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Reactions of Cyclopentadienyl-Amidinate Titanium Imido Compounds with CS_2, COS, Isocyanates, and Other Unsaturated Organic Compounds

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New single-, double-, and cross-coupling and imido group transfer reactions of cyclopentadienyl-amidinate titanium imido complexes are described. Reaction of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)Cl(py)$ (R = Me or H) with the lithiated benzamidinate $Li[PhC(NSiMe_3)_2]$ or acetamidinate $Li[MeC(N^iPr)_2]$ afforded the *tert*-butyl imido complexes $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (R = Me (**5**) or H (**7**)) and $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{MeC(N^iPr_2)_2\}$ (R = Me (**6**) or H (**8**)), respectively. Reaction of **6** with $ArNH_2$ or $TolNH_2$ (Ar = 2,6-$C_6H_3Me_2$, Tol = 4-C_6H_4Me) afforded the corresponding aryl imido complexes $Ti(\eta\text{-}C_5Me_5)(NR)\{MeC(N^iPr_2)_2\}$ (R = Ar (**9**) or Tol (**10**)). Complexes **5**, **7**, and **8** underwent cycloaddition/extrusion reactions with CS_2 and COS to form μ-sulfido dimers and ^tBuNCS and ^tBuNCO, respectively. Compound **6** reacted with COS to form ^tBuNCO and $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$, but with CS_2 additional insertion into an amidinate ligand $Ti-N^iPr$ bond occurred to form $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{N(^iPr)C(Me)N(^iPr)C(S)S\}]_2$. For the aryl imido compounds **9** and **10** the intermediate cycloaddition products $Ti(\eta\text{-}C_5Me_5)\{N(R)C(E)S\}\{MeC(N^iPr)_2\}$ (E = S or O) were observed. No further insertion of CS_2 or COS into the Ti−NR bonds occurred. All *tert*-butyl imido compounds reacted slowly with ^tBuNCO or ArNCO to form μ-oxo-bridged dimers and $^tBuNCN^tBu$ or $^tBuNCNAr$, respectively. Reaction of **9** with ^tBuNCO gave the N,O-bound ureate $Ti(\eta\text{-}C_5Me_5)\{N(Ar)C(N^tBu)O\}\{MeC(N^iPr)_2\}$, which extruded $^tBuNCNAr$ to form $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$. Reaction of **9** or **10** with aryl isocyanates gave the N,O-bound ureates $Ti(\eta\text{-}C_5Me_5)\{N(R^1)C(NR^2)O\}\{MeC(N^iPr)_2\}$ (R^1 = Ar, R^2 = Ar or Tol; R^1 = Tol, R^2 = Ar or Tol (**25**)), which did not undergo extrusion. Reaction of **25** with TolNCO gave the net cycloaddition−insertion product $Ti(\eta\text{-}C_5Me_5)\{OC(NTol)NTolC(NTol)O\}\{MeC(N^iPr)_2\}$. Several heterocumulene cross-coupling cycloaddition−insertion reactions were studied: for example, the sequential reaction of **10** with TolNCO and CO_2 gave $Ti(\eta\text{-}C_5Me_5)\{OC(O)NTolC(NTol)O\}\{MeC(N^iPr)_2\}$. Aryl imides **9** and **10** reacted with TolNCNTol to form the guanidinate complexes $Ti(\eta\text{-}C_5Me_5)\{N(Tol)C(NTol)N(R)\}\{MeC(N^iPr)_2\}$ (R = Ar or Tol). Reaction of **5** and **6** with PhNO gave $^tBuN{=}NPh$ and μ-oxo-bridged dimers; the aryl imides **9** and **10** reacted similarly. Ketone and aldehyde C═O/Ti═NR bond metathesis reactions occurred for certain *tert*-butyl and aryl imido compounds with MeCOMe, PhCOPh, PhCOH, and PhCOMe, and in some instances intermediates were observed. Slow imide/imine metathesis occurred between $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{PhC(N^iPr_2)_2\}$ and PhCH(NTol). Compound **6** rapidly converted $PhCONH_2$ and $Me(CH_2)_4CONH_2$ to the corresponding nitriles, but the analogous reaction with $^tBuCONH_2$ was slower. Several other titanium imido compounds and $Ti(NMe_2)_2Cl_2$ were also evaluated for the $PhCONH_2$ dehydration reaction.

Introduction

Terminal transition metal imido compounds have been of continuing interest for over two decades, and a good deal of this chemistry has been reviewed.[1−20] In terms of reaction chemistry, the imido ligand (NR, where R is typically an organic group) can act as either a spectator ligand (as found in imido-supported olefin metathesis[7,10,16] or Ziegler−Natta polymerization[19] catalysts) or as a reactive site (typically via coupling of the M═NR bond with unsaturated substrates, but also via C−H bond activation). Some of the most reactive metal−imido

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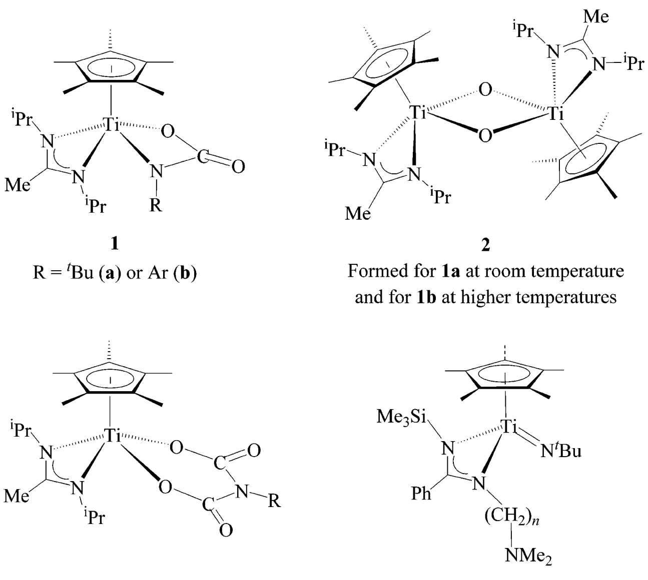
Chart 1



1

R = ^{t}Bu (**a**) or Ar (**b**)

2

Formed for **1a** at room temperature and for **1b** at higher temperatures

3

Formed for **1b** only

4

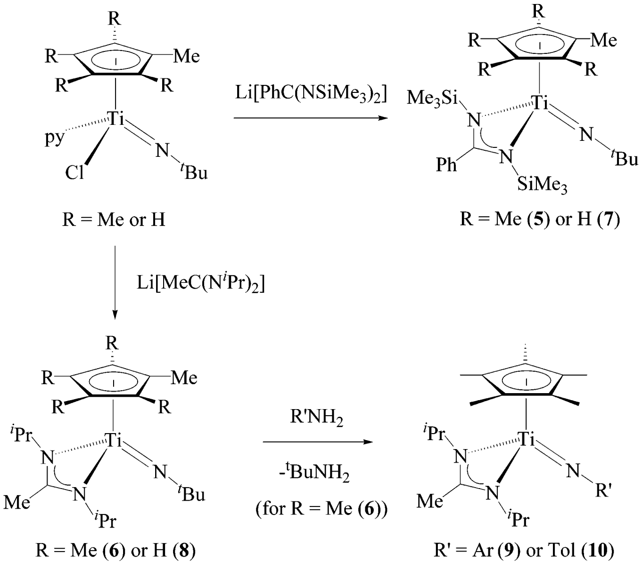
$n = 2$ or 3

linkages have been found for the group 4 elements.[3,4,11,12,15,20,21] In this contribution we focus on titanium imido chemistry in particular.[22]

As part of our program in this area,[4,11,20] we reported preliminary results for the reaction of the new cyclopentadienyl-amidinate systems Ti(η-C_5Me_5)(NR){MeC(N^{i}Pr)$_2$}[23] (R = ^{t}Bu or Ar (2,6-$C_6H_3Me_2$)) with CO_2.[23] Cycloaddition reactions of titanium imides with CO_2 have been reported for a number of other systems,[24−27] but the cyclopentadienyl-amidinate systems were especially interesting because the reaction products ultimately formed showed a marked dependency on the imido NR group. In the case when R = ^{t}Bu, CO_2 cycloaddition (to form N,O-bound carbamate complex **1a**, Chart 1) was followed by cycloreversion (extrusion of ^{t}BuNCO) to yield the μ-oxo-bridged dimer **2**, whereas the corresponding reaction for **1b** (R = Ar) yielded exclusively the double CO_2 activation product **3** where a second CO_2 molecule has inserted into the carbamate Ti−N bond of **1b**. Motivated by the potential of cyclopentadienyl-amidinate titanium imido complexes to offer additional variation or control of CO_2 reactivity, we recently reported comprehensive experimental and DFT computational studies of the reactions of various pendant arm functionalized complexes (for example **4**, Chart 1) with CO_2.[28] The nature of the pendant arm affected both the CO_2 and isocyanate extrusion reaction steps.

In this paper we report the synthesis and characterization of new cyclopentadienyl-amidinate titanium imido complexes, together with a detailed study of their reactions with other organic substrates, namely, CS_2, COS, isocyanates, carbodiimides, PhNO, ketones, PhCOH, PhC(NTol)H, and primary organic amides. A part of the work was communicated previously.[23]

Scheme 1. Synthesis of Cyclopentadienyl-Amidinate Imido Compounds



Results and Discussion

Synthesis of Cyclopentadienyl-Amidinate Imido Compounds. The half-sandwich *tert*-butyl imido compounds Ti(η-C_5R_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (R = H or Me (**5**))[29,30] have previously been prepared from the imido-benzamidinate complex Ti(N^{t}Bu){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$.[31] To develop the chemistry of cyclopentadienyl-amidinate imido compounds further, it was necessary to be able to vary the imido and amidinate ligand N-substituents, as well as the cyclopentadienyl ligand substituents. However, our attempts to develop a wider range of amidinate-imido starting complexes Ti(NR){R^2C(NR^1)$_2$}Cl(py)$_2$ (R^2, R^1 other than phenyl, SiMe$_3$; R = ^{t}Bu or aryl) met with frustration, the products being ill-defined and rather capricious in their handling. This is consistent with our previous report that although reaction of Li[PhC(NSiMe$_3$)$_2$] with Ti(N^{t}Bu)Cl$_2$(py)$_3$ afforded the monomeric benzamidinate compound Ti(N^{t}Bu){PhC(NSiMe$_3$)$_2$}Cl(py)$_2$,[31] the corresponding reaction with Li[MeC(NCy)$_2$] (Cy = cyclohexyl) gave a poorly soluble, dimeric product,[30] thus showing the sensitivity of the reaction and products to the particular amidinate ligand employed.

