Inorg. Chem. **2008**, *47*, 12049−12062

Inorganic Chemistry
Article

Synthesis, Structures and Reactivity of Group 4 Hydrazido Complexes Supported by Calix[4]arene Ligands

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Received September 9, 2008

Reaction of $TiCl_2(Me_2Calix)$ with 2 equiv of LiNHNRR′ afforded the corresponding terminal hydrazido(2-) complexes Ti(NNRR′)(Me_2Calix) (R = Ph, R′ = Ph (**1**) or Me; R = R′ = Me (**3**)) which were all structurally characterized. The X-ray structure of Ph_2NNH_2 is reported for comparison. Compound **1** was also prepared from $Na_2[Me_2Calix]$ and $Ti(NNPh_2)Cl_2(py)_3$. Reaction of $ZrCl_2(Me_2Calix)$ with 2 equiv of $LiNHNR_2$ afforded only the bis(hydrazido(1-)) complexes $Zr(NHNR_2)_2(Me_2Calix)$ (R = Ph or Me). Treatment of $Ti(NNMe_2)(Me_2Calix)$ (**3**) with MeI gave the zwitterionic hydrazidium species $Ti(NNMe_3)(MeCalix)$ (**6**) via a net isomerization reaction which was found to be catalytic in MeI. The corresponding reaction of **3** with CD_3I gave $Ti(NNMe_2CD_3)(MeCalix)$ (**6-*d*$_3$**) with concomitant elimination of MeI. Reaction of **3** with 1 equiv of MeOTf gave $[Ti(NNMe_3)(Me_2Calix)][OTf]$ (**7-OTf**) which in turn reacted with $^nBu_4NI$ to form **6** and MeI. Addition of PhCHO to **3** gave the μ-oxo dimer $[Ti(\mu\text{-}O)(Me_2Calix)]_2$ and benzaldehyde-dimethylhydrazone. Reaction of either **3** or **6** with ^tBuNCO gave the zwitterionic species $Ti\{^tBuNC(NNMe_3)O\}(MeCalix)$ (**10**) which has been crystallographically characterized. Compound **10** is the formal product of insertion of an isocyanate into the $Ti{=}N_\alpha$ bond of a titanium hydrazide or hydrazidium species (Me_2Calix or MeCalix = dianion or trianion of the di- or monomethyl ether of *p*-*tert*-butyl calix[4]arene, respectively).

Introduction

The chemistry of hydrazido complexes $(L)M{=}NNR_2$ continues to be of considerable interest, particularly in the context of the biological and synthetic activation and fixation of dinitrogen.[1−9] Although the structures, properties, and reactivity of such compounds are well-established for the Groups 5−7 transition metals, there remains a paucity of examples for Group 4.[10] This is in contrast to the situation for the apparently related imido complexes (L)M=NR (R = alkyl or aryl) which are very well established for titanium and zirconium in particular.[11−16] In our group, we have become interested in developing the chemistry of titanium hydrazido complexes.[17−21] This contribution describes our recent results using calix[4]arenes as supporting ligands.

Although Wiberg reported the first terminal titanium hydrazido complex in 1978 ($Cp_2Ti\{NN(SiMe_3)_2\}$[22]), the first structurally authenticated example was described only recently by Odom, namely, $Ti(dpma)(NNMe_2)(^tBubipy)$ (dpma = *N*,*N*-di(pyrrolyl-R-methyl)-*N*-methylamine; ^{t}Bubipy =

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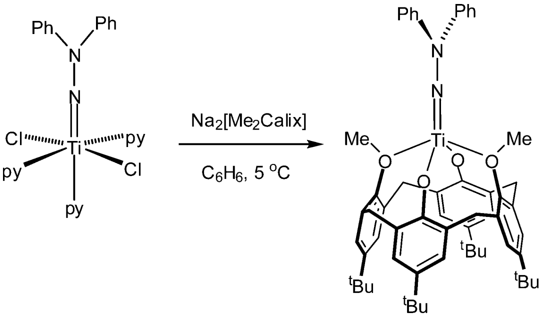
5,5′-di-*tert*-butyl-2,2′-bipyridine).[23] Since this report in 2004, only a handful of other terminal titanium hydrazides have been structurally characterized.[18−20,24,25] Certain Ti═NNR_2 species have been implicated in the catalytic hydrohydrazination[23,26−32] and iminohydrazination[24,31] of alkynes and in the synthesis of indoles[13,28,30] and tryptamines.[29] In these reactions, a [2 + 2] cycloaddition reaction between Ti═NNR_2 and an alkyne (or allene) is considered to be the key N−C bond forming step. Little is directly known about these catalytic processes or the intermediates involved.

Very few papers have addressed the stoichiometric reactions of titanium (or zirconium[33,34]) hydrazides. We found that the macrocycle-supported complex $Ti(NNPh_2)(Me_4taa)$ underwent [2 + 2] cycloaddition reactions of the Ti═N_α bond with CO_2 and *p*-tolyl isocyanate (Me_4taa = dianion of tetramethyl dibenzotetraaza[14]annulene).[17] Woo subsequently observed hydrazone formation on reaction of porphyrin-supported hydrazides with certain aldehydes[35] via a Ti═NNR_2/C═O metathesis reaction. Odom found that $Ti(dpma)(NNMe_2)(^tBubipy)$ reacted with MeI to form the corresponding hydrazidium salt $[Ti(dpma)(NNMe_3)(^tBubipy)]I$ via electrophilic attack at the hydrazido β-nitrogen.[23] In all of these reactions the hydrazide $N_\alpha-N_\beta$ bonds remained intact. In constrast, we recently found that the diamide-amine supported complex $Ti(NNPh_2)\{MeN(CH_2CH_2NSiMe_3)_2\}(py)$ reacted with MeCCR (R = Me or Ph) via an apparent insertion reaction into the $N_\alpha-N_\beta$ bond.[19] Possibly related $N_\alpha-N_\beta$ bond cleavage chemistry has been found for a couple of types of zirconium hydrazide.[33,34]

To explore further the chemistry of the Ti═NNR_2 functional group we have been developing routes to new types of titanium hydrazide complexes.[19] Ligand choices have been guided by our and others experience from the area of Group 4 imido chemistry. Calixarene ligands (and in particular calix[4]arenes) have been widely used platforms for coordination, supramolecular and organometallic chemistry over the past 10−15 years.[36−43] In particular, such ligands have been used for a range of metal-imido complexes of Group 4 (including reactions of Ti═NR multiple bonds with unsaturated substrates)[44−46] and one example of a Group 6 hydrazide(2-).[47] In a recent communication we found that $[Ti(NNPh_2)Cl_2(py)_2]_2$ reacted with $Na_2[Bn_2Calix]$ to form $Ti(NNPh_2)(Bn_2Calix)$ (Bn_2Calix = dianion of 1,3-dibenzyl ether of *p*-*tert*-butyl calix[4]arene).[19] No structure was reported and no reactivity studies were carried out. In this paper we build on these preliminary results using the related Me_2Calix ligand (Me_2Calix = dianion of 1,3-dimethyl ether of *p*-*tert*-butyl calix[4]arene).

Results and Discussion

Synthesis of New Hydrazido(2-) and Hydrazido(1-) Complexes. Building on our recent communication[19] we found that reaction of $Na_2[Me_2Calix]$ with monomeric $Ti(NNPh_2)Cl_2(py)_3$ in cold C_6H_6 gave the terminal hydrazido derivative $Ti(NNPh_2)(Me_2Calix)$ (**1**) in 35% isolated yield as a brown solid (eq 1). The ^1H and ^{13}C NMR spectra of **1** indicated the presence of a C_{2v} symmetric $Me_2Calix[4]arene$ ligand on the NMR time scale, consistent with the solid state X-ray structure discussed below.



1

(1)

The low yield of **1** by this method was disappointing. This prompted us to seek a higher yielding and more versatile route which could also lead to alternative terminal hydrazides. Terminal hydrazide synthons such as $Ti(NNPh_2)Cl_2(py)_3$ are not yet available for titanium with dialkyl or monoalkyl NNR_2 ligands. Although the dimeric species $Ti_2(\mu\text{-}\eta^1{:}\eta^2\text{-}NNMe_2)_2Cl_4(py)_4$ has been reported,[18] its reactions with $Na_2[Me_2calix]$ gave intractable mixtures. Therefore we developed the route summarized in eq 2.

Reaction of the previously reported[46] $TiCl_2(Me_2Calix)$ with 2 equiv of the lithiated hydrazides LiNHNRR′ (R = Ph, R′ = Ph or Me; R = R′ = Me) at 60 °C afforded the corresponding terminal hydrazides $Ti(NNRR')(Me_2Calix)$ (R = Ph, R′ = Ph (**1**) or Me (**2**); R = R′ = Me (**3**)) in 75−91% isolated yield along with 1 equiv of the corresponding $RR'NNH_2$ (observed when followed in C_6D_6). Analogous dehydrohalogenative routes were used previously for the corresponding imido complexes $M(NR)(Me_2Calix)$ (M = Ti or Zr, R = ^{t}Bu or certain aryl groups).[46] The NMR spectra

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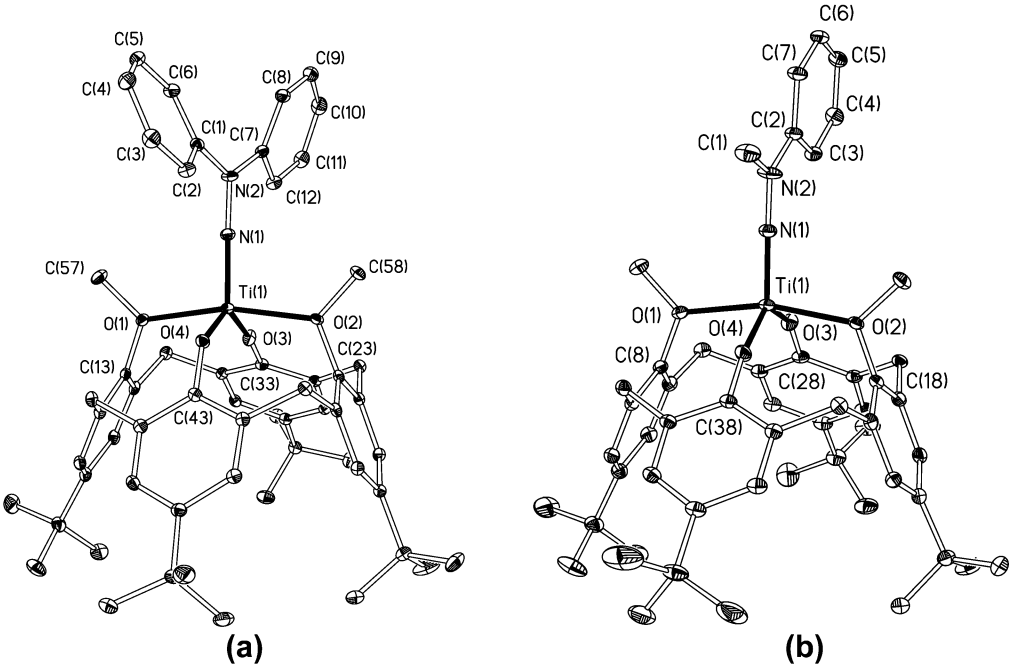
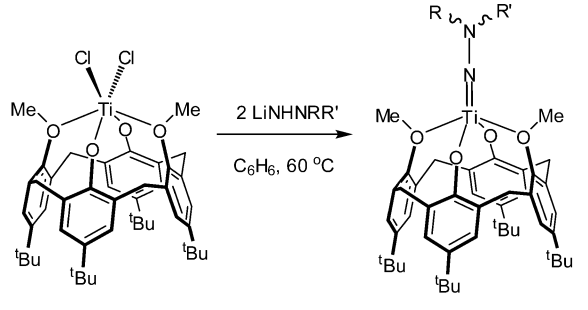


Figure 1. Displacement ellipsoid plots (20% probability) with H atoms and solvent molecules of crystallization omitted for clarity. (a) $Ti(NNPh_2)(Me_2Calix)$ (**1**). (b) $Ti\{NN(Me)Ph\}(Me_2Calix)$ (**2**).

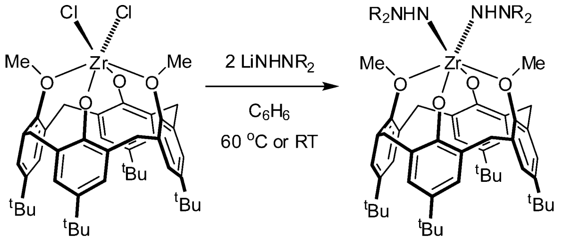
of **2** and **3** were analogous to that of **1** and their X-ray structures have also been determined (see below). The EI mass spectra of **1** and **2** each showed the expected molecular ions as well as peaks for $[TiNN(Me)Ph_2]^+$ and $[TiNN(Me_2)Ph]^+$, respectively; the EI-MS of **3** showed only $[TiNNMe_3]^+$ as the highest *m*/*z* titanium fragment. The formation of β-N-methylated fragments (potentially arising from transfer of a calix[4]arene O-Me group) may be relevant to the attempted alkylations and other reactions described later in this paper.



