# Synthesis and Reactivity of Titanium Hydrazido Complexes Supported by Diamido-Ether Ligands

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S *Supporting Information*

ABSTRACT: The synthesis and reactivity of titanium diphenyl hydrazido(2−) complexes supported by the diamido-ether ligands $O(2\text{-}C_6H_4NSiMe_3)_2$ ($N_2^{Ar}O$) and $O\text{-}(CH_2CH_2NSiMe_3)_2$ (N_2O) are described. Reaction of $Li_2N_2^{Ar}O$ or Li_2N_2O with $Ti(NNPh_2)Cl_2(py)_3$ afforded $Ti(N_2^{Ar}O)(NNPh_2)(py)_2$ (**14**) or $Ti(N_2O)(NNPh_2)(py)_2$ (**15**) with $\kappa^3\text{-}mer$-bound diamido-ether ligands. Reaction with ^tBu-bipy (4,4′-di-*tert*-butyl-2,2′-bipyridyl) or bipy (2,2′-bipyridyl) gave a switch to $\kappa^3\text{-}fac$-coordination. Reaction of **15** with Ar′NCO (Ar′ = 2,6-$C_6H_3^iPr_2$) gave $Ti\{O(CH_2CH_2NSiMe_3)\text{-}(CH_2CH_2NC(O)N(SiMe_3)Ar')\}\text{-}\{N(NPh_2)C(O)N(Ar')\}$, in which the substrate has inserted into a $Ti–N_{amide}$ bond of N_2O as well as adding to the $Ti\equiv N_\alpha$ multiple bond. With Ar′NCS the [2+2] cycloaddition product $Ti(N_2O)\{N(NPh_2)C(NAr')S\}(py)$ was obtained, and with Ar′NCSe a mixture was formed including $Ti_2(N_2O)_2(\mu\text{-}Se)_2$. Both **14** and **15** reacted with $Ar^{Fx}CN$ ($Ar^{Fx} = C_6H_3F_2$ or C_6F_5) to give $Ti\equiv N_\alpha$ bond insertion products of the type $Ti(L)\{NC(Ar^{Fx})NNPh_2\}(py)_2$ (L = $N_2^{Ar}O$ or N_2O) containing hydrazonamide ligands. Reaction of **14** with XylNC (Xyl = 2,6-$C_6H_3Me_2$) gave only the isonitrile σ-adduct $Ti(N_2^{Ar}O)(NNPh_2)(py)(CNXyl)$, whereas **15** underwent $N_\alpha–N_\beta$ bond reductive cleavage with ^tBuNC or XylNC forming $Ti(N_2O)(NPh_2)(NCN^tBu)$ or $Ti\{O(CH_2CH_2NSiMe_3)(CH_2CH_2NCN(SiMe_3)Xyl)\}(NPh_2)(NCNXyl)$ (**27**). Both contain metalated carbodiimide ligands, but in **27** an additional reaction of XylNC with the $Ti–N_{amide}$ bond of N_2O has taken place. Compound **15** also reacted with a number of internal alkynes RCCR′ (R = R′ = Me or Ph; R = Me, R′ = aryl) to give $N_\alpha–N_\beta$ bond reductive cleavage products of the type $Ti\{O(CH_2CH_2NSiMe_3)(CH_2CH_2NC(R)C(R')NSiMe_3\}(NPh_2)$, again involving a reaction of a $Ti–N_{amide}$ bond.
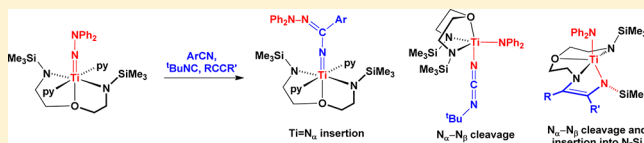
INTRODUCTION

The stoichiometric and catalytic chemistry of group 4 alkyl and aryl imido complexes (L)M≡N−R (M = Ti, Zr, Hf; R = alkyl or aryl; L = supporting ligand (set)) has been extensively studied for over 20 years, as summarized in a series of reviews.[1] The polar and unsaturated M≡N multiple bond (a $\sigma^2\pi^4$ triple bond in most cases[2]) can undergo a range of reactions with both saturated and unsaturated substrates. In contrast, the chemistry of group 4 dialkyl or diaryl hydrazido(2−) compounds (L)M≡N-NR_2, first reported by Wiberg (M = Ti)[3] and Bergman (M = Zr),[4] was initially fairly slow to develop, as has also been the case for their alkylidene hydrazido (i.e., (L)M≡N−N≡CRR′)[5] and alkoxy imido (i.e., (L)M≡N−OR)[6] counterparts. Nonetheless, in the past decade in particular, a wide range of titanium[7] and zirconium and hafnium[8] hydrazido complexes have been isolated or generated *in situ*, and the small-molecule reaction chemistry of the M≡N−NR_2 functional group has been explored. In addition to hydrohydrazination and related catalytic transformations involving alkynes and allenes,[7d−i,k,n,s,aa,ab,9] stoichiometric reactions with a large number of substrates including CO, isonitriles, nitriles, ^tBuCP, alkynes, allenes and heteroallenes (e.g., CO_2, CS_2, isocyanates, and their congeners), organic azides, silanes and halosilanes, boranes, alkyl halides, and Brønsted acids have been reported. These reactions lead to a range of outcomes including addition to either the N_α or N_β

atom, cycloaddition to (or insertion into) the $Ti\equiv N_\alpha$ bond, and also cleavage of (or insertion into) the $N_\alpha–N_\beta$ bond.[7a−u,w−ac,8]

Of the various types of supporting ligands used in group 4 hydrazido chemistry, one of the most effective with regard to promoting new chemistry of the M≡N−NR_2 functional group has been the diamido-pyridine ligands $(2\text{-}NC_5H_4)CMe\text{-}(CH_2NSiMe_2R)_2$ (R = Me (N_2N^{py}) or ^tBu ($N_2^*N^{py}$))[7p,q,t,w,8a,c−g,i−m] or the closely related diamido-amine ligand $MeN(CH_2CH_2NR)_2$ (R = $SiMe_3$ (N_2N^{Me}) or ^iPr)[7m,p,t,u,w,ab] illustrated by way of example for complexes **1**−**4** in Figure 1. As shown by structural and DFT studies,[7p] the π-donor N_{amide} atoms of N_2N^{Me}- and N_2N^{py}-type ligands tend to destabilize the M≡N_α multiple bond (again a $\sigma^2\pi^4$ triple bond in most cases[5f,7j,l,p,x]). This, together with the relatively open coordination sphere provided by these ligands, leads to a more reactive M≡N−NR_2 moiety and access to a range of reaction products. Thus treatment of **3** with Ar′NCE (E = O, S, Se) gives well-defined $Ti\equiv N_\alpha$ [2+2] cycloaddition products **5**.[7t,w] However, with $Ar^{Fx}CN$ ($Ar^{Fx} = C_6F_5$ or 2,6-$C_6H_3F_2$) the corresponding cycloaddition products are not stable and the $Ti\equiv N_\alpha$ bond net insertion products **6** result.[7t,w] All of the compounds **1**−**3** react with isonitriles to undergo $N_\alpha−N_\beta$ bond
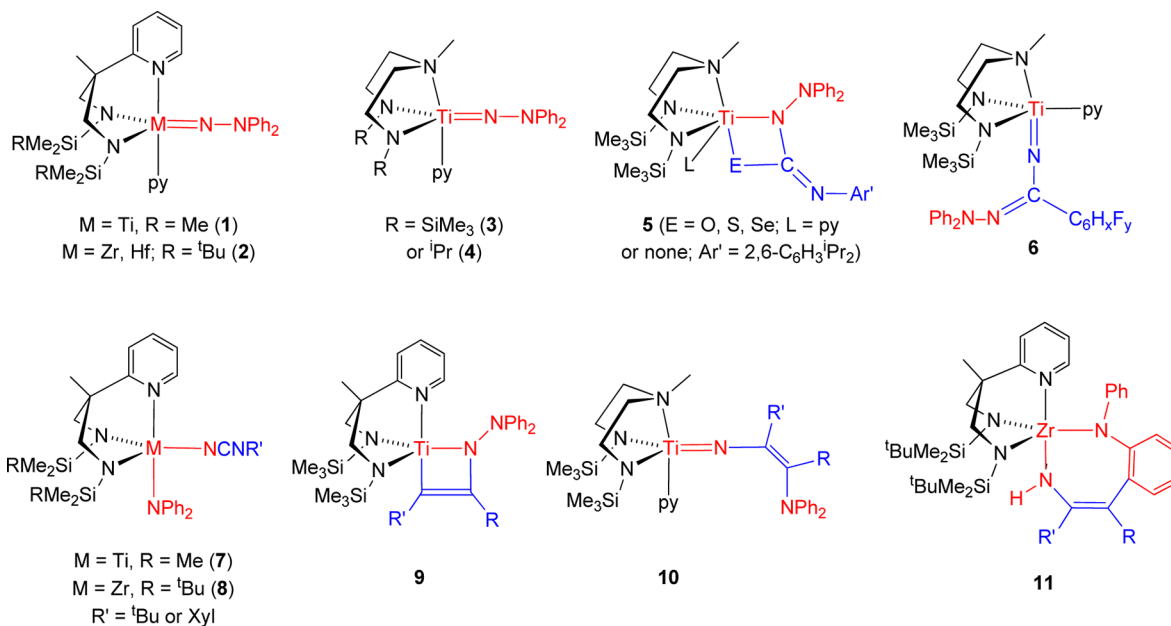
Figure 1. Examples of group 4 hydrazido complexes supported by diamido-amine ligands (**1**−**4**) and selected reaction products with isocyanates, nitriles, isonitriles, and alkynes. The atoms of the original M=NNR$_2$ group are shown in red, and those of the substrate are in blue.

cleavage and net N$_\alpha$ atom transfer to form a metalated carbodiimide ligand (e.g., **7** and **8**).[7t,w,8a] Furthermore, with alkynes a range of reaction products (**9**−**11**) can be isolated depending upon the alkyne, metal, and supporting ligand.[7m,q,t,8h,l,m]

Use of more sterically demanding versions of N$_2$N^{Me} (Me$_3$SiN(CH$_2$CH$_2$NSiMe$_3$)$_2$ or MeN(CH$_2$CH$_2$CH$_2$N-SiMe$_3$)$_2$)[7p] or the four-coordinate version (2-NC$_5$H$_4$)CH$_2$N-(CH$_2$NSiMe$_3$)$_2$[7p] tends to close down this reactivity or lead to mixtures of reaction products.[10] In contrast, we very recently showed that changing the N$_{amide}$ substituent "R" from −SiMe$_3$ in **3** to −^{i}Pr in **4** gave a change in reactivity from 1,2-diamination catalysis[7m,t] (via intermediates of the type **10**) to hydrohydrazination catalysis via an unprecedented titanium acetylide/vinyl hydrazido(1−) resting state and intermediate.[7ab]

Given the range of different M=N-NR$_2$ group reactivity as a function of supporting ligand sets (and the success of diamido-amine-type ligands in general), we thought it would be of interest to replace the neutral pyridyl or amine N-donors in the N$_2$N^{py} or N$_2$N^{Me} ligands to (even) less sterically demanding and weaker O-donor ether groups. We therefore modified the N$_2$N^{Me} ligand by introducing an oxygen in place of NMe to give O(CH$_2$CH$_2$NSiMe$_3$)$_2$ (referred to as "N$_2$O" hereafter). We also used a diaryl version of this ligand, namely, O(2-C$_6$H$_4$NSiMe$_3$)$_2$ ("N$_2^{Ar}$O") reported previously by Schrock et al. in the development of new group 4 olefin polymerization catalysts.[11] Figure 2 shows the protio forms of the diamido-ether ligands used and their abbreviations. In this contribution we report the
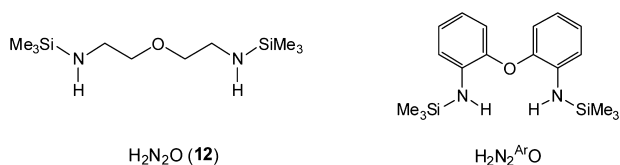
use of these diamido-ether ligands as platforms for the synthesis of titanium hydrazido complexes and their subsequent reactivity with a representative range of small unsaturated molecules.

RESULTS AND DISCUSSION

Synthesis of New Diphenyl Hydrazido Complexes Supported by Diamido-Ether Ligands. The lithiated ligand Li$_2$N$_2^{Ar}$O was synthesized according to literature methods.[11] The new protio-ligand H$_2$N$_2$O (**12**) was synthesized starting from O(CH$_2$CH$_2$NH$_2$)$_2$,[12] which was then silylated using Me$_3$SiCl and Et$_3$N to form **12** as a colorless oil in 75% yield. Lithiation using BuLi in hexanes on a multigram scale afforded Li$_2$N$_2$O (**13**) in 87% isolated yield as a colorless crystalline solid. Diffraction-quality crystals of **13** were grown from a pentane solution at RT. The molecular structure is shown in Figure 3, and metric details are provided in the Supporting Information.

Compound **13** is dimeric in the solid state, consisting of two crystallographically distinct Li$_2$N$_2$O moieties linked through bridging Li atoms (Li(2) and Li(4)), resulting in an unusual open cage-like structure. The Li−O and Li−N$_{amide}$ distances lie within the expected ranges,[13] but analogous lithiated diamido-amine ligands have ladder-like structures with the N$_{amide}$ and Li atoms in an approximately coplanar arrangement with the N$_{amine}$ donors bound to only one Li atom.[14] In **13** the O donors are able to bridge two Li atoms, therefore leading to a different structural motif. This flexibility of the N$_2$O ligands in **13** compared to their N$_2$N^{Me} and related analogues is also manifested in the structural and reaction chemistry of the hydrazido complexes described later on. Interestingly, while structurally characterized lithiated diamido-amine and mono-amido-ether compounds are well established,[13] only one example of a lithiated polyamine-ether has been reported previously.[15] The ^{1}H, ^{13}C, and ^{7}Li spectra of **13** at RT and at −80 °C in toluene-d_8 are consistent with a highly fluxional complex in solution, showing only one type of Li environment (δ = 1.9 ppm) and apparent C_{2v} symmetry at all temperatures.
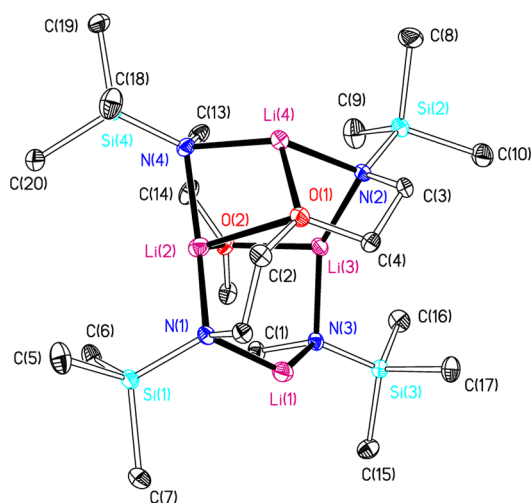

Figure 2. Protio forms of the diamido-ether ligands used and their abbreviations.

H$_2$N$_2$O (**12**)

H$_2$N$_2^{Ar}$O

Figure 3. Displacement ellipsoid plot (20% probability) of Li_2N_2O (**13**). H atoms are omitted for clarity. See Figure S1 of the Supporting Information for further details.

We have previously found that diamido-amine-supported titanium diphenyl hydrazido complexes such as **1**, **2**, and **3** (Figure 1) can be conveniently prepared from $Ti(NNPh_2)Cl_2(py)_3$.[7p,ab] As summarized in Scheme 1, reaction of $Li_2N_2^{Ar}O$ or Li_2N_2O (**13**) with $Ti(NNPh_2)Cl_2(py)_3$ in toluene at −40 or −78 °C proceeds smoothly to yield $Ti(N_2^{Ar}O)(NNPh_2)(py)_2$ (**14**) or $Ti(N_2O)(NNPh_2)(py)_2$ (**15**) in 59% and 71% isolated yield, respectively. The ^1H and ^{13}C NMR spectra of **14** and **15** show resonances attributable to two chemically equivalent, coordinated pyridine ligands, a $NNPh_2$ moiety and a κ^3-*mer*-bound diamido-ether ligand. Each exists as the single isomer illustrated in Scheme 1, possessing approximate C_{2v} symmetry. Diffraction-quality crystals of **14** and **15** were grown from hexanes, and the solid-state structures (*vide infra*) confirm those shown in the scheme.

The κ^3-*mer* coordination modes of the $N_2^{Ar}O$ and N_2O ligands in **14** and **15** contrast with the κ^3-*fac* coordination of the diamido-amine ligands in **1**, **2**, and **3**[7p,ab] and related imido[16] and alkoxy-imido[6b] compounds. It has been shown previ-

ously[11,17] that $N_2^{Ar}O$ can adopt either a *fac* or *mer* coordination geometry, and its analogue N_2O appears to have the same flexibility. To explore this aspect further, we found that addition of ^tBu-bipy (4,4′-di-*tert*-butyl-2,2′-bipyridyl) to **14**, or bipy (2,2′-bipyridyl) to **15**, gave $Ti(N_2^{Ar}O)(NNPh_2)(^tBu$-bipy) (**16**) or $Ti(N_2^{Ar}O)(NNPh_2)(bipy)$ (**17**), respectively, in 50% and 62% isolated yield. When followed on the NMR tube scale in C_6D_6, the reactions were quantitative as expected. Compounds **16** and **17** exist as single isomers in solution, and the ^1H and ^{13}C NMR spectra are consistent with the C_s-symmetric structures illustrated in Scheme 1, which were confirmed by X-ray crystallography (*vide infra*). The compounds each contain a κ^3-*fac*-bound diamido-ether ligand and are analogous to the previously reported hydrazido and alkoxyimido complexes of N_2N^{Me}, namely, $Ti(N_2N^{Me})(NNPh_2)(bipy)$ and $Ti(N_2N^{Me})(NO^tBu)(bipy)$ (with $NNPh_2$ or NO^tBu *trans* to NMe), formed in a similar way from $Ti(N_2N^{Me})(NNPh_2)(py)$[7t] or $Ti(N_2N^{Me})(NO^tBu)(py)$.[6b]

The solid-state structures of $Ti(N_2^{Ar}O)(NNPh_2)(py)_2$ (**14**) and $Ti(N_2O)(NNPh_2)(py)_2$ (**15**) are shown in Figure 4, and those of $Ti(N_2^{Ar}O)(NNPh_2)(^tBu$-bipy) (**16**) and $Ti(N_2^{Ar}O)$-$(NNPh_2)(bipy)$ (**17**) are given in Figure 5. Selected bond distances and angles are listed in Table 1. Compound **15** crystallizes with three crystallographically independent molecules in the asymmetric unit, but there are no chemically significant differences between the metric parameters and only one set of values are listed in Table 1 (see Table S1 of the Supporting Information for full details).