Our presently favored route to cyclopentadienyl-amidinate imido compounds is summarized in Scheme 1 and starts from the previously reported[32] half-sandwich compounds Ti(η-C_5R_4Me)(N^{t}Bu)Cl(py) (R = Me or H). As proof of method, we found that reaction of Ti(η-C_5Me_5)(N^{t}Bu)Cl(py) with Li[PhC(NSiMe$_3$)$_2$] gave Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**5**) in 41%

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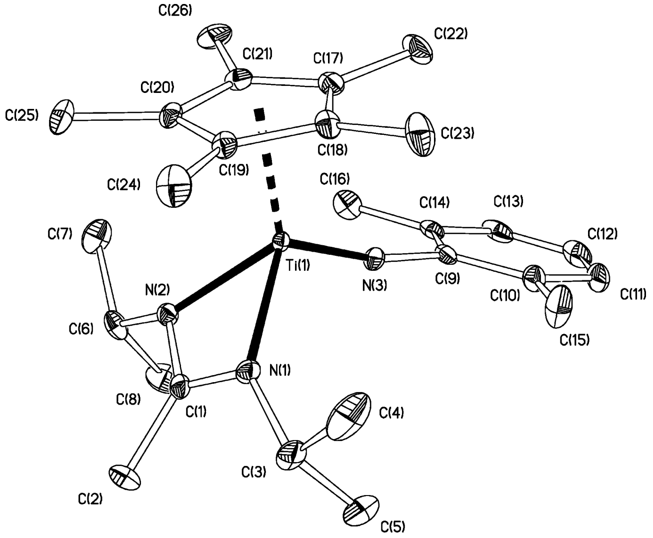


Figure 1. Displacement ellipsoid plot (25% probability) of $Ti(\eta\text{-}C_5Me_5)(NAr)\{MeC(N^iPr)_2\}$ (**9**). H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ti(\eta\text{-}C_5Me_5)(NAr)\{MeC(N^iPr)_2\}$ (9)[a]

Ti(1)−N(1)	2.094(2)	$Ti(1)\cdots Cp_{cent}$	2.085
Ti(1)−N(2)	2.099(2)	C(1)−N(1)	1.335(4)
Ti(1)−N(3)	1.738(2)	C(1)−N(2)	1.339(4)
Ti(1)−N(3)−C(9)	168.9(2)	$Cp_{cent}\cdots Ti(1)-N(2)$	119.5
$Cp_{cent}\cdots Ti(1)-N(1)$	119.1	$Cp_{cent}\cdots Ti(1)-N(3)$	121.4

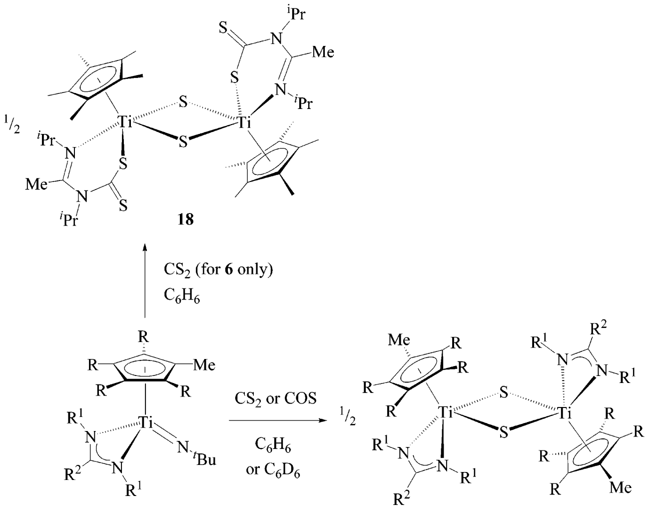
[a] Cp_{cent} refers to the C_5Me_5 ring carbon centroid.

yield after high-vacuum sublimation (Scheme 1). This yield is somewhat lower than the 79% reported for the previous route starting from LiC_5Me_5 and $Ti(N^tBu)\{PhC(NSiMe_3)_2\}Cl(py)_2$.[30] However, the new benzamidinate and diisopropylacetamidinate complexes $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**6**, 98% yield) and $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{R^2C(NR^1)_2\}$ (R^1 = $SiMe_3$, R^2 = Ph (**7**, 93% yield); R^1 = Me, R^2 = ^iPr (**8**, 96% yield)) were obtained in excellent yield.

Since it is known[23−25] that the cycloaddition chemistry of aryl imido complexes can be rather different from that of the *tert*-butyl imido homologues, we also targeted aryl imido compounds with sterically different imido *N*-aryl substituents, focusing on the pentamethylcyclopentadienyl-diisopropylacetamidinate-supporting ligand set. An arylamine/*tert*-butyl imide exchange protocol[33] was used, and reaction (Scheme 1) of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**6**) with $ArNH_2$ (Ar = 2,6-$C_6H_3Me_2$) or $TolNH_2$ (Tol = 4-C_6H_4Me) at room temperature afforded the compounds $Ti(\eta\text{-}C_5Me_5)(NR)\{MeC(N^iPr)_2\}$ (R = Ar (**9**, 95% yield) or Tol (**10**, 50% yield)).

The molecular structure of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**9**) determined by single crystal X-ray diffraction is shown in Figure 1. The compound is monomeric with a three-legged piano stool geometry and is consistent with the solution NMR data. The selected bond distances and angles listed in Table 1 are within the previously reported ranges[34,35] for titanium(IV) complexes of the three types of ligand present. The reasonably linear Ti═N−Ar linkage (Ti(1)−N((3)−C(9) = 168.9(2)°) suggests that the arylimido nitrogen (N(3)) is formally sp-hybridized and able to act as a four-electron donor to the titanium center, which achieves an overall valence electron count of 16. As seen previously with the $MeC(N^iPr)_2$ ligand,[36] the methyl groups of the isopropyl substituents are oriented away from the backbone methyl group (C(2)), presumably to minimize intraligand steric repulsions. Although structural data for nearly 100 cyclopentadienyl-amidinate transition metal compounds are listed in the Cambridge Crystallographic Database, including ca. 10 for titanium systems in particular,[37−41] compound **9** is the first crystallographically characterized group 4 imido complex within this family.

Scheme 2. Reactions of Cyclopentadienyl-Amidinate *tert*-Butyl Imido Compounds with CS_2 and COS



	R	R^1	R^2
5	Me	$SiMe_3$	Ph
6	Me	^iPr	Me
7	H	$SiMe_3$	Ph
8	H	^iPr	Me

	R	R^1	R^2
11	Me	$SiMe_3$	Ph
12	Me	^iPr	Me (*not for CS_2*)
13	H	$SiMe_3$	Ph
14	H	^iPr	Me

The rest of this contribution describes the reactions of the cyclopentadienyl-amidinate imido complexes with a range of organic substrates.

Reactions with CS_2 and COS. As mentioned, our previous studies of the reactivity of Ti═NR bonds in cyclopentadienyl-amidinate complexes have focused exclusively on the reactions with CO_2.[23,28] We therefore start our discussion with the reactions with sulfur-containing analogues of CO_2. A number of reactions of imido compounds with CS_2 have been described previously,[25,26,42−44] and the usual reaction pathway is cycloaddition followed by extrusion to form the corresponding isothiocyanate and metal sulfide. Reactions between the *tert*-butyl imido compounds **5**−**8** and CS_2 and COS are summarized in Scheme 2. The corresponding reactions of the aryl imido

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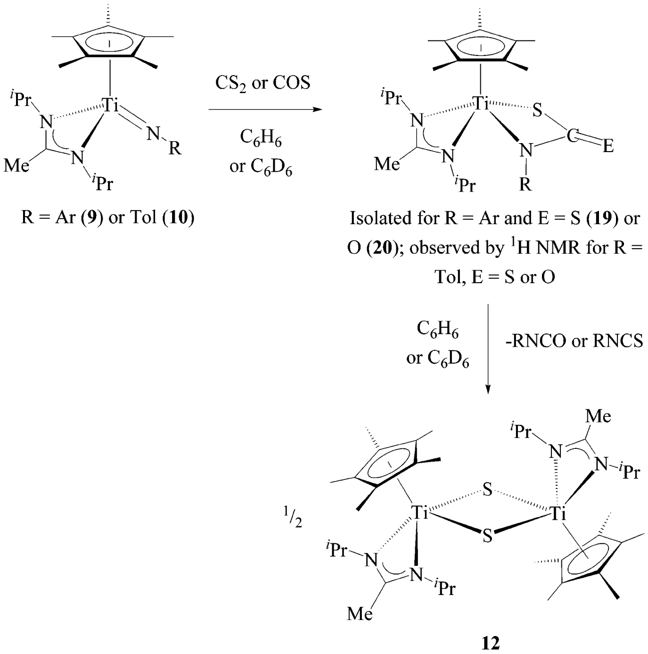
Scheme 3. Reactions of Ti(η-C_5Me_5)(NR){MeC(N^iPr)$_2$} (R = Ar (9) or Tol (10))



compounds **9** and **10** are summarized in Scheme 3 and discussed below.

The reactions with CS_2 and COS were all slower than the ones reported previously for CO_2,[23,28] with those for CS_2 being the slowest. For example, when followed by ^{1}H NMR in C_6D_6, the reaction of Ti(η-C_5H_4Me)(N^tBu){PhC($NSiMe_3$)$_2$} (**7**) with COS (to form **13**) was complete within 14 h, whereas that with CS_2 took 4−5 days under otherwise identical conditions. These relative rates of reaction are consistent with previous reports for reactions of multiple bonds with these substrates.[45] Second, for a given substrate, the more sterically encumbered C_5Me_5-supported compounds reacted at the slowest rates. With the exception of that between **6** and CS_2 (see below), the reactions of **5**−**8** with CS_2 formed the dimeric sulfido-bridged complexes [Ti(η-C_5R_4Me)(μ-S){R^2C(NR^1)$_2$}]$_2$ (Scheme 2) and *tert*-butyl isothiocyanate. The compounds **11**, **13**, and **14** were isolated on a preparative scale (30−68% yield), and **11** and **13** were crystallographically characterized (see below). Compound **12** (Scheme 2) could not be obtained this way and was made on a preparative scale from **6** and COS. NMR tube scale reactions between COS and **5**, **7**, and **8** showed that the corresponding μ-sulfido dimers (and ^{t}BuNCO) were also quantitatively formed. The reactions to form **11**−**14** are assumed to proceed via a cycloaddition−extrusion mechanism, although no NMR evidence for the likely (di)thiocarbamate intermediates Ti(η-C_5R_4-Me){N(^{t}Bu)C(E)S}{R^2C(NR^1)$_2$} (E = S or O) was found. The reactions of COS with **5**−**8** were exclusively selective for C=S bond cleavage and, when followed by ^{1}H NMR, showed no evidence for the formation of ^{t}BuNCS or the corresponding oxo-bridged dimers [Ti(η-C_5R_4Me)(μ-O){R^2C(NR^1)$_2$}]$_2$ (R^1 = $SiMe_3$, R^2 = Ph, R = Me (**15**) or H (**16**);[46,47] R^1 = ^{i}Pr, R^2 = Me, R = Me (**2**)[23] or H (**17**)[46,47]). Selective C=S bond cleavage of COS in reactions with multiply bonded compounds is precedented.[45]

Table 2. Selected Distances (Å) and Angles (deg) for [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (11) and [Ti(η-C_5H_4Me)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (13)[a]

compound 11		compound 13	
Ti(1)−N(1)	2.193(3)	Ti(1)−N(1)	2.135(3)
		Ti(1)−N(1B)	2.197(3)
Ti(1)−S(1)	2.259(1)	Ti(1)−S(1)	2.304(1)
		Ti(1)−S(1B)	2.363(1)
Ti(1)−Cp_{cent}	2.101	Ti(1)−Cp_{cent}	2.061
Cp_{cent}−Ti(1)−N(1)	111.2	Cp_{cent}−Ti(1)−N(1)	112.5
		Cp_{cent}−Ti(1)−N(1B)	108.2
Cp_{cent}−Ti(1)−S(1)	113.6	Cp_{cent}−Ti(1)−S(1)	119.3
		Cp_{cent}−Ti(1)−S(1B)	110.1
Ti(1)−S(1)−Ti(1C)	92.44(7)	Ti(1)−S(1)−Ti(1B)	91.73(4)

[a] Cp_{cent} refers to the C_5Me_5 or C_5H_4Me ring carbon centroid.