(2)

R = Ph, R ' = Ph (**1**) or Me (**2**)
R = R' = Me (**3**)

Reactions of $LiNHNPh_2$ and $LiNHNMe_2$ with $ZrCl_2(Me_2Calix)$ have also been carried out using analogous methods (eq 3). In each of these cases the bis(hydrazido-(1-)) compounds $Zr(NHNR_2)_2(Me_2Calix)$ (R = Ph (**4**) or Me (**5**)) were obtained as the only products. The NMR spectra were again consistent with C_{2v} symmetric species and the IR spectra showed characteristic ν(N−H) bands. Heating these compounds either in the presence or in the absence of a base (e.g., DMAP) failed to promote elimination of H_2NNR_2 to afford terminal hydrazide(2-) derivatives. We note that in the corresponding imido chemistry, reaction of $ZrCl_2(Me_2Calix)$ with $LiNH^tBu$ or LiNHPh gave bis(amido) derivatives $Zr(NHR)_2(Me_2Calix)$, and only with the sterically demanding LiNHAr (Ar = 2,6-$C_6H_3{}^iPr_2$) was a terminal imide $Zr(NAr)(Me_2Calix)$ and free $ArNH_2$ formed.[46] It appears that the hydrazines used in our studies to date are insufficiently bulky to promote formation of terminal hydrazido(2-) zirconium complexes. Nonetheless, zirconium hydrazido(1-) species are relatively uncommon[33] and have been structurally characterized only very recently, this being for a κ^2- coordinated $NHNMe_2$ moiety.[48] The spectroscopic data do not distinguish between κ^1- or κ^2- coordinated $NHNR_2$ ligands in the case of **4** or **5**.



(3)

R = Ph (**4**) or Me (**5**)

Gade has shown that the zirconium hydrazides $Zr(NNRR')(N_2N^{py})(L)$ (R = Ph, R′ = Ph or Me; L = py or DMAP; N_2N^{py} is a diamide-amine ligand) can be obtained via treatment of the mono(chloride), mono(hydrazido(1-)) species $Zr(NHNRR')Cl(N_2N^{py})$ with $Li[N(SiMe_3)_2]$ in the presence of the donor L.[34,48] We have attempted to obtain analogous hydrazide(1-)-chloride complexes of the type $Zr(NHNR_2)Cl(Me_2Calix)$ (R = Ph or Me) starting from $ZrCl_2(Me_2Calix)$ and 1 equiv of $LiNHNR_2$. In each case a mixture containing the bis(hydrazido(1-)) species (**4** or **5**) was ultimately obtained. In the reaction of $ZrCl_2(Me_2Calix)$

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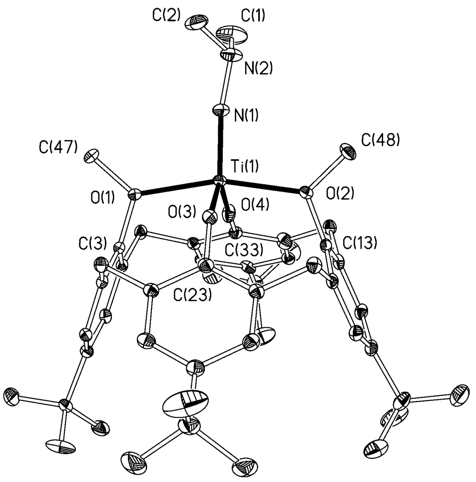

Figure 2. Displacement ellipsoid plot (20% probability) of $Ti(NNMe_2)(Me_2Calix)$ (**3**). H atoms and toluene molecules of crystallization are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (°) for $Ti(NNPh_2)(Me_2Calix)$ (**1**), $Ti\{NN(Me)Ph\}(Me_2Calix)$ (**2**), and $Ti(NNMe_2)(Me_2Calix)$ (**3**)

	1	2	3
Ti(1)−N(1)	1.717(2)	1.727(3)	1.729(4)
N(1)−N(2)	1.352(3)	1.344(2)	1.373(6)
N(2)−C(1)	1.418(3)	1.450(5)	1.448(10)
N(2)−C(2)/C(7)[a]	1.422(3)	1.397(4)	1.421(9)
Ti(1)−O(1)	2.142(2)	2.150(2)	2.166(3)
Ti(1)−O(2)	2.144(2)	2.155(2)	2.147(3)
Ti(1)−O(3)	1.849(2)	1.874(2)	1.883(3)
Ti(1)−O(4)	1.885(2)	1.857(2)	1.861(3)
Ti(1)−N(1)−N(2)	177.3(2)	175.8(3)	170.4(4)
N(1)−N(2)−C(2)/C(7)[a]	116.6(2)	118.1(3)	111.5(6)
N(1)−N(2)−C(2)/C(7)[a]	118.4(2)	120.5(3)	113.9(5)
C(1)−N(2)−C(2)/C(7)[a]	125.0(2)	121.4(3)	112.5(6)
O(1)−Ti(1)−O(2)	165.3(6)	164.2(8)	162.5(1)
O(3)−Ti(1)−O(4)	134.1(8)	131.9(1)	125.9(2)

[a] C(2) for $Ti\{NN(Me)Ph\}(Me_2Calix)$ (**2**) and $Ti(NNMe_2)(Me_2Calix)$ (**3**); C(7) for $Ti(NNPh_2)(Me_2Calix)$ (**1**).

with $LiNHNPh_2$, minor ^1H NMR resonances indicating C_s symmetry were tentatively assigned to a species $Zr(NHNPh_2)Cl(Me_2Calix)$, but these disappeared over several hours with an increase in the intensity of those for the starting $ZrCl_2(Me_2Calix)$ and the bis(hydrazide(1-)) **4**.

Structural Investigations. As mentioned, the X-ray structures of Ti(NNRR′)(Me_2Calix) (R = Ph, R′ = Ph (**1**) or Me (**2**); R = R′ = Me (**3**)) have all been determined. Views of the complexes are given in Figures 1 and 2, and key distances and angles are compared in Table 1.

All three compounds contain a 5-coordinate titanium center possessing an approximately trigonal bipyramidal geometry. The hydrazido N_α atom and the two Me_2Calix anionic phenolate O donors occupy the equatorial sites and the ether O-donors the apical positions. An analogous geometry was found for $Ti(N^tBu)(Me_2Calix)$[46] and for Group 4 imido bis(phenolate) complexes $Ti(NR)(OAr)_2(L)_2$ in general.[49−52] The Ti−O distances for the Ti(Me_2Calix) fragments in **1**−**3** and associated parameters are comparable to those reported previously for titanium calix[4]arene complexes.[46,53−55] There are no significant differences between the three structures in these regards.

The principal structural interest in **1**−**3** is the Ti═NNRR′ functional group and how the bond parameters change with the N_β substituents. Several structural reports of terminal $Ti{=}NNPh_2$ groups have now appeared (seven examples).[18−20] The $Ti{=}N_\alpha$ distances span the range 1.718(2)−1.751(1) Å (avg. 1.737 Å) and the $N_\alpha{-}N_\beta$ distances span the range 1.353(2)−1.369(3) Å (avg. 1.362 Å). The mono(phenyl) hydrazide $Ti\{NN(H)Ph\}(dmpa)(^tBubipy)$ has also been structurally characterized ($Ti{=}N_\alpha$ 1.712(4), $N_\alpha{-}N_\beta$ 1.350(5) Å).[25] There have been three structural reports of terminal $Ti{=}NNMe_2$ groups: $Ti(NNMe_2)(dpma)(^tBubipy)$ ($Ti{=}N_\alpha$ 1.708(3), $N_\alpha{-}N_\beta$ 1.388(4) Å),[23] $Cp^*Ti(NNMe_2)\{MeC(N^iPr)_2\}$ ($Ti{=}N_\alpha$ 1.723(2), $N_\alpha{-}N_\beta$ 1.386(2) Å),[19] and $Ti(NNMe_2)(dap)\{^tBuNCHCHC(^nBu)NNMe_2\}$($Ti{=}N_\alpha$ 1.709(3), $N_\alpha{-}N_\beta$ 1.403(4) Å; dap = 2-(dimethylaminomethyl)pyrrolyl).[24]

Within these groups of compounds there appears to be no discernible trend in $Ti{=}N_\alpha$ distances, while the $Ti{=}N_\alpha{-}N_\beta$ angles are all approximately linear (range ca. 160−178°). However, the large variation in supporting ligand set could easily lead to significant differences in individual $Ti{=}N_\alpha$ values, masking any effects of the N_β substituents. Within the NNR_2 units themselves the $N_\alpha{-}N_\beta$ distances for the $NNPh_2$ and NN(H)Ph species appear to be shorter than for the $NNMe_2$ systems. The N_β for the two $NNPh_2$ species are effectively planar (sums of angles subtended at N_β ca. 357−360°), whereas for the $NNMe_2$ compounds the N_β is highly pyramidalized with sums of angles at N_β in the range ca. 334−337°.[56]

The homologous series **1**−**3** provides the first systematic comparison of the bond parameters of phenyl, alkyl and mixed aryl/alkyl N_β-substituted hydrazides within the same supporting ligand framework. The Ti═NNRR′ linkages are all effectively linear and the range of values for $Ti{=}N_\alpha{-}N_\beta$ is 170.4(4) to 177.3(2)°. The N_β atom (N(2)) for **3** is pyramidalized (sum of angles 338(2)°), whereas in **1** and **2** it is planar (sum of angles 360(1)°). As suggested by Odom,[25] this appears to be due to conjugation between N_β and the phenyl rings. In **2** the N_β−Me and N_β−Ph distances are 1.450(5) and 1.397(4) Å, respectively, and the Ph ring is effectively coplanar with Ti(1)−N(1)−N(2) to within 1 to 2 degrees. The N_β−Ph distances in **1** are slightly longer since the phenyl rings are more twisted out of coplanarity by ca. 10−20° for steric reasons.

The $Ti{=}N_\alpha$ distances all lie in the range expected for titanium−nitrogen multiple bonds and are comparable to those previously found (see above). They can be compared

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(56) The N_β-bound H for $Ti\{NN(H)Ph\}(dmpa)(^tBubipy)$ was not located, but the $N_\alpha{-}N_\beta$−Ph angle (123.2(4)°) is indicative of a trigonal planar geometry.

to the ranges found for titanium imido complexes: Ti═N^{t}Bu range *ca.* 1.66 − 1.74 Å (mean *ca.* 1.70 Å); Ti═NAr range *ca.* 1.69−1.76 Å (mean *ca.* 1.72 Å).[53,54] The Ti═N^{t}Bu distance in Ti(N^{t}Bu)(Me$_2$Calix) is 1.706(2) Å.[46] The $N_\alpha-N_\beta$ distances in **1** (1.352(3) Å) and **3** (1.373(6) Å) appear a little shorter than in previous complexes with Ti═NNPh$_2$ and Ti═NNMe$_2$ groups.

DFT calculations for Ti(NNPh$_2$){HC(Me$_2$pz)$_3$}Cl$_2$[18] and other compounds[20,25] have suggested that NNR$_2$ groups bound to titanium are best considered as "hydrazide(2-)" ligands, $[N\text{-}NR_2]^{2-}$, as opposed to neutral isodiazenes (:N═NR$_2$), which is more typically the case for later transition metals.[57−60] Calculations have also suggested that $[N\text{-}NH_2]^{2-}$ should possess a long $N_\alpha-N_\beta$ bond (1.57 Å) and highly pyramidal N_β, while singlet isodiazene (:N═NH$_2$) is predicted to be planar with a $N_\alpha-N_\beta$ distance of 1.23 Å.[61] Based on the structural data compounds **1**−**3** are clearly hydrazide(2-) species with the inherent tendency for N_β pyramidalization suppressed by conjugation with the phenyl group(s).

The differences between the Ti═N_α distances for **1** or **2** and that for **3** (0.012(4) and 0.002(5) Å, respectively) are at or below the limits of statistical significance at the 3σ level. Likewise there is no significant difference between the Ti═N_α or $N_\alpha-N_\beta$ distances for **1** and **2**. However, the differences between $N_\alpha-N_\beta$ distances for **1** and **2** (both possessing a planar N_β) and **3** are indicative of a lengthening of this bond ($\Delta N_\alpha-N_\beta$ = 0.021(7) or 0.029(6) Å) upon pyramidalization of N_β, and are consistent in this regard with the literature data mentioned above.

In general terms the $N_\alpha-N_\beta$ distances in **1**−**3** lie in between those expected for N═N double (*ca.* 1.22−1.26 Å) and N−N single (*ca.* 1.40−1.45 Å) bonds.[53,54,62] Note that these N−N single bond averages vary significantly depending on the formal hybridization of the nitrogen ($N(sp^2)-N(sp^2) < N(sp^2)-N(sp^3) < N(sp^3)-N(sp^3)$). The experimental $N_\alpha-N_\beta$ distance in Me$_2$NNH$_2$ (both nitrogens formally sp^3 hybridized) is 1.436(2) Å,[63] and is clearly much longer than the $N_\alpha-N_\beta$ distance in **3**.