Complexes **14** and **15** have an approximately octahedral titanium center, with the diamido-ether ligand coordinated meridonally and the two pyridine ligands positioned mutually *trans*. The $Ti−N_{py}$ bond lengths are typical of neutral nitrogen σ-only interactions with titanium.[13] The $Ti(1)−N(1)$ bond lengths of 1.739(3) and 1.736(4) Å for **14** and **15**, with approximately linear $Ti(1)−N(1)−N(2)$ angles of 176.1(2)° and 170.0(3)° suggest a formal $Ti\equiv N_\alpha$ triple bond as expected.[7p] The $N(1)−N(2)$ bond distances of 1.373(4) and 1.379(5) Å are within the usual range for group 4 hydrazides and somewhat shorter compared to the N−N bond distance of Ph_2NNH_2 (1.418(2) Å),[7o] consistent with some residual

Scheme 1. Synthesis of New Titanium Hydrazido Complexes Supported by Diamido-Ether Ligands
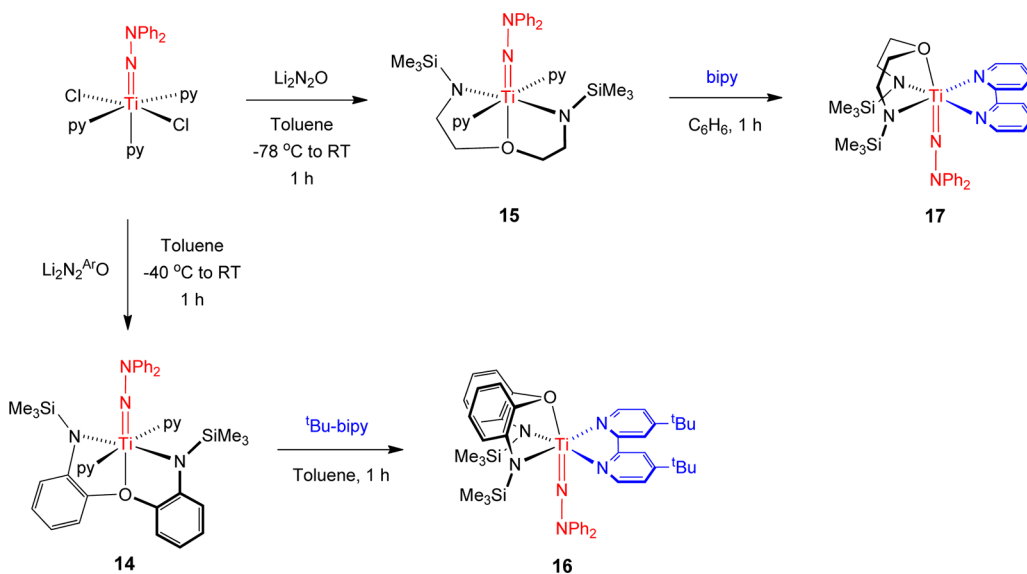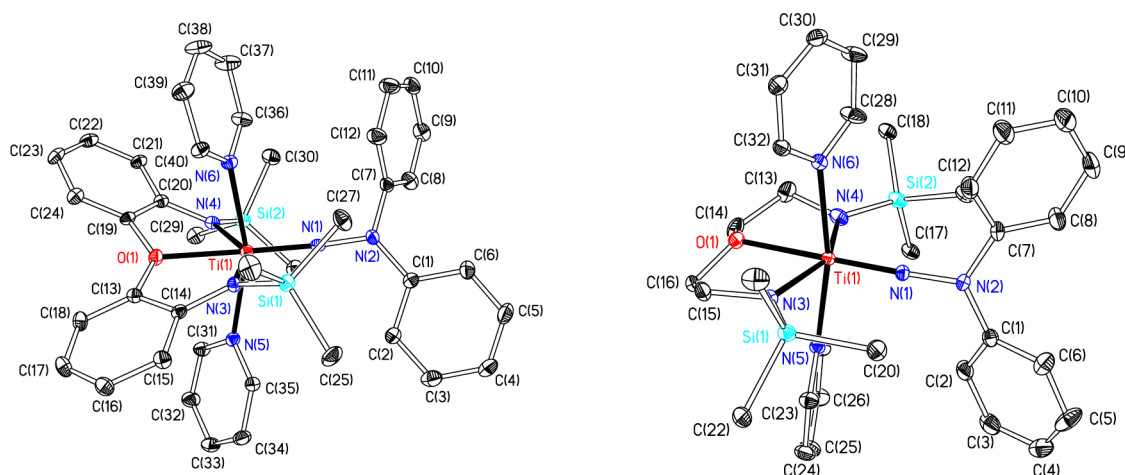
Figure 4. Displacement ellipsoid plot (20% probability) of Ti(N$_2^{Ar}$O)(NNPh$_2$)(py)$_2$ (**14**) (left) and Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (**15**) (right). H atoms are omitted for clarity.
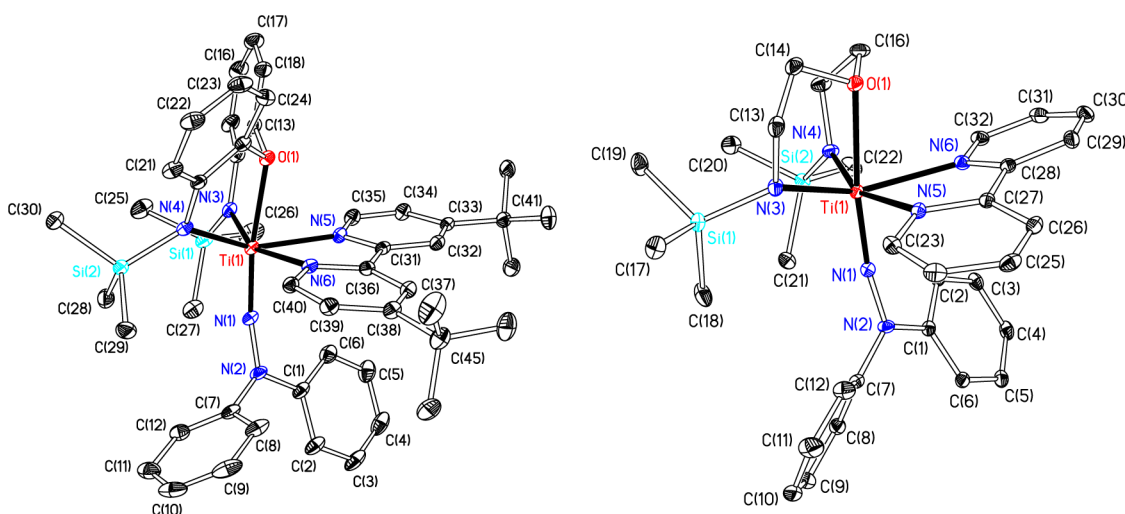
Figure 5. Displacement ellipsoid plot (20% probability) of Ti(N$_2^{Ar}$O)(NNPh$_2$)(^{t}Bu-bipy) (**16**) (left) and Ti(N$_2$O)(NNPh$_2$)(bipy) (**17**) (right). H atoms are omitted for clarity.

multiple-bond character. The sum of angles subtended at N(2) in both compounds is ca. 360°, indicating sp^2 hybridization and conjugation of the N$_\beta$ lone pair with the phenyl rings, a known feature for diphenyl hydrazide ligands of the early transition metals. These metric parameters for the Ti=NNPh$_2$ ligands in **14** and **15** are similar to those found in other diamide-donor-supported complexes such as **3**.[7p] The Ti–N$_{amide}$ bond distances for **14** (Ti(1)–N(3 or 4) = 2.099(3) or 2.102(3) Å) are slightly longer than those in **15** (2.081(4) or 2.054(3) Å), and both are longer than in Ti(N$_2$N^{Me})(NNPh$_2$)(py) (**3**) (2.029(5) or 2.026(5) Å), reflecting the different coordination geometry and number in the diamido-ether complexes. Both N$_{amide}$ atoms are approximately trigonal planar, as indicated by the sum of the angles subtended at N(3) and N(4) being ca. 360°. Finally we note that the Ti(1)–O(1) distances are within the expected ranges.[13] The solid-state structures of the bipyridyl complexes **16** and **17** also feature approximately octahedral titanium centers but with the diamido-ether ligand κ^3-*fac* coordinated. The Ti=N$_\alpha$, Ti–O, and Ti–N$_{amide}$ bond lengths are similar to those in **14** and **15** and are comparable to those in Ti(N$_2$N^{Me})(NNPh$_2$)(bipy).[7t] The similarity of the metric parameters of bis(pyridine) and bipyridyl structures suggest

that both *mer-* and *fac-*coordination modes should be accessible to the diamido-ether ligands in **14** and **15** during reaction sequences.

Reaction with Isocyanates. As a starting point for reactivity studies of **14** and **15**, we chose to probe their reactions with isocyanates and their heavier sulfur and selenium congeners. Group 4 imido complexes have a well-established chemistry with isocyanates and other heterocumulenes,[1b,c,e,18] and these reactions can lead to isolated [2+2] cycloaddition products or cycloaddition–extrusion (net metathesis of M= NR with E=C=E′ (E and/or E′ = O, S, NR) or "double insertion", in which two heterocumulene moieties effectively insert into the M=NR multiple bond. Group 4 hydrazides also have an established and, in many ways, similar chemistry with allenes and heterocumulenes both for titanium[5f,7a,o,r,u,w,z] and its heavier congeners.[8i−k] By way of example, Figure 1 shows the reaction products (compounds of the type **5**) of Ti(N$_2$N^{Me})(NNPh$_2$)(py) (**3**) with Ar′NCE (E = O, S, Se; Ar′ = 2,6-C$_6$H$_3$^{i}Pr$_2$).[7w] The bulky Ar′ group was necessary to prevent unwanted side-reactions such as insertion into the Ti– N$_{amide}$ bonds, which is a known complication with diamide-donor supporting ligand sets and these substrates for a number

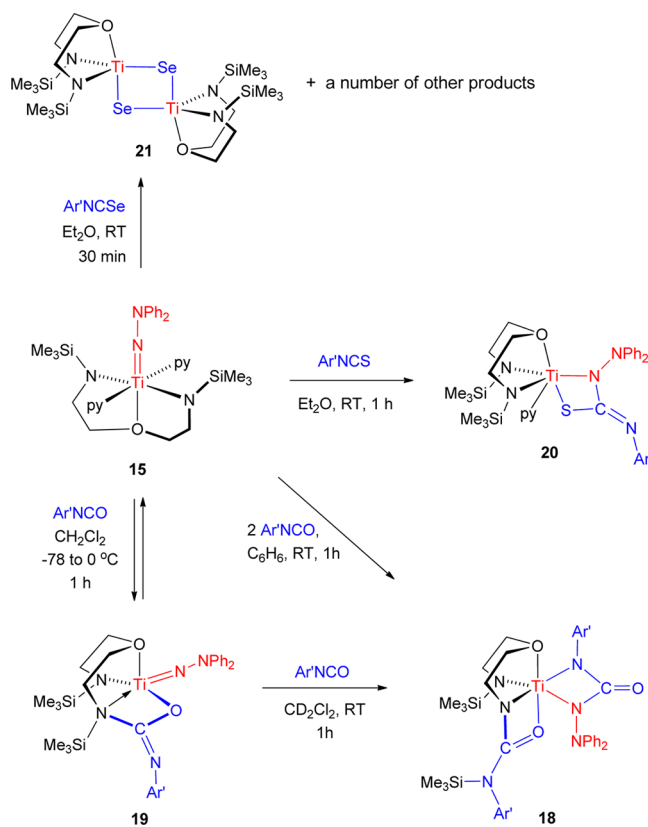**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ti(N₂^{Ar}O)(NNPh₂)(py)₂ (14), Ti(N₂O)(NNPh₂)(py)₂ (15), Ti(N₂^{Ar}O)(NNPh₂)(^{t}Bu-bipy) (16), and Ti(N₂O)(NNPh₂)(bipy) (17)**

	14	15	16	17
Ti(1)−N(1)	1.739(3)	1.736(4)	1.734(3)	1.743(2)
Ti(1)−N(3)	2.099(3)	2.081(4)	2.073(3)	2.039(2)
Ti(1)−N(4)	2.102(3)	2.054(3)	2.100(3)	2.045(2)
Ti(1)−N(5)	2.276(3)	2.315(4)	2.259(3)	2.278(2)
Ti(1)−N(6)	2.266(3)	2.273(4)	2.252(3)	2.304(2)
Ti(1)−O(1)	2.180(2)	2.217(3)	2.221(3)	2.297(2)
N(1)−N(2)	1.373(4)	1.379(5)	1.366(5)	1.371(3)
Ti(1)−N(1)−N(2)	176.1(2)	178.0(3)	169.0(3)	170.86(16)
N(1)−Ti(1)−N(3)	107.20(12)	105.08(16)	106.25(15)	108.43(8)
N(1)−Ti(1)−N(4)	105.07(13)	103.56(16)	108.65(15)	102.51(8)
N(1)−Ti(1)−N(5)	100.52(12)	95.60(15)	95.75(15)	90.20(8)
N(1)−Ti(1)−N(6)	98.80(12)	96.26(16)	88.97(14)	95.11(8)
N(1)−Ti(1)−O(1)	178.55(11)	179.0(3)	171.41(14)	173.12(8)
N(3)−Ti(1)−O(1)	74.18(10)	75.12(13)	78.72(12)	77.76(7)
N(4)−Ti(1)−O(1)	73.54(10)	76.24(13)	76.32(12)	78.09(7)
N(5)−Ti(1)−O(1)	79.96(10)	84.65(12)	77.26(11)	87.29(6)
N(6)−Ti(1)−O(1)	80.75(10)	83.49(13)	84.08(11)	78.01(6)
N(3)−Ti(1)−N(4)	147.69(11)	151.3(2)	103.91(13)	106.25(8)
N(5)−Ti(1)−N(6)	160.65(11)	168.1(1)	71.30(12)	70.32(7)

Scheme 2. Reactions of Ti(N₂O)(NNPh₂)(py)₂ (15) with Ar′NCE (Ar′ = 2,6-C₆H₃^{i}Pr₂; E = O, S, or Se)

of early transition metals.[19] Using these same Ar′NCE substrates we found that complicated mixtures of unknown products were formed with Ti(N₂^{Ar}O)(NNPh₂)(py)₂ (14) when assessed on the NMR tube scale in C₆D₆, so no further reactions were attempted with this complex. More success was found with Ti(N₂O)(NNPh₂)(py)₂ (15), as shown in Scheme 2.

Addition of 1 equiv of Ar′NCO to 15 on the NMR tube scale in C₆D₆ consumed all of the isocyanate to form a single new product (18) but with half of the 15 remaining apparently unreacted. Addition of a further equivalent of substrate gave complete conversion to the new product along with 2 equiv of free pyridine. The reaction was successfully scaled up using 2 equiv of Ar′NCO in benzene at RT to give Ti{O-(CH₂CH₂NSiMe₃)(CH₂CH₂NC(O)N(SiMe₃)Ar′)}{N-(NPh₂)C(O)N(Ar′)} (18, Scheme 2) in 46% isolated yield. Single crystals were obtained but diffracted poorly (overall $I/\sigma(I)$ = 0.8 for the diffraction data) but could nonetheless be used to establish the connectivity as shown in the scheme (see also Figure S2 of the Supporting Information). The solid-state structure confirms that 2 equiv of Ar′NCO have been incorporated. One Ar′NCO has evidently undergone a [2+2] cycloaddition with the Ti=NNPh₂ bond, forming a κ²N,N′-coordinated ureato moiety, {N(NPh₂)C(O)N(Ar′)}, of the type observed previously,[7a] although κ²N,E-bound ureate-type ligands (E = O, S, Se) are usually preferred on steric grounds.[7r,w] The other Ar′NCO group has reacted with one of the Ti−N_{amide} bonds followed by a 1,3-sigmatropic SiMe₃

group migration from the N_{amide} atom of the N₂O ligand to the isocyanate-derived nitrogen. This overall type of sequence has been observed for a number of imido complexes including Ti(N₂N^{py})(N^{t}Bu)(py), M(N₂N^{py})(N^{t}Bu)Cl(py) (M = Nb or Ta), and [W(N₂N^{py})(NPh)Me]⁺, including direct observation of the intermediate formed prior to SiMe₃ group migration.[19] The solution-state structure of 18 was unequivocally established by 1D and 2D and NOE NMR spectroscopy, allowing the full assignment of the ¹H and ¹³C NMR spectra. An IR band at 1658 cm⁻¹, absent in 15 and the intermediate 19 (*vide infra*), was assigned to ν(C=O) of the ureate moiety by comparison with literature examples.[7a]

The reaction between 15 and 1 equiv of Ar′NCO was followed in CD₂Cl₂ from −78 °C to ca. 0 °C, at which temperature a reaction proceeded to consume all of the Ar′NCO and also the 15, giving a C_1-symmetric species assigned as the Ti−N_{amide} insertion product Ti{O-(CH₂CH₂NSiMe₃)(CH₂CH₂N(SiMe₃)C(O)NAr′)}(NNPh₂) (19), shown in Scheme 2. Addition of a further equivalent of Ar′NCO and warming to RT forms 18 as expected. Interestingly, warming the solution of 19 to RT in the absence of additional Ar′NCO gave half of an equivalent of starting hydrazide 15 and also 18. Thus the reaction of 15 with Ar′NCO to form 19 appears to be reversible. It was nonetheless possible to prepare 19 on the preparative scale by using 1:1 stoichiometric quantities of 15 and Ar′NCO at temperatures below 0 °C and then crystallizing at −78 °C. In this manner 19 was isolated as an analytically pure solid in 61% yield, which is stable for days at RT in the solid state.