Unexpectedly, the reaction of Ti(η-C_5Me_5)(N^tBu){MeC(N^iPr)$_2$} (**6**) with an excess of CS_2 gave [Ti(η-C_5Me_5)(μ-S){N(^{i}Pr)C(Me)N(^{i}Pr)C(S)S}]$_2$ (**18**, Scheme 2) in 80% isolated yield after 10 days at room temperature. Compound **18** is formed by net CS_2 insertion into a Ti−$N_{amidinate}$ bond as well as attack at the Ti=N^tBu bond (CS_2 cycloaddition/^{t}BuNCS extrusion). The NMR and IR spectra and combustion elemental analysis of **18** were consistent with the proposed structure, and the EI mass spectrum showed the expected parent ion at m/z = 864 with the correct isotope distribution. When the reaction between **6** and exactly 1 equiv of CS_2 was followed by ^{1}H NMR in C_6D_6, ca. 50% conversion to **18** and ^{t}BuNCS was observed, and the rest of the **6** remained unreacted. No reaction was observed between the dimeric sulfide [Ti(η-C_5Me_5)(μ-S){MeC(N^iPr)$_2$}]$_2$ (**12**, prepared from **6** and COS) and CS_2 over three weeks. These observations suggest that formation of **18** proceeds via initial CS_2 insertion into a Ti−$N_{amidinate}$ followed by a relatively fast cycloaddition to the Ti=N^tBu bond (or vice versa), extrusion of ^{t}BuNCS, and dimerization of the so-formed transient terminal monomeric sulfide Ti(η-C_5Me_5)(S){N(^{i}Pr)C(Me)N(^{i}Pr)C(S)S}. Although the insertion of CS_2 into a metal−$N_{amidinate}$[48] or related[49] bond is precedented, it is not apparent why the reaction of **6** with CS_2 differs from those of the other imides studied.

The molecular structures of [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**11**) and [Ti(η-C_5H_4Me)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**13**) are compared in Figure 2, and selected distances and angles are listed in Table 2. The structures are very similar and reveal the mutual *trans* arrangement of the cyclopentadienyl rings as well as the dimeric nature of the products, which may be described as edge-shared, four-legged piano stools. The distances and angles are within previously reported ranges for the ligands present.[34,35] The slightly longer Ti−Cp_{cent} distance in **11** may be attributed to greater steric influence of the C_5Me_5 ring, as may the slightly longer Ti(1)−N(1) distance compared to the average value in **13**. The observation of longer average Ti−S distances in **13** may be a consequence of these other shorter bond distances (i.e., Ti−Cp_{cent}, Ti−N) leading to more repulsion between the metal centers (note also that the cyclopentadienyl ring methyl groups in **13** are oriented over the Ti_2(μ-S)$_2$ moiety, toward the adjacent Ti{PhC($NSiMe_3$)$_2$} moiety).

Scheme 3 summarizes the reactions of the aryl imido compounds Ti(η-C_5Me_5)(NR){MeC(N^iPr)$_2$} (R = Ar (**9**) or Tol (**10**)) with CS_2 and COS. These were all faster than those of the *tert*-butyl imides **6** and **8**. Again, the reactions with CS_2 were slower that those with COS, and the tolyl imido compound

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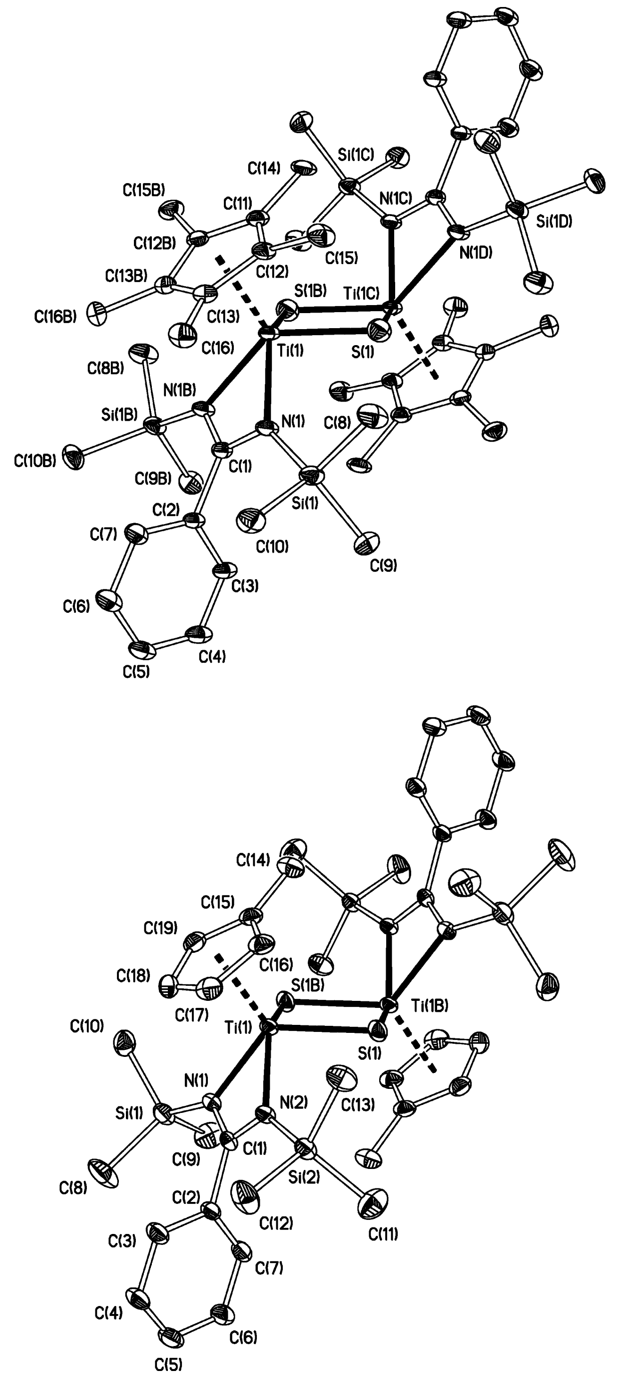

Figure 2. Displacement ellipsoid plots (25% probability) of [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**11**, top) and [Ti(η-C_5H_4Me)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**13**, bottom). H atoms are omitted for clarity.

10 reacted more quickly than the more sterically crowded **9**. NMR tube scale experiments showed that the ultimate products of these reactions were the sulfide-bridged dimer **12** and either RNCS (CS_2 reactions; R = Ar for **9** or Tol for **10**) or RNCO (COS reactions). At intermediate stages of reaction resonances attributable to likely (di)thiocarbamate intermediates were observed (Scheme 3). In preparative scale reactions of **9** with CS_2 and COS the compounds Ti(η-C_5Me_5){N(Ar)C(S)S}{MeC-(N^iPr)$_2$} (**19**, 60% yield) and Ti(η-C_5Me_5){N(Ar)C(O)S}{MeC-(N^iPr)$_2$} (**20**, 70% yield), respectively, could be isolated. The IR spectrum of **20** showed a ν(C=O) band at 1672 cm^{-1}, which was absent in the IR spectrum of **19**. This, and the quantitative formation of **12** and ArNCO on decomposition of **20**, supports the N,S-bound thiocarbamate isomers proposed in Scheme 3. The (di)thiocarbamate intermediates formed from the tolyl imide **10** and CS_2 or COS extruded TolNCS or TolNCO (forming **12**) much more quickly than **19** or **20**. NMR tube scale reactions of **10** showed that the extrusion products had started to be formed in significant amounts even before all of **10** had finished reacting, and the likely (di)thiocarbamate intermediates could not be isolated on a preparative scale.

In no cases were products of a second CS_2 or COS insertion into a Ti−N$_{\text{carbamate}}$ bond of **19** or **20** seen, in contrast to the corresponding reactions with CO_2 (e.g., reaction of **1b** (Chart 1) to form dicarboxylate **3**[23]). It is interesting that the more sterically crowded intermediate carbamates **19** and **20** (formed from **9**) are *more stable* to isocyanate extrusion than their homologues formed from **10**. This recurrent theme (vide infra and ref 28) in the reactions of cyclopentadienyl-amidinate systems contrasts with reports for other systems[12,43] and may reflect difficulties associated with accessing the appropriate transition state for the more sterically crowded cyclopentadienyl-amidinate systems.[50]

Reactions with Organic Isocyanates and Carbodiimides. Reactions with Isocyanates (1:1 ratio). The reactions of metal imido compounds (L)M=NR with isocyanates R′NCO are well established and in the first instance can lead to either N,O- or N,N-bound ureate complexes, (L)M{N(R)C(NR′)O} or (L)M-{N(R)C(O)N(R′)}. These can often be isolated[24,25,51−59] but can also extrude either a molecule of carbodiimide (RN=C=NR′) to form the corresponding metal oxo compound[44,55−57] or a molecule of a different isocyanate (RNCO), leading to a new metal imido compound (L)M=NR′.[26,53,58] In addition, we have previously shown that certain first-formed titanium ureate species can reversibly insert a further equivalent of isocyanate, forming transient N,N-bound biuret species (i.e., compounds analogous to **3** (Chart 1) but with the metal-bound O atoms replaced by NR).[24] Later transition metal N,N-bound biuret complexes have also been formed (sometimes reversibly) from the reactions of metal ureate complexes with isocyanates,[49,60−62] although in these cases metal imido compounds were not the precursors to the ureates themselves. Given their interesting reactions with CO_2 and the rich chemistry of metal imido