To make a better comparison between Ti═NNPh$_2$ and Ti═NNMe$_2$ distances and those of the free hydrazines we have determined the X-ray structure of Ph$_2$NNH$_2$. The molecular strucuture is shown in Figure 3 and selected distances and angles for the two crystallographically independent molecules are given in Table 2. There are no significant differences between the two molecules and we will refer to one set of values. Similarly, there are no supramolecular (e.g., H-bonding) interactions which could perturb the geometric features. Interestingly, Ph$_2$NNH$_2$ contains a pyramidal N_α (sp^3 hybridized) atom and a trigonal planar N_β (sp^2, sum of angles 357.9(4)°). The N_β−Ph distances are within the range spanned by **1** and **2**, consistent with significant conjugation. The N−N single bond in Ph$_2$NNH$_2$ (1.418(2) Å) is shorter than that in Me$_2$NNH$_2$ (1.436(2) Å). Furthermore, the difference between $N_\alpha-N_\beta$ values in these two organic species ($\Delta N_\alpha-N_\beta$ = 0.018(3) Å) is the same within error as that between **1** and **3** ($\Delta N_\alpha-N_\beta$ = 0.021(7) Å) or **2** and **3** ($\Delta N_\alpha-N_\beta$ = 0.029(6) Å). Therefore any discussions of differences between Ti═NNPh$_2$ and Ti═NNMe$_2$ group $N_\alpha-N_\beta$ bond lengths should take into account variations in single bond radii on changing from sp^2 to sp^3 hybridization for N_β. Depending upon individual cases, these hybridization effects could make a major contribution to observed bond length variations.

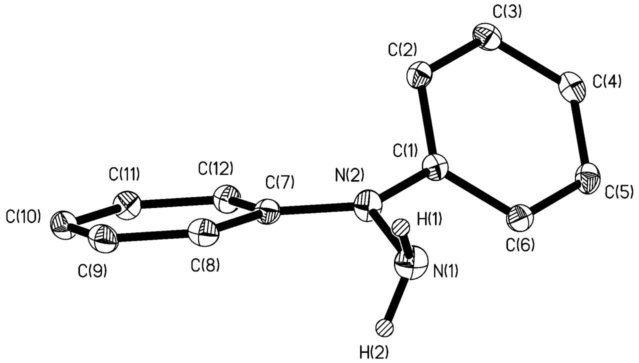

Figure 3. Displacement ellipsoid plot (20% probability) of one of the two independent molecules of Ph$_2$NNH$_2$ in the asymmetric unit. C-bound H atoms omitted for clarity. H atoms drawn as sphere of arbitrary radius.

Reactivity Studies: Alkylating Agents. As mentioned in the introduction, few reactivity studies of titanium hydrazides have been reported. Encouraged by the success of Me$_2$Calix as a supporting ligand platform in reactivity studies of Ti(NR)(Me$_2$Calix) we screened the hydrazides **1**−**3** against a range of substrates, starting with alkylating agents.

Odom has reported alkylation reactions of terminal hydrazides to form the corresponding hydrazidium complexes [(L)Ti═NNR$_2$R′]$^+$.[23,25] Analogous reactions have been reported for other transition metal hydrazides.[64] We found that none of **1**−**3** reacted with MeI at room temperature. In the case of **1** and **2** no reaction occurred even after heating at 100 °C for 16 h. However, heating a sample of Ti(NNMe$_2$)(Me$_2$Calix) (**3**) with an excess of MeI at 100 °C for 20 min gave conversion to a new product **6** as a pale orange solid. The ^{1}H NMR spectrum of **6** featured three resonances attributed to *t*-butyl groups of a calix[4]arene ligand in a relative ratio of 9:9:18 H, along with four doublets for the calix[4]arene methylene linkages between *ca.* 3.5 and 5.5 ppm. A singlet of relative intensity 9 H at 2.75 ppm was consistent with a Ti═NNMe$_3^+$ moiety, but the O-Me resonance at 4.03 ppm integrated as only 3 H compared to the other groups. Overall these and other data were not consistent with the expected product of N_β methylation, namely, [Ti(NNMe$_3$)(Me$_2$Calix)]I containing a C_{2v} symmetric cation isoelectronic with Ti(N^{t}Bu)(Me$_2$Calix). Compound **6**

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(58) Studt, F.; Tuczek, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5639.
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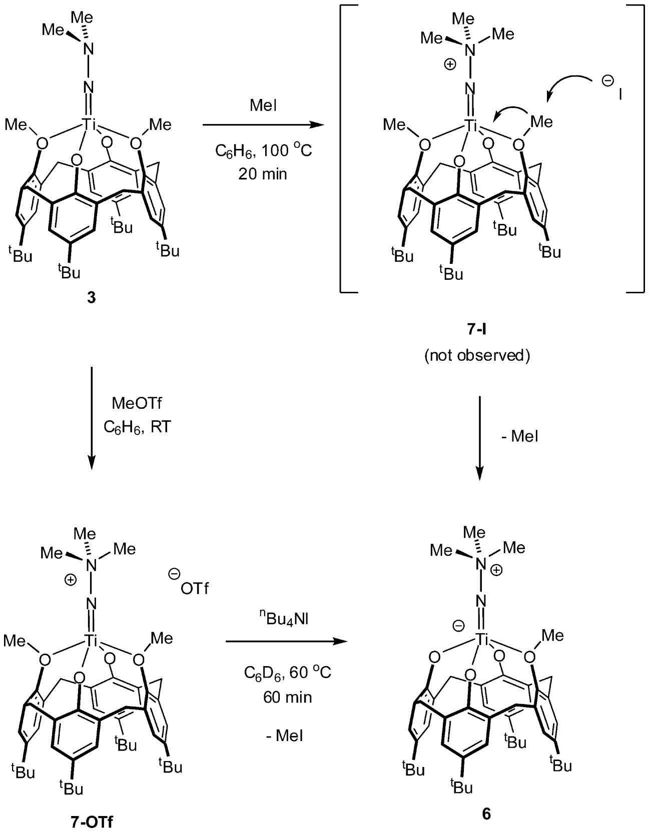
(64) Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 2767.

Table 2. Selected Bond Distances (Å) and Angles (°) for Ph_2NNH_2[a]

N(1)−N(2)	1.418(2) [1.415(2)]	N(1)−H(1)	0.94(3) [0.97(3)]
N(2)−C(1)	1.411(2) [1.406(2)]	N(1)−H(2)	0.97(3) [0.94(3)]
N(2)−C(7)	1.401(2) [1.408(2)]		
N(1)−N(2)−C(1)	114.19(13) [114.86(13)]	N(2)−N(1)−H(1)	106(2) [106.4(14)]
N(1)−N(2)−C(7)	119.95(14) [119.61(14)]	N(2)−N(1)−H(2)	111(2) [112(2)]
C(1)−N(2)−C(7)	123.71(13) [124.49(13)]	H(1)−N(1)−H(2)	114(2) [105(2)]

[a] Values in brackets are for the other crystallographically independent molecule.

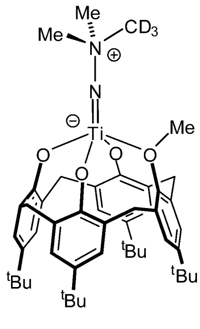
Scheme 1. Reactions Leading to $Ti(NNMe_3)(Me_2Calix)$ (**6**) and Proposed Mechanism for the Reaction with MeI



is in fact the zwitterionic hydrazidium complex $Ti(NNMe_3)(MeCalix)$ containing a trianionic, monomethyl calix[4]arene ligand.

Scheme 1 illustrates the proposed structure of **6** and a likely mechanism for formation. Demethylation reactions of Ti-bound Me_2Calix to form MeCalix have been reported previously, for example, for $TiCl_2(Me_2Calix)$[65] and $Ti(OAr)_2(Me_2Calix)$ (Ar = *p*-Tol or 4-$C_6H_4{}^tBu$).[46] The proposed intermediate $[Ti(NNMe_3)(Me_2Calix)]^+$ ($\mathbf{7}^+$) is not observed under the reaction conditions but, as mentioned, is isoelectronic with the previously reported *t*-butyl imide $Ti(N^tBu)(Me_2Calix)$. Scheme 1 also implies that the transformation of **3** to **6** should not appear to consume MeI, and several NMR tube scale reactions have been carried out to probe this.

When the reaction between **3** and MeI was followed by ^1H NMR spectroscopy the resonance for MeI did not diminish. Treating **3** with 0.12 equiv of MeI also led to quantitative conversion to **6**, again without decrease in intensity of the MeI resonance. When the reaction was carried out with CD_3I the ^1H and ^2D spectra were consistent with the formation of $Ti\{NN(Me_2)CD_3\}(MeCalix)$ (**6-*d*₃**) and the ^1H NMR spectrum showed the formation of 1 equiv of natural abundance MeI. Compound **6-*d*₃** did not scramble the CD_3 label into the MeCalix over time in solution. Furthermore, exposure of **6** to CD_3I did not lead to incorporation of CD_3 into the complex (as judged by ^2H NMR spectroscopy) showing that the formation of **6** from the intermediate $\mathbf{7}^+$ (Scheme 1) is irreversible.



6-*d*₃

Further attempts to extend and probe this novel catalytic demethylation of **6** were carried out. Reaction of **3** with 3 equiv of $PhCH_2Br$ in C_6D_6 gave (according to NMR data) the corresponding zwitterion $Ti\{NN(Me_2)CH_2Ph\}(MeCalix)$ (**8**) after 16 h at 60 °C. Using a smaller excess of $PhCH_2Br$ led to a small amount of **6** also being formed, presumably due to reaction of **3** with the eliminated MeBr. Unfortunately, attempts to obtain a pure sample of **8** on the preparative scale were unsuccessful, giving only mixtures of products. Reaction of **3** with Me_2SO_4 (1 equiv) on the NMR tube scale immediately gave a new Me_2Calix-containing product, but this was found to be the previously reported *μ*-oxo dimer $Ti_2(\mu\text{-}O)_2(Me_2Calix)_2$.[46]

Reaction of **3** with MeOTf in C_6D_6 was more successful (Scheme 1), and a C_{2v} symmetric species, $[Ti(NNMe_3)(Me_2Calix)][OTf]$ (**7-OTf**), was formed quantitatively. Attempts to isolate **7-OTf** on the preparative scale were complicated by the ready formation of mixtures, among which $Ti_2(\mu\text{-}O)_2(Me_2Calix)_2$ was again present, presumably due to Ti=N/S=O metathesis side-reactions. However, reaction of a concentrated solution of **3** with MeOTf in C_6H_6 gave a precipitate of pure **7-OTf** (albeit in low yield) which could be successfully characterized. Although the ^{19}F NMR spectrum of **7-OTf** does not unambiguously eliminate OTf^- anion coordination (free and coordinated OTf^- have very

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(65) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270*, 298.

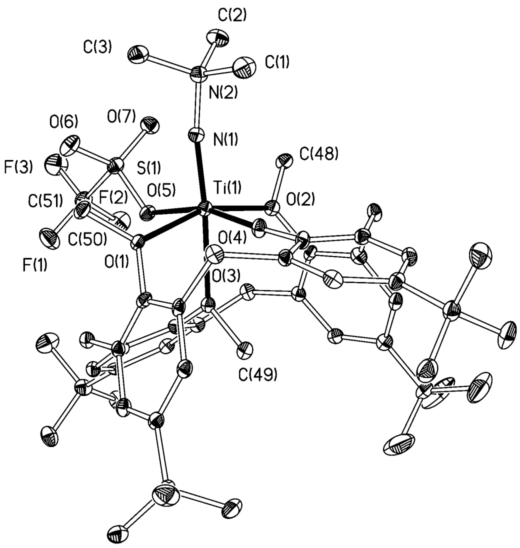


Figure 4. Displacement ellipsoid plot (20% probability) of $[Ti(NNMe_3)(Me_3Calix)(OTf)][OTf]$ (**9-OTf**). H atoms, $[OTf]^-$ anion, and benzene molecules of crystallization are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (°) for $[Ti(NNMe_3)(Me_3Calix)(OTf)]^+$ ($\mathbf{9^+}$)

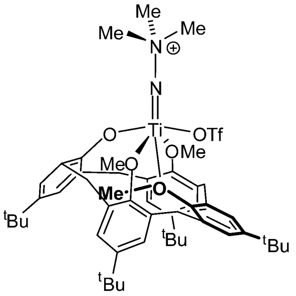
Ti(1)−O(1)	2.135(3)	Ti(1)−O(5)	2.079(3)
Ti(1)−O(2)	2.139(3)	Ti(1)−N(1)	1.705(3)
Ti(1)−O(3)	2.301(2)	N(1)−N(2)	1.418(4)
Ti(1)−O(4)	1.794(3)	S(1)−O(5)	1.486(3)
S(1)−O(6)	1.424(3)	S(1)−O(7)	1.432(3)
N(1)−Ti(1)−O(1)	99.93(13)	N(1)−Ti(1)−O(4)	102.47(14)
N(1)−Ti(1)−O(2)	100.09(13)	N(1)−Ti(1)−O(5)	94.89(13)
N(1)−Ti(1)−O(3)	172.94(13)	Ti(1)−N(1)−N(2)	165.6(3)
N(1)−N(2)−C(1)	108.7(3)	N(1)−N(2)−C(2)	110.1(3)
N(1)−N(2)−C(3)	108.9(3)		

similar ^{19}F shifts[66,67]), its infrared spectrum is consistent with a free OTf^- anion as indicated by strong, broad bands between 1260 and 1295 cm^{-1}.[68] Attempts to observe $\mathbf{7^+}$ by electrospray mass spectrometry were unsuccessful.