Reaction of 15 with Ar′NCS proceeds smoothly at RT to yield the [2+2] cycloaddition product Ti(N₂O){N(NPh₂)C-

(NAr′)S}(py) (**20**) in 57% yield (Scheme 2). This complex is the analogue of the diamido-amine complexes Ti(N$_2$N^{Me}){N-(NPh$_2$)C(NAr′)E}(py)$_n$ (**5**; E = O, n = 1; E = S or Se, n = 0)[7w] and Zr(N$_2$*N^{py}){N(NPh$_2$)C(NAr′)S}(py)$_n$ (n = 0 or 1).[8k] The molecular structure of **20** is shown in Figure 6 along with
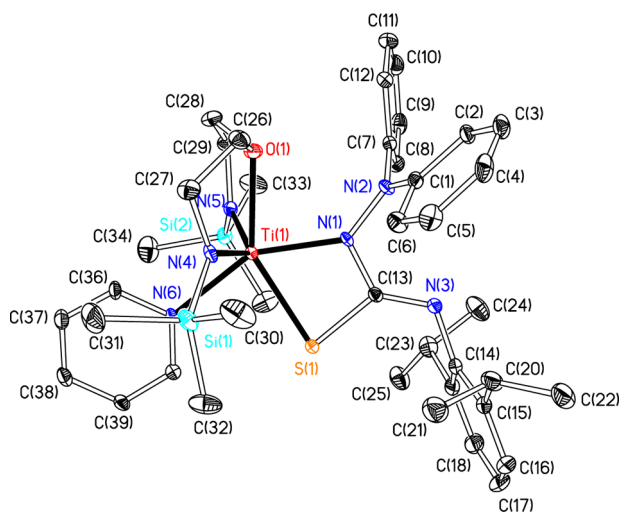
Figure 6. Displacement ellipsoid plot (20% probability) of Ti(N$_2$O)-{N(NPh$_2$)C(NAr′)S}(py) (**20**). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−S(1) 2.419(1), Ti(1)−O(1) 2.240(2), Ti(1)−N(1) 2.051(3), Ti(1)−N(4) 1.954(3), Ti(1)−N(5) 1.959(3), Ti(1)−N(6) 2.289(3), N(1)−N(2) 1.408(4), S(1)−C(13) 1.777(3), N(1)−C(13) 1.360(5), N(3)−C(13) 1.280(4), N(4)−Ti(1)−N(5) 130.7(1), Ti(1)−S(1)−C(13) 81.6(1), S(1)−Ti(1)−N(1) 66.9(8), S(1)−C(13)−N(1) 103.8(2).

selected bond lengths and angles. The NMR spectra and other data are fully consistent with the solid-state structure, and when followed on the NMR tube scale, the reaction was quantitative. Compound **20** contains a κ^3-*fac*-coordinated N$_2$O ligand and a κ^{2}N,S-coordinated thioureato moiety as unambiguously established by the solid-state structure. The main difference between Ti(N$_2$N^{Me}){N(NPh$_2$)C(NAr′)S} and **20** is the presence of a coordinated pyridine ligand, possibly suggesting a reduced electron-donating capacity or steric profile of the N$_2$O ligand compared to N$_2$N^{Me}, although we note that Gade was able to isolate Zr(N$_2$*N^{py}){N(NPh$_2$)C(NAr′)S}(py)$_n$ either with or without a coordinated pyridine ligand.[8k] The distances and angles associated with the N(NPh$_2$)C(NAr′)S moiety in **20** are comparable to those in the related complexes, and the parameters associated with the titanium coordination center are likewise analogous to those in the complex **5** in general and the starting complex **15**.

Whereas the thiourea complex **20** is stable for days in solution at RT, reaction with Ar′NCSe yielded a mixture of products from which the μ-selenido-bridged dimer Ti$_2$(N$_2$O)$_2$(μ-Se)$_2$ (**21**) was crystallized from Et$_2$O solution at −30 °C as a few red, diffraction-quality crystals. The molecular structure of **21** is shown in Figure 7 together with selected bond lengths and angles. It was not possible to obtain a pure sample of **21** because it crystallized among oily side-products and could not be separated. The formation of the bridged dimer is thought to occur via [2+2] cycloaddition of Ar′NCSe to the Ti=NNPh$_2$ bond (forming an intermediate analogous to **20**) and Ti(N$_2$N^{Me}){N(NPh$_2$)C(NAr′)Se}), followed by retro-cycloaddition and extrusion of the organic product
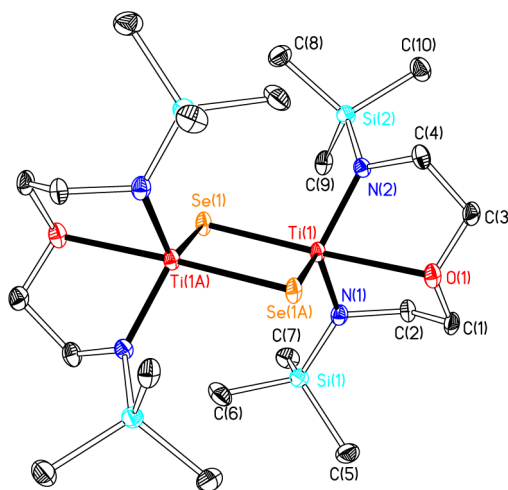
Figure 7. Displacement ellipsoid plot (20% probability) of Ti$_2$(N$_2$O)$_2$(μ-Se)$_2$ (**21**). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−Se(1A) 2.460(1), Ti(1)−Se(1) 2.429(1), Ti(1)−N(1) 1.902(7), Ti(1)−N(2) 1.924(6), Ti(1)−O(1) 2.359(5), Se(1A)−Ti(1)−Se(1) 93.5(5), Ti(1A)−Se(1)−Ti(1) 86.5(5), Se(1)−Ti(1)−O(1) 176.7(2), N(1)−Ti(1)−N(2) 115.8(3).

Ar′NCNNPh$_2$,[7z] which was observed among the reaction products but not isolated.

Structurally authenticated titanium selenido-bridged dimers are relatively rare, and **21** represents only the third example.[20] The metric parameters of the Ti$_2$Se$_2$ core are similar to those found in Ti$_2$(μ-Se)$_2${Ar′NCH$_2$CH$_2$CH$_2$NAr′}$_2$, synthesized by Piers et al. from Ti{Ar′NCH$_2$CH$_2$CH$_2$NAr′}Me$_2$ and elemental selenium.[20b] The Ti−Se bonds in **21** are slightly dissimilar in length (Ti(1)−Se(1) = 2.429(1) Å, Ti(1)−Se(1A) = 2.460(1) Å), which distorts the Ti$_2$Se$_2$ core to some extent (Se(1A)−Ti(1)−Se(1) = 93.5(5), Ti(1A)−Se(1)−Ti(1) = 86.5(5)°).

Reaction with Organic Nitriles. The reactions of organic nitriles with transition metal imides (L)M=NR are almost unknown and give rise to dimeric complexes of the type (L)$_2$Ti$_2${μ-NC(R′)(NR)}$_2$.[21] This is in contrast to the position for metal nitrides,[22] alkylidenes,[23] and alkylidynes.[24] We found recently that Ti(N$_2$N^{py})(NNPh$_2$)(py) (**1**) reacts with MeCN to give an analogous dimeric species, whereas Ti(N$_2$N^{Me})-(NNPh$_2$)(py) (**3**) gave mixtures with this substrate or PhCN.[7w] However, reaction of both **1** and **3** with fluorinated benzonitriles Ar^{Fx}CN (Ar^{Fx} = Ar^{F2} (2,6-C$_6$H$_3$F$_2$) or Ar^{F5} (C$_6$F$_5$)) gave unexpected Ti=N$_α$ insertion products such as Ti(N$_2$N^{Me}){NC(Ar^{Fx})NNPh$_2$}(py) (**6**, Figure 1), containing a hydrazonamide ligand. DFT studies showed that this reaction proceeds via a cycloaddition/reverse cycloaddition reaction sequence. Mono- and dimetalated hydrazonamides have been reported by sequential reaction of AlMe$_3$ or dialkyl zincs with Me$_2$NNH$_2$ and MeCN, forming polynuclear clusters.[25] Very recently we found that the alkylidene hydrazido complex Cp*Ti{MeC(N^{i}Pr)$_2$}(NNCPh$_2$) reacted with 2 equiv of ArCN (Ar = Ph or Ar^{F5}) to form unusual "double insertion" products, Cp*Ti{MeC(N^{i}Pr)$_2$}{N(NCPh$_2$)C(Ar)NC(Ar)N}.[5f]

Compounds **14** and **15** gave unknown mixtures with PhCN but with Ar^{F5}CN or Ar^{F2}CN (for **15**) clean and quantitative (when followed by NMR in C$_6$D$_6$) conversion to the new terminal hydrazonide complexes Ti(N$_2^{Ar}$O){NC(Ar^{F5})-NNPh$_2$}(py)$_2$ (**22**), Ti(N$_2$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (**23**), and Ti(N$_2$O){NC(Ar^{F2})NNPh$_2$}(py)$_2$ (**24**) within 2 to 3 h. The reaction for **14** proceeded readily at RT (as was the case
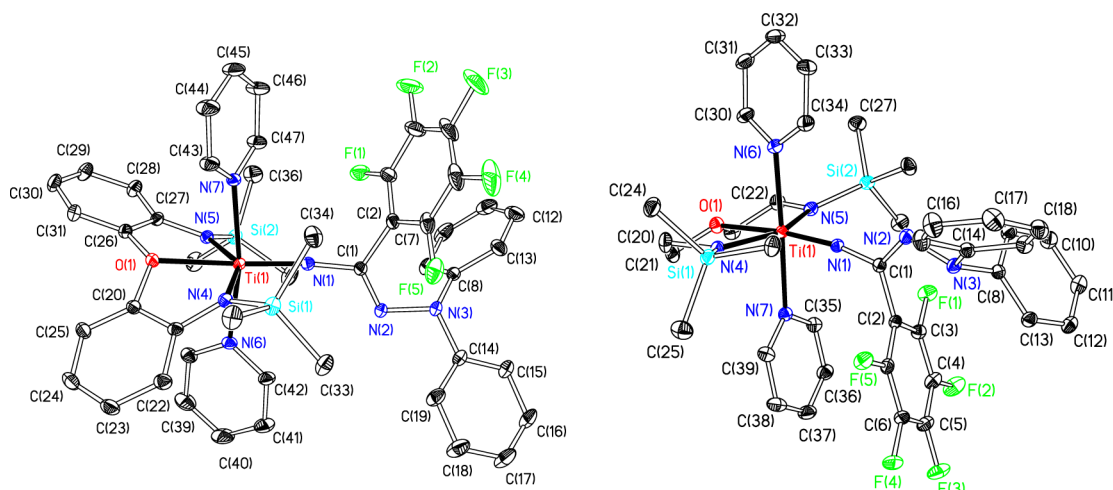
Figure 8. Displacement ellipsoid plot (20% probability) of Ti(N$_2^{Ar}$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (**22**) (left) Ti(N$_2$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (**23**) (right). H atoms are omitted for clarity.

with the diamido-amine complexes **1** and **3**), whereas that with **15** required heating at 70 °C. The new compounds were isolated in 47−52% yield on the preparative scale, and diffraction-quality crystals of **22** and **23** were obtained. The molecular structures are shown in Figure 8, and selected bond lengths and angles are compared in Table 2. The solid-state

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ti(N$_2^{Ar}$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (22) and Ti(N$_2$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (23)

	22	23
Ti(1)−N(1)	1.760(2)	1.774(2)
Ti(1)−N(4)	2.059(2)	2.022(2)
Ti(1)−N(5)	2.071(2)	2.029(2)
Ti(1)−N(6)	2.237(2)	2.247(2)
Ti(1)−N(7)	2.231(2)	2.288(2)
Ti(1)−O(1)	2.222(2)	2.221(2)
N(1)−C(1)	1.356(3)	1.342(3)
C(1)−C(2)	1.514(4).	1.518(4)
C(1)−N(2)	1.298(2)	1.304(3)
N(2)−N(3)	1.432(3)	1.447(3)
Ti(1)−N(1)−C(1)	173.7(2)	170.0(2)
O(1)−Ti(1)−N(1)	173.72(9)	173.20(9)
N(4)−Ti(1)−N(5)	145.92(9)	149.61(9)
N(1)−Ti(1)−N(4)	103.84(9)	105.20(10)
N(1)−Ti(1)−N(5)	109.94(9)	105.19(9)
N(6)−Ti(1)−N(7)	169.60(8)	174.36(8)
N(5)−Ti(1)−O(1)	74.71(8)	74.68(8)
N(6)−Ti(1)−O(1)	89.69(8)	90.77(8)
N(7)−Ti(1)−O(1)	80.59(7)	84.53(8)
N(1)−C(1)−N(2)	121.2(2)	122.2(2)
N(1)−C(1)−C(2)	115.4(2)	115.9(2)
N(2)−C(1)−C(2)	123.4(2)	121.9(2)
C(1)−N(2)−N(3)	114.1(2)	113.5(2)

structures and solution NMR and other data are consistent with the structures illustrated in Scheme 3. No intermediate species were observed when followed by NMR. It is assumed, based on our previous studies,[7w] that the reactions proceed via [2+2] cycloaddition reactions between Ti≡NNPh$_2$ and the nitrile followed by reverse cycloaddition to give an overall net insertion reaction of Ar^{Fx}CN into Ti≡N$_\alpha$.

Scheme 3. Reactions of Ti(N$_2^{Ar}$O)(NNPh$_2$)(py)$_2$ (14) and Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (15) with Ar^{Fx}CN (Ar^{Fx} = 2,6-C$_6$H$_3$F$_2$ or C$_6$F$_5$)
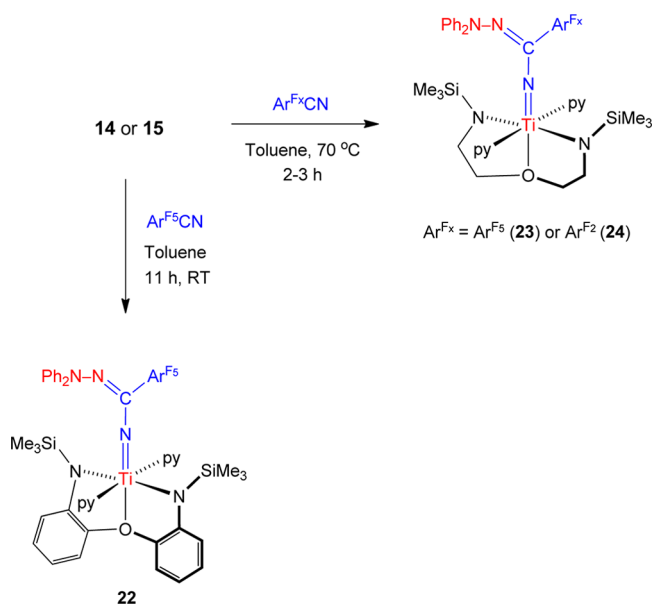
Compounds **22** and **23** have an approximately octahedral titanium center bonded to terminal hydrazonamido ligands. Their overall geometries are very similar to those of their hydrazido precursors **14** and **15** with κ^3-*mer* coordination modes of the N$_2^{Ar}$O and N$_2$O ligands and mutually *trans* pyridines. The Ti−N$_{py}$ and Ti−O distances in **22** and **23** are not significantly different from those in **14** and **15**. The N$_{amide}$ atoms of the N$_2^{Ar}$O and N$_2$O ligands are trigonal planar, implying sp^2 hybridization. The Ti(1)−N(1)−C(1) linkages are approximately linear (Ti(1)−N(1)−C(1) = 173.7(2)° or 170.0(2)°), implying sp hybridization at the new N$_\alpha$ atom. The Ti−N$_\alpha$ distances in **22** and **23** (1.760(2) and 1.774(2) Å) are significantly longer than in their hydrazido analogues **14** and **15** (1.739(3) and 1.736(4) Å), suggesting reduced Ti≡N$_\alpha$ multiple-bond character (the Ti−N(1) bond lengths are nonetheless still indicative of a formal Ti≡N$_\alpha$ triple bond). The Ti−N$_{amide}$ distances in **22** and **23** (av 2.060(2) and 2.025(2) Å) are, in contrast, shorter than their counterparts in

14 and **15** (av 2.101(2) and 2.067(3) Å), indicating better $N_{amide} \rightarrow Ti$ π-donation. This would follow from the longer $Ti=N_\alpha$ bonds. Analogous features were previously found for the diamido-amine analogues **6** in comparison with their hydrazido starting material **3** and can be attributed to the electron-withdrawing nature of the $-C(Ar^{Fx})NNPh_2$ groups bound to N_α in these hydrazonamido complexes. A degree of multiple bonding is indicated by the N(1)−C(1) (1.356(3) and 1.342(3) Å) and N(2)−C(1) (1.298(2) and 1.304(3) Å) bond lengths. The N(2)−C(1) formal double bond has the shorter bond distance of the two, confirming the valence bond representations in Scheme 3.