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(50) For example, structurally characterized pentamethylcyclopentadienyl complexes Ti(η-C_5Me_5){N^{t}BuC(O)O}{$Me_3SiNC(Ph)N(CH_2)_nNMe_2$} (formed from CO_2 and **4**) undergo ^{t}BuNCO extrusion over 1−2 h at room temperature, whereas the monomethylcyclopentadienyl homologues Ti(η-C_5H_4Me){N^{t}BuC(O)O}{$Me_3SiNC(Ph)N(CH_2)_nNMe_2$} undergo first-order, concentration-independent decay rapidly above −25 °C.[28]

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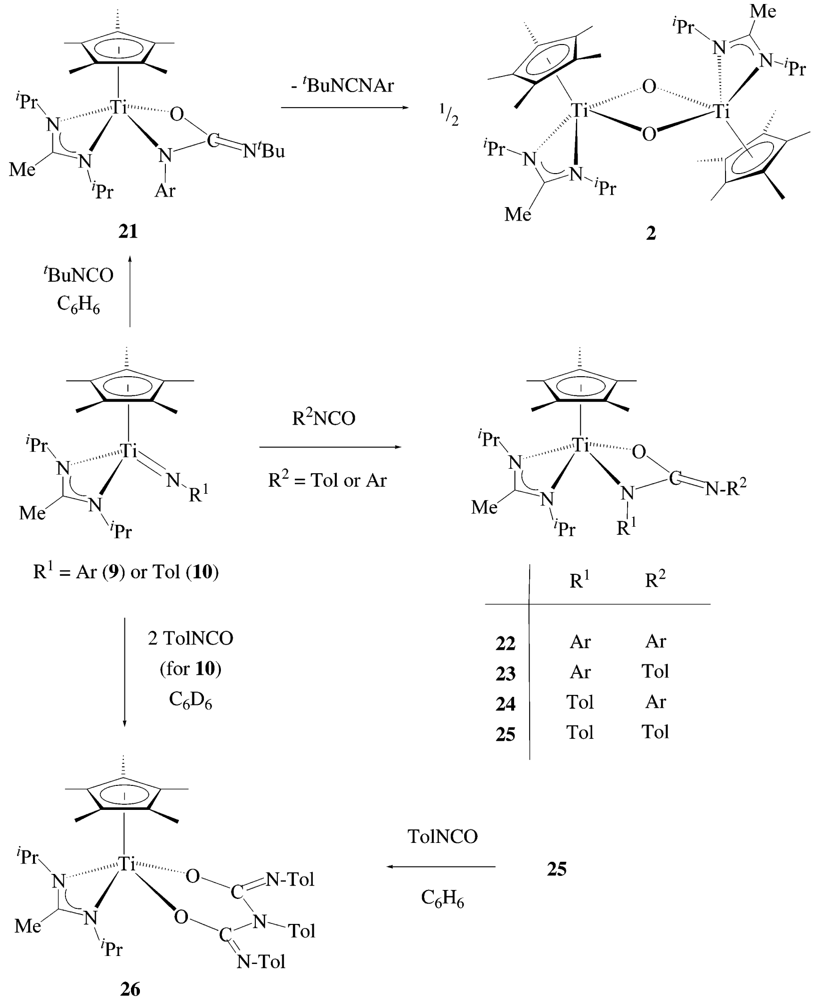
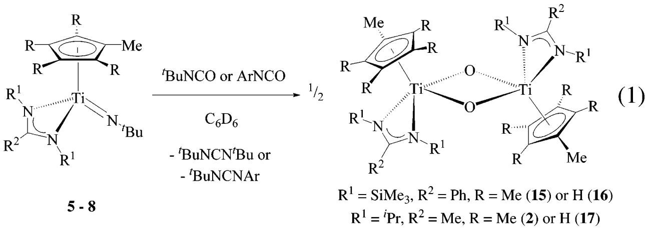
Scheme 4. Reactions of Arylimido Compounds Ti(η-C$_5$Me$_5$)(NR){PhC(N^{i}Pr$_2$)$_2$} (R = Ar (9) or Tol (10)) with *tert*-Butyl and Aryl Isocyanates



	R^1	R^2
22	Ar	Ar
23	Ar	Tol
24	Tol	Ar
25	Tol	Tol

compounds with isocyanates in general, we decided to explore in detail reactions of cyclopentadienyl-amidinate titanium imido compounds with isocyanates.

 (1)

R^1 = SiMe$_3$, R^2 = Ph, R = Me (**15**) or H (**16**)
R^1 = ^{i}Pr, R^2 = Me, R = Me (**2**) or H (**17**)

The *tert*-butyl imido compounds gave different final products from the aryl imido analogues. Equation 1 summarizes the NMR tube scale (C$_6$D$_6$) reactions of compounds **5**−**8** with ^{t}BuNCO and of **6** and **7** with ArNCO. In all cases the products were the known[63,64] carbodiimide ^{t}BuNCN^{t}Bu or ^{t}BuNCNAr (identified by their GC-MS and/or ^{1}H NMR spectra) and the corresponding μ-oxo-bridged dimer **2** or **15**−**17**. The reactions with ^{t}BuNCO were very slow indeed at room temperature, with half-lives ranging from 4 to 18 days (this being for the reaction of **5** with ^{t}BuNCO). The reactions are considerably slower that those of **6** with CO$_2$, in which instantaneous formation of carbamate **1a** (Chart 1) occurs.[23] Since μ-oxo-bridged dimers are ultimately formed, it is likely that N,O-bound ureate intermediates are involved, but no resonances for such species were observed except in the reaction of the least sterically crowded *tert*-butyl imide, namely, **8**. However, these were minor peaks compared to the starting compound **8** and μ-oxo product **17**, and it was not deemed feasible to attempt to isolate this compound on a preparative scale. Structurally characterized N,O-bound ureate products are described in due course below.

The reactions of **6** or **7** with ArNCO were noticeably faster, with half-lives of ca. 24 and 12 h, respectively, for consumption of the starting imides. The slightly faster rate of reaction may reflect the reduced steric factors associated with ArNCO in comparison with ^{t}BuNCO and perhaps the different electrophilicities of the central carbon in these substrates. As mentioned, the ultimate products of the reactions are the oxo dimers **2** and **16** and ^{t}BuNCNAr. Additional resonances attributed to N,O-bound ureate intermediates Ti(η-C$_5$R$_4$Me){N(^{t}Bu)C(NAr)O}{MeC(NR^1)$_2$} were seen at intermediate reaction times. However, these were always alongside those of the starting materials and final reaction products, and again no attempt was made to isolate them on a preparative scale. The ready collapse of all these presumed cycloaddition products to the final μ-oxo products in eq 1 parallels the behavior found with CO$_2$, CS$_2$, and COS. We therefore turned our attention to reactions of aryl imido compounds, which we hoped would give more stable metallocyclic products. Scheme 4 summarizes the reactions of the aryl imides **9** and **10** with various isocyanates. Variation of

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the imido N-substituents 2,6-$C_6H_3Me_2$ and *p*-tolyl provided for some control of steric influence. Reaction of **9** with ^{t}BuNCO ultimately gave quantitative conversion to the μ-oxo dimer **2** and ^{t}BuNCNAr[64] after ca. 12 h. In contrast to the reactions of **5**−**8**, however, conversion of **9** to the N,O-bound ureate Ti(η-C_5Me_5){N(Ar)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$} (**21**) intermediate was complete after ca. 4 h and before significant decay to **2** and ^{t}BuNCNAr had occurred, thus allowing its isolation as a sticky oil in 27% yield. The tolyl imido compound **10** also reacted with ^{t}BuNCO to form μ-oxo-bridged dimer **2** (together with ^{t}BuNCNTol). However, although the initial reaction to form the likely intermediate Ti(η-C_5Me_5){N(Tol)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$} was faster than for the corresponding reaction of **9**, the subsequent extrusion reaction to form **2** was also faster (complete within ca. 3 h) and it was not possible to isolate this intermediate. Again (as noted above) it appears that the bulkier N-Ar substituent in **21** confers slightly greater stability on the intermediate cycloaddition species than the smaller N-Tol substituent.

The instability of **21** in solution hindered further purification, but its NMR and IR spectra support the structure shown in Scheme 4. The MeC(N^{i}Pr)$_2$ ligand isopropyl groups appear as two sharp apparent septets and four doublets in the ^{1}H NMR spectrum. The *ortho*-methyl groups of the Ar N-substituent are sharp and inequivalent at room temperature, consistent with restricted rotation about the N−C$_{ipso}$ bond and thus this group being attached to the metal-bound nitrogen in a rather crowded position (rather than being attached to the less crowded exocyclic C═*N* nitrogen). These spectroscopic features are analogous to the structurally characterized compounds **22** and **23** (Scheme 4) described below, which only differ in having Ar or Tol groups in place of the ^{t}Bu group in **21**. A band at 1652 cm^{-1} in the IR spectrum of **21** is consistent with a C═N^{t}Bu functional group. Finally we note that the resonances for **21** are not the same as those tentatively assigned to the putative intermediate Ti(η-C_5Me_5){N(^{t}Bu)C(NAr)O}{MeC(N^{i}Pr)$_2$} (an isomer of **21**) formed in the reaction of **6** with ArNCO (eq 1).

In contrast to the instability of **21**, the cycloaddition products **22**−**25** (Scheme 4) formed between **9** and **10** and TolNCO or ArNCO were stable for weeks at room temperature (decomposition to unidentified mixtures occurred only at elevated temperatures). The compounds **23** and **24** are isomers of each other (the structure of **23** was confirmed by X-ray crystallography; see below) but do not interconvert or equilibrate in solution even after several weeks. This is in contrast to Woo's N,O-ureate compound Zr{N(−2,6-$C_6H_3{}^iPr_2$)C(N^{t}Bu)O}(TTP) (formed from Zr(N-2,6-$C_6H_3{}^iPr_2$)(TTP) and ^{t}BuNCO), which slowly isomerizes to Zr{N(^{t}Bu)C(N-2,6-$C_6H_3{}^iPr_2$)O}(TTP) (H_2TTP = *meso*-tetra-*p*-tolylporphyrin) over a number of weeks.[57]

The NMR spectra of **22**−**25** show the absence of molecular symmetry (inequivalent ^{i}Pr groups for the MeC(N^{i}Pr)$_2$ ligand). For **22** and **25** this is good evidence for the proposed N,O-bound complexes (alternative isomers with N,N-bound ureate ligands would be C_s symmetrical species); the symmetry of the N,N-bound ureate isomers of **23** and **24**, however, would also be C_1. The methyl groups of the Ar moiety in **23** appear as two sharp resonances, consistent with this group being rather sterically hindered (see also the crystal structure of this compound below). In its isomer **24**, however, the two methyl groups appear as a singlet (relative intensity 6 H), showing that the exocyclic C═NAr site is significantly less crowded. In structurally characterized **22** one Ar substituent exhibits hindered rotation (presumably the one closest to the titanium) and the other does not.