The compound **7-OTf** is the triflate analogue of the proposed intermediate (**7-I**, Scheme 1) in the reaction of **3** with MeI to form $Ti(NNMe_3)(Me_2Calix)$ (**6**). Consistent with this mechanism, we found that heating an NMR sample of **7-OTf** with $^nBu_4NI$ for 60 min gave clean conversion to **6** and free MeI.

During our attempts to isolate **7-OTf**, a few diffraction-quality crystals of the new compound **9-OTf** were obtained. These contain the cation $[Ti(NNMe_3)(Me_3Calix)(OTf)]^+$ ($\mathbf{9^+}$) and a noncoordinated $[OTf]^-$ anion. The molecular structure of $\mathbf{9^+}$ is shown in Figure 4 and selected distances and angles are listed in Table 3. **9-OTf** is the product of the reaction of **3** with 2 equiv of MeOTf. Attempts to isolate pure **9-OTf** on a preparative scale were unsuccessful, and a mixture of products were formed when the reaction between isolated **7-OTf** and MeOTf was followed by NMR.

The $\mathbf{9^+}$ cation contains an approximately octahedral titanium center coordinated to a formally monoanionic



$\mathbf{9^+}$

*tri*methyl calix[4]arene ligand in a partial cone conformation. The Me_3Calix ligand is formed by O-methylation of the Me_2Calix moiety in $Ti(NNMe_2)(Me_2Calix)$ (**3**) or $[Ti(NNMe_3)(Me_2Calix)][OTf]$ (**7-OTf**). **9-OTf** is the first structurally characterized example of a metal complex of Me_3Calix although the protio-form of the ligand itself has previously been the subject of an X-ray diffraction study.[69] The titanium coordination sphere is completed by a monodentate OTf ligand and a trimethyl hydrazidium ligand. The additional $[OTf]^-$ anion makes no significant contact to the $\mathbf{9^+}$ cation.

The compound **9-OTf** is the second structurally characterized example of a Group 4 alkyl hydrazidium complex, the other being $[Ti(dpma)(NNMe_3)(^tBubipy)]I$[23] (examples from the later metals are better established[53,54]). The $Ti{=}N_\alpha$ and $N_\alpha{-}N_\beta$ distances of 1.705(3) and 1.418(4) Å in $\mathbf{9^+}$ are the same within error to those in this previous example. The $Ti{=}N_\alpha$ distance in $\mathbf{9^+}$ is shorter than in **3** (1.729(4) Å) while the $N_\alpha{-}N_\beta$ distance is longer (1.373(6) Å in **3**). Although there are significant changes in the supporting ligand set between neutral, 5-coordinate $Ti(NNMe_2)(Me_2Calix)$ (**3**) and cationic $[Ti(NNMe_3)(Me_3Calix)(OTf)]^+$ ($\mathbf{9^+}$) which could in principle perturb the bonding parameters of the $Ti{=}NNMe_3$ group, we note that analogous variations in $Ti{=}N_\alpha$ and $N_\alpha{-}N_\beta$ distances were found by Odom on going from neutral $Ti(dpma)(NNMe_2)(^tBubipy)$ to cationic $[Ti(dpma)(NNMe_3)(^tBubipy)]^+$ (both complexes being 6-coordinate). There are several likely origins for the relative shortening and lengthening of the $Ti{=}N_\alpha$ and $N_\alpha{-}N_\beta$ distances between $(L)Ti{=}NNMe_2$ and $(L')Ti{=}NNMe_3^+$ species, including loss of any residual $N_\alpha{-}N_\beta$ multiple bond character and electrostatic repulsion between N_α and the formally cationic N_β.

Reactivity Studies: Unsaturated Substrates. As mentioned, 5-coordinate, macrocycle-supported titanium hydrazido complexes have been shown to undergo successful [2 + 2] cycloaddition reactions with TolNCO and CO_2,[17] and also $Ti{=}NNR_2/C{=}O$ metathesis reactions with certain aldehydes.[35] In order to try to develop the underexplored chemistry of the $Ti{=}NNR_2$ functional group we have screened the reactions of **1**−**3** with a range of unsaturated substrates including CO_2, CS_2, alkyl- and aryl-isocyanates, nitriles, isonitriles and internal and terminal alkynes under a range of conditions. Regrettably almost all of these reactions gave either rather complex mixtures or (particularly

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[67] Yi, X.-Y.; Williams, I. D.; Leung, W.-H. *J. Organomet. Chem.* **2006**, *691*, 1315.

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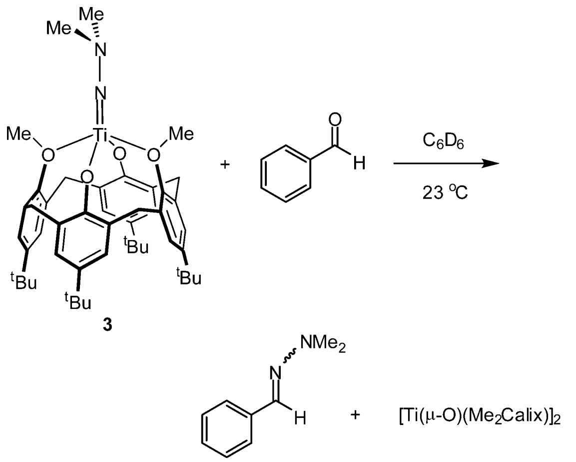
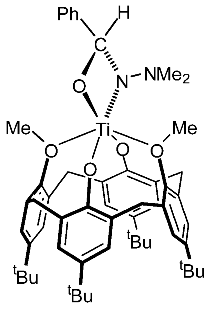
[69] Grootenhuis, P. D. J.; Kollman, P. A.; Groenen, L. C.; van Hummel, G. J.; Ugozzoli, F.; reetti, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 4165.

in the case of **1** and **2**) no reaction under forcing conditions. In two instances, however, reasonably well-defined reactions were observed.



(4)

Reaction of Ti(NNMe$_2$)(Me$_2$Calix) (**3**) with benzaldehyde gave quantitative conversion by ^{1}H NMR to benzaldehyde-dimethylhydrazone (mixture of isomers[70]) at room temperature after 16 h (eq 4). However, complex mixtures were observed with acetophenone upon heating (no reaction occurred at room temperature) and no reaction occurred with benzophenone. No reaction occurred between **1** and benzaldehyde at room temperature and upon heating a complex mixture was formed. The side-product of the reaction of **3** with PhCHO was Ti$_2$(μ-O)$_2$(Me$_2$Calix)$_2$. The metathesis reaction in eq 4 probably proceeds via a [2 + 2] cycloaddition reaction and intermediate Ti{OC(H)PhNNMe$_2$}(Me$_2$Calix) (**3-PhCHO-int**). Adducts of this type have been observed previously in titanium imido chemistry.[71] Under these reaction conditions, no Me$_2$Calix demethylation products were observed.



3-PhCHO-int

Reactions of **3** with arylisocyanates at room temperature gave immediate formation of complex mixtures. However, reaction with ^{t}BuNCO at 70 °C gave modest yields of Ti{N^{t}BuC(NNMe$_3$)O}(MeCalix) (**10**) (eq 5). Diffraction-quality crystals of **10** were obtained from a saturated benzene solution. The molecular structure is shown in Figure 5 and important bond distances and angles are presented in Table 4.

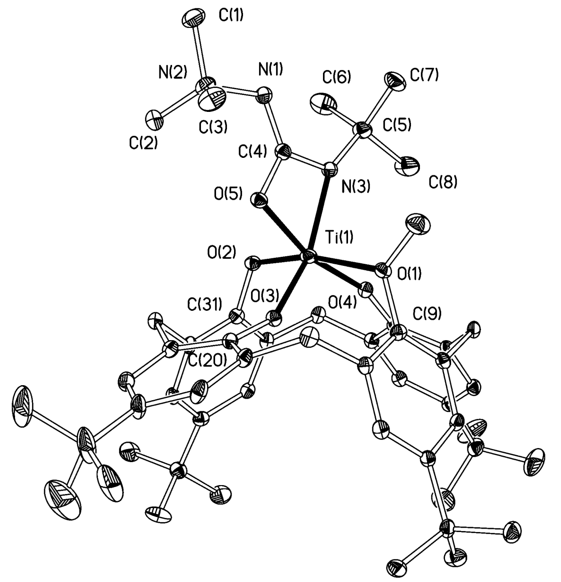
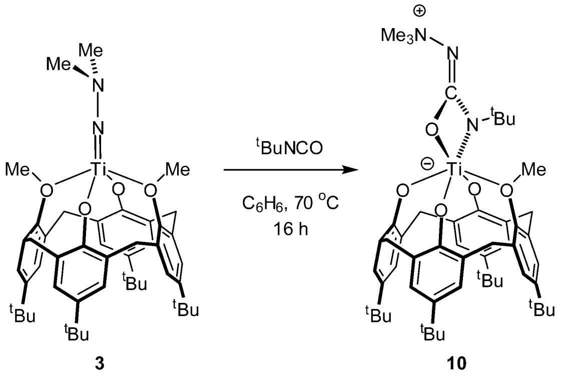


Figure 5. Displacement ellipsoid plot (20% probability) of Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (**10**). H atoms and benzene molecules of crystallization are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (°) for Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (**10**)

Ti(1)−O(1)	2.326(3)	N(3)−C(5)	1.462(7)
Ti(1)−O(2)	1.907(3)	C(4)−N(1)	1.318(7)
Ti(1)−O(3)	1.839(3)	C(4)−O(5)	1.330(6)
Ti(1)−O(4)	1.815(3)	C(4)−N(3)	1.359(6)
Ti(1)−O(5)	2.054(3)	N(1)−N(2)	1.477(6)
Ti(1)−N(3)	2.019(4)		
O(3)−Ti(1)−O(4)	105.3(2)	N(1)−C(4)−O(5)	127.9(4)
O(1)−Ti(1)−O(2)	167.4(1)	N(1)−C(4)−N(3)	123.0(5)
N(3)−Ti(1)−O(5)	65.0(2)	C(4)−N(1)−N(2)	113.5(4)
C(4)−N(3)−C(5)	123.5(4)		



(5)

Compound **10** is another zwitterionic species containing a demethylated MeCalix ligand. The Ti(MeCalix) fragment is coordinated to a κ(N,O)-bound ^{t}BuNC(NNMe$_3$)O ligand. The latter features an exocyclic NNMe$_3^+$ group, presumably formed by demethylation of Me$_2$Calix by the Ti=NNMe$_2$ at some stage of the reaction (see below). Note that the assignment of the N(1) and N(3) substituents as NMe$_3^+$ and the isoelectronic CMe$_3$ (as shown in Figure 5) is consistent

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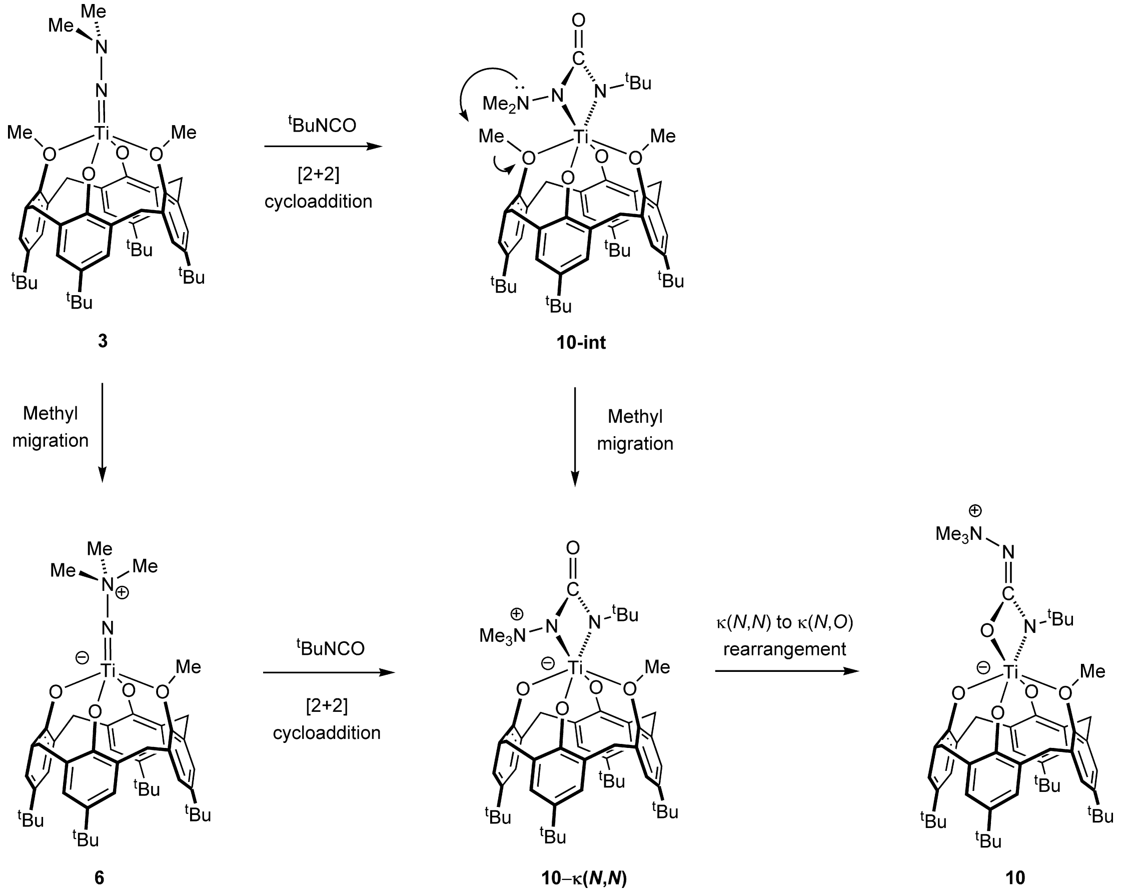
(70) Petroski, R. J. *Synth. Commun.* **2006**, *36*, 1727.