Overall, the geometries within the hydrazonamide fragments are similar to those we reported previously for **6** and its analogues. Close contacts are also observed between certain carbons in the C_6F_5 rings and those of the pyridine ligands or one carbon of the $NNPh_2$ rings (for **22** C(36)···C(4) = 3.474(5) Å, C(35)···C(3) = 3.376(4) Å, and C(2)···C(8) = 2.964(4) Å; for **23** C(47)···C(3) = 3.507(5) Å and C(2)···C(8) = 2.948(4) Å). Such π-stacking-type interactions are well known in general for fluorinated aryl rings,[26] including between the N-substituents of titanium imido compounds,[27] and were observed in $Ti(N_2N^{Me})\{NC(Ar^{F5})NNPh_2\}(py)$.[7w]

Reactions with Isonitriles. One of the distinctive types of reaction of certain group 4 diphenyl- and alkylidene-hydrazido complexes is their propensity to undergo reductive $N_\alpha−N_\beta$ bond cleavage with oxidizable substrates. This was first observed by Bergman and Andersen for the reactions of $Cp_2Zr(NNPh_2)(DMAP)$[4] or $Cp^*_2Ti\{\eta^2-NNC(H)Tol\}$[5c] with CO, giving mixed diphenylamide/isocyanate or alkylidene imido/isocyanate products $Cp_2Zr(NPh_2)(NCO)$ and $Cp^*_2Ti-(NCO)\{NC(H)Tol\}$, respectively. Subsequently, both Gade[8a] and then our group[7w] found that reactions of XylNC (Xyl = 2,6-$C_6H_3Me_2$) or ^tBuNC with $Ti(N_2N^{py})(NNPh_2)(py)$ (**1**), $Zr(N_2^*N^{py})(NNPh_2)(py)$ (**2**), and $Ti(N_2N^{Me})(NNPh_2)(py)$ (**3**) gave mixed diphenylamide-metalated carbodiimide complexes such as **7** and **8** (Figure 1). Our DFT studies found that the reactions for **1** and **3** (and most likely the other example mentioned) proceed via RNC addition to $M=N_a$ followed by NR_2 transfer to the metal and $N_\alpha−N_\beta$ bond cleavage.[7w]

Reaction of **14** with an excess of XylNC at RT in C_6D_6 resulted in quantitative substitution of one pyridine ligand and formation of the XylNC σ-adduct $Ti(N_2^{Ar}O)(NNPh_2)(py)-(CNXyl)$ (**25**). No further reaction was observed even upon prolonged heating at 80 °C in C_6D_6. The scaled-up reaction (eq 1) afforded **25** in 62% isolated yield as a crystalline, brown
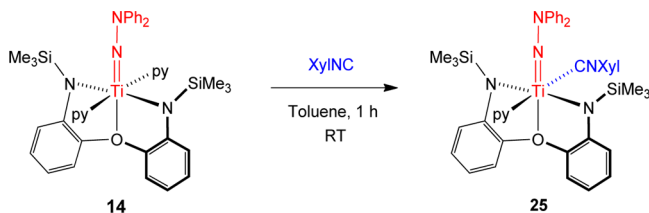
powder. The ^1H and ^{13}C NMR spectra are consistent with a C_s-symmetric octahedral complex in solution, with one bound pyridine remaining. The assignment of **25** as an σ-adduct is supported by its IR spectrum, which shows a band for $\nu(N\equiv C)$ at 2159 cm^{-1}, which is higher than that for the free ligand (ν = 2110 cm^{-1}). The increased $\nu(C\equiv N)$ compared to the uncoordinated isonitrile is consistent with coordination to the electron-deficient titanium in **25**.[5f,28] In addition, reaction of **14**

with 1 equiv of ^tBu-bipy in C_6D_6 immediately formed $Ti(N_2^{Ar}O)(NNPh_2)(^tBu-bipy)$ (**16**) and free XylNC and pyridine, consistent with the proposed structure of **25**. Finally, preliminary studies of the reaction between **14** and ^tBuNC on the NMR tube scale immediately gave a similar spectrum to that of **25**, indicative of adduct formation, either at RT or on heating. This reaction was not scaled up.

In contrast to the limited reactivity of **14**, compound **15** undergoes $N_\alpha−N_\beta$ bond cleavage and new Ti−C and/or N−C bond forming reactions with ^tBuNC and XylNC, as summarized in Scheme 4. On the NMR tube scale no reaction

Scheme 4. Reactions of Ti(N₂O)(NNPh₂)(py)₂ (15) with Isonitriles
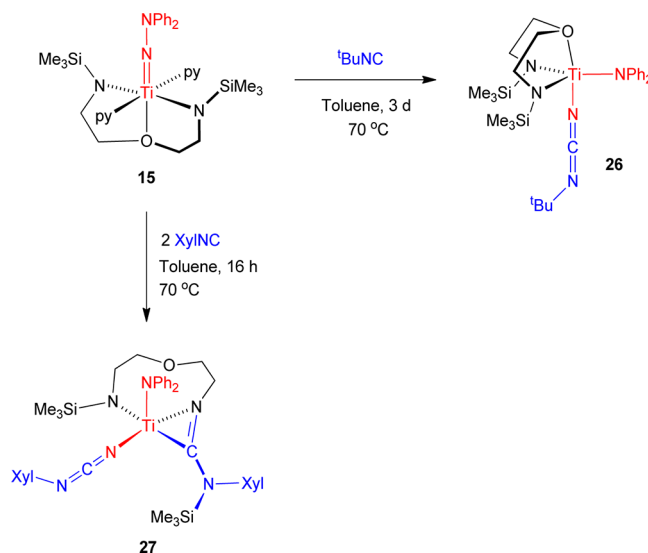
was observed at RT between a 1:1 mixture of **15** and ^tBuNC. However, after heating for three days at 70 °C a single new product, $Ti(N_2O)(NPh_2)(NCN^tBu)$ (**26**), was formed along with 2 equiv of free pyridine. No further reaction was observed when an excess of ^tBuNC was used, and no intermediates were observed. The reaction was scaled up (Scheme 4) to give **26** in 46% isolated yield. The NMR and IR spectra for **26** (band for $\nu(NCN^tBu)$[7w] at 2102 cm^{-1}) are indicative of a C_s-symmetric complex possessing a *fac*-coordinated N_2O ligand (two types of CH_2 environment with diastereotopic hydrogens), a new NCN^tBu ligand, and a NPh_2 moiety, as illustrated in Scheme 4.[7w] The solid-state structure of **26** is shown in Figure 9, along with selected bond distances and angles, and is consistent with the spectroscopic and other analytical data.

Compound **26** contains a five-coordinated titanium center possessing a trigonal bipyramidal geometry. In addition to the *fac*-coordinated N_2O ligand (occupying one axial and two equatorial sites) there is an equatorially positioned NPh_2 group and the expected metalated carbodiimide fragment, which is positioned *trans* to the O donor of the diamido-ether ligand. An analogous structure was found for $Ti(N_2N^{Me})(NPh_2)-(NCNXyl)$, prepared from $Ti(N_2N^{Me})(NNPh_2)(py)$ (**4**) and XylNC,[7w] although this compound formed much more readily (3 h at RT), as were the diamido-pyridine complexes **7** and **8** (Figure 1). Interestingly, **8** has the NCNR ligand positioned in the equatorial plane and NPh_2 located axially,[8a] whereas **7** exists as two positional isomers in a ca. 3:2 ratio.[7w] The metric data for **26** are comparable to those of $Ti(N_2N^{Me})(NPh_2)-(NCNXyl)$. As mentioned, the N_2O ligand is *fac* coordinated

Figure 9. Displacement ellipsoid plot (30% probability) of Ti(N$_2$O)-(NPh$_2$)(NCN^{t}Bu) (**26**). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−O(1) 2.188(1), Ti(1)−N(1) 1.909(2), Ti(1)−N(2) 1.960(2), Ti(1)−N(4) 1.944(2), Ti(1)−N(5) 1.954(2), N(1)−C(13) 1.210(2), N(3)−C(13) 1.213(2), N(4)−Ti(1)−N(5) 122.3(7), Ti(1)−N(1)−C(13) 179.7(2), N(1)−C(13)−N(3) 172.9(2).

Figure 10. Displacement ellipsoid plot (20% probability) of Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NCN(SiMe$_3$)Xyl)}(NPh$_2$)-(NCNXyl) (**27**). H atoms are om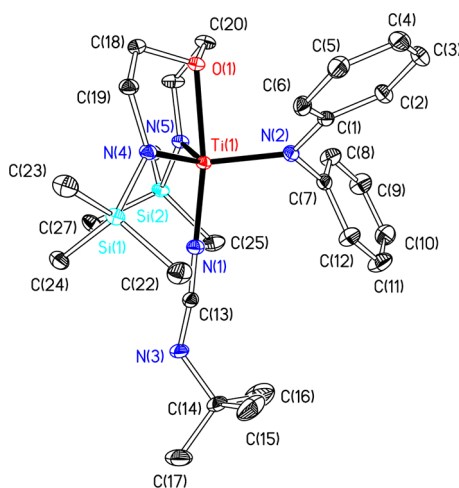itted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−N(1) 2.021(3), Ti(1)−N(2) 1.969(3), Ti(1)−N(3) 1.883(3), Ti(1)−N(4) 1.971(3), Ti(1)−C(23) 2.079(3), N(1)−C(32) 1.151(5), N(5)−C(32) 1.267(6), N(4)−C(23) 1.291(5), N(4)−C(14) 1.463(5), N(6)−C(23) 1.349(5), N(3)−Ti(1)−N(4) 99.9(1), Ti(1)−N(1)−C(32) 168.4(3), N(1)−C(32)−N(5) 167.4(4), Ti(1)−N(4)−C(23) 76.0(2), Ti(1)−C(23)−N(4) 66.9(2), N(4)−Ti(1)−C(23) 37.1(1).

and the O(1)−Ti(1)−N(1) linkage is almost linear. The Ti(1)−N(4,5) bonds for the N$_2$O ligand in **26** (av 1.949(2) Å) are shorter than in **15** (av 2.067(3) Å), reflecting the lower coordination number of titanium and the absence of the strongly π-donating NNPh$_2$ ligand in the latter. The Ti(1)−N(2) distance of 1.960 Å is comparable as expected, and all three equatorially positioned N$_{amide}$ atoms have a trigonal planar geometry and sp^2 hybridization.

The Ti(1)−N(1) distance (1.909(2) Å) for the NCN^{t}Bu group is somewhat shorter than those in Ti(N$_2$N^{py})(NPh$_2$)-(NCN^{t}Bu) (1.973(6) Å) and Ti(N$_2$N^{py})(NPh$_2$)(NCNXyl) (1.970(3) Å), which probably reflects the weaker *trans* influence of the axial O-donor for N$_2$O compared to the pyridyl or tertiary amine donors in these previous complexes. A number of metalated carbodiimides of the type (L)M-NCNR have been structurally characterized.[13] The N(1)−C(13) and C(13)−N(3) distances are within the usual ranges for these other examples. Similar observations were made for Ti-(N$_2$N^{Me})(NPh$_2$)(NCNXyl) and Ti(N$_2$N^{py})(NPh$_2$)(NCN^{t}Bu)

As for the reaction with ^{t}BuNC, no reaction occurred between Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (**15**) and XylNC (1 equiv) at RT in C$_6$D$_6$. Heating at 70 °C for 14 h consumed all of the isonitrile but only half of the hydrazido complex, leading to a single new product, **27** (no intermediates or other species were observed). Addition of a further equivalent of XylNC gave complete conversion of **15**. The reaction was scaled up to give Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NCN(SiMe$_3$)Xyl)}(NPh$_2$)-(NCNXyl) (**27**, Scheme 4) in 50% yield. Although the NMR and IR data for **27** were consistent with new NPh$_2$ and NCNXyl (ν(NCNXyl) at 2129 cm^{-1}) groups being formed, the NMR spectra showed a further set of xylyl group resonances, along with two SiMe$_3$ groups and four inequivalent CH$_2$ linkages with diastereotopic hydrogens. The data are consistent with the structure proposed for **27** in Scheme 4, which is supported by X-ray crystallography (Figure 10). Compound **27** is reminiscent of that of **18** (Scheme 2), formed from **15** and 2 equiv of Ar′NCO. Thus 1 equiv of XylNC has reductively cleaved the N$_a$−N$_b$ bond of **15**, forming new NPh$_2$ and

NCNXyl ligands, while a second has reacted with one of the Ti−N$_{amide}$ bonds to the N$_2$O ligand with concomitant SiMe$_3$ group migration to form a new metalated amidinyl functional group. It is unclear in what order the two equivalents react, as no intermediates were observed. The ^{13}C NMR resonance for the Ti-bound carbon (C(23) in Figure 10) was found at 203.9 ppm, which is characteristic for metal-bound η^2-RC≡NCR$_2$ ligands.[29]

As shown in Figure 10, compound **27** contains an approximately square-based pyramidal Ti center with the diphenylamido ligand occupying the apical site. The square base is formed by N(1) of the metalated carbodiimide ligand and the former N$_2$O ligand acting as a tridentate ligand that binds though one silyl amide (N(3)) and one η^2-N,C-bound amidinyl functional group (N(4), C(23)). The ether oxygen O(1) does not coordinate to the metal center, as evidenced by the O(1)···Ti(1) distance of 3.576(3) Å. The Ti−N(1−4) bond distances are within the range found for Ti−N single bonds in general.[13] The Ti−NPh$_2$ distance of 1.969(3) Å is the same as in **26**, whereas Ti−NCNXyl (2.021(3) Å) is longer than in **26** (1.909(2) Å) or Ti(N$_2$N^{py})(NPh$_2$)(NCNXyl) (1.970(3) Å). The N(4)−C(23) distance of 1.291(5) Å in the η^2-C,N-bound amidinyl moiety is consistent with a formal double bond and significantly shorter than N(4)−C(14) (1.463(5) Å) or N(6)−C(23) (1.349(5) Å), the latter showing evidence of conjugation from the trigonal planar N(6). The Ti(1)−N(4) and Ti(1)−C(23) distances of 2.021(3) and 2.079(3) Å indicate significant bonding interactions with both of these atoms in the amidinyl moiety.

Reaction with Alkynes. As was described in the Introduction, their stoichiometric and catalytic reactions with alkynes has been one of the main focuses of interest in group 4 hydrazido compounds.[4,7d−i,k,m,n,q,s,t,aa,ab,8h,l,m,9b] For the diamido-amine-supported complexes **1**−**3** the chemistry has been particularly rich, affording a variety of reaction products as exemplified by **9**−**11** (Figure 1).[7m,q,t,8h,l,m] Under appropriate

catalytic conditions these types of compounds are intermediates in alkyne hydrohydrazination,[7ab] 1,2-diamination,[10b] or indole synthesis.[4,8l,m] The sensitivity of the reaction outcome of titanium hydrazides to the particular diamide-donor ligand type is exemplified by the reactions of **1** (diamide-pyridine ligand) and **3** (diamido-amine ligand type): with the former, [2+2] cycloaddition products were obtained (cf. **9**) for internal and terminal alkynes; for the latter, only N_α–N_β insertion products could be isolated, and only for internal alkynes. Therefore we were interested in exploring the reactions of $Ti(N_2^{Ar}O)$-$(NNPh_2)(py)_2$ (**14**) and $Ti(N_2O)(NNPh_2)(py)_2$ (**15**) with various representative alkynes.

Unfortunately **14** did not react with terminal or internal alkynes (TolCCH, MeCCMe, PhCCMe, $(4\text{-}C_6H_4CF_3)CCMe$, or PhCCPh) at RT in benzene or toluene. Upon heating to 70 °C, these reactions yielded unknown mixtures of products. In contrast, **15** did show interesting reactivity with internal alkynes at elevated temperatures, although again no reaction occurred at RT. This is in contrast to the reactions of **1** and **3** with the same substrates that occur at RT or below.[7m,t] The reactions of **15** with the internal alkynes ArCCMe (Ar = Ph, $4\text{-}C_6H_4OMe$, or $4\text{-}C_6H_4CF_3$), PhCCPh, and MeCCMe are summarized in Scheme 5. The reactions were initially assessed on the NMR

Scheme 5. Reactions of $Ti(N_2O)(NNPh_2)(py)_2$ (15) with Alkynes
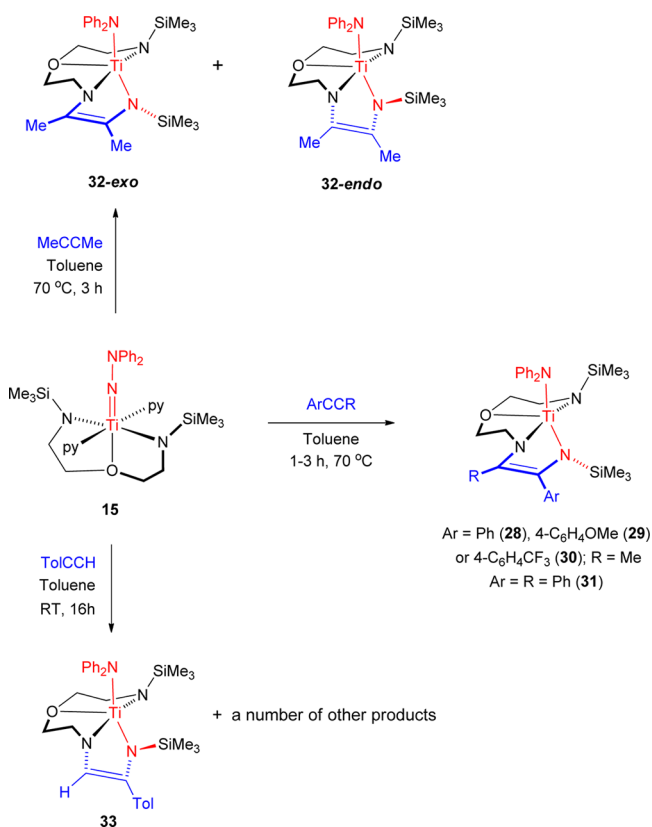
tube scale in C_6D_6 at 80 °C. After 2 h quantitative conversion to free pyridine and single products for ArCCMe or PhCCPh were observed; in the case of MeCCMe two isomeric products were formed, the relative proportion of which did not change over time. The reactions were scaled up in toluene at 70 °C, to give $Ti\{O(CH_2CH_2NSiMe_3)(CH_2CH_2NC(R)C(Ar)$-$NSiMe_3)\}(NPh_2)$ (R = Me, Ar = Ph (**28**), $4\text{-}C_6H_4OMe$ (**29**),

$4\text{-}C_6H_4CF_3$ (**30**); R = Ar = Ph (**31**)) or $Ti\{O$-$(CH_2CH_2NSiMe_3)(CH_2CH_2NC(Me)\text{-}C(Me)NSiMe_3)\}$-$(NPh_2)$ (two isomers: **32-exo** and **32-endo**) in ca. 40–80% isolated yield. The ^1H and ^{13}C NMR spectra of **28–32** are consistent with the C_1-symmetric complexes depicted in Scheme 5. Each shows resonances for a new NPh_2 moiety, a ArCCR (R = Me or Ph) or MeCCMe moiety, inequivalent $SiMe_3$ groups, and four inequivalent CH_2 groups with diastereotopic hydrogens. These spectral features are reminiscent of those for the Ar'NCO- and XylNC-derived products **18** and **27** described above (Schemes 2 and 4). The solid-state structures (*vide infra*) support those depicted in Scheme 5.