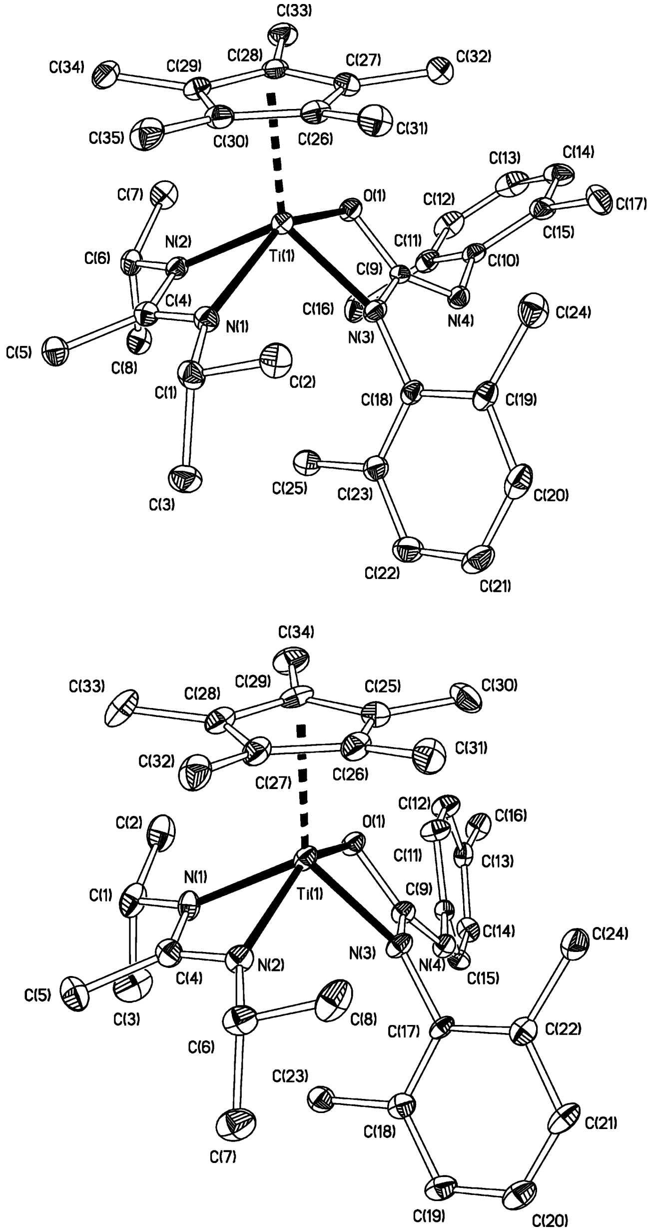


Figure 3. Displacement ellipsoid plots (20% probability) of Ti(η-C_5Me_5){N(Ar)C(NR)O}{MeC(N^{i}Pr)$_2$} (R = Ar (**22**, top) or Tol (**23**, bottom)). H atoms are omitted for clarity.

The IR data for the new compounds are consistent with the proposed structures and feature ν(C═N) bands in the range 1609−1616 cm^{-1} (somewhat lower than the corresponding band in **21**). The ν(C═O) band in the corresponding CO_2 cycloaddition product Ti(η-C_5Me_5){N(Ar)C(O)O}{MeC(N^{i}Pr)$_2$} (**1b**) was higher, as expected (ν(C═O) = 1669 cm^{-1}).[23] The ν(C═O) bands in the N,N-bound ureates Ti{N(Ph)C(O)N(R)}(Me$_4$taa) (H_2Me_4taa = tetramethyldibenzotetraaza[14]annulene; R = Ph or Tol) appear in the range 1626−1630 cm^{-1}.[24] Conclusive evidence of the N,O-coordination is provided by the X-ray structures of **22** and **23**, which are shown in Figure 3. Selected distances and angles are given in Table 3.

The molecular structures of **22** and **23** confirm those proposed in Scheme 4. The four-legged piano stool molecules contain η^5-bound C_5Me_5 and bidentate MeC(N^{i}Pr)$_2$ ligands along with the expected N,O-bound ureate ligands. The associated distances and angles are very similar for the two compounds, as expected, since they differ only in the identity of the exocyclic N(4) substituent. However, the orientation of these rings differs

Table 3. Selected Distances (Å) and Angles (deg) for $Ti(\eta\text{-}C_5Me_5)\{N(Ar)C(NR)O\}\{MeC(N^iPr)_2\}$ (R = Ar (22) or Tol (23))[a]

parameter	compound **22**	compound **23**
Ti(1)−N(1)	2.149(3)	2.024(5)
Ti(1)−N(2)	2.027(3)	2.150(5)
Ti(1)−N(3)	1.995(3)	1.994(4)
Ti(1)−O(1)	1.981(3)	1.973(4)
Ti(1)−Cp_{cent}	2.094	2.106
C(9)−N(4)	1.283(5)	1.283(7)
N(1)−Ti(1)−N(2)	63.83(13)	63.8(2)
N(3)−Ti(1)−O(1)	66.84(12)	66.6(2)
Cp_{cent}−Ti(1)−N(1)	112.2	115.2
Cp_{cent}−Ti(1)−N(2)	114.7	111.7
Cp_{cent}−Ti(1)−N(3)	136.1	135.7
Cp_{cent}−Ti(1)−O(1)	104.1	105.4
C(9)−N(4)−C(10)	119.0(3)	121.5(4)
C(9)−N(4)−C(10)−C(15)	109.3	14.4

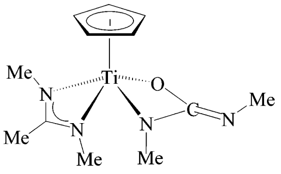
[a] Cp_{cent} refers to the C_5Me_5 ring carbon centroid.

significantly. For **22** the aryl ring lies approximately perpendicular to the {Ti(1)O(1)C(9)N(3)} titanocyclic core (dihedral angle C(9)−N(4)−C(10)−C(15) = 109.3°), whereas in **23** the tolyl ring is nearly coplanar with the titanocycle (dihedral angle C(9)−N(4)−C(10)−C(15) = 14.4°). This is due to the presence of the *ortho*-methyl substituents in **22**. However, since these methyls appear as a singlet in the ^1H and ^{13}C NMR spectra (vide supra), the barrier to rotation about the N(4)−C_{ipso} bond must be relatively small. The average distances and angles subtended at Ti(1) in the two structures are within the usual ranges,[34,35] and those to the C_5Me_5 and amidinate ligands are comparable to the ones found in the starting imide **9** and the dicarboxylate $Ti(\eta\text{-}C_5Me_5)\{OC(O)N(Ar)C(O)O\}\{MeC(N^iPr)_2\}$ (**3**).[23] However, within both **22** and **23** the individual Ti−$N_{amidinate}$ distances are significantly different (Δ(Ti−N) = 0.122(6) and 0.126(10) Å), with the bond *cis* to the carbamate N-Ar moiety being longer. This is attributed to steric effects of the bulky aryl substituent. The Cp_{cent}−Ti(1)−N(3) angles (av 135.9°) are significantly larger than the Cp_{cent}−Ti(1)−O(1) (av 104.8°) angles, and this also reflects the steric influence of the bulky Ar substituent at N(3). This aryl ring lies perpendicular to the {Ti,N,C,O} titanocycle core and is consistent with the NMR spectra, which showed two resonances for the individual *ortho*-methyl groups. The greater barrier to rotation about the N(3)−C_{ipso} bond in **22** compared to rotation about N(4)−C_{ipso} (as implied by the solution NMR data) is consistent with the greater steric crowding around the former and the higher coordination number of N(3) compared to N(4).

Although only one other crystallographically characterized ureate complex of titanium has been reported,[25] they are in general well established (a further 10 such structures for other metals are recorded in the Cambridge Structural Database[34,35]). However, only two crystallographically characterized N,O-ureate complexes have been reported for any metal, namely, Woo's $Zr\{N(-2,6\text{-}C_6H_3{}^iPr_2)C(N^tBu)O\}(TTP)$ and its isomer $Zr\{N(^tBu)C(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)O\}(TTP)$.[57]

The factors controlling the preferred ureate ligand coordination mode may be rather finely balanced. Thus while $Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(TTP)$ reacts with ^tBuNCO to form the N,O-bound ureate complex $Zr\{N(-2,6\text{-}C_6H_3{}^iPr_2)C(N^tBu)O\}(TTP)$,[57] we found that the closely related $Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)(Me_4taa)$ (with the same imido N-substituent) reacts with the same isocyanate to give the structurally authenticated N,N-bound ureate $Zr\{N(-2,6\text{-}C_6H_3{}^iPr_2)C(O)N(^tBu)\}(Me_4taa)$ as the only observed product.[24] Since Me_4taa provides a more "open" zirconium coordination site than TTP, it would appear that steric factors may be important in selecting the preferred ureate coordination mode. We also found that $Ti(N^tBu)(Me_4taa)$ reacts with $OCN\text{-}4\text{-}C_6H_4NO_2$ to give an N,N-bound ureate product, whereas with ^tBuNCO an N,O-bound ureate was formed, presumably to minimize steric repulsions between *tert*-butyl groups and the $Ti(Me_4taa)$ moiety.[24] Chirik recently reported that $Ti\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(NSiMe_3)$ forms an N,O-bound ureate derivative on reaction with Me_3SiNCO.[59]

If steric factors are indeed important in the reactions shown in Scheme 4, then the observation that even the least sterically crowded product **25** (Scheme 4) possesses an N,O-bound ureate ligand would suggest that the $C_5Me_5/MeC(N^iPr)_2$ supporting ligand set is relatively sterically demanding. To probe this aspect, DFT (density functional theory) calculations were carried out on the simple hypothetical models $Ti(\eta\text{-}C_5H_5)\{N(Me)C(NMe)O\}\{MeC(NMe)_2\}$ (**I**, N,O-bound ureate) and $Ti(\eta\text{-}C_5H_5)\{N(Me)C(O)N(Me)\}\{MeC(NMe)_2\}$ (**II**, N,N-bound ureate). Details of the calculations are provided in the Experimental Section and Supporting Information. The N,O-bound isomer **I** was *less* stable than **II**, but by only 11.7 $kJ \cdot mol^{-1}$ (electronic energies). Even the sterically unencumbered model system **II** is apparently strained, as indicated by inequivalent Cp_{cent}−Ti−N_{ureate} angles of 140.3° and 109.2° (cf. a Cp_{cent}−Ti−N_{ureate} angle of 125.9° and Cp_{cent}−Ti−O angle of 112.3° in **I**). Similarly, the Ti−$N_{amidinate}$ distances of 2.035 and 2.190 Å in **II** are significantly more different than those in **I** (2.060 and 2.120 Å). The DFT results imply that increased crowding in cyclopentadienyl-amidinate-supported ureate complexes would lead to N,O-bound isomers.