(71) Guiducci, A. E.; Boyd, C. L.; Mountford, P. *Organometallics* **2006**, *25*, 1167.

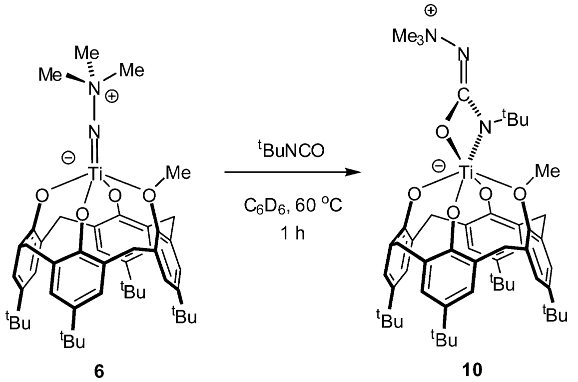
Scheme 2. Two Possible Mechanisms for the Formation of Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (**10**) from Ti(NNMe$_2$)(Me$_2$Calix) (**3**)



with the computed displacment parameters for N(2) and C(5). The solution NMR spectra and other data (2D NOESY) for **10** are consistent with the X-ray structure.

The ^{t}BuNC(NNMe$_3$)O moiety (or its homologues) in **10** has not been strucurally authenticated before. It is related to well-known ureate ligands RNC(O)NR′ (which can be κ(*N,O*) or κ(*N,N'*)-bound), formed, for example, by cycloaddition of carbodiimides to M═O bonds or isocyanate addition to M═NR bonds.[12,14,17] A related and structurally authenticated precedent for the ^{t}BuNC(NNMe$_3$)O ligand in **10** is the κ(*N,O*)-Me$_2$NC(NNMe$_2$)O moiety in Si{Me$_2$NC(NNMe$_2$)O}$_2$Ph$_2$.[72] A closely related (isoelectronic) example from titanium ureate chemistry is Ti{κ(*N,O*)-^{t}BuNC(N^{t}Bu)O}(Me$_4$taa) formed from ^{t}BuNCO and Ti(N^{t}Bu)(Me$_4$taa).[17] The ^{t}BuNC(NNMe$_3$)O ligand in **10** is the N$_\beta$-methylated homologue of the TolNC(O)NNPh$_2$ moiety formed when Ti(NNPh$_2$)(Me$_4$taa) reacts with TolNCO to give Ti{TolNC(O)NNPh$_2$}(Me$_4$taa).[17]

Compound **10** could also be formally viewed as the product of the net insertion of ^{t}BuNCO into the Ti═NNMe$_3^+$ bond of Ti(NNMe$_3$)(MeCalix) (**6**). To test this experimentally we carried out the reaction of **6** with ^{t}BuNCO on the NMR tube scale. After 1 h the ^{1}H NMR spectrum showed 70% conversion of **6** to **10** along with minor unknown products (eq 6). This formal insertion of a substrate into the Ti═N$_\alpha$ bond of a hydrazidium complex appears to be a new reaction type. Typically hydrazidium complexes undergo reductive cleavage of the N$_\alpha$–N$_\beta$ bond.[8,9] Although the reaction in eq 6 is far from well-behaved, it does suggest that early metal hydrazidium complexes (L)M═NNR$_3^+$ could have M═N$_\alpha$ bond coupling chemistry with unsaturated substrates of the type well-established for the isoelectronic imides (L)M═NCR$_3$.



(6)

Scheme 2 outlines two potential mechanisms for the formation of **10** from **3**. The upper pathway proceeds via an initial [2 + 2] cycloaddition with ^{t}BuNCO which is well-established in imido chemistry and observed previously for the reaction of Ti(NNPh$_2$)(Me$_4$taa) with TolNCO or CO$_2$. Formation of PhCH(NNMe$_2$) from **3** and PhCHO (eq 4) probably also proceeds via a [2 + 2] cycloaddition species (**3-PhCHO-int**). Migration of a Me$_2$Calix O-methyl group to the N$_\beta$ of intermediate **10-int** would generate **10-*κ*(*N,N*)**

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(72) Kalikhman, I.; Gostevskii, B.; Botoshansky, M.; Kaftory, M.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. *Organometallics* **2006**, *25*, 1252.

Table 5. X-ray Data Collection and Processing Parameters for Ti(NNPh$_2$)(Me$_2$Calix)·Et$_2$O (**1·Et$_2$O**), Ti{NN(Me)Ph}(Me$_2$Calix)·2(C$_7$H$_8$) (**2·2(C$_7$H$_8$)**), Ti(NNMe$_2$)(Me$_2$Calix)·1.75(C$_7$H$_8$) (**3·1.75(C$_7$H$_8$)**), Ph$_2$NNH$_2$, [Ti(NNMe$_3$)(Me$_3$Calix)(OTf)][OTf] (**9-OTf·1.75(C$_6$H$_6$)**) and Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (**10·3(C$_6$H$_6$)**)

	1·Et$_2$O	**2·2(C$_7$H$_8$)**	**3·1.75(C$_7$H$_8$)**
empirical formula	$C_{58}H_{68}N_2O_4Ti·C_4H_{10}O$	$C_{53}H_{66}N_2O_4Ti·2(C_7H_8)$	$C_{48}H_{64}N_2O_4Ti·1.75(C_7H_8)$
fw	979.21	1027.30	942.19
temp/K	150	150	150
wavelength/Å	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$
a/Å	13.45820(10)	20.9438(3)	12.8906(2)
b/Å	21.6566(3)	13.0864(2)	13.5333(2)
c/Å	19.2699(3)	23.3105(5)	18.6807(3)
α/deg	90	90	74.0201(5)
β/deg	103.8770(6)	111.6514(6)	80.0566(5)
γ/deg	90	90	62.9365(6)
V/Å^3	5452.46(12)	5938.15(18)	2785.63(8)
Z	4	4	2
d (calcd)/Mg·m^{-3}	1.193	1.149	1.123
abs coeff/mm^{-1}	0.207	0.192	0.199
R indices^a	$R_1 = 0.0497^b$ $R_w = 0.0424^b$	0.0593^b 0.0628^b	0.0881^b 0.0899^b

	Ph$_2$NNH$_2$	**9-OTf·1.75(C$_6$H$_6$)**	**10·3(C$_6$H$_6$)**
empirical formula	$C_{12}H_{12}N_2$	$C_{52}H_{70}F_6N_2O_{10}S_2Ti·1.75(C_6H_6)$	$C_{53}H_{73}N_3O_5Ti·3(C_6H_6)$
fw	184.24	1245.85	1114.42
temp/K	150	150	150
wavelength/Å	0.71073	0.71073	0.71073
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	9.5104(2)	15.998(3)	13.0664(3)
b/Å	11.1230(2)	25.675(6)	23.5233(6)
c/Å	11.6530(3)	16.425(3)	23.6745(7)
α/deg	116.1926(11)	90	90
β/deg	112.4355(12)	108.1990(10)	93.0525(11)
γ/deg	94.348(2)	90	90
V/Å^3	977.05(4)	6409(2)	7266.4(3)
Z	4	4	4
d (calcd)/Mg·m^{-3}	1.252	1.291	1.019
abs coeff/mm^{-1}	0.076	0.272	0.163
R indices^a	$R_1 = 0.0443^b$ $R_w = 0.0522^b$	$R_1 = 0.0677^c$ $wR_2 = 0.1885^d$	$R_1 = 0.0888^c$ $wR_2 = 0.2808^d$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w\,(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}}$; $wR_2 = \sqrt{\{\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}}$. [b] $I > 3\sigma(I)$. [c] $I > 2\sigma(I)$. [d] All data.

an isomer of the final product **10**. Demethylation of the Me$_2$Calix of **10-int** is precedented by the Me-X elimination reactions of TiX$_2$(Me$_2$Calix) (X = Cl or OAr),[46,65] but in the present case dissociation of a side-product "Me-X" cannot occur. Rearrangment of **10-κ(*N,N*)** to the κ(*N,O*)-coordinated isomer **10** results in a less sterically crowded metal center. A related rearrangment has been observed previously in the reaction of Ti(O)(Me$_4$taa) with TolNCNTol to form Ti{κ(*N,N'*)-TolNC(O)NTol}(Me$_4$taa) via a κ(*N,O*)-coordinated intermediate. It has previously been found by DFT that κ(*N,N'*)-coordination of ureate ligands can be favored electronically,[71] but that steric factors can favor κ(*N,O*)-coordination.[17,71] Interestingly, **10** can in principle exist as one of two κ(*N,O*)-coordinated isomers, namely, with the $\underline{\text{N}}{}^t$Bu bound to Ti (as found) or with $\underline{\text{N}}$NMe$_3^+$ bound. We proposed that the likely better sigma donor ability of $\underline{\text{N}}{}^t$Bu compared to $\underline{\text{N}}$NMe$_3^+$ is responsible for the observed structure.

As shown in eq 6, compound **10** could in principle also be formed from a first-formed hydrazidium zwitterion **6**, suggesting that an alternative mechanism for the conversion of **3** to **10** might involve initial rearrangement of **3**–**6** (Scheme 2). However, we have found no evidence for the isomerization of pure **3** to **6**, even after 18 h at 100 °C. Addition of a strong base such as DMAP likewise does not promote O-Me migration via a potential 6-coordinate intermediate Ti(NNMe$_2$)(DMAP)(Me$_2$Calix) which could be a model for an initial adduct Ti(NNMe$_2$)(σ-^{t}BuNCO)-(Me$_2$Calix).

Conclusions

Reactions of TiCl$_2$(Me$_2$Calix) with lithiated hydrazides give high-yielding dehydrohalogenative routes to terminal titanium hydrazides. Unfortunately, the larger radius of zirconium prevented this methodology being extended to the heavier congener. The X-ray structures of the series of compounds Ti{NNRR′}(Me$_2$Calix) (**1**–**3**) show, by structural comparisons with titanium imido complexes and the free hydrazines Me$_2$NNH$_2$ and Ph$_2$NNH$_2$, that (i) the NNR$_2$ ligands are best viewed as hydrazide(2-) groups, (ii) a significant contribution to N$_\alpha$–N$_\beta$ bond length variations in these and other Group 4 systems may arise from the change in hybridization at N$_\beta$, and (iii) the planarity of N$_\beta$ is attributed to conjugation with one or both phenyl rings. This conjugation (possibly along with steric constraints) appears to limit the reactions of the Ti=NNR$_2$ functional groups except in the case of Ti(NNMe$_2$)(Me$_2$Calix) (**3**).

However, few well-defined reaction products could be obtained for this system and possible reasons include (i) the limitations of a rigid tetradentate ligand environment, (ii) an absence of strongly π-donating (labilizing) coligands (in comparison with recent diamide-amine supported systems),[19] (iii) facile calix[4]arene O-Me bond cleavage side-reactions and (iv) apparently facile formation of Ti═O groups (leading to $Ti(\mu\text{-}O)_2Ti$ moieties) via cycloaddition/extrusion pathways (for example in the reaction of **3** with PhCHO, Me_2SO_4 or MeOTf). Despite the widespread use of calixarenes in organometallic, coordination and metal−ligand multiple bond chemistry, the dimethyl ethers are insufficiently robust to act as a platform to develop the chemistry of the $Ti{=}NNR_2$ functional group.