Overall, in compounds **28–32** the hydrazide ligand in **15** has undergone reductive N_α–N_β bond cleavage to form a new Ti–NPh_2 moiety, presumably (based on our previous detailed mechanistic studies[7t]) via a [2+2] cycloaddition product of the type $Ti(N_2O)\{N(NPh_2)C(R)CR'\}(py)$ (**34**, not observed). However, rather than forming a N_α–N_β bond insertion species such as $Ti(N_2O)\{NC(R')C(R)NPh_2\}(py)$ (**35**, the analogue of **10** in Figure 1), the observed products show the net insertion of a RC≡CR'N moiety into one of the N–$SiMe_3$ bonds of the N_2O ligand. In addition, in the case of the products **28–30** formed with the unsymmetrical alkynes ArCCMe, the regiochemistry of this net insertion reaction is very specific with the CMe carbon bound to the N_2O-derived N atom (Scheme 5). We recently reported an analogous reaction of the titanium alkoxyimido complex $Ti(N_2N^{Me})(NO^tBu)(py)$ with PhCCMe to give $Ti\{MeN(CH_2CH_2NSiMe_3)(CH_2CH_2NC\text{-}(Me)C(Ph)NSiMe_3)\}(NPh_2)$ (**36**).[6a] DFT calculations found that **36** was formed via azirinyl intermediate $Ti(N_2N^{Me})\{NC\text{-}(Me)C(Ph)\}(O^tBu)$ (**37**) followed by attack by an N_{imide} atom of the N_2N^{Me} ligand on the azirine ligand and then a 1,3-sigmatropic $SiMe_3$ migration.[6a] Interestingly, azirinyl intermediates related to **37** also precede the N_α–N_β bond insertion products **10** (Figure 1)[7t] and C–H activation products such as **11** reported by Bergman[4] and Gade.[8l] We therefore propose that the products **28–32** arise by a similar mechanism, namely, via the [2+2] cycloaddition compound **34** and then an azirinyl intermediate analogous to **37**. The first-formed cycloaddition species **34** is also likely to be the source of the regioselectivity with ArCCMe.[7q,t]
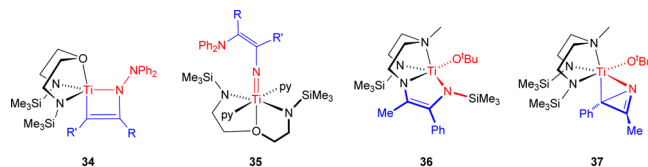
As mentioned, the product formed with MeCCMe exists as a mixture of isomers denoted "**32-exo**" and "**32-endo**" in a 5:2 ratio according to NMR integration. They have very similar ^1H and ^{13}C NMR spectra and are believed to differ only with regard to the orientation of the alkyne-derived fragment, which may be oriented "up" toward the Ti–NPh_2 moiety (as found by crystallography for **28** and **30**) or "down", away from it. The isomers were assigned in solution through the use of NOE spectroscopy. It was not possible to separate the isomeric products **32-exo** and **32-endo** by fractional crystallization.

Diffraction-quality crystals of **28** and **30** were grown from saturated hexanes solutions at RT. The molecular structures are shown in Figure 11, and selected bond lengths and angles are listed in Table 3. Each possesses a distorted square base pyramidal geometry with the new NPh_2 group in the axial

Figure 11. Displacement ellipsoid plot (20% probability) of Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(Ph)NSiMe$_3$}(NPh$_2$) (**28**) (left) and Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(C$_6$H$_4$CF$_3$)NSiMe$_3$}(NPh$_2$) (**30**) (right). H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(Ph)NSiMe$_3$}-(NPh$_2$) (28) and Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(C$_6$H$_4$CF$_3$)-NSiMe$_3$}(NPh$_2$) (30)
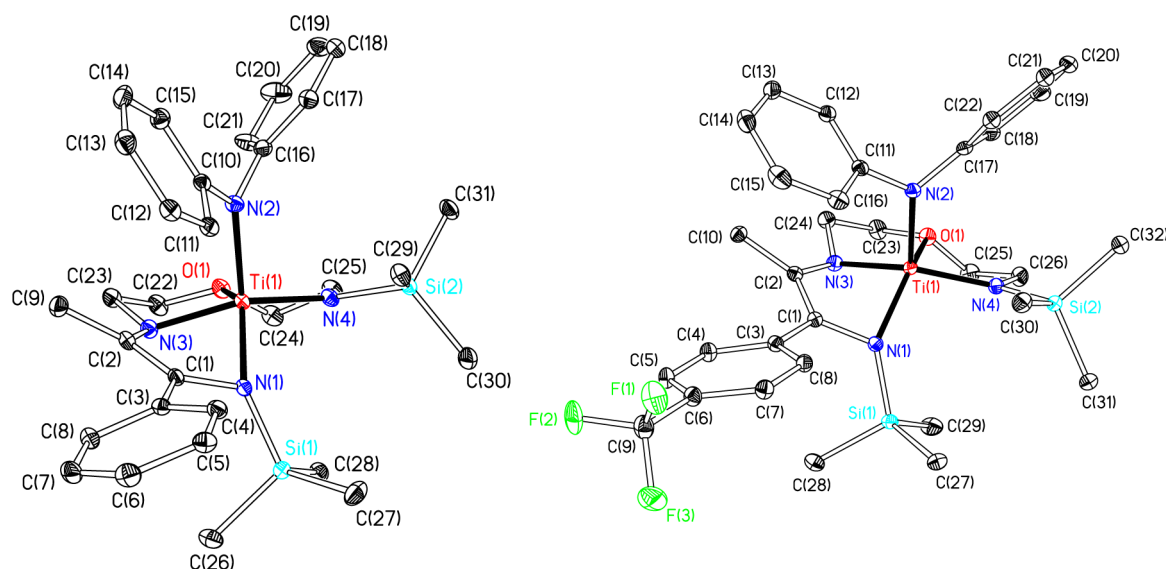
	28	30
Ti(1)–N(1)	1.9499(18)	1.9381(9)
Ti(1)–N(2)	2.0297(19)	2.0006(10)
Ti(1)–N(3)	1.9485(18)	1.9601(10)
Ti(1)–N(4)	1.9562(18)	1.9542(10)
Ti(1)–O(1)	2.2347(16)	2.2537(9)
N(1)–C(1)	1.422(3)	1.4130(14)
C(1)–C(2)	1.387(3)	1.3938(15)
C(1)–C(3)	1.492(3)	1.4788(15)
N(3)–C(2)	1.371(3)	1.3715(15)
O(1)–Ti(1)–N(1)	129.54(7)	132.95(4)
O(1)–Ti(1)–N(2)	105.49(7)	104.48(4)
O(1)–Ti(1)–N(3)	70.28(7)	71.00(4)
O(1)–Ti(1)–N(4)	75.55(7)	75.23(4)
N(1)–Ti(1)–N(2)	123.11(8)	120.41(4)
N(1)–Ti(1)–N(3)	83.70(7)	83.95(4)
N(1)–Ti(1)–N(4)	104.59(8)	104.76(4)
N(2)–Ti(1)–N(3)	105.33(8)	104.79(4)
N(2)–Ti(1)–N(4)	101.63(8)	103.75(4)
N(3)–Ti(1)–N(4)	140.87(8)	140.06(4)
N(1)–C(1)–C(2)	117.14(18)	117.76(10)
N(1)–C(1)–C(3)	118.91(18)	119.11(9)
N(3)–C(2)–C(1)	114.05(19)	113.79(10)

position and Ti(1) lying 0.66−0.68 Å out of the plane formed by N(1), N(3), N(4), and O(1). As mentioned, the MeCCAr moiety is folded "up" toward the NPh$_2$ ligand. Overall the structures are reminiscent of that for Ti{O(CH$_2$CH$_2$NSiMe$_3$)-(CH$_2$CH$_2$NCN(SiMe$_3$)Xyl)}(NPh$_2$)(NCNXyl) (**27**, Figure 10), except that in **28** and **30** O(1) is coordinated to the metal (Ti(1)−O(1) = 2.2347(16) and 2.2537(9) Å). The Ti−NPh$_2$ bond distances (2.0297(19) and 2.0006(10) Å) are consistent with formal single bonds but are a little longer than the other three Ti−N(1,3,4) distances (range 1.9381(9)−1.9601(10) Å). Both C(1) and C(2) have a trigonal planar

geometry, and the C(1)−C(2) bond distances of 1.387(3) Å (**28**) and 1.3938(15) Å (**30**) indicate significant double-bond character.

We have previously reported that reactions of Ti(NNPh$_2$)-(N$_2$N^{Me})(py) (**3**) with terminal alkynes form unidentified mixtures of products.[7t] In contrast, Ti(NNPh$_2$)(N$_2$N^{py})(py) (**1**) reacted cleanly with both internal and terminal alkynes to form metallacyclobutene products.[7q,t] Unfortunately, although the reactions of **15** with terminal alkynes such as TolCCH proceeded without heating at RT in toluene over 16 h, a complex mixture of products was formed. In the case of TolCCH a small number of red, diffraction-quality crystals identified as Ti(NPh$_2$){O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(H)-C(Tol)NSiMe$_3$)} (**33**, Scheme 5) were isolated from a hexanes solution at 0 °C. The molecular structure of **33** is given in Figure S3 of the Supporting Information along with selected bond lengths and angles. Interestingly the alkyne-derived HC≡CTol moiety in **33** is oriented "down" away from the Ti−NPh$_2$ moiety in the manner proposed for **32-endo** (*vide supra*).

■ CONCLUSIONS

In this contribution we have reported the synthesis and reactivity of two new titanium diphenyl hydrazido(2−) complexes supported by two different diamido-ether ligands, N$_2^{Ar}$O and N$_2$O. As expected from previous literature for N$_2^{Ar}$O,[11] these ligands exhibit a larger degree of flexibility with respect to *mer*- or *fac*-coordination than is the case for the previously employed diamido-amines (e.g., N$_2$N^{Me} and related) in this area. This is exemplified by Ti(L)(NNPh$_2$)(py)$_2$ (L = N$_2^{Ar}$O (**14**) and N$_2$O (**15**)) or Ti(L){NC(Ar^{Fx})NNPh$_2$}(py)$_2$ (**22−24**) with *mer*-bound diamido-ether ligands, but Ti(N$_2$O)-(NNPh$_2$)(bipy) (**17**), Ti(N$_2$O){N(NPh$_2$)C(NAr′)S}(py) (**20**), or Ti(N$_2$O)(NPh$_2$)(NCN^{t}Bu) (**26**) with *fac*-coordinated ones. In general, the reactions with Ar′NCE, Ar^{Fx}CN, and RNC follow the recently established reactivity patterns in terms of leading to [2+2] cycloaddition to Ti=N$_\alpha$ with Ar′NCE, insertion into Ti=N$_\alpha$ with Ar^{Fx}CN, and reductive N$_\alpha$−N$_\beta$ bond cleavage with isonitriles. However, there are several difference between the reactions of **14** and **15**: although both

give insertion reactions with Ar^{Fx}CN, with RNC the N$_2^{Ar}$O-supported system forms only the σ-adduct Ti(N$_2^{Ar}$O)-(NNPh$_2$)(py)(CNXyl), and with alkynes no reaction took place for **14**. The reasons for these difference are not clear. The reactions of **15** are more like those of its diamido-amine-supported counterparts Ti(L)(NNPh$_2$)(py) (L = N$_2$N^{py} (**1**) or N$_2$N^{Me} (**3**)), but with three of the four classes of substrate studied there are clear complications arising from competing or alternative reactions of the Ti−N$_{amide}$ bond of N$_2$O. This is most clearly seen in the reactions with alkynes (Scheme 5), which give exclusively Ti−N$_{amide}$ bond activation products, and also with Ar′NCO, which forms **18**, and with XylNC to give **27**. It seems that, in general, the greater flexibility of the N$_2$O ligand opens up these other pathways. It would be interesting in the future to use alternative diamido-ether ligands with different N$_{amide}$ substituents to try to block these deleterious alternatives.

■ EXPERIMENTAL SECTION

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over potassium (C$_6$D$_6$), sodium (toluene-d_8), or P$_2$O$_5$ (CDCl$_3$·CD$_2$Cl$_2$), distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise, referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F spectra were referenced externally to CFCl$_3$. ^{7}Li spectra were referenced externally to LiCl, and the ^{2}H NMR spectrum was referenced to the natural abundance deuterium resonance of the protio solvent (C$_6$H$_6$). Assignments were confirmed using two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm$^{−1}$). Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University or Elemental Microanalysis Ltd., Devon.

Starting Materials. O(CH$_2$CH$_2$NH$_2$)$_2$,[12] Ti(NNPh$_2$)Cl$_2$(py)$_3$,[7p] (4-C$_6$H$_4$OMe)CCMe,[30] (4-C$_6$H$_4$CF$_3$)CCMe,[30] Ar′NCSe,[7w] and Li$_2$N$_2^{Ar}$O[11] were synthesized according to literature procedures. Other reagents were purchased from Sigma-Aldrich or Alfa-Aesar and used without further purification.

H$_2$N$_2$O (12). A solution of O(CH$_2$CH$_2$NH$_2$)$_2$ (8.14 g, 78.2 mmol) and Et$_3$N (43.6 mL, 0.31 mol) in THF (30 mL) was cooled to 0 °C. Me$_3$SiCl (21.8 mL, 0.17 mol) was added dropwise to the cooled solution, a white precipitate immediately formed, and the reaction was warmed to RT. After 3 h the slurry was filtered and volatiles were removed under reduced pressure. The product was extracted into pentane (30 mL) and the solvent was removed *in vacuo* to give a colorless oil. Yield: 14.5 g (75%). ^{1}H NMR (CDCl$_3$, 299.9 MHz): δ 3.32 (4H, t, ^3J = 5.7 Hz, OC$\underline{H}_2$), 2.80 (4H, t, ^3J = 5.7 Hz, NC$\underline{H}_2$), 0.71 (2H, s, N$\underline{H}$), −0.3 (18H, s, Si$\underline{Me}_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 73.9 (N$\underline{C}$H$_2$), 41.5 (O$\underline{C}$H$_2$), 0.0 (Si$\underline{Me}_3$). IR (NaCl plates, Nujol mull, cm$^{−1}$): 2361 (s), 2336 (m), 1653 (s), 1456 (s), 1248 (s), 1115 (m), 949 (w), 836 (s), 668 (s). FI-MS: [M + H]$^+$ *m/z* = 249.1825 (calcd for C$_{10}$H$_{28}$N$_2$OSi$_2$: *m/z* = 249.1818).

Li$_2$N$_2$O (13). BuLi (23.5 mL, 37.7 mmol, 1.6 M in hexanes) was added dropwise to a solution of **12** (4.45 g, 17.9 mmol) in hexanes (60 mL) at −78 °C. A white precipitate immediately formed, and the solution was then warmed to RT. After 3 h the white solid was filtered, washed with pentane (3 × 5 mL), and dried *in vacuo*. Yield: 4.07 g

(87%). Diffraction-quality crystals were grown from a concentrated pentane solution at RT. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz): δ 3.24 (4H, t, ^3J = 4.9 Hz, OC$\underline{H}_2$), 3.07 (4H, t, ^3J = 4.9 Hz, NC$\underline{H}_2$), 0.16 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz): δ 77.9 (N$\underline{C}$H$_2$), 45.6 (O$\underline{C}$H$_2$), 1.9 (Si$\underline{Me}_3$) ppm. ^{7}Li NMR (toluene-d_8, 117 MHz): 1.9 (N$\underline{Li}$) ppm. IR (NaCl plates, Nujol mull, cm$^{−1}$): 1570 (m), 1419 (w), 1358 (w), 1345 (m), 1271 (w), 1242 (s), 1084 (s), 1052 (s), 1022 (s), 952 (s), 913 (w), 823 (s), 763 (m), 734 (s), 668 (m), 618 (m). Anal. Found (calcd for C$_{10}$H$_{26}$N$_2$OSi$_2$Li$_2$): C, 46.43 (46.13); H, 10.21 (10.06); N, 10.76 (10.20).