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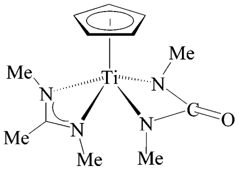
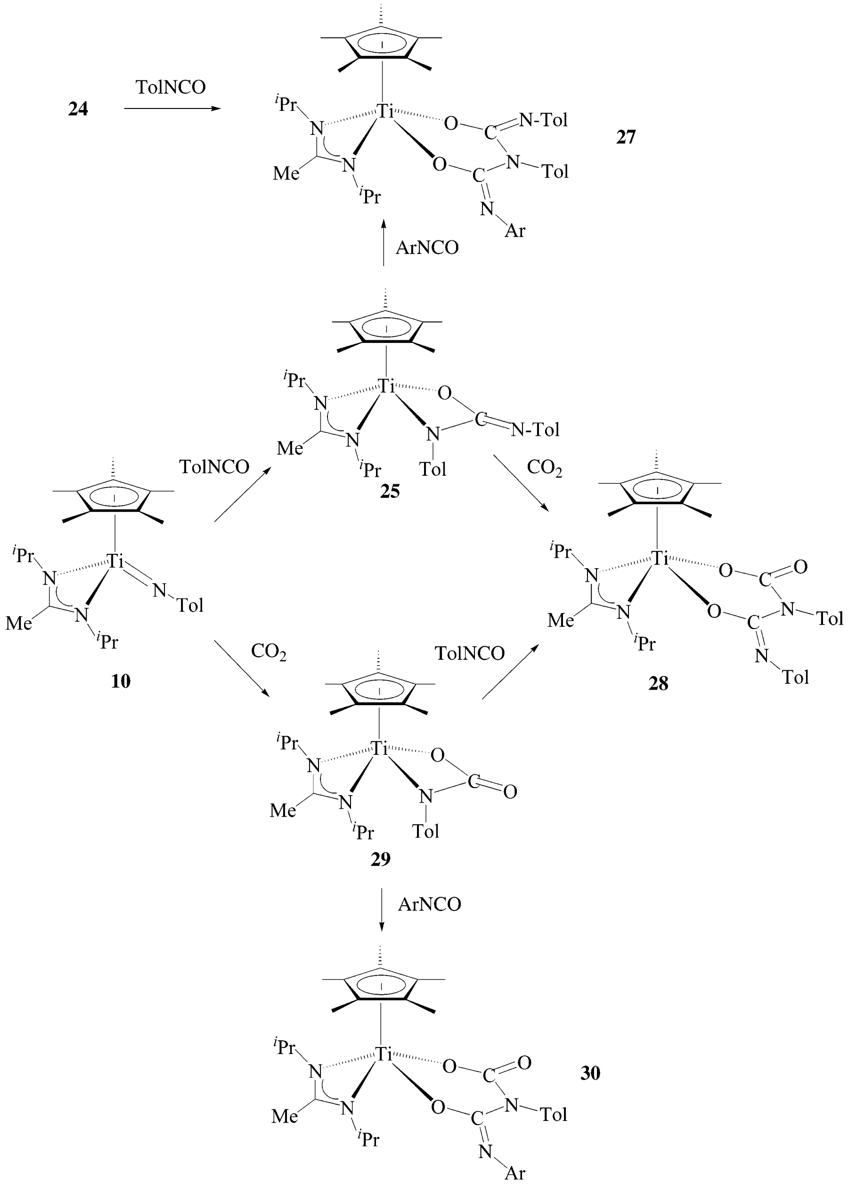


II

Multiple Coupling of Heterocumulenes. As mentioned, the N-aryl-substituted carbamate complex **1b** (Chart 1) reacts with further CO_2 to form the novel dicarboxylate **3**.[23] Furthermore, certain metal N,N-bound ureates undergo insertion of isocyanates into one of the metal−nitrogen bonds.[24,49,60−62] We therefore decided to study the reactions of the new N,O-bound ureates with additional isocyanate or CO_2. The new chemistry is summarized in Schemes 4 and 5.

Reaction of $Ti(\eta\text{-}C_5Me_5)\{N(Tol)C(NTol)O\}\{MeC(N^iPr)_2\}$ (**25**) with TolNCO afforded the new compound $Ti(\eta\text{-}C_5Me_5)\{OC(NTol)N(Tol)C(NTol)O\}\{MeC(N^iPr)_2\}$ (**26**) in 51% isolated yield. The same compound was also formed directly from $Ti(\eta\text{-}C_5Me_5)(NTol)\{MeC(N^iPr)_2\}$ (**10**) and TolNCO (2 equiv) in C_6D_6. Unfortunately we were not able to grow diffraction-quality crystals of **26** or any of the related products (Scheme 5) described below. The NMR spectra of **26** suggest molecular C_s symmetry and feature one isopropyl group environment (two inequivalent diastereotopic Me groups) and two *p*-tolyl groups in a 2:1 ratio. Although in principle these data are consistent with the presence of either an O,O- or N,N-bound $C_2O_2(NTol)_2$-NTol biuret ligand, the O,O-bound isomer depicted for **26** is favored on the basis of further spectroscopic data. First, no NOE interactions were found between the tolyl group hydrogens and those of the $C_5Me_5/MeC(N^iPr)_2$ ligand set. Second, the IR spectrum shows two new bands at 1655 and 1609 cm^{-1} (assigned to the in- and out-of-phase $\nu(C{=}N)$ modes (A′ and A″), respectively), which differ significantly from the in- and out-of-phase $\nu(C{=}O)$ modes found for the dicarboxylate **3** (1694 and 1656 cm^{-1}).[23]

Scheme 5. Cross-Coupling Reactions with Heterocumulenes



Biuret and related compounds with two different hetercumulene residues can be prepared as shown in Scheme 5. NMR tube scale reaction between **24** and TolNCO or **25** and ArNCO formed the same O,O-bound biuret product, namely, Ti(η-C$_5$Me$_5$){OC(NTol)N(Tol)C(NAr)O}{MeC(N^{i}Pr)$_2$} (**27**). The reaction starting from **24** was complete within 5 min, whereas that starting from **25** required ca. 2 h. Compound **27** was isolated in 81% yield on a preparative scale starting from **24**. The NMR and IR data for **27** are consistent with the non-C_s-symmetric structure illustrated.

The totally regioselective cross-coupling of aryl isocyanates and CO$_2$ can be also achieved. NMR tube scale reactions showed that the sequential treatment of **10** with TolNCO and CO$_2$ (or vice versa) led exclusively to a common product, Ti(η-C$_5$Me$_5$)-{OC(O)N(Tol)C(NTol)O}{MeC(N^{i}Pr)$_2$} (**28**) via **25** or the carbamate Ti(η-C$_5$Me$_5$){N(Tol)C(O)O}{MeC(N^{i}Pr)$_2$} (**29**),[46,47] respectively. The NMR spectra for **28** (obtained in 55% isolated yield from **29** and TolNCO) featured two inequivalent isopropyl and *para*-tolyl groups as expected, and the IR spectrum showed bands at 1681 and 1618 cm^{-1} assigned to ν(C=O) and ν(C=N), respectively. We were also able to prepare the mixed-heterocumulene compound **30** (with different biuret N-substituents) from **29** and ArNCO in 65% isolated yield. The IR spectrum showed bands at 1680 and 1620 cm^{-1}, again assigned to ν(C=O) and ν(C=N), respectively. However, there was no reaction between the more sterically crowded carbamate Ti(η-C$_5$Me$_5$){N(Ar)C(O)O}{MeC(N^{i}Pr)$_2$} (**1b**) and either ArNCO or TolNCO.

As mentioned above, a number of compounds with N,N-bound biuret ligands have been reported previously,[49,60–62,65–67] and several have been crystallographically characterized.[60,65–67] However, neither O,O-bound biuret ligands or the related monocarboxylate ligands in **28** and **30** have been reported before. The totally selective insertion of RNCO or CO$_2$ into the Ti–N bonds of the ureate complexes is consistent with previous reports of M–N versus M–O bond reactivity toward unsaturated substrates[68] and the exclusive formation of O,O-bound dicarboxylate complex **3** (Chart 1) from N-aryl carbamate **1b**.

The overall "double substrate activation" reactions leading to **26**–**28** and **30** are rare in transition metal imido chemistry.

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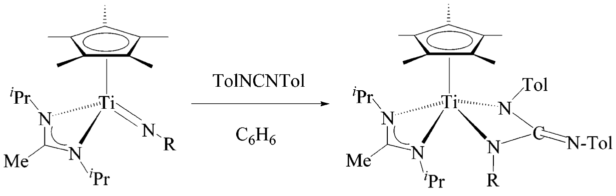
The first example was for the reaction of Bergman's Ir(η-C_5Me_5)(N^{t}Bu) with $C_2(CO_2Me)_2$ to form Ir(η-C_5Me_5){η^4-$C_4(CO_2Me)_4$N^{t}Bu}.[69] Our reports of the reversible insertion of PhNCO into a Ti−N bond of the imido-derived ureato complex Ti{N(Ph)C(O)N(Tol)}(Me_4taa)[24] and the formation of dicarboxylate **3** (Chart 1)[23] are the only other such examples for titanium. Bergman has studied in detail the highly selective sequential coupling of certain alkynes and carbodiimides with Zr═NR bonds to form six-membered metallacycles.[70]

Reactions with Carbodiimides. The reactions of group 4 imido compounds with carbodiimides also have been of recent interest,[24,43,62,70−72] especially with regard to new C−N forming reactions. Me_4taa,[24] bis(cyclopentadienyl),[43,62] and bis(guanidinate)[71,72] supporting ligand sets have so far been employed in this chemistry, and so it was of interest to explore the reactions of the cyclopentadienyl-amidinate imido systems.

The reactions of **5**−**10** with carbodiimides were considerably slower than the corresponding ones with CO_2 or isocyanates (and in some cases did not proceed at all). This probably reflects the increased steric interactions arising around the metal center in the target guanidinate complexes. None of the *tert*-butyl imido compounds **5**−**8** reacted with either ^{i}PrNCN^{i}Pr or TolNCNTol at room temperature or upon heating. Similarly, **10** also failed to react with ^{i}PrNCN^{i}Pr. However, the reactions between **9** and **10** and TolNCNTol proceeded slowly (24 and 1 h, respectively) at room temperature to form the guanidinate complexes Ti(η-C_5Me_5){N(Tol)C(NTol)N(R)}{MeC(N^{i}Pr)$_2$} (R = Ar (**31**) or Tol (**32**)) in ca. 70% isolated yields (eq 2). The NMR and IR spectra support the proposed structures, with the latter showing a ν(C═N) band at 1655 cm^{-1} in both cases. The NMR spectra of **32** indicated molecular C_s symmetry, showing two *p*-tolyl groups in a 1:2 ratio. The spectra for **31** showed two different *p*-tolyl groups in a 1:1 ratio and the absence of any molecular symmetry, as expected for the structure depicted in eq 2.



