles under vacuum left a white solid residue. ^{1}H NMR established the presence of two products, **6** (75% based on $C\mathit{H}_2Si(C\mathit{H}_3)_3$ resonances) and **7** (25%), that do not exchange on the NMR time scale upon warming the solution to 60 °C. Slow recrystallization of this crude material from toluene at −30 °C gave analytically pure crystals of **6**, which proved suitable for X-ray diffraction (0.032 g, 48%). Complex **6** (major product): ^{1}H NMR (C_6D_6, 500 MHz): δ 3.97 (m, 4H, THF), 2.73 (d, $^2J_{H-H}$ = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.60 (d, $^2J_{H-H}$ = 15.4, 2H, $NCH_2C(CF_3)_2$), 2.14 (s, 6H, NCH_3), 1.85 (m, 2H, CH_2CH_2), 1.68 (m, 2H, CH_2CH_2), 1.31 (m, 4H, THF), 0.39 (s, 12H, $SiMe_3$), −0.95 (d, J_{H-Y} = 3.1, 2H, YCH_2). ^{13}C{^{1}H} NMR (C_6D_6, 500 MHz): δ 128.4 (q, $^1J_{C-F}$ = 287, $C(\mathit{C}F_3)_2$), 82.0 (br m, $\mathit{C}(CF_3)_2$), 61.8 (s, $N\mathit{C}H_2C(CF_3)_2$), 57.7 ($CH_2\mathit{C}H_2$), 45.8 (NCH_3), 27.3 (d, $^1J_{C-Y}$ = 78.7, YCH_2), 4.8 ($SiMe_3$). ^{19}F NMR (toluene-d_8): δ −76.6 (q, $^4J_{F-F}$ = 10.5, 6F), −79.7 (q, $^4J_{F-F}$ = 10.5, 6F). Anal. Calcd for $C_{20}H_{33}F_{12}N_2O_3SiY$: C, 34.58; H, 4.79; N, 4.03. Found: C, 34.15; H, 5.21; N, 3.96. **Minor product** (**7**): ^{1}H NMR (C_6D_6, 500 MHz): δ 3.97 (m, 4H, THF), 2.73 (d, $^2J_{H-H}$ = 15.5, 2H, $NCH_2C(CF_3)_2$), 2.60 (d, $^2J_{H-H}$ = 15.4, 2H, $NCH_2C(CF_3)_2$), 2.06 (s, 6H, NCH_3), 1.85 (m, 2H, CH_2CH_2), 1.68 (m, 2H, CH_2CH_2), 1.31 (m, 4H, THF), 0.38 (m, 12H, $SiMe_3$), −0.59 (dd, $^2J_{H-H}$ = 10.1, J_{H-Y} = 3.1, 2H, YCH_2). ^{13}C{^{1}H} NMR (C_6D_6, 500 MHz): δ 128.4 (q, $^1J_{C-F}$ = 287, $C(\mathit{C}F_3)_2$), 82.0 (br m, $\mathit{C}(CF_3)_2$), 61.8 (s, $N\mathit{C}H_2C(CF_3)_2$), 57.7 ($CH_2\mathit{C}H_2$), 45.8 (NCH_3), 28.2 (d, $^1J_{C-Y}$ = 79.0, YCH_2), 4.8 ($SiMe_3$).

Crystal Structure Determination of 3, 4, and 6. Suitable single crystals of all investigated compounds were mounted onto glass fibers using the "oil-drop" method. Diffraction data for **3** and **4** were collected at 100 K and those for **6** at 120 K, all using a NONIUS Kappa CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A combination of ω- and φ-scans was carried out to obtain at least a unique data set. Crystal structures were solved by means of the Patterson method, and remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[28] Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement are given in Table 1. Atomic coordinates, thermal parameters, and complete listings of bond lengths and angles are available as Supporting Information.

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Supporting Information Available: X-ray diffraction data for complexes **3**, **4**, and **6** in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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