Ti(N$_2^{Ar}$O)(NNPh$_2$)(py)$_2$ (14). To a mixture of Li$_2$N$_2^{Ar}$O (0.23 g, 0.63 mmol) and Ti(NNPh$_2$)Cl$_2$(py)$_3$ (0.32 g, 0.63 mmol) cooled to −40 °C was added cold toluene (20 mL, −40 °C). The stirred green-brown suspension was allowed to warm to RT and stirred for a further hour, resulting in a dark brown solution. The volatiles were removed under reduced pressure, and the dark brown solid was extracted into toluene (2 × 15 mL) and filtered. The volatiles were removed under reduced pressure. The residue was washed with hexanes (2 × 5 mL), and the supernatant was removed by filtration. The solid was dried *in vacuo* to yield the product as a dark brown powder. Yield: 0.27 g (59%). Diffraction-quality crystals were grown from a saturated hexanes solution at 4 °C. ^{1}H NMR (C$_6$D$_6$, 499.9 MHz, 293 K): δ 9.12 (4H, d, ^3J = 5 Hz, o-C$_6$H$_5$N), 7.23 (4H, app. d, app. ^3J = 7.2 Hz, o-C$_6$H$_5$), 7.08 (4H, app. t, app. ^3J = 7 Hz, m-C$_6$H$_5$), 6.95 (2H, dd, ^3J = 7 Hz, p-C$_6$H$_4$O), 6.86−6.89 (4H, overlapping m, p-C$_6$H$_5$ and o-C$_6$H$_4$O), 6.71 − 6.76 (4H, overlapping m, p-C$_6$H$_5$N and m-C$_6$H$_4$O), 6.52 (4H, m, m-C$_6$H$_5$N), 6.20 (2H, m, o-C$_6$H$_4$N), 0.46 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 293 K): 152.4 (o-$\underline{C}_6$H$_5$N), 150.1 (*ipso*-$\underline{C}_6$H$_4$O), 147.0 (m-$\underline{C}_6$H$_5$N), 145.2 (*ipso*-$\underline{C}_6$H$_4$N), 137.4 (p-$\underline{C}_6$H$_5$N), 128.6 (m-$\underline{C}_6$H$_5$), 123.9 (m-$\underline{C}_6$H$_4$O), 123.0 (m-$\underline{C}_6$H$_5$N), 122.0 (o-$\underline{C}_6$H$_5$), 119.1 (p-$\underline{C}_6$H$_4$O), 114.3(o-$\underline{C}_6$H$_4$N), 112.1 (o-$\underline{C}_6$H$_4$O), 2.7 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm$^{−1}$): 1603 (m), 1597 (m), 1586 (m), 1576 (w), 1559 (w), 1493 (m), 1475 (s), 1444 (s), 1317 (w), 1279 (s), 1240 (s), 1212 (w), 1189 (m), 1169 (w), 1158 (w), 1111 (w), 1068 (w), 1040 (w), 1011 (w), 928 (s), 875 (w), 842 (m), 779 (w), 751 (m), 736 (m), 724 (w), 694 (s), 669 (w), 637 (w), 629 (w), 581 (w), 484 (br, m), 402 (w). Anal. Found (calcd for C$_{22}$H$_{35}$N$_3$OSi$_2$Ti·C$_5$H$_5$N): C, 64.35 (64.50); H, 6.45 (6.34); N, 10.88 (10.75).

Ti(N$_2^{Ar}$O)(NNPh$_2$)(^{t}Bu-bipy) (16). To a stirred solution of Ti-(N$_2^{Ar}$O)(NNPh$_2$)(py)$_2$ (**14**) (0.29 g, 0.40 mmol) in toluene (20 mL) was added a solution of ^{t}Bu-bipy (0.11 g, 0.40 mmol) in toluene (10 mL) at RT. An immediate change of color from dark brown to dark green was observed. After stirring for 1 h, the volatiles were removed under reduced pressure. The residue was triturated in hexanes (2 × 10 mL), and the supernatant was removed by filtration. The resulting solid was dried *in vacuo* to yield the product as a dark green powder. Yield: 0.17 g (50%). Diffraction-quality crystals were grown from a saturated toluene/hexanes solution at 4 °C. ^{1}H NMR (C$_6$D$_6$, 499.9 MHz, 293 K): δ 9.35 (2H, d, ^3J = 6 Hz, 6-(4,4′-*tert*-butyl)C$_5$$\underline{H}_3$N)$_2$), 7.48 (2H, d, ^4J = 1.5 Hz, 3-((4,4′-*tert*-butyl)C$_5$$\underline{H}_3$N)$_2$), 7.32 (2H, dd, ^3J = 7.3 Hz, ^4J = 1.5 Hz, o-C$_6$$\underline{H}_4$O), 7.03 (4H, dd, ^3J = 7.0 Hz, ^4J = 1.5 Hz, o-C$_6$$\underline{H}_5$), 6.97 (2H, m, m-C$_6$$\underline{H}_4$O), 6.92 (4H, m, m-C$_6$$\underline{H}_5$), 6.84 (2H, dd, ^3J = 6.8 Hz, ^4J = 1.5 Hz, o-C$_6$$\underline{H}_4$N), 6.82 (2H, dd, ^4J = 1.5 Hz, ^3J = 6.8 Hz, 5-(4,4′-*tert*-butyl)C$_5$$\underline{H}_3$N)$_2$), 6.69 (2H, m, p-C$_6$$\underline{H}_5$), 6.26 (2H, m, p-C$_6$$\underline{H}_4$), 0.85 (18H, s, (4,4′-C$\underline{Me}_3C_5H_3$N)$_2$), 0.80 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 293 K): 162.5 (4-(4,4′-*tert*-butyl)$\underline{C}_5$H$_3$N)$_2$), 152.7 (2-(4,4′-*tert*-butyl)$\underline{C}_5$H$_3$N)$_2$), 152.2 (6-(4,4′-*tert*-butyl)$\underline{C}_5$H$_3$N)$_2$), 151.3 (*ipso*-$\underline{C}_6$H$_4$O), 150.3 (*ipso*-$\underline{C}_6$H$_4$N), 146.8 (*ipso*-$\underline{C}_6$H$_5$), 128.5 (m-$\underline{C}_6$H$_5$), 125.5 (m-$\underline{C}_6$H$_4$O), 122.3 (5-(4,4′-*tert*-butyl)$\underline{C}_5$H$_3$N)$_2$), 121.7 (p-$\underline{C}_6$H$_5$), 119.9 (o-$\underline{C}_6$H$_5$), 119.8 (o-$\underline{C}_6$H$_4$O), 119.5 (o-$\underline{C}_6$H$_4$N), 116.9 (3-(4,4′-*tert*-butyl)$\underline{C}_5$H$_3$N)$_2$), 114.9 (p-$\underline{C}_6$H$_4$O), 34.6 (4,4′-$\underline{C}$Me$_3$C$_5$H$_3$N)$_2$), 29.8 (4,4′-C$\underline{Me}_3$C$_5$H$_3$N)$_2$), 4.1 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm$^{−1}$): 1617 (w), 1594 (w), 1586 (w), 1489 (m), 1482 (m), 1403 (w), 1304 (w), 1281 (w), 1247 (m), 1151 (w), 1101 (w), 946 (w), 914 (w), 845 (m), 736 (m), 698 (w), 623 (w), 488 (br, s). EI-MS: *m/z* =572 [Ti(N$_2$O)(NNPh$_2$)]$^+$ (5%), 269 [^{t}Bu-bipy]$^+$ (14%), 73 [SiMe$_3$]$^+$ (46%). Anal. Found (calcd for C$_{48}$H$_{60}$N$_6$OSi$_2$Ti·0.75(C$_7$H$_8$)): C, 70.18 (70.27); H, 7.26 (7.31); N, 9.00 (9.23).

Ti(N₂O)(NNPh₂)(py)₂ (15). To a stirred mixture of $Ti(NNPh_2)Cl_2(py)_3$ (2.07 g, 3.84 mmol) and Li_2N_2O (13) (1.00 g, 3.84 mmol), cooled to −78 °C, was added cold toluene (60 mL, −78 °C). The reaction was allowed to warm to RT, and the solution gradually changed color from green to dark brown. After 1 h the volatiles were removed *in vacuo* and the dark brown oily solid extracted into Et_2O (3 × 15 mL), which was then removed *in vacuo*. The product was recrystallized from a concentrated hexanes solution at RT. Yield: 1.72g (71%). Diffraction-quality crystals were grown from a saturated hexanes solution at RT. ^1H NMR (C_6D_6, 299.9 MHz): δ 9.09 (4H, d, ^3J = 4.8 Hz, *o*-py), 7.11 (4H, t, ^3J = 8.6 Hz, *o*-NPh₂), 7.01 (2H, t, ^3J = 7.6 Hz, *p*-py), 6.89 (2H, t, ^3J = 7.1 Hz, *p*-NPh₂), 6.78−6.65 (8H, m, *m*-NPh₂ and *m*-py), 3.53 (4H, t, ^3J = 5.4 Hz, OC$\underline{H}_2$), 3.10 (4H, t, ^3J = 5.4 Hz, NC$\underline{H}_2$), 0.42 (18H, s, Si$\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 152.6 (*o*-py), 146.8 (*i*-NPh₂), 137.4 (*p*-py), 128.2 (*p*-NPh₂), 23.6 (*m*-py), 120.4 (*m*-NPh₂), 119.0 (*o*-NPh₂), 74.1 (N$\underline{C}H_2$), 51.0 (O$\underline{C}H_2$), 2.7 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1597 (s), 1581 (s), 1559 (w), 1539 (w), 1506 (w), 1489 (s), 1442 (s), 1419 (w), 1351 (w), 1293 (m), 1276 (m), 1256 (m), 1242 (m) 1206 (m), 1183 (w), 1167 (m), 1150 (w), 1115 (w), 1068 (m), 1036 (m), 1024 (w), 1007 (w), 995 (w), 958 (s), 938 (m), 885 (w), 841 (s), 824 (s), 787 (m), 743 (s), 693 (s), 668 (m), 660 (w), 634 (s), 624 (m). EI-MS: *m/z* = 168 (98%) [NPh₂]⁺, 73 (85%) [SiMe₃]⁺. Anal. Found (calcd for $C_{27}H_{41}N_5OSi_2Ti$): C, 58.36 (58.36); H, 7.30 (7.44); N, 11.80 (12.60).

Ti{O(CH₂CH₂NSiMe₃)(CH₂CH₂NC(O)N(SiMe₃)Ar′)}{N(NPh₂)C(O)N-(Ar′)} (18). Ar′NCO (0.20 mL, 0.95 mmol) was added to a solution of $Ti(N_2O)(NNPh_2)(py)_2$ (15, 0.30 g, 0.47 mmol) in benzene (10 mL). After 1 h the brown precipitate formed was filtered, washed with benzene (3 × 10 mL), and dried *in vacuo*. Yield: 0.19 g (46%). ^1H NMR (CD_2Cl_2, 299.9 MHz): δ 7.51 (4H, d, ^3J = 7.5 Hz, *o*-NPh₂), 7.38−7.07 (7H, m, *p*-Ar′NCO, *m*-NPh₂, *m*-Ar′NCO), 7.03 (2H, t, ^3J = 7.3 Hz, *p*-NPh₂), 6.93 (2H, d, ^3J = 7.8 Hz, *m*-Ar′NSiMe₃), 6.70 (1H, t, ^3J = 7.2 Hz, *p*-Ar′NSiMe₃), 4.22−4.06 (2H, m, OC$\underline{H}_2$CH₂NSiMe₃), 3.69−3.33 (5H, m, C$\underline{H}_2$NSiMe₃, OCH₂CH₂NCO, $\underline{H}$CC₆H₃NSiMe₃), 3.29−3.01 (2H, m, $\underline{H}$CC₆H₃NSiMe₃, $\underline{H}$CC₆H₃NCO), 3.01−2.85 (1H, m, $\underline{H}$CC₆H₃NCO), 2.76 (1H, dt, ^3J = 12.4, 6.1 Hz, C$\underline{H}_2$NCO), 2.60−2.40 (1H, m, C$\underline{H}_2$NCO), 1.43 (3H, d, ^3J = 6.7 Hz, $\underline{Me}_2$CHC₆H₃NSiMe₃), 1.28 (3H, d, ^3J = 5.5 Hz, $\underline{Me}_2$CHC₆H₃NSiMe₃), 1.26 (3H, d, ^3J = 3.5 Hz, $\underline{Me}_2$CHC₆H₃NSiMe₃), 1.24 (3H, d, ^3J = 4.7 Hz, $\underline{Me}_2$CHC₆H₃NCO), 1.18 (3H, d, ^3J = 6.8 Hz, $\underline{Me}_2$CHC₆H₃NSiMe₃), 1.13 (3H, d, ^3J = 7.0 Hz, $\underline{Me}_2$CHC₆H₃NCO), 1.10 (3H, d, ^3J = 6.8 Hz, $\underline{Me}_2$CHC₆H₃NCO), 0.94 (3H, d, ^3J = 6.8 Hz, $\underline{Me}_2$CHC₆H₃NCO), 0.13 (9H, s, Ar′NSi$\underline{Me}_3$), −0.11 (9H, s, CH₂NSi$\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 169.1 (CO), 166.4 (CO), 148.2 (*i*-Ar′NCO), 147.6 (*i*-Ar′NSiMe₃), 147.2 (*o*-Ar′NSiMe₃), 146.5 (*o*-Ar′NCO), 145.1 (*o*-Ar′NSiMe₃), 143.6 (*o*-Ar′NCO), 134.7 (*i*-NPh₂), 128.9 (*p*-Ar′NCO), 125.3 (*o*-NPh₂), 124.2 (*m*-Ar′NCO), 123.4 (*m*-NPh₂), 122.8 (*p*-NPh₂), 118.2 (*p*-Ar′NSiMe₃), 114.0 (*m*-Ar′NSiMe₃), 74.2 (O$\underline{C}H_2$CH₂NSiMe₃), 72.4 (O$\underline{C}H_2$CH₂NCO), 52.0 ($\underline{C}H_2$NSiMe₃), 45.2 ($\underline{C}H_2$NCO), 29.2 (H$\underline{C}C_6H_3$NCO), 29.0 (H$\underline{C}C_6H_3$NCO), 28.3 (H$\underline{C}C_6H_3$NSiMe₃), 28.2 (H$\underline{C}C_6H_3$NSiMe₃), 25.8 ($\underline{Me}_2$CHC₆H₃NCO), 25.4 ($\underline{Me}_2$CHC₆H₃NSiMe₃), 25.2 ($\underline{Me}_2$CHC₆H₃NCO), 24.2 ($\underline{Me}_2$CHC₆H₃NCO), 24.0 ($\underline{Me}_2$CHC₆H₃NSiMe₃), 23.6 ($\underline{Me}_2$CHC₆H₃NSiMe₃), 23.2 ($\underline{Me}_2$CHC₆H₃NSiMe₃), 22.8 ($\underline{Me}_2$CHC₆H₃NCO), 0.3 (Ar′NSi$\underline{Me}_3$), −0.2 (CH₂NSi$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1684 (m), 1658 (s), 1636 (m), 1623 (m), 1617 (m), 1587 (s), 1576 (m), 1559 (m), 1554 (w), 1539 (m), 1517 (s), 1492 (s), 1457 (s), 1420 (s), 1362 (m), 1342 (m), 1331 (s), 1292 (s), 1254 (s), 1244 (m), 1197 (m), 1173 (m), 1068 (m), 1030 (m), 1006 (m), 938 (m), 925 (m), 902 (s), 840 (s), 792 (m), 769 (m), 748 (m), 740 (s), 725 (w), 699 (s), 679 (m), 668 (w), 641 (m), 590 (s). EI-MS: *m/z* =701 (5%) [M − NNPh₂]⁺, 168 (100%) [NPh₂]⁺. Anal. Found (calcd for $C_{48}H_{70}N_6O_3Si_2Ti$): C, 65.22 (65.28); H, 8.00 (7.99); N, 9.40 (9.52).