Nonetheless, we have been able to observe the first catalytic demethylation of a Me_2Calix ligand leading to the unusual zwitterionic hydrazidium derivative $Ti(NNMe_3)$(MeCalix) (**6**) and its reaction with ^tBuNCO leading to overall insertion into the $Ti{=}N_\alpha$ bond (formation of **10**). This is a departure from the previously observed chemistry of such species (for both Group 4 and Group 6) which focused on $N_\alpha{-}N_\beta$ cleavage reaction, but is of the type expected for a terminal imido species ($Ti{=}N{-}NMe_3^+$ being isoelectronic with $Ti{=}N{-}CMe_3$, for example). Furthermore, $Ti\{^tBuNC(NNMe_3)O\}$(MeCalix) (**10**) provides the first structurally authenticated example of any Group 4 hydrazidium cycloaddition product.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or drybox techniques. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of activated alumina.[73] Deuterated solvents were dried over sodium (C_6D_6) or P_2O_5 ($CDCl_3$ and CD_2Cl_2), distilled under reduced pressure and stored under dinitrogen in Young's Teflon valve ampoules. Solution NMR samples were prepared under a dinitrogen atmosphere in a drybox, in 5 mm Wilmad NMR tubes possessing Young's Teflon valves. ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 or a Varian Unity Plus 500 spectrometer at ambient temperature. The ^1H and ^{13}C spectra were initially referenced to either residual solvent (^1H) or (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F spectra were referenced externally to $CFCl_3$. Chemical shifts are quoted in δ (ppm) and coupling constants (J) in Hz. Where necessary, ^1H and ^{13}C experiments were assisted by $^1H{-}^1H$ and $^1H{-}^{13}C$ correlation experiments. IR spectra were recorded on a Nicolet Magna 560 ESP FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates. IR data are quoted as wavenumbers (cm^{-1}) within the range 4000−400 cm^{-1}. Mass spectra were recorded by the departmental service and elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

Starting Materials. $Na_2[Me_2Calix]$,[74] $Ti(NNPh_2)Cl_2(py)_3$,[20] $TiCl_2(Me_2Calix)$ and $ZrCl_2(Me_2Calix)$[46] were prepared according to literature procedures. 1,1-Diphenylhydrazine was obtained from Sigma-Aldrich as the hydrogen chloride salt, from which the free hydrazine was obtained by basification, drying and removal of residual solvent, followed by distillation under inert atmospheric conditions. 1,1-Dimethylhydrazine and 1-methyl-1-phenylhydrazine and pyridine were dried over freshly ground CaH_2 and distilled before use. Lithiated hydrazines were prepared by reaction of 1 equiv of ^nBuLi with the corresponding 1,1-disubstituted hydrazine in hexanes at −78 °C. Other organic reagents were obtained commercially, dried over CaH_2 or P_2O_5, distilled under reduced pressure and stored in Young's Teflon valve ampoules.

$Ti(NNPh_2)(Me_2Calix)$ (1). *Method (a), f*rom $Ti(NNPh_2)Cl_2(py)_3$: A solution of $Na_2[Me_2Calix]$ (0.750 g, 1.04 mmol) in benzene (40 mL) was added to a solution of $Ti(NNPh_2)Cl_2(py)_3$ (1.120 g, 2.08 mmol) in benzene (40 mL) at 0 °C. The solution was allowed to warm to rt and stirred for 16 h, resulting in a dark brown slurry. Volatiles were removed under reduced pressure, and the brown solid remaining was extracted into diethylether (2 × 15 mL) and filtered. Volatiles were removed under reduced pressure yielding a brown solid which was washed with hexane (3 × 10 mL). The brown solid product was dried in vacuo. Yield: 0.416 g (35%). *Method (b)*, from $TiCl_2(Me_2Calix)$: A solution of $LiNHNPh_2$ (0.719 g, 3.78 mmol) in benzene (100 mL) was added to a solution of $TiCl_2(Me_2Calix)$ (1.500 g, 1.89 mmol) in benzene (60 mL) at rt. The solution was heated at 60 °C and stirred for 16 h, resulting in a dark brown solution. Volatiles were removed under reduced pressure, and the brown solid remaining was extracted into benzene (2 × 30 mL) and filtered. Volatiles were removed under reduced pressure yielding a brown solid which was washed with hexane (1 × 20 mL). The brown solid product was dried in vacuo. Yield: 1.550 g (91%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.04 (4 H, d, $^3J = 7.6$ Hz, $o\text{-}NC_6H_5$), 7.31 (4 H, s, $OC_6\underline{H}_2{}^tBu$), 7.24 (4 H, app. t, app. $^3J = 8.5$ and 7.4 Hz, $m\text{-}NC_6H_5$), 6.87 (2 H, t, $^3J = 7.3$ Hz, $p\text{-}NC_6H_5$), 6.83 (4 H, s, $MeOC_6\underline{H}_2{}^tBu$), 4.74 (4 H, d, $^2J = 12.3$ Hz, $ArC\underline{H}_2Ar$ proximal to OMe), 4.06 (6 H, s, OMe), 3.33 (4 H, d, $^2J = 12.3$ Hz, $ArC\underline{H}_2Ar$ distal to OMe), 1.50 (18 H, s, $OC_6H_2{}^tBu$), 0.69 (18 H, s, $MeOC_6H_2{}^tBu$). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 160.0 ($i\text{-}OC_6H_2{}^tBu$), 150.6 ($i\text{-}MeOC_6H_2{}^tBu$), 149.1 ($p\text{-}MeOC_6H_2{}^tBu$), 146.6 ($i\text{-}NC_6H_5$), 140.6 ($p\text{-}OC_6H_2{}^tBu$), 132.8 ($o\text{-}MeOC_6H_2{}^tBu$), 129.3 ($m\text{-}NC_6H_5$ and $o\text{-}OC_6H_2{}^tBu$), 127.0 ($m\text{-}MeOC_6H_2{}^tBu$), 125.0 ($m\text{-}OC_6H_2{}^tBu$), 122.5 ($p\text{-}NC_6H_5$), 117.5 ($o\text{-}NC_6H_5$), 72.1 (OMe), 34.2 ($OC_6H_2\underline{C}Me_3$), 33.6 ($ArCH_2Ar$ and $MeOC_6H_2\underline{C}Me_3$), 31.9 ($OC_6H_2C\underline{Me_3}$), 30.6 ($MeOC_6H_2C\underline{Me_3}$). IR (KBr plates, Nujol mull, cm^{-1}): ν 1592 (s), 1544 (m), 1479 (s), 1392 (m), 1362 (m), 1330 (s), 1308 (s), 1274 (s), 1211 (m), 1185 (m), 1166 (m), 1121 (m), 1091 (m), 1028 (w), 1004 (m), 942 (w), 913 (m), 873 (m), 858 (m), 848 (m), 796 (m), 779 (w), 748 (m), 697 (m), 680 (w), 627 (m), 567 (s). EI-MS: *m/z* 904 $[M]^+$ (100%), 707 $[M\text{-}NNPh_2Me]^+$ (38%), 197 $[NNPh_2Me]^+$ (17%). Anal. found (calcd. for $C_{58}H_{68}N_2O_4Ti$): C 76.84 (76.97), H 7.60 (7.57), N 3.12 (3.10) %.

$Ti\{NN(Me)Ph\}(Me_2Calix)$ (2). A slurry of LiNHNMePh (0.500 g, 3.90 mmol) in benzene (80 mL) was added to a solution of $TiCl_2(Me_2Calix)$ (1.549 g, 1.95 mmol) in benzene (50 mL). The solution was heated at 60 °C and stirred for 16 h, resulting in a dark brown solution. Volatiles were removed under reduced pressure, the remaining brown solid was extracted into benzene (2 × 25 mL) and filtered. Volatiles were removed under reduced pressure yielding a brown solid which was washed with hexane (1 × 20 mL). The brown solid was dried in vacuo. Yield: 1.449 g (88%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.70 (2 H, d, $^3J = 7.9$ Hz, $o\text{-}NC_6H_5$), 7.34 (2 H, app. t, $^3J = 7.9$ and 7.2 Hz, $m\text{-}NC_6H_5$), 7.33 (4 H, s, $OC_6\underline{H}_2{}^tBu$), 6.85 (4 H, s, $MeOC_6\underline{H}_2{}^tBu$), 6.81 (1 H, t, $^3J = 7.2$ Hz, $p\text{-}NC_6H_5$), 4.80 (4 H, d, $^2J = 12.3$ Hz, $ArC\underline{H}_2Ar$ proximal to OMe), 4.06 (6 H, s, OMe), 3.44 (3 H, s, NMe), 3.37 (4 H, d, $^2J = 12.3$ Hz, $ArC\underline{H}_2Ar$ distal to OMe), 1.51 (18 H, s, $OC_6H_2{}^t\underline{Bu}$), 0.70 (18 H, s, $MeOC_6H_2{}^t\underline{Bu}$). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 159.7 ($i\text{-}OC_6H_2{}^tBu$), 150.2 ($i\text{-}MeOC_6H_2{}^tBu$),

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148.6 (p-MeOC$_6$H$_2{}^t$Bu), 148.2 (i-NC$_6$H$_5$), 140.0 (p-OC$_6$H$_2{}^t$Bu), 132.4 (m-MeOC$_6$H$_2{}^t$Bu), 129.1 (m-NC$_6$H$_5$), 128.9 (m-OC$_6$H$_2{}^t$Bu), 126.6 (m-MeOC$_6$H$_2{}^t$Bu), 142.4 (m-OC$_6$H$_2{}^t$Bu), 118.6 (p-NC$_6$H$_5$), 110.1 (m-NC$_6$H$_5$), 71.7 (OMe), 41.7 (NMe), 33.9 (ArCH$_2$Ar), 33.4 and 33.4 (overlapping MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$ and OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 31.9 (OC$_6$H$_2$C$\underline{\mathrm{Me}_3}$), 30.3 (MeOC$_6H_2C\underline{\mathrm{Me}_3}$). IR (KBr plates, Nujol mull, cm^{-1}): ν 1593 (m), 1466 (s), 1363 (m), 1332 (s), 1319 (s), 1278 (w), 1261 (w), 1210 (m), 1165 (w), 1120 (m), 1093 (m), 1012 (m), 935 (w), 914 (w), 873 (m), 859 (m), 844 (w), 807 (m), 796 (m), 750 (w), 692 (w). EI-MS: m/z 842 [M]$^+$ (100%), 135 [NNPhMe$_2$]$^+$ (5%), 121 [NPhMe$_2$]$^+$ (17%). Anal. found (calcd. for C$_{53}$H$_{66}$N$_2$O$_4$Ti): C 75.59 (75.51), H 7.86 (7.89), N 3.29 (3.32) %.

Ti(NNMe$_2$)(Me$_2$Calix) (3). A solution of LiNHNMe$_2$ (0.483 g, 7.31 mmol) in benzene (20 mL) was added to a solution of TiCl$_2$(Me$_2$Calix) (2.900 g, 3.65 mmol) in benzene (100 mL). The reaction mixture was heated at 60 °C and stirred for 16 h, resulting in a brown solution. Volatiles were removed under reduced pressure, and the remaining brown solid was extracted into diethylether (4 × 25 mL) and filtered. Volatiles were removed under reduced pressure yielding a light brown solid that was dried in vacuo. Yield: 2.136 g (75%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.33 (4 H, s, OC$_6\underline{\mathrm{H}_2}{}^t$Bu), 6.86 (4 H, s, MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu), 4.80 (4 H, d, ^{2}J = 12.4 Hz, ArC$\underline{\mathrm{H}_2}$Ar proximal to OMe), 4.32 (6 H, s, OMe), 3.37 (4 H, d, ^{2}J = 12.4 Hz, ArC$\underline{\mathrm{H}_2}$Ar distal to OMe), 2.82 (6 H, s, NMe$_2$), 1.51 (18 H, s, OC$_6$H$_2\underline{{}^t\mathrm{Bu}}$), 0.71 (18 H, s, MeOC$_6H_2\underline{{}^t\mathrm{Bu}}$). ^{13}C-{^{1}H} NMR (C$_6D_6$, 75.4 MHz, 293 K): δ 160.1 (i-OC$_6$H$_2{}^t$Bu), 150.6 (i-MeOC$_6$H$_2{}^t$Bu), 148.8 (p-MeOC$_6$H$_2{}^t$Bu), 139.9 (p-OC$_6$H$_2{}^t$Bu), 132.8 (o-MeOC$_6$H$_2{}^t$Bu), 129.2 (o-OC$_6$H$_2{}^t$Bu), 126.8 (m-MeOC$_6$H$_2{}^t$Bu), 124.7 (m-OC$_6$H$_2{}^t$Bu), 72.5 (OMe), 49.0 (NMe$_2$), 34.2 (OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.7 (overlapping MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$ and Ar$\underline{\mathrm{C}}$H$_2$Ar), 32.3 (OC$_6$H$_2$C$\underline{\mathrm{Me}_3}$), 30.5 (MeOC$_6H_2C\underline{\mathrm{Me}_3}$). IR (KBr plates, Nujol mull, cm^{-1}): ν 1599 (m), 1480 (s), 1392 (m), 1361 (s), 1319 (s), 1212 (s), 1166 (m), 1119 (s), 1093 (m), 1002 (s), 937 (m), 921 (m), 891 (m), 871 (s), 856 (m), 810 (m), 796 (s), 782 (m), 758 (m), 709 (w), 677 (s), 637 (w), 608 (m), 565 (s). EI-MS: m/z 121 [TiNNMe$_3$]$^+$ (16%), 105 [TiNNMe$_2$]$^+$ (8%), 58 [NNMe$_2$]$^+$ (31%). Anal. found (calcd. for C$_{48}$H$_{64}$N$_2$O$_4$Ti): C 73.84 (73.83), H 8.24 (8.26), N 3.58 (3.59) %.