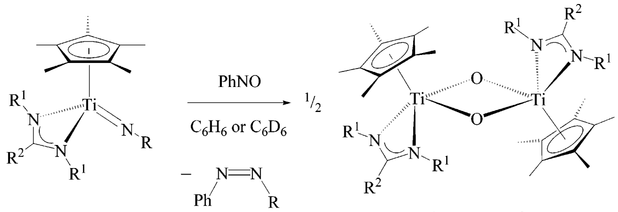
(2)

R = Ar (**9**) or Tol (**10**)   R = Ar (**31**) or Tol (**32**)

Heating a sample of **31** in C_6D_6 at 80 °C for 30 min gave complete conversion to the starting imide Ti(η-C_5Me_5)(NAr){MeC(N^{i}Pr)$_2$} (**9**) and the symmetrical starting carbodiimide TolNCNTol. After 24 h at room temperature the slow cycloaddition reaction had re-formed **31**. Compound **31** is analogous to Bergman's zirconocene complex Cp_2Zr{N(Tol)C(NTol)N-(2,6-$C_6H_3{}^i$Pr$_2$)} (formed from Cp_2Zr(N-2,6-$C_6H_3{}^i$Pr$_2$)(THF) and TolNCNTol),[43] which, on heating at 75 °C, isomerizes to the C_s symmetrical guanidinate Cp_2Zr{N(Tol)C(N-2,6-$C_6H_3{}^i$Pr$_2$)N-(Tol)}, most likely via a cycloreversion/cycloaddition process involving transient Cp_2Zr(NTol) and TolNCN-2,6-$C_6H_3{}^i$Pr$_2$. The driving force of this isomerization is believed to be relief of steric strain in the first-formed (asymmetric) metallacycle. It is not clear why **31** does not behave in a similar way to release the unsymmetrical carbodiimide TolNCNAr and form Ti(η-C_5Me_5)(NTol){MeC(N^{i}Pr)$_2$} (**10**) (which in turn could recombine with TolNCNAr).

Reactions with Non-cumulene N═O, C═O, and C═NR Functional Groups. In addition to the cumulenes CO_2, CS_2, COS, RNCO, and RNCNR, some of the cyclopentadienyl-amidinate titanium imido compounds also react with nitrosobenzene, aldehydes, ketones, imines, and certain organic amides.

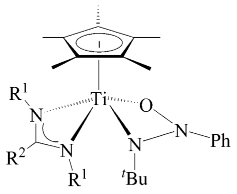
Reactions with PhNO. Transition metal-mediated metathesis reactions of nitroso compounds are relatively rare.[73−77] Metathesis reactions of terminal imido compounds (L)$_n$M═NR with PhNO to form metal oxo species and diazo compounds RN═NPh have recently been reported for titanium and zirconium.[73,76,77]



(3)

R = ^{t}Bu (**5**, **6**), Ar (**9**) or Tol (**10**)   **15** (R^1 = SiMe$_3$, R^2 = Ph) or **2** (R^1 = ^{i}Pr, R^2 = Me)

The reactions between PhNO and the *tert*-butyl imido compounds **5** and **6** were monitored by NMR tube scale reactions (eq 3). In each case complete consumption of PhNO had occurred after ca. 5 min and resonances attributed to *cis*-^{t}BuN═NPh (formed quantitatively) were observed.[78] In the reaction of **5** the appearance of a fine yellow precipitate signaled the formation of the highly insoluble μ-oxo dimer [Ti(η-C_5Me_5)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**15**)[46,47] as the organometallic side-product. In the reaction of **6** the side-product was [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**2**).[23] The reaction between **5** and PhNO was scaled up in benzene, giving **15** in 53% isolated yield. Compound **2** could not be isolated in pure form this way owing to difficulties in separating it from the organic side-product (both **15** and **2** can also be cleanly prepared by reaction of **5** or **6** with CO_2 in 19 and 70% isolated yield[23,46,47]). The diazo species *cis*-^{t}BuN═NPh is the kinetic product of these reactions and over several hours underwent the known thermal rearrangement to *trans*-^{t}BuN═NPh.[79] The initial formation of *cis*-^{t}BuN═NPh implies that the first-formed intermediates are cycloaddition products of the type **III** (analogous intermediates have been proposed previously[73]).



III

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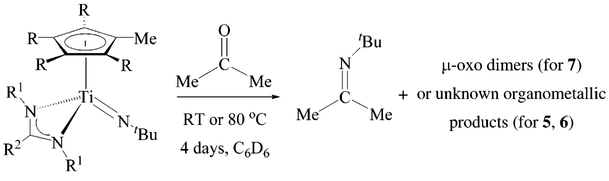
It was hoped that use of aryl imido compound **9** or **10** would lead to more stable intermediates of this type (cf. the reactions with CO_2[23] and RNCO). However, preliminary screening by NMR tube scale reactions in C_6D_6 showed the rapid (within ca. 3 min) consumption of the aryl imido compound in each case and the formation of μ-oxo-bridged dimers (eq 3). Resonances attributable to *cis*- and *trans*-^{t}BuN=NR (R = Ar or Tol)[64,80] were again observed, and the expected molecular ions were also identifed by APCI mass spectrometry.

The metathesis reactions between **5**, **6**, **9**, and **10** and PhNO follow the trends previously observed.[73,76,77] As in the corresponding zirconium chemistry,[73,77] the putative metallocyclic intermediates were not observed. This is consistent with the inherently weak nature of O−N and N−N single bonds, which is typically attributed to secondary electron−electron repulsion.[81]

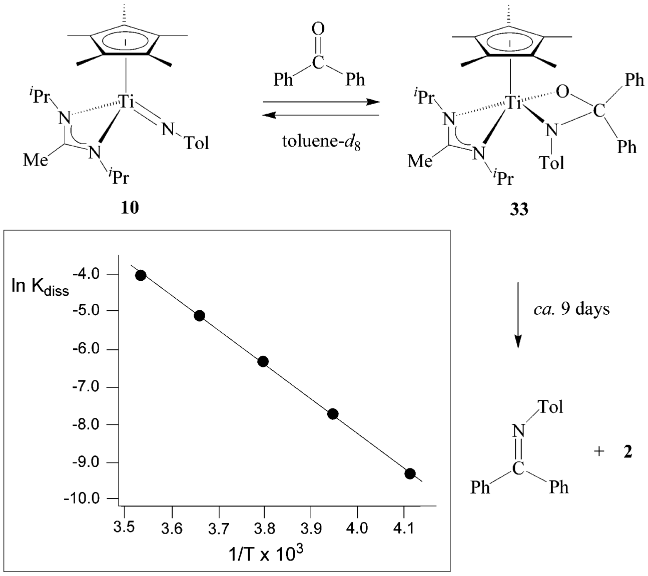
Reactions with Aldehydes and Ketones. The metathesis reactions between metal imido compounds and organic carbonyls to form ketimines or aldimines via cyclcoaddition reactions is well-established.[2,12,42,44,55,59,76,82−86] Of particular relevance to our contribution are the reports for titanium[44,59,76,83,85] and zirconocene systems.[12,55,82]

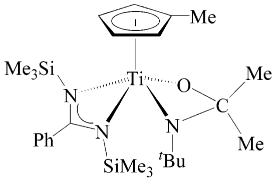


5 - 7 (4)

The reactions between certain cyclopentadienyl-amidinate titanium imido compounds and representative carbonyl compounds, namely, MeCOMe, PhCOPh, PhCOH, and PhCOMe, were assessed, mainly by NMR tube scale reactions. Initial studies focused on the reactions of the *tert*-butyl imides **5**−**7** with MeCOMe (eq 4). The reactions of **6** and **7** proceeded at room temperature (but only slowly, with **6** being the slower of the two). No reaction was observed between MeCOMe and the bulkiest imido compound **5** at room temperature, and this solution was heated at 80 °C. After 4 days all three reactions showed incomplete conversion of MeCOMe to the corresponding imine MeC(N^{t}Bu)Me, which was identified by NMR spectroscopy.[87,88] The organometallic product of the reaction with **7** was the μ-oxo dimer [Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$,[46,47] as would be expected if the mechanism proceeds via a imide-ketone cycloaddition reaction[82] to form a metallocycle such as Ti(η-C_5H_4Me){N(^{t}Bu)C(Me)$_2$O}{PhC(NSiMe$_3$)$_2$} (**IV**, not observed). Subsequent collapse of this metallocycle via extrusion of MeC(N^{t}Bu)Me would lead to transient Ti(η-C_5Me_5)(O){PhC(NSiMe$_3$)$_2$}, which would, in turn, self-trap to form the observed μ-oxo dimers. The several organometallic side-products (not isolable) in the reactions of **5** and **6** were not the expected μ-oxo dimers, and it is possible in these cases (and perhaps also for **7**) that concomitant side-reactions stemming from the enol tautomer of MeCOMe (CH$_2$-CH(OH)Me) may also or alternatively be occurring. Bergman has previously shown[82] that increased steric bulk in the reactions of zirconocene imido compounds with organic ketones possessing enolizable protons afforded amide-enolate complexes.

Scheme 6. Reaction of Ti(η-C_5Me_5)(NTol){PhC(N^{i}Pr$_2$)$_2$} (10) with PhCOPh. Inset: Plot of ln K_{diss} vs 1/T (K^{-1}) for the Dissociation of Ti(η-C_5Me_5){N(Tol)C(Ph)$_2$O}{PhC(N^{i}Pr$_2$)$_2$} (33) to Ph_2CO and 10





IV

No reaction occurred between **6** or **9** and PhCOPh in C_6D_6. In contrast, reaction with the tolyl imide **10** almost immediately gave an equilibrium mixture containing **10**, PhCOPh, and a new compound formulated as the cycloaddition product Ti(η-C_5Me_5)-{N(Tol)C(Ph)$_2$O}{MeC(N^{i}Pr$_2$)$_2$} (**33**, Scheme 6). No further change in the relative amounts of **10** and product **33** was seen after 10 min, but after ca. 9 days the resonances for both the starting materials and **33** were virtually absent, and those of the μ-oxo dimer **2** and PhC(NTol)Ph (identified by comparison with literature NMR data[89] and a parent ion in the APCI mass spectrum) had appeared. Attempts to isolate **33** led to recovered starting materials, and so this complex was characterized by ^{1}H NMR spectroscopy in situ, which showed the absence of molecular symmetry, as suggested by two inequivalent isopropyl substituents, each with diasterotopic methyl groups. Two inequivalent phenyl group environments were also observed, consistent with the proposed structure. Since the resonances for **10**, PhCOPh, and **33** are all sharp, any exchange between free and coordinated PhCOPh must be slow on the NMR time scale.