Ti{O(CH₂CH₂NSiMe₃)(CH₂CH₂N(SiMe₃)C(NAr′)O)}(NNPh₂) (19). Ar′NCO (0.14 mL, 0.63 mmol) was added to a solution of $Ti(N_2O)(NNPh_2)(py)_2$ (15, 0.40 g, 0.63 mmol) in CH_2Cl_2 cooled to −78 °C. The solution was allowed to warm to 0 °C over 2 h and

then cooled to −78 °C. Hexanes (10 mL) were then added, and the so-formed dark red solid was filtered, washed with cold hexanes and dried *in vacuo* at 0 °C. Yield: 0.30 g, (61%). ^1H NMR (CD_2Cl_2, 499.9 MHz, 0 °C): δ 7.84 (4H, dd, ^3J = 6.3, 1.6 Hz, *o*-NPh₂), 7.75−7.59 (2H, m, *p*-NPh₂), 7.10−6.96 (5H, m, *m*-NPh₂, *m*-Ar′), 6.85 (1H, t, ^3J = 7.6 Hz, *m*-Ar′), 6.65 (1H, dd, ^3J = 7.6, 1.4 Hz, *p*-Ar′), 4.41−4.11 (2H, m, OC$\underline{H}_2$CH₂NSiMe₃, C$\underline{H}_2$NC), 4.11−3.86 (2H, m, OC$\underline{H}_2$CH₂NC, OC$\underline{H}_2$CH₂NSiMe₃), 3.86−3.62 (2H, m, OCH₂C$\underline{H}_2$NC, C$\underline{H}_2$NSiMe₃), 3.20 (1H, dt, ^3J = 6.8, 5.7 Hz, C$\underline{H}$Me₂), 3.09 (1H, dd, ^3J = 13.4, 3.3 Hz, C$\underline{H}_2$NSiMe₃), 2.98 (1H, dt, ^3J = 13.7, 6.8 Hz, C$\underline{H}$Me₂), 2.91 (1H, d, ^3J = 15.2 Hz, C$\underline{H}_2$NC), 1.14 (3H, d, ^3J = 6.8 Hz, $\underline{Me}$C), 1.09 (3H, d, ^3J = 6.9 Hz, $\underline{Me}$C), 0.98 (3H, d, ^3J = 6.9 Hz, $\underline{Me}$C), 0.62 (3H, d, ^3J = 6.9 Hz, $\underline{Me}$C), 0.29 (9H, s, CNSi$\underline{Me}_3$), −0.46 (9H, s, CH₂NSi$\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, 0 °C): δ 157.7 (NCO), 150.3 (*o*-NPh₂), 147.4 (*i*-Ar′), 141.3 (*o*-Ar′), 140.2 (*o*-Ar′), 138.2 (*p*-NPh₂), 136.0 (*i*-NPh₂), 124.3 (*m*-NPh₂), 122.9 (*p*-Ar′), 121.2 (*m*-Ar′), 120.7 (*m*-Ar′), 80.7 (O$\underline{C}H_2$CH₂NSiMe₃), 77.8 (O$\underline{C}H_2$CH₂NC), 47.6 ($\underline{C}H_2$NSiMe₃), 42.5 ($\underline{C}H_2$NC), 28.0 ($\underline{C}$HMe₂), 27.4 ($\underline{C}$HMe₂), 24.2 ($\underline{Me}$C), 23.8 ($\underline{Me}$C), 23.3 ($\underline{Me}$C), 22.5 ($\underline{Me}$C), 1.3 (NCSi$\underline{Me}_3$), 0.3 (CH₂NSi$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1586 (m), 1566 (m), 1521 (w), 1491 (s), 1457 (s), 1339 (m), 1327 (m), 1247 (m), 1216 (w), 1153 (w), 1100 (w), 1069 (w), 1057 (w), 1043 (w), 1008 (w), 948 (w), 842 (s), 802 (w), 744 (m), 694 (m). EI-MS: *m/z* 679 (5%) [M]⁺, 496 (5%) [M − NNPh₂]⁺, 91 (100%) [NPh]⁺. Anal. Found (calcd for $C_{35}H_{53}N_5O_2Si_2Ti$): C, 61.48 (61.83); H, 7.53 (7.86); N, 10.35 (10.30).

Ti(N₂O){N(NPh₂)C(NAr′)S}(py) (20). A solution of Ar′NCS (0.14 g, 0.63 mmol) in Et_2O (10 mL) was added to a solution of $Ti(N_2O)(NNPh_2)(py)_2$ (15, 0.40 g, 0.63 mmol) in Et_2O (10 mL). After 1 h the resulting suspension was filtered and the red solid dried *in vacuo*. Yield: 0.28 g (57%). Diffraction-quality crystals were grown from a concentrated benzene solution, layered with hexanes. ^1H NMR (CD_2Cl_2, 299.9 MHz): δ 8.81 (2H, d, ^3J = 4.7 Hz, *o*-py), 7.81 (1H, dd, ^3J = 10.6, 4.6 Hz, *p*-py), 7.49−7.35 (3H, m, *o*-NPh₂, *m*-py), 7.28−7.15 (4H, m, *m*-NPh₂), 7.01−6.78 (8H, m, *p*-Ar′, *m*-Ar′, *p*-NPh₂), 3.98 (4H, t, ^3J = 5.4 Hz, OC$\underline{H}_2$), 3.76 (2H, dt, ^3J = 12.0, 5.8 Hz, NC$\underline{H}_2$), 3.22 (2H, dt, ^3J = 13.1, 4.8 Hz, NC$\underline{H}_2$), 3.08 (2H, dq, ^3J = 13.7, 6.9 Hz, C$\underline{H}$Me₂), 1.18 (6H, d, ^3J = 5.9 Hz, CH$\underline{Me}_2$), 0.87 (6H, d, ^3J = 5.9 Hz, CH$\underline{Me}_2$), −0.09 (18H, s, Si$\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 150.6 (*o*-py), 147.4 (*i*-NPh₂), 145.0 (*o*-Ar′), 141.1 (*i*-Ar′), 128.7 (*m*-NPh₂), 124.4 (*m*-py), 122.4 (*p*-Ar′), 122.2 (*p*-NPh₂), 120.3 (*m*-Ar′), 119.0 (*o*-NPh₂), 77.7 (O$\underline{C}H_2$), 53.6 (N$\underline{C}H_2$), 28.1 ($\underline{C}$HMe₂), 24.1 (CH$\underline{Me}_2$), 23.3 (CH$\underline{Me}_2$), 1.1 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1609 (s), 1578 (s), 1492 (s), 1332 (w), 1279 (w), 1246 (m), 1220 (w), 1164 (w), 1072 (w), 1053 (w), 1030 (w), 990 (w), 953 (w), 939 (m), 922 (m), 871 (m), 837 (s), 794 (m), 758 (m), 740 (s), 700 (m), 690 (m). EI-MS: *m/z* 775 (2%) [M]⁺, 696 (3%) [M − py]⁺, 169 (42%) [NPh₂]⁺. Anal. Found (calcd for $C_{40}H_{58}N_6OSSi_2Ti$): C, 61.80 (61.99); H, 7.24 (7.54); N, 10.46 (10.84).

Ti(N₂^{Ar}O){NC(Ar^{F5})NNPh₂}(py)₂ (22). To a stirred solution of $Ti(N_2^{Ar}O)(NNPh_2)(py)_2$ (14, 0.28 g, 0.38 mmol) in toluene (20 mL) was added a solution of Ar^F5CN (48.4 μL, 0.38 mmol) in toluene (10 mL) at RT, leading to an immediate change of color from dark brown to bright orange. After stirring for 2 h, the volatiles were removed under reduced pressure. The residue was washed with hexanes (2 × 10 mL), and the resulting solid was dried *in vacuo* to give **22** as an orange powder. Yield: 0.17 g (52%). Diffraction-quality crystals were grown from a saturated toluene/pentane solution. ^1H NMR (C_6D_6, 499.9 MHz, 293 K): δ 9.02 (4H, br, s, *o*-NC₅$\underline{H}_5$), 7.18 (4H, d, ^3J = 7.1 Hz, *o*-C₆$\underline{H}_5$), 7.04−7.07 (6H, m, overlapping *m*-C₆$\underline{H}_5$ and *o*-OC₆$\underline{H}_4$), 6.82 (2H, m, *p*-C₆$\underline{H}_5$), 6.64−6.67 (4H, m, overlapping m, *p*-NC₅$\underline{H}_5$ and *m*-OC₆$\underline{H}_4$), 6.60 (2H, m, *o*-NC₆$\underline{H}_4$), 6.49 (4H, m, *m*-NC₅$\underline{H}_5$), 6.35 (2H, m, *p*-OC₆$\underline{H}_4$), 0.43 (18H, s, Si$\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 151.1 (*o*-NC₅$\underline{H}_5$), 149.7 (*i*-C₆$\underline{H}_5$), 149.3 (*i*-OC₆$\underline{H}_4$), 144.8 (*i*-NC₆$\underline{H}_4$), 138.0 (*p*-NC₅$\underline{H}_5$), 128.8 (*m*-C₆$\underline{H}_5$), 124.3 (*m*-OC₆$\underline{H}_4$), 123.2 (*m*-NC₅$\underline{H}_5$), 122.5 (*p*-C₆$\underline{H}_5$), 121.8 (*o*-C₆$\underline{H}_5$), 118.3 (*o*-NC₆$\underline{H}_4$), 115.6 (*p*-OC₆$\underline{H}_4$), 112.1 (*o*-OC₆$\underline{H}_4$), 3.1 (Si$\underline{Me}_3$) ppm. ^{19}F NMR NMR (C_6D_6, 282.5 MHz, 293 K): −164.1 (*o*-

C_6F_5), −158.0 (*m*-C_6F_5), −136.1 (*p*-C_6F_5) ppm. Resonances corresponding to N$\underline{C}$(C_6F_5)NNPh$_2$ were not observed. IR (NaCl plates, Nujol mull, cm^{-1}): 1603 (m), 1588 (w), 1517 (m), 1502 (m), 1493 (m), 1293 (w), 1280 (m), 1247 (m), 1189 (w), 1112 (w), 1042 (w), 1013 (w), 991 (w), 951 (w), 922 (w), 871 (w), 833 (m), 786 (w), 753 (m), 736 (w), 712 (w), 697 (w), 636 (w), 487 (br, s). EI-MS: *m/z* = 241 [TiNC(C_6F_5)]$^+$ (25%), 192 [C_6F_5CN]$^+$ (29%), 169 [NPh$_2$]$^+$ (100%), 167 [C_6F_5]$^+$ (84%). Anal. Found (calcd for $C_{47}H_{47}N_7OSi_2Ti·0.4(C_7H_8)$): C, 62.07 (62.19); H, 5.31 (5.26); N, 9.74 (10.19).

Ti(N$_2$O){NC(Ar^{F5})NNPh$_2$}(py)$_2$ (23). Ar^{F5}CN (0.09 mL, 0.69 mmol) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (15, 0.40 g, 0.63 mmol) in toluene and heated to 70 °C. After 2 h the volatiles were removed under reduced pressure to give a dark red, viscous oil. This was dissolved in a minimum volume of hexanes at 40 °C and allowed to cool slowly to form an orange solid, which was washed with pentane and dried *in vacuo*. Yield: 0.25 g (47%). Diffraction-quality crystals were grown from a saturated hexanes solution at 0 °C. ^{1}H NMR (C_6D_6, 299.9 MHz): δ 8.93 (2H, d, ^3J = 3.1, *o*-py), 7.24 (4H, d, ^3J = 7.8, *o*-NPh$_2$), 7.08 (4H, t, ^3J = 7.9, *m*-NPh$_2$), 6.91 (1H, t, ^3J = 7.6 *p*-py), 6.80 (2H, t, ^3J = 7.3, *p*-NPh$_2$), 6.61 (2H, m, *m*-py), 3.36 (4H, t, ^3J = 5.6, O$\underline{C}$H$_2$), 3.13 (4H, t, ^3J = 5.6, N$\underline{C}$H$_2$), 0.41 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 151.4 (*o*-py), 149.9 (*i*-NPh$_2$), 136.7 (*p*-py), 128.7 (*m*-NPh$_2$), 123.5 (*m*-py), 122.1 (*o*-NPh$_2$), 122.0 (*p*-NPh$_2$) 73.9 (N$\underline{C}$H$_2$), 52.3 (O$\underline{C}$H$_2$), 2.4 (Si$\underline{Me}_3$) ppm. Selected ^{13}C{^{19}F} NMR (C_6D_6, 75.4 MHz): 157.6 (*i*-C_6F_5), 141.5 (*m*-C_6F_5), 138.9 (*p*-C_6F_5), 135.5 (*o*-C_6F_5) ppm. ^{19}F{^{1}H} NMR (C_6D_6, 470.4 MHz): −136.3 (*o*-C_6F_5), −160.4 (*p*-C_6F_5), −164.6 (*m*-C_6F_5) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1599 (m), 1587 (w), 1517 (s), 1351 (s), 1289 (w), 1268 (w), 1246 (m), 1236 (m), 1217 (w), 1207 (w), 1150 (w), 1106 (w), 1069 (m), 1039 (w), 1008 (w), 986 (m), 951 (m), 931 (m), 884 (w), 830 (s), 752 (s), 711 (w), 702 (s), 692 (m) 670 (m), 624 (m). EI-MS: *m/z* = 377 (5%) [NC(NNPh$_2$)-C_6F_5]$^+$, 193 (35%) [NCC_6F_5]$^+$. Anal. Found (calcd for $C_{29}H_{36}F_5N_5OSi_2Ti$): C, 56.47 (56.58); H, 5.59 (5.60); N, 11.22 (11.84).

Ti(N$_2$^{Ar}O)(NNPh$_2$)(py)(CNXyl) (25). To a stirred solution of Ti(N$_2$^{Ar}O)(NNPh$_2$)(py)$_2$ (14, 0.30 g, 0.40 mmol) in toluene (20 mL) was added a solution of XylNC (0.05 g, 0.40 mmol) in toluene (10 mL) at RT, leading to an immediate change of color from dark brown to yellow-brown. After stirring for 1 h, the volatiles were removed under reduced pressure. The residue was washed with hexanes (2 × 10 mL), and the resulting solid was dried *in vacuo* to give 25 as a brown powder. Yield: 0.20 g (62%). ^{1}H NMR (C_6D_6, 499.9 MHz, 293 K): δ 9.16 (4H, br, s, *o*-N$C_5\underline{H}_5$), 7.60 (4H, br, s, *o*-$C_6\underline{H}_5$), 7.26 (4H, t, ^3J = 7.3 Hz, *m*-$C_6\underline{H}_5$), 7.14 (4H, br, s, overlapping *m*-O$C_6\underline{H}_4$ and *p*-O$C_6\underline{H}_4$), 7.01 (2H, t, ^3J = 7.0 Hz, *p*-$C_6\underline{H}_5$), 6.91 (2H, t, ^3J = 6.9 Hz, *o*-O$C_6\underline{H}_4$), 6.86 (1H, t, ^3J = 6.9 Hz, *p*-N$C_5\underline{H}_5$), 6.79 (1H, t, ^3J = 6.9 Hz, *p*-(2,6-$C_6\underline{H}_3$Me$_2$CN)), 6.62−6.64 (4H, m, overlapping *m*-(2,6-$C_6\underline{H}_3$Me$_2$CN) and *m*-N$C_5\underline{H}_5$), 6.41 (2H, br, t, *o*-N$C_6\underline{H}_4$), 2.16 (6H, s, 2,6-$C_6H_3\underline{Me}_2$CN) and 0.60 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 293 K): 151.8 (*o*-N$\underline{C}_5$H$_5$), 150.1 (*i*-O$\underline{C}_6$H$_5$), 146.4 (*i*-$\underline{C}_6$H$_5$), 145.8 (*i*-N$\underline{C}_6$H$_4$), 137.5 (*p*-N$\underline{C}_5$H$_5$), 135.6 (*o*-(2,6-$\underline{C}_6$H$_3$Me$_2$CN)), 129.2 (*p*-(2,6-$\underline{C}_6$H$_3$Me$_2$CN)), 128.7 (*m*-$\underline{C}_6$H$_5$), 127.7 (*m*-(2,6-$\underline{C}_6$H$_3$Me$_2$CN)), 125.5 (*i*-(2,6-$\underline{C}_6$H$_3$Me$_2$CN)), 124.4 (*o*-O$\underline{C}_6$H$_4$), 123.1 (*m*-N$\underline{C}_5$H$_5$), 122.0 (*p*-$\underline{C}_6$H$_5$), 120.1 (*o*-$\underline{C}_6$H$_5$), 119.0 (*p*-O$\underline{C}_6$H$_4$), 114.4 (*o*-N$\underline{C}_6$H$_4$), 112.4 (*m*-O$\underline{C}_6$H$_4$), 18.6 (2,6-$C_6H_3\underline{Me}_2$CN), 3.0 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 2159 (m), 1595 (s), 1586 (s), 1570 (w), 1560 (w), 1506 (w), 1490 (s), 1476 (s), 1443 (s), 1317 (m), 1280 (s), 1244 (s), 1213 (s), 1185 (m), 1172 (w), 1160 (m), 1114 (m), 1069 (w), 1048 (w), 1041 (m), 1027 (w), 990 (w), 921 (s), 874 (w), 843 (s), 829 (s), 780 (m), 740 (m), 752 (m), 697 (s), 668 (w), 636 (m), 581 (m), 558 (m), 464 (br, s). EI-MS: *m/z* = 703 [M − py]$^+$ (5%), 572 [Ti(NNPh$_2$)(N$_2$O)]$^+$ (5%), 390 [Ti(L)]$^+$ (5%), 344 [L]$^+$ (85%), 169 [NPh$_2$]$^+$ (82%), 131 [XylNC]$^+$ (75%). Anal. Found (calcd for $C_{44}H_{50}N_6OSi_2Ti$): C, 66.96 (67.50); H, 6.49 (6.44); N, 10.15 (10.73).

Ti(N$_2$O)(NPh$_2$)(NCN^{t}Bu) (26). ^{t}BuNC (0.71 mL, 0.63 mmol) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (15, 0.40 g, 0.63 mmol) in toluene (10 mL) and heated to 70 °C. After 72 h the

volatiles were removed under reduced pressure. The resultant dark red oil was dissolved in a minimum volume of hexanes (5 mL) and cooled to −78 °C. The solid formed was filtered and dried *in vacuo* and then dissolved in a minimum amount of pentane and cooled to −30 °C. The red powder was again filtered and then dried *in vacuo*. Yield: 0.16 g (46%). Diffraction-quality crystals were grown from a concentrated hexanes solution at RT. ^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.25−7.02 (8H, m, *o*-NPh$_2$, *m*-NPh$_2$), 6.84 (2H, m, *p*-NPh$_2$), 3.53 (2H, m, O$C\underline{H}_2$), 3.22 (2H, m, N$C\underline{H}_2$), 3.13−3.01 (4H, m, O$C\underline{H}_2$, N$C\underline{H}_2$), 1.25 (9H, s, $C\underline{Me}_3$), 0.31 (18H, s, Si$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 153.45 (*i*-NPh$_2$), 129.1 (*o*-NPh$_2$), 123.3 (*m*-NPh$_2$), 122.7 (*p*-NPh$_2$), 118.5 (N$\underline{C}$N), 74.1 (O$\underline{C}$H$_2$), 52.9 (N$\underline{C}$H$_2$), 42.8 ($\underline{C}$Me$_3$), 32.0 (C$\underline{Me}_3$), 2.1 (Si$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 2102 (s), 1592 (m), 1247 (m), 1172 (m), 1092 (w), 1077 (m), 1028 (w), 939 (m), 922 (m), 859 (s), 841 (s), 785 (m), 755 (m), 694 (m). EI-MS: *m/z* = 559 (5%) [M]$^+$, 391 (100%) [M − NPh$_2$]$^+$, 168 (62%) [NPh$_2$]$^+$, 73 (67%) [SiMe$_3$]$^+$. Anal. Found (calcd for $C_{27}H_{45}N_5OSi_2Ti$): C, 58.04 (57.94); H, 8.00 (8.10); N, 12.38 (12.51).

Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(SiMe$_3$)Xyl)}(NPh$_2$)(NCNXyl) (27). A solution of XylNC (0.17 g, 1.26 mmol) in toluene (10 mL) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (15, 0.40 g, 0.63 mmol) in toluene (10 mL) and heated to 70 °C. After 16 h the volatiles were removed under reduced pressure. The solid was dissolved in pentane (5 mL) and cooled to −78 °C, giving 27 as a red solid, which was filtered and dried *in vacuo*. Yield: 0.23 g (50%). Diffraction-quality crystals were grown from a concentrated hexanes solution at RT. ^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.33 (4H, d, ^3J = 8.4 Hz, *o*-NPh$_2$), 7.30−7.12 (6H, m, *m*-NPh$_2$, *m*-XylNCN), 7.06−6.76 (6H, m, *p*-NPh$_2$, *p*-XylNCN, *p*-XylNSiMe$_3$, *m*-XylNSiMe$_3$), 3.94 (1H, m, $C\underline{H}_2$NSiMe$_3$), 3.78 (1H, m, O$C\underline{H}_2$CH$_2$NSiMe$_3$), 3.60−3.49 (2H, m, O$C\underline{H}_2$CH$_2$NC), 3.42 (1H, m, $C\underline{H}_2$NC), 3.15 (1H, d, ^3J = 10.6 Hz, O$C\underline{H}_2$CH$_2$NSiMe$_3$), 2.88 (1H, d, ^3J = 14.9 Hz, $C\underline{H}_2$NC), 2.77 (6H, s, $\underline{Me}$C$_6$H$_3$NCN), 2.47 (1H, d, ^3J = 12.4 Hz, $C\underline{H}_2$NC), 2.13 (3H, s, $\underline{Me}$C$_6$H$_3$NSiMe$_3$), 1.70 (3H, s, $\underline{Me}$C$_6$H$_3$NSiMe$_3$), 0.52 (9H, s, Si$\underline{Me}_3$NXyl), 0.38 (9H, s, Si$\underline{Me}_3$NCH$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 203.9 (Ti$\underline{C}$N), 152.3 (*i*-XylNSiMe$_3$), 142.5 (*i*-XylNCN), 136.1 (*o*-XylNSiMe$_3$), 134.2 (*o*-XylNSiMe$_3$), 132.0 (*o*-XylNCN), 129.5 (*i*-NPh$_2$), 129.3 (*o*-NPh$_2$), 129.0 (*m*-XylNCN), 128.4 (*m*-XylNSiMe$_3$), 127.4 (*m*-XylNSiMe$_3$), 123.6 (*m*-NPh$_2$), 122.7 (*p*-NPh$_2$), 121.6 (*p*-XylNSiMe$_3$), 121.1 (*p*-XylNCN), 118.1 (N$\underline{C}$N), 73.8 (O$\underline{C}$H$_2$CH$_2$NSiMe$_3$), 68.9 (O$\underline{C}$H$_2$CH$_2$NC), 52.3 ($\underline{C}$H$_2$NSiMe$_3$), 51.2 ($\underline{C}$H$_2$NC), 20.0 ($\underline{Me}$C$_6$H$_3$NCN), 19.2 ($\underline{Me}$C$_6$H$_3$NSiMe$_3$), 18.9 ($\underline{Me}$C$_6$H$_3$NSiMe$_3$), 2.1 (Si$\underline{Me}_3$NXyl), 0.4 (Si$\underline{Me}_3$NCH$_2$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 2184 (w), 2129 (s), 1591 (m), 1485 (m), 1269 (m), 1189 (w), 1174 (w), 1134 (w), 1114 (w), 1080 (m), 1061 (w), 1029 (w), 1011 (w), 988 (w), 925 (w), 910 (w), 879 (w), 844 (s), 780 (m), 756 (s), 698 (m), 503 (s). EI-MS: *m/z* = 740 (2%) [M]$^+$, 607 (5%) [M − XylNC]$^+$, 439 (90%) [M − XylNC-NPh$_2$]$^+$, 169 (100%) [NPh$_2$]$^+$. Anal. Found (calcd for $C_{40}H_{54}N_6OSi_2Ti$): C, 65.14 (65.02); H, 7.23 (7.37); N, 11.21 (11.37).

Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(Ph)NSiMe$_3$)}(NPh$_2$) (28). PhCCMe (0.12 mL, 0.95 mmol) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (15, 0.50 g, 0.79 mmol) in toluene (10 mL) and heated to 70 °C. After 2 h the volatiles were removed under reduced pressure, and the resultant dark brown, viscous oil was dissolved in a minimum amount of hexanes (5 mL) at 40 °C. Upon cooling to RT the brown crystalline powder that formed was filtered and dried *in vacuo*. Yield: 0.23 g (48%). Brown, diffraction-quality needles were grown from a saturated hexanes solution at RT. ^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.65 (2H, d, ^3J = 7.9, *o*-PhCC), 7.24 (2H, t, ^3J = 7.6 Hz, *m*-PhCC), 7.06 (9H, m, ^3J = 27.5 Hz, 17.0, 7.4, *p*-PhCC, *o*-NPh$_2$, *m*-NPh$_2$), 6.80 (2H, t, ^3J = 7.1 Hz, *p*-NPh$_2$), 3.90−2.78 (8H, m, O$C\underline{H}_2$, N$C\underline{H}_2$), 1.51 (3H, s, $\underline{Me}$CC), 0.27 (9H, s, CH$_2$NSi$\underline{Me}_3$), 0.09 (9H, s, CNSi$\underline{Me}_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 154.5 (*i*-NPh$_2$), 140.9 (*i*-PhCC), 131.6 (*o*-PhCC), 128.7 (*m*-NPh$_2$), 127.9 (*m*-PhCC), 126.5 (*o*-NPh$_2$), 124.6 (*p*-PhCC), 122.0 (Me$\underline{C}$C), 121.6 (*p*-NPh$_2$), 118.4 (Ph$\underline{C}$C), 76.1 (O$\underline{C}$H$_2$CH$_2$NSiMe$_3$), 73.4 (O$\underline{C}$H$_2$CH$_2$NC), 51.6 (CN$\underline{C}$H$_2$), 51.0 (SiMe$_3$N$\underline{C}$H$_2$), 14.8 ($\underline{Me}$CC), 3.1 (CNSi$\underline{Me}_3$), 1.2 (CH$_2$NSi$\underline{Me}_3$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1592 (m), 1581 (m), 1572 (m), 1560 (w), 1467

(s), 1422 (w), 1363 (s), 1323 (w), 1291 (w), 1243 (s), 1204 (w), 1193 (s), 1172 (m), 1152 (m), 1119 (w), 1107 (w), 1088 (s), 1051 (m), 1035 (m), 999 (w), 981 (m), 942 (s), 914 (m), 894 (s), 849 (s), 825 (s), 777 (m), 753 (s), 708 (m), 695 (s), 682 (w), 668 (w), 657 (w), 617 (w), 609 (m), 570 (s). EI-MS: m/z = 592 (30%) $[M]^+$, 424 (70%) $[M - NPh_2]^+$, 169 (100%) $[HNPh_2]^+$. Anal. Found (calcd for $C_{31}H_{44}N_4OSi_2Ti$): C, 63.00 (62.81); H, 7.63 (7.48); N, 9.28 (9.45).

Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Me)C(Me)NSiMe$_3$)}(NPh$_2$) **(32).** MeCCMe (0.25 mL, 3.15 mmol) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (**15**, 0.40 g, 0.63 mmol) in toluene (10 mL) and heated to 70 °C. After 3 h volatiles were removed under reduced pressure. The resultant dark brown, viscous oil was dissolved in a minimum amount of pentane (5 mL) and cooled to −78 °C. The brown solid (**32**) that formed was filtered and dried *in vacuo*. Yield: 0.26 g (78%). Anal. Found (calcd for $C_{26}H_{42}N_4OSi_2Ti$): C, 59.01 (58.85); H, 7.63 (7.98); N, 8.64 (8.37). IR (NaCl plates, Nujol mull, cm^{-1}): 1596 (s), 1501 (w), 1288 (m), 1201 (m), 1175 (w), 876 (m), 753 (m), 700 (w). Compound **32** exists as a mixture of isomers denoted "**32-exo**" and "**32-endo**" in a 5:2 ratio according to NMR integration.

Data for 32-exo. ^{1}H NMR (C$_6$D$_6$, 499.9 MHz): δ 7.12−7.07 (4H, m, *i*-NPh$_2$), 6.97 (2H, dd, ^3J = 8.3, 0.9 Hz, *p*-NPh$_2$), 6.83−6.78 (4H, m, *o*-NPh$_2$), 3.95 (1H, ddd, ^3J = 13.3, 11.2, 3.5 Hz, C<u>H</u>$_2$NC), 3.76 (1H, td, ^3J = 10.8, 3.7 Hz, OC<u>H</u>$_2$CH$_2$NSiMe$_3$), 3.40−3.29 (2H, m, OC<u>H</u>$_2$CH$_2$NC), 3.18 (1H, ddd, ^3J = 10.3, 3.4, 1.7 Hz, OC<u>H</u>$_2$CH$_2$NSiMe$_3$), 2.87−2.77 (3H, m, C<u>H</u>$_2$NSiMe$_3$, C<u>H</u>$_2$NSiMe3), 2.24 (3H, s, <u>Me</u>CNSiMe$_3$), 2.06 (3H, s, <u>Me</u>CNCH$_2$), 0.01 (9H, s, CH$_2$NSi<u>Me</u>$_3$), −0.10 (9H, s, MeCNSi<u>Me</u>$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz): δ 143.6 (*i*-NPh$_2$), 137.6 (<u>C</u>CNCH$_2$), 129.5 (*o*-NPh$_2$), 123.4 (<u>C</u>CNSiMe$_3$), 121.3 (*p*-NPh$_2$), 121.1 (*m*-NPh$_2$), 76.1 (O<u>C</u>H$_2$CH$_2$NSiMe$_3$), 74.4 (O<u>C</u>H$_2$CH$_2$NC), 51.1 (<u>C</u>H$_2$NC), 41.9 (<u>C</u>H$_2$NSiMe$_3$), 23.3 (<u>Me</u>CNSiMe$_3$), 21.5 (<u>Me</u>CNCH$_2$), 1.2 (CH$_2$NSi<u>Me</u>$_3$), 1.1 (MeCNSi<u>Me</u>$_3$) ppm.

Data for 32-endo. ^{1}H NMR (C$_6$D$_6$, 499.9 MHz): δ 7.19−7.16 (4H, m, *o*-NPh$_2$), 6.99−6.94 (2H, m, *p*-NPh$_2$), 6.88−6.83 (4H, m, *m*-NPh$_2$), 3.70−3.60 (1H, m, OC<u>H</u>$_2$CH$_2$NSiMe$_3$), 3.61−3.47 (2H, m, C<u>H</u>$_2$NC, OC<u>H</u>$_2$CH$_2$NC), 3.40−3.28 (2H, m, C<u>H</u>$_2$NSiMe$_3$), 3.11−2.97 (2H, m, OC<u>H</u>$_2$CH$_2$NSiMe$_3$, C<u>H</u>$_2$NC), 2.97−2.88 (1H, m, OC<u>H</u>$_2$CH$_2$NC), 2.01 (3H, s, <u>Me</u>CNSiMe$_3$), 1.54 (3H, s, <u>Me</u>CNCH$_2$), 0.29 (9H, s, CH$_2$NSi<u>Me</u>$_3$), 0.22 (9H, s, MeCNSi<u>Me</u>$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz): δ 153.7 (*i*-NPh$_2$), 128.8 (*o*-NPh$_2$), 123.8 (*p*-NPh$_2$), 118.7 (<u>C</u>CNCH$_2$), 118.1 (*m*-NPh$_2$), 110.7 (<u>C</u>CNSiMe$_3$), 75.0 (O<u>C</u>H$_2$CH$_2$NSiMe$_3$), 72.1 (O<u>C</u>H$_2$CH$_2$NC), 51.7 (<u>C</u>H$_2$NC), 50.1 (<u>C</u>H$_2$NSiMe$_3$), 19.9 (<u>Me</u>CNCH$_2$), 13.6 (<u>Me</u>CNCH$_2$), 2.7 (CH$_2$NSi<u>Me</u>$_3$), 1.6 (MeCNSi<u>Me</u>$_3$) ppm.

Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(Ph)C(Ph)NSiMe$_3$)}(NPh$_2$) **(31).** A solution of PhCCPh (0.11 g, 0.63 mmol) in toluene (10 mL) was added to a solution of Ti(N$_2$O)(NNPh$_2$)(py)$_2$ (**15**, 0.40 g, 0.63 mmol) in toluene (10 mL) and heated to 70 °C. After 1.5 h the volatiles were removed under reduced pressure. The resultant dark brown oil was dissolved in a minimum amount of hexanes (5 mL) and then cooled to −30 °C. The brown solid (**31**) that formed was filtered and dried *in vacuo*. Yield: 0.19 g (45%). ^{1}H NMR (C$_6$D$_6$, 499.9 MHz): δ 7.55−7.46 (4H, m, *o*-CPh), 7.21 (4H, t, ^3J = 7.8 Hz, *o*-NPh$_2$), 7.18−7.12 (2H, m, *p*-NPh$_2$), 7.04−6.93 (4H, m, *m*-CPh), 6.93−6.78 (6H, m, *m*-NPh$_2$, *p*-CPh), 3.59−3.41 (2H, m, C<u>H</u>$_2$NC), 3.26 (2H, ddt, ^3J = 10.0, 8.6, 5.0 Hz, OC<u>H</u>$_2$CH$_2$NSiMe$_3$, OC<u>H</u>$_2$CH$_2$NC), 3.20−2.97 (2H, m, C<u>H</u>$_2$NSiMe$_3$), 2.83 (1H, ddd, ^3J = 12.6, 7.3, 2.6 Hz, OC<u>H</u>$_2$CH$_2$NSiMe$_3$), 2.51 (1H, dd, ^3J = 13.4, 7.9 Hz, OC<u>H</u>$_2$CH$_2$NC), 0.32 (9H, s, CH$_2$NSi<u>Me</u>$_3$), 0.17 (9H, s, CNSi<u>Me</u>$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz): δ 153.8 (*i*-NPh$_2$), 140.1 (*i*-CPh), 137.1 (*i*-CPh), 132.7 (*o*-CPh), 131.3 (*o*-CPh), 129.1 (*o*-NPh$_2$), 128.1 (*m*-NPh$_2$), 127.4 (*m*-CPh), 127.0 (<u>C</u>CNSiMe$_3$), 126.6 (<u>C</u>CNCH$_2$), 124.3 (*p*-NPh$_2$), 120.0 (*p*-CPh), 118.1 (*p*-CPh), 75.2 (O<u>C</u>H$_2$CH$_2$NSiMe$_3$), 72.5 (O<u>C</u>H$_2$CH$_2$NC), 52.1 (<u>C</u>H$_2$NC), 51.5 (<u>C</u>H$_2$NSiMe$_3$), 2.8 (CNSi<u>Me</u>$_3$), 1.7 (CH$_2$NSi<u>Me</u>$_3$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1594 (w), 1485 (m), 1246 (m), 1187 (m), 1099 (w), 1071 (w), 1029 (w), 950 (w), 926 (m), 892 (w), 840 (s), 753 (m), 699 (m). EI-MS: m/z 654 (5%) $[M]^+$, 486 (10%) $[M - NPh_2]^+$, 73 (95%)

$[SiMe_3]^+$. Anal. Found (calcd for $C_{36}H_{46}N_4OSi_2Ti$): C, 65.87 (66.03); H, 6.93 (7.08); N, 8.58 (8.56).

X-ray Structure Determinations. X-ray data collection and processing parameters are given in the Supporting Information. 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 an Enraf-Nonius KappaCCD diffractometer. Absorption and decay corrections were applied to the data, and equivalent reflections merged.[31] The structures were solved with SIR92[32] or SHELXS-97,[33] and further refinements and all other crystallographic calculations were performed using either the CRYSTALS program suite[34] or SHELXL-97.[35] Other details of the structure solution and refinements are given in the Supporting Information (CIF data). 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 Center.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Crystallographic data in CIF format and data collection and processing parameters for the X-ray structure determinations; further details of the X-ray structures of Li$_2$N$_2$O (**13**), Ti{O(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NC(O)N(SiMe$_3$)Ar′)}{N-(NPh$_2$)C(O)N(Ar′)} (**18**), and Ti{O(CH$_2$CH$_2$NSiMe$_3$)-(CH$_2$CH$_2$NC(H)C(Tol)NSiMe$_3$)}(NPh$_2$) (**33**) and a listing of selected bond distances for all three moleucles of **15** in the asymmetric unit; additional experimental information (experimental details for **17**, **21**, **24**, **29**, **30**, **33**). This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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