Zr(NHNPh$_2$)$_2$(Me$_2$Calix) (4). A solution of LiNHNPh$_2$ (0.227 g, 1.19 mmol) in benzene (50 mL) was added to a slurry of ZrCl$_2$(Me$_2$Calix) (0.500 g, 0.60 mmol) in benzene (50 mL). The mixture was heated at 60 °C and stirred for 1 h, yielding a turbid yellow solution. Volatiles were removed under reduced pressure, and the product was extracted into benzene (2 × 40 mL) and filtered. The volatiles were removed under reduced pressure, and the product was extracted into hexane (2 × 5 mL) and filtered. Repeated crystallizations from this saturated hexane solution at −30 °C yielded the title product as a beige solid that was dried in vacuo. Yield: 0.118 g (21%). ^{1}H NMR (C$_6$H$_6$, 299.9 MHz, 293 K): δ 7.34 (8 H, d, ^{3}J = 7.4 Hz, o-NHN$\underline{\mathrm{Ph}_2}$), 7.24 (4 H, s, OC$_6\underline{\mathrm{H}_2}{}^t$Bu), 7.13 (8 H, app. t, ^{3}J = 7.2 and 7.4 Hz, m-NHN$\underline{\mathrm{Ph}_2}$), 6.88 (4 H, t, ^{3}J = 7.2 Hz, p-NHN$\underline{\mathrm{Ph}_2}$), 6.80 (4 H, s, MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu), 4.17 (4 H, d, ^{2}J = 12.7 Hz, ArC$\underline{\mathrm{H}_2}$Ar proximal to OMe), 3.86 (6 H, s, OMe), 3.16 (4 H, d, ^{2}J = 12.7 Hz, ArC$\underline{\mathrm{H}_2}$Ar distal to OMe), 1.48 (18 H, s, OC$_6$H$_2\underline{{}^t\mathrm{Bu}}$), 0.71 (18 H, s, MeOC$_6H_2\underline{{}^t\mathrm{Bu}}$). ^{13}C-{^{1}H} NMR (C$_6D_6$, 75.4 MHz, 293 K): δ 158.2 (i-OC$_6$H$_2{}^t$Bu), 153.7 (i-MeOC$_6$H$_2{}^t$Bu), 151.9 (i-NHNPh$_2$), 148.8 (p-MeOC$_6$H$_2{}^t$Bu), 141.0 (p-OC$_6$H$_2{}^t$Bu), 131.8 (o-MeOC$_6$H$_2{}^t$Bu), 130.6 (o-OC$_6$H$_2{}^t$Bu), 128.9 (m-NHNPh$_2$), 127.3 (m-MeOC$_6$H$_2{}^t$Bu), 124.5 (m-OC$_6$H$_2{}^t$Bu), 121.2 (p-NHNPh$_2$), 120.5 (o-NHNPh$_2$), 69.7 (OMe), 34.3 (OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.7 (ArCH$_2$Ar and MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 32.2 (OC$_6$H$_2$C$\underline{\mathrm{Me}_3}$), 30.6 (MeOC$_6H_2C\underline{\mathrm{Me}_3}$). IR (KBr plates, Nujol mull, cm^{-1}): ν 3583 (w, ν(N−H)), 1587 (m), 1480 (s), 1464 (s), 1363 (m), 1320 (s), 1276 (m), 1214 (m), 1169 (m), 1118 (m), 1090 (m), 1063 (w), 1029 (w), 991 (m), 935 (w), 873 (m), 856 (m), 792 (m), 746 (m), 732 (m), 691 (m), 665 (m), 641 (m). Anal. found (calcd. for C$_{70}$H$_{80}$N$_4$O$_4$Zr): C 74.15 (74.23), H 7.08 (7.12), N 4.91 (4.95) %.

Zr(NHNMe$_2$)$_2$(Me$_2$Calix) (5). A solution of LiNHNMe$_2$ (0.158 g, 2.39 mmol) in benzene (40 mL) was added to a slurry of ZrCl$_2$(Me$_2$Calix) in benzene (40 mL). The mixture was heated at 60 °C and stirred for 1 h, yielding a cloudy beige solution. Volatiles were removed under reduced pressure, the product was extracted into benzene (2 × 40 mL) and filtered. Volatiles were removed under reduced pressure, yielding the title product as a beige solid that was dried in vacuo. Yield: 0.601 g (60%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.38 (4 H, s, OC$_6\underline{\mathrm{H}_2}{}^t$Bu), 6.98 (4 H, s, MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu), 4.53 (4 H, d, ^{2}J = 11.7 Hz, ArC$\underline{\mathrm{H}_2}$Ar proximal to OMe), 3.65 (6 H, s, OMe), 3.39 (4 H, d, ^{2}J = 12 Hz, ArC$\underline{\mathrm{H}_2}$Ar distal to OMe), 3.20 (2 H, s, N$\underline{\mathrm{H}}$NMe$_2$), 2.67 (12 H, s, NHN$\underline{\mathrm{Me}_2}$), 1.53 (18 H, s, OC$_6H_2\underline{{}^t\mathrm{Bu}}$), 0.83 (18 H, s, MeOC$_6H_2\underline{{}^t\mathrm{Bu}}$). ^{13}C-{^{1}H} NMR (C$_6D_6$, 75.4 MHz, 293 K): δ 160.2 (i-OC$_6$H$_2{}^t$Bu), 154.4 (i-MeO$_6$H$_2{}^t$Bu), 147.7 (p-MeOC$_6$H$_2{}^t$Bu), 138.1 (p-OC$_6$H$_2{}^t$Bu), 132.3 (o-OC$_6$H$_2{}^t$Bu), 130.5 (o-MeOC$_6$H$_2{}^t$Bu), 126.4 (m-OC$_6$H$_2{}^t$Bu), 124.7 (m-MeOC$_6$H$_2{}^t$Bu), 66.3 (OMe), 52.6 (NHNMe$_2$), 34.6 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 34.2 (OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.7 (MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 32.4 (OC$_6$H$_2$C$\underline{\mathrm{Me}_3}$), 30.8 (MeOC$_6H_2C\underline{\mathrm{Me}_3}$). IR (KBr plates, Nujol mull, cm^{-1}): ν 3583 (w, ν(N−H)), 2814 (m), 1603 (w), 1481 (s), 1392 (m), 1362 (m), 1334 (s), 1321 (s), 1285 (m), 1262 (m), 1215 (s), 1167 (m), 1123 (m), 1097 (m), 1015 (s), 982 (m), 943 (w), 926 (m), 916 (m), 870 (m), 847 (s), 797 (m), 787 (m), 760 (w), 702 (w), 666 (m). EI-MS: m/z 208 [Zr(NHNMe$_2$)$_2$]$^+$ (50%). Anal. found (calcd. for C$_{50}$H$_{72}$N$_4$O$_4$Zr): C 67.86 (67.91), H 8.19 (8.21), N 6.25 (6.34) %.

NMR Tube Scale Reaction of Ti(NNMe$_2$)(Me$_2$Calix) (3) with PhCHO. Benzaldehyde (2.6 μL, 0.026 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.020 g, 0.026 mmol) in C$_6$D$_6$ (0.75 mL). After 16 h at rt the ^{1}H NMR spectrum showed quantitative conversion to [Ti(μ-O)(Me$_2$Calix)]$_2$ in addition to a mixture of the geometrical isomers of benzaldehyde-dimethylhydrazone.[70]

Ti(NNMe$_3$)(MeCalix) (6). MeI (71.7 μL, 1.150 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.300 g, 0.384 mmol) in benzene (20 mL). The solution was heated at 100 °C for 20 min and the volatiles were removed under reduced pressure. The remaining orange solid was washed with pentane (1 × 10 mL) leaving a pale orange solid that was dried in vacuo. Yield: 0.126 g, (42%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.44 (2 H, d, ^{4}J = 2.3 Hz, MeOAr-OC$_6\underline{\mathrm{H}_2}{}^t$Bu-ArO proximal to ArO), 7.36 (2 H, d, ^{4}J = 2.3 Hz, MeOAr-OC$_6\underline{\mathrm{H}_2}{}^t$Bu-ArO proximal to MeOAr), 7.02 (4 H, s, overlapping MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu and OAr-OC$_6\underline{\mathrm{H}_2}{}^t$Bu-ArO), 5.21 (2 H, d, ^{2}J = 11.8 Hz, OAr-C$\underline{\mathrm{H}_2}$-ArO proximal to OMe), 4.64 (2 H, d, ^{2}J = 11.8 Hz, MeOAr-C$\underline{\mathrm{H}_2}$-ArO proximal to OMe), 4.03 (3 H, s, OMe), 3.48 (2 H, d, ^{2}J = 11.8 Hz, OAr-C$\underline{\mathrm{H}_2}$-ArO distal to OMe), 3.45 (2 H, d, ^{2}J = 11.8 Hz, MeOAr-C$\underline{\mathrm{H}_2}$-ArO distal to OMe), 2.75 (9 H, s, NNMe$_3$), 1.51 (18 H, s, MeOAr-OC$_6$H$_2\underline{{}^t\mathrm{Bu}}$-ArO), 0.91 (9 H, s, MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}_2}{}^t$Bu-ArO), 0.82 (9 H, s, MeOC$_6\underline{\mathrm{H}_2}{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}_2}{}^t$Bu-ArO). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 159.3 (i-MeOAr-OC$_6$H$_2{}^t$Bu-ArO), 155.0 (i-OAr-OC$_6$H$_2{}^t$Bu-ArO), 150.7 (i-MeOC$_6$H$_2{}^t$Bu), 147.9 (p-MeOC$_6$H$_2{}^t$Bu or p-OAr-OC$_6$H$_2{}^t$Bu-ArO), 140.9 (p-MeOC$_6$H$_2{}^t$Bu or p-OAr-OC$_6$H$_2{}^t$Bu-ArO), 140.7 (p-MeO-OC$_6$H$_2{}^t$Bu-ArO), 132.9 (o-MeO-C$_6$H$_2{}^t$Bu or o-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 131.7 (o-OAr-OC$_6$H$_2{}^t$Bu-ArO or o-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to OAr), 129.3 (o-MeO-C$_6$H$_2{}^t$Bu or o-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 128.6 (o-OAr-OC$_6$H$_2{}^t$Bu-ArO or o-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to OAr), 126.4 (m-MeOC$_6$H$_2{}^t$Bu or m-OAr-OC$_6$H$_2{}^t$Bu-ArO), 125.0 (m-MeOC$_6$H$_2{}^t$Bu or m-OAr-OC$_6$H$_2{}^t$Bu-ArO), 124.9 (m-

MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to ArO), 123.4 (*m*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 67.0 (OMe), 59.8 (NMe$_3$), 34.10 (MeO-OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$-ArO), 33.9 (OAr-$\underline{\mathrm{C}}$H$_2$−ArO), 33.9 (OAr-OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$-ArO or MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.4 (overlapping MeOAr-$\underline{\mathrm{C}}$H$_2$−ArO and OAr-OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$-ArO or MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 31.9 (MeOAr-OC$_6$H$_2$C$\underline{\mathrm{Me}}_3$-ArO), 30.9 (MeOC$_6H_2C\underline{\mathrm{Me}}_3$ or OAr-OC$_6$H$_2$C$\underline{\mathrm{Me}}_3$-ArO), 30.5 (MeOC$_6H_2C\underline{\mathrm{Me}}_3$ or OAr-OC$_6$H$_2$C$\underline{\mathrm{Me}}_3$-ArO). IR (KBr plates, Nujol mull, cm^{-1}): ν 1595 (w), 1544 (w), 1465 (s), 1393 (m), 1361 (m), 1322 (s), 1310 (s), 1281 (m), 1260 (m), 1239 (m), 1207 (s), 1167 (w), 1124 (m), 1012 (m), 941 (w), 919 (m), 872 (m), 850 (m), 827 (m), 819 (m), 798 (s), 780 (w), 758 (m), 722 (w), 699 (w), 675 (w), 617 (m), 563 (s). Anal. found (calcd. for $C_{48}H_{64}N_2O_4Ti$): C 73.84 (73.83), H 8.19 (8.26), N 3.56 (3.59) %.

NMR Tube Scale Synthesis of Ti(NNMe$_2$CD$_3$)(MeCalix) (6-*d*$_3$). CD$_3$I (4.8 μL, 0.077 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.020 g, 0.026 mmol) in C$_6$D$_6$ (0.75 mL). The mixture was heated at 100 °C for 20 min. The ^{1}H NMR spectrum showed quantitative conversion to Ti(NNMe$_2$CD$_3$)-(MeCalix) (**8-*d*$_3$**) with the concomitant evolution of one equivalent of MeI.

^{2}H NMR (C$_6$H$_6$, 76.7 MHz, 293 K): δ 2.59 (s, NCD$_3$).

NMR Tube Scale Reaction of Ti(NNMe$_2$)(Me$_2$Calix) with 0.12 equiv MeI. MeI (0.6 μL, 0.009 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.050 g, 0.064 mmol) in C$_6$D$_6$. The mixture was heated at 100 °C for 30 min. The ^{1}H NMR spectrum revealed the quantitative conversion of **3** to **6** with MeI present in the product mixture in the same proportions as at the start of the reaction.

NMR Tube Scale Synthesis of Ti{NN(Me)$_2$CH$_2$Ph}(MeCalix) (8). Benzyl bromide (9.1 μL, 0.077 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.020 g, 0.026 mmol) in C$_6$D$_6$ (0.75 mL). The solution was heated at 60 °C for 16 h. The ^{1}H NMR spectrum revealed quantitative conversion to Ti(NNMe$_2$Bz)(MeCalix) (**8**). The ^{1}H NMR spectrum of 8 was assigned by analogy with the resonances of **6**. Attempts to isolate **8** on a preparative scale were unsuccessful. When a smaller excess of benzyl bromide is used in this reaction, small amounts of Ti(NNMe$_3$)(MeCalix) (**6**) are also observed. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.52 (1 H, d, ^{3}J = 7.9 Hz, *p*-NCH$_2\underline{\mathrm{Ph}}$), 7.35 (2 H, d, ^{4}J = 2.0 Hz, MeOAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO proximal to ArO), 7.28 (2 H, d, ^{4}J = 2.0 Hz, MeOAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO proximal to MeOAr), 7.05 (2 H, app. t, app. ^{3}J = 7.9 and 7.4 Hz, *m*-NCH$_2\underline{\mathrm{Ph}}$), 6.95 (2 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 6.91 (2 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 6.90 (1 H, t, ^{3}J = 7.4 Hz, *p*-NCH$_2\underline{\mathrm{Ph}}$), 5.01 (2 H, d, ^{2}J = 12.6 Hz, OAr-C$\underline{\mathrm{H}}_2$-ArO proximal to OMe), 4.26 (2 H, s, NC$\underline{\mathrm{H}}_2$Ph), 4.07 (2 H, d, ^{2}J = 12.1 Hz, MeOAr-C$\underline{\mathrm{H}}_2$-ArO proximal to OMe), 3.46 (2 H, d, ^{2}J = 12.6 Hz, OAr-C$\underline{\mathrm{H}}_2$-ArO distal to OMe), 3.29 (3 H, s, OMe), 3.21 (2 H, d, ^{2}J = 12.1 Hz, MeOAr-C$\underline{\mathrm{H}}_2$-ArO distal to OMe), 2.77 (6 H, s, $\underline{\mathrm{NMe}}_2$), 1.48 (18 H, s, MeOAr-OC$_6$H$_2{}^t\underline{\mathrm{Bu}}$-ArO), 0.91 (9 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 0.77 (9 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO).

NMR Tube Scale Reaction of Ti(NNMe$_2$)(Me$_2$Calix) (3) with Me$_2$SO$_4$. Dimethyl sulfate (2.4 μL, 0.026 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.020 g, 0.026 mmol) in C$_6$D$_6$ (0.75 mL). After 16 h a yellow precipitate had formed, and the ^{1}H NMR spectra (taken in CD$_2$Cl$_2$ and C$_6$D$_6$) showed that [Ti(μ-O)(Me$_2$Calix)]$_2$ had been formed as the major product.[46]

Synthesis of [Ti(NNMe$_3$)(Me$_2$Calix)][OTf] (7-OTf). Methyl triflate (45 μL, 0.40 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.300 g, 0.38 mmol) in benzene (20 mL). The resultant red solution was stirred for 16 h, during which time a pale orange solid formed. This was was filtered, washed with cold pentane (3 × 20 mL) and dried in vacuo to give **7-OTf** as a pale yellow powder. Yield: 0.08 g, (22%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.24 (4H, s, OC$_6\underline{\mathrm{H}}_2{}^t$Bu), 6.81 (4H, s, MeOC$_6H_2{}^t$Bu), 4.56 (4H, d, ^{2}J = 12.7 Hz, ArC$\underline{\mathrm{H}}_2$Ar proximal to OMe), 4.41 (6H, s, OMe), 3.50 (9H, s, NMe), 3.34 (4H, d, ^{2}J = 12.7 Hz, ArC$\underline{\mathrm{H}}_2$Ar distal to OMe), 1.45 (18H, s, OC$_6$H$_2{}^t\underline{\mathrm{Bu}}$), 0.70 (18H, s, MeOC$_6H_2{}^t\underline{\mathrm{Bu}}$). ^{13}C-{^{1}H} NMR (C$_6D_6$, 75.4 MHz, 293 K): δ 160.0 (*i*-OC$_6$H$_2{}^t$Bu), 151.3 (*i*-MeOC$_6$H$_2{}^t$Bu), 149.6 (*p*-MeOC$_6$H$_2{}^t$Bu), 142.7 (*p*-OC$_6$H$_2{}^t$Bu), 132.0 (*o*-MeOC$_6$H$_2{}^t$Bu), 129.5 (*o*-OC$_6$H$_2{}^t$Bu), 127.1 (*m*-MeOC$_6$H$_2{}^t$Bu), 124.8 (*m*-OC$_6$H$_2{}^t$Bu), 74.3 (OMe), 60.8 (NMe), 34.3 (OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.7 (MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 33.5 (Ar-$\underline{\mathrm{C}}$H$_2$−Ar), 32.0 (OC$_6$H$_2$C$\underline{\mathrm{Me}}_3$), 30.6 (MeOC$_6H_2C\underline{\mathrm{Me}}_3$). ^{19}F-{^{1}H} NMR (C$_6D_6$, 282.4 MHz, 293 K): δ −77.82 (CF$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1563 (w), 1506 (w), 1464 (s), 1394 (w), 1377 (m), 1364 (m), 1272 (s), 1258 (s), 1212 (m), 1164 (s), 1115 (w), 1092 (w), 1043 (m), 1032 (s), 993 (w), 941 (w), 932 (w), 874 (w), 862 (w), 796 (w), 756 (w), 722 (w), 665 (w), 641 (s), 573 (m). Anal. found (calcd. for $C_{50}H_{67}F_3N_2O_7STi$): C 63.45(63.55), H 7.10 (7.15), N 3.06 (2.96) %.

Reaction of [Ti(NNMe$_3$)(Me$_2$Calix)][OTf] (7-OTf) with ^{n}Bu$_4$NI. Methyl triflate (2.9 μL, 0.026 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.020 g, 0.026 mmol) to form a red solution of [Ti(NNMe$_3$)(Me$_2$Calix)][OTf] (**7-OTf**) as above. Bu$_4$NI (0.009 g, 0.026 mmol) was added to this solution, leading to a color change from red back to orange. After heating at 60 °C for 1 h the ^{1}H NMR spectrum showed the near-quantitative formation of Ti(NNMe$_3$)(MeCalix) (**6**) along with MeI.

Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (10). ^{t}BuNCO (87.7 μL, 0.768 mmol) was added to a solution of Ti(NNMe$_2$)(Me$_2$Calix) (0.500 g, 0.640 mmol) in benzene (30 mL). The solution was heated at 70 °C for 16 h and the volatiles were removed under reduced pressure leaving an orange/brown solid. Washing with pentane (2 × 5 mL) yielded an orange solid that was dried in vacuo. Yield: 0.162 g, (29%). ^{1}H NMR (C$_6$D$_6$, 299.9 Hz, 293 K): δ 7.38 (2 H, d, ^{4}J = 2.4 Hz, MeOAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO proximal to ArO), 7.34 (2 H, d, ^{4}J = 2.4 Hz, MeOAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO proximal to MeOAr), 7.06 (2 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 7.03 (2 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 5.35 (2 H, d, ^{2}J = 12.6 Hz, OAr-C$\underline{\mathrm{H}}_2$-ArO proximal to OMe), 4.70 (2 H, d, ^{2}J = 12.3 Hz, OAr-C$\underline{\mathrm{H}}_2$-ArO distal to OMe), 3.81 (3 H, s, OMe), 3.54 (2 H, d, ^{2}J = 12.6 Hz, OAr-C$\underline{\mathrm{H}}_2$-ArO distal to OMe), 3.46 (2 H, d, ^{2}J = 12.3 Hz, MeOAr-C$\underline{\mathrm{H}}_2$-ArO distal to OMe), 2.28 (9 H, s, NNMe$_3$), 1.85 (9 H, s, N^{t}Bu), 1.46 (18 H, s, MeOAr-OC$_6$H$_2{}^t\underline{\mathrm{Bu}}$-ArO), 0.91 (9 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO), 0.85 (9 H, s, MeOC$_6\underline{\mathrm{H}}_2{}^t$Bu or OAr-OC$_6\underline{\mathrm{H}}_2{}^t$Bu-ArO). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 172.0 (^{t}BuN$\underline{\mathrm{C}}$(NNMe$_3$)O), 162.9 (*i*-OAr-OC$_6$H$_2{}^t$Bu-ArO), 162.3 (*i*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO), 154.1 (*i*-MeOC$_6$H$_2{}^t$Bu), 147.3 (*p*-OAr-OC$_6$H$_2{}^t$Bu-ArO), 142.5 (*p*-MeOC$_6$H$_2{}^t$Bu), 141.6 (*p*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO), 133.3 (*o*-MeOC$_6$H$_2{}^t$Bu or *o*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 133.2 (*o*-OAr-OC$_6$H$_2{}^t$Bu-ArO or *o*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to OAr), 131.1 (*o*-MeOC$_6$H$_2{}^t$Bu or *o*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 127.0 (*o*-OAr-OC$_6$H$_2{}^t$Bu-ArO or *o*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to OAr), 126.5 (*m*-MeOC$_6$H$_2{}^t$Bu), 125.4 (*m*-OAr-OC$_6$H$_2{}^t$Bu-ArO), 125.0 (*m*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to OAr), 123.6 (*m*-MeOAr-OC$_6$H$_2{}^t$Bu-ArO proximal to MeOAr), 63.5 (OMe), 56.2 (NNMe$_3$), 55.1 (N$\underline{\mathrm{C}}$Me$_3$), 35.2 (OAr-CH$_2$−ArO), 34.7 (MeOAr-CH$_2$−ArO), 34.3 (MeOAr-OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$-ArO), 33.7 (OAr-OC$_6$H$_2\underline{\mathrm{C}}$Me$_3$-ArO), 33.5 (MeOC$_6$H$_2\underline{\mathrm{C}}$Me$_3$), 32.1 (MeOAr-OC$_6$H$_2$C$\underline{\mathrm{Me}}_3$-ArO), 31.9 (MeOC$_6H_2C\underline{\mathrm{Me}}_3$), 31.4 (NC$\underline{\mathrm{Me}}_3$), 31.2 (OAr-OC$_6H_2C\underline{\mathrm{Me}}_3$-ArO). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1568 (w), 1519 (m), 1465 (s), 1392 (w), 1377 (s), 1362 (m), 1313 (w), 1278 (m), 1239 (w), 1209 (s), 1170 (w), 1124 (w), 1070 (w), 1014 (w), 937 (w), 920 (w), 871 (w), 858 (w), 825 (w), 819 (s), 792 (m), 756 (w), 723 (w), 677 (m), 665 (m), 601 (s). Anal. found (calcd. for $C_{53}H_{73}N_3O_5Ti$): C 72.36 (72.33), H 8.30 (8.36), 7.83 (7.77) %.

NMR Tube Scale Synthesis of Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (10) from Ti(NNMe$_3$)(MeCalix) (6) and ^{t}BuNCO. ^{t}BuNCO (2.9 μL, 0.026 mmol) was added to a solution of Ti(NNMe$_3$)(MeCalix) (0.020 g, 0.026 mmol) in C_6D_6 (0.75 mL). The mixture was heated at 60 °C for 1 h. The ^{1}H NMR spectrum showed formation of **10** in 70% yield.

Crystal Structure Determinations of Ti(NNPh$_2$)(Me$_2$Calix)·Et$_2$O (1·Et$_2$O), Ti{NN(Me)Ph}(Me$_2$Calix)·2(C$_7$H$_8$) (2·2(C$_7$H$_8$)), Ti(NNMe$_2$)(Me$_2$Calix)·1.75(C$_7$H$_8$) (3·1.75(C$_7$H$_8$)), Ph$_2$NNH$_2$, [Ti(NNMe$_3$)(Me$_3$Calix)(OTf)][OTf] (9-OTf·1.75(C$_6$H$_6$)) and Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (10·3(C$_6$H$_6$)). Crystal data collection and processing parameters are given in Table 5. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using either an Enraf-Nonius KappaCCD diffractometer. Intensity data were processed using the DENZO-SMN package.[75] The structures were solved using the direct-methods program SIR92,[76] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[77] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined (see additional comments below). H atoms bonded to C were placed geometrically while the N−H atoms for Ph$_2$NNH$_2$ were located from Fourier difference maps and refined isotropically. Further details of the refinements are provided in the CIF in Supporting Information. A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Acknowledgment. We thank the EPSRC and the Nuffield Foundation for support.

Note Added after ASAP Publication. There was an error in Scheme 2 in the version published ASAP November 11, 2008; the corrected version was published ASAP November 18, 2008.

Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of Ti(NNPh$_2$)(Me$_2$Calix)·Et$_2$O (**1·Et$_2$O**), Ti{NN(Me)Ph}(Me$_2$Calix)·2(C$_7$H$_8$) (**2·2(C$_7$H$_8$)**), Ti(NNMe$_2$)(Me$_2$Calix)·1.75(C$_7$H$_8$) (**3·1.75(C$_7$H$_8$)**), Ph$_2$NNH$_2$, [Ti(NNMe$_3$)(Me$_3$Calix)(OTf)][OTf] (**9-OTf·1.75(C$_6$H$_6$)**), and Ti{^{t}BuNC(NNMe$_3$)O}(MeCalix) (**10·3(C$_6$H$_6$)**). This information is available free of charge via the Internet at http://pubs.acs.org.

IC801735C

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