Potentially **33** could alternatively be formulated as a σ (Lewis base) adduct between an oxygen lone pair of the ketone and titanium. To probe this hypothesis, a CD_2Cl_2 solution of **10** was

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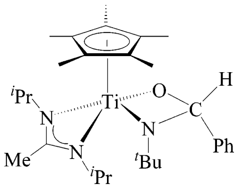
cooled to −90 °C in the presence of pyridine (1 equiv). No complexation was observed. However, when PhCOPh was added to the mixture and the spectrum again recorded, the quantitative formation of **33** was observed. Since pyridine is a superior Lewis base to PhCOPh, these NMR experiments militate against **33** being a simple Lewis base adduct (as does the eventual formation of the imine and μ-oxo products).

Warming the mixture to 50 °C (toluene-d_8) displaced the equilibrium completely in favor of the reactants, whereas on cooling to −40 °C, the mixture was completely converted to **33**. The equilibrium constants for dissociation (K_{diss}) of **33** were measured at 5 °C intervals in the range −30 to −10 °C. A plot of ln K_{diss} versus $1/T$ is shown in the inset to Scheme 6, and the derived thermodynamic parameters are $\Delta H_{\mathrm{diss}} = 75.1 \pm 1.9$ kJ·mol^{-1} and $\Delta S_{\mathrm{diss}} = 230 \pm 10$ J·mol^{-1}·K^{-1}. The positive ΔS_{diss} is in accord with the dissociative process **33** → **10** + PhCOPh, and the ΔH_{diss} value shows that the metallacycle is reasonably enthalpically favored. Compound **33** is the first observed cycloaddition product between a Ti═NR bond and a ketonic $R_2C{=}O$ bond. The formation of the imine PhC(NTol)Ph from **33** suggests that the reactions with MeCOMe described above could also follow this cycloaddition/extrusion pathway.

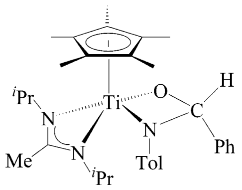
Reasoning that steric factors should inhibit the formation of metallacycles with PhCOPh, we also examined reactions with PhCOH (again on the NMR tube scale in C_6D_6, focusing on the C_5Me_5/MeC(N^{i}Pr)$_2$ systems **6** and **10**). Reaction of the *tert*-butyl imide **6** with PhCOH was essentially complete within 5 min to form Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr$_2$)$_2$} (**34**) with only a trace of unreacted imide and aldehyde present at this stage. The metallocyclic compound **34** quickly ($t_{1/2}$ ca. 30 min) underwent extrusion to form the known aldimine PhC(N^{t}Bu)H (identified by comparison with literature NMR data[89] and a parent ion in the APCI mass spectrum) and the μ-oxo-bridged dimer **2**. The instability of **34** prevented its isolation on the preparative scale, and it was characterized by in situ ^{1}H NMR spectroscopy. The stereochemistry around the C(Ph)H carbon in the metallocycle is assumed to be the less sterically hindered alternative (i.e., with the phenyl group oriented away from the η-C_5Me_5 ring, as found in the related PhCOMe cycloaddition product **36** (see below)).



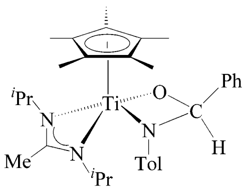
34

Reaction of the tolyl imide **10** with PhCOH was also complete after 5 min, but the reaction was more complicated than for **6**. The ^{1}H NMR spectrum after 5 min showed resonances attributed to *two* new metallacyclic products, **35a** (major, ca. 80%) and **35b** (minor), which are believed to be isomers of each other, namely, Ti(η-C_5Me_5){N(Tol)C(Ph)(H)O}{MeC(N^{i}Pr$_2$)$_2$}. After 20 min the ratio of the isomers was ca. 1:1 with some μ-oxo dimer **2** being visible. After 1 h **2** was the dominant organometallic species. The aldimine PhC(NTol)H was the organic side-product of this reaction (identified by comparison with a commercial sample). The compounds **35a** and **35b** are probably diastereomers (the titanium center and the C(Ph)H carbon both being stereocenters). Two possible structures are illustrated below, but the instability of the compounds and the complicated NMR spectra, which contain a number of overlapping resonances, prevented a more comprehensive assignment.

It is not clear why the PhCOPh cycloaddition product **33** undergoes the retrocyclization reaction (Scheme 6) so much more slowly than **35a**/**35b**, but one possibility could again be steric hindrance in the more highly crowded metallocycle **33,** making access to the necessary transition state more difficult.

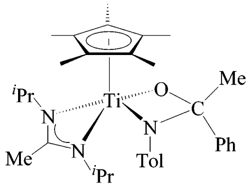


35a



35b

From the reactions with PhCOPh and PhCOH it appeared that while too much steric hindrance inhibits or prevents the formation of the cycloaddition products, some stabilization toward extrusion is gained by increasing steric bulk around the metallocyle ring. As a further probe of this, we carried out reactions of **6**, **9**, and **10** with PhCOMe. No reaction was seen after 16 h at room temperature for the more sterically crowded imides **6** and **9**. Trace amounts of μ-oxo species were seen among other unknown products after heating at 80 °C for 24 h. However, the tolyl imide **10** reacted smoothly with PhCOMe in C_6D_6 within 10 min to give greater than 90% conversion to the cycloaddition product Ti(η-C_5Me_5){N(Tol)C(Ph)(Me)O}{MeC(N^{i}Pr$_2$)$_2$} (**36**). Under otherwise identical conditions the conversion of **10** to **33** with PhCOPh was ca. 40%. Compound **36** is relatively stable toward imine extrusion, and the reaction mixture remained effectively unchanged for at least 1 h. After 16 h ca. 25% conversion to the anticipated metathesis products PhC(NTol)Me and the μ-oxo dimer **2** was observed. The somewhat higher stability of **36** compared to that of Ti(η-C_5Me_5){N(Tol)C(Ph)(H)O}{MeC(N^{i}Pr$_2$)$_2$} (**35a**/**35b**, almost complete extrusion after 1 h) allowed its isolation as a brown wax in 57% yield on the preparative scale (the intrinsic instability and waxy nature prevented us from obtaining an analytically pure sample). The ^{1}H and ^{13}C NMR data are consistent with the structure depicted below (the orientation of the C(Me)Ph group being determined from a ROESY spectrum). The absence of a ν(C═O) band in the IR spectrum of **36** is further support for the incorporation of the PhCOMe carbonyl group into the metallocyclic core.



36

Reactions with Imines. The metathesis reaction between terminal imides (L)$_n$M═NR and organic imines of the type R′C(NR″)H to afford the corresponding imide (L)$_n$M═NR″ and imine R′C(NR)H is still in the early stages of development.[90−97]

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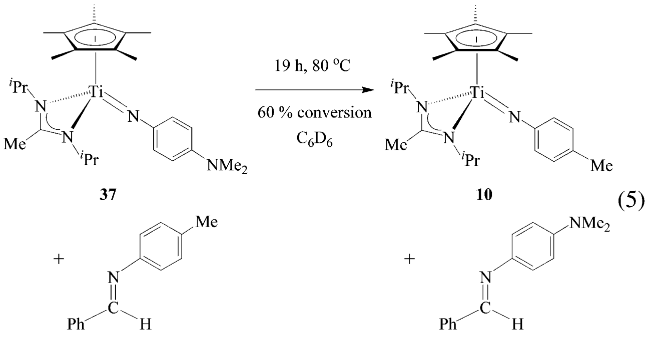
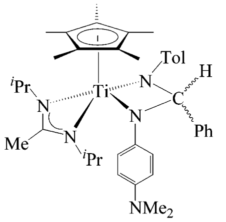
Without doubt these reactions are in principle able to proceed via a [2+2] cycloaddition/extrusion process (Chauvin-type[98] mechanism, cf. olefin metathesis), as clearly demonstrated by Bergman for zirconocene imido systems.[90,91,97] However, in other instances (so far specifically where ancillary chloride ligands are present) it appears that an acid-mediated (non-Chauvin-type) mechanism could also be operative.[92,93] Since certain of our cyclopentadienyl-amidinate titanium imido systems undergo cycloaddition and subsequent metathesis (extrusion) reactions with aldehydes and ketones, we hoped that they could be used to gain further experimental data on the imide/imine metathesis reaction.

Previous studies showed that the aldimine PhC(NTol)H would be a suitable substrate (aryl aldimines are more reactive than alkyl aldimines or ketimines). For comparison with the chemistry so far described, reactions between PhC(NTol)H and the imido compounds **6**, **9**, and **10** were screened by NMR tube scale experiments in C_6D_6. No reaction was observed (even for **10**) either at room temperature or at 80 °C, in contrast to the analogous reactions with PhCOH (vide supra). However, although a cycloaddition product between **10** and the imine was not observed, it is nonetheless possible that a degenerate metathesis reaction (i.e., exchange of Ti=NTol and C=NTol) could be occurring via a short-lived intermediate and therefore not detected by NMR spectroscopy.



37 **10** (5)

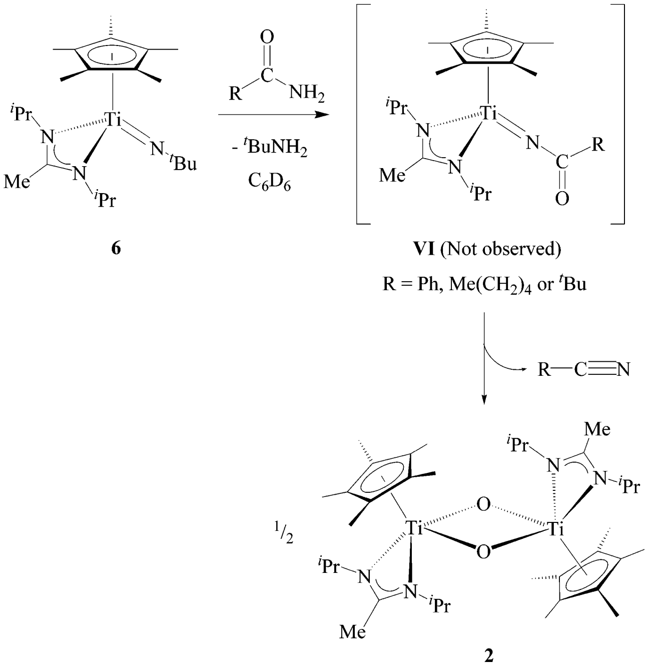
To further probe this possibility, we used the *p*-dimethylaminophenyl analogue of **10**, namely, Ti(η-C_5Me_5)(N-4-C_6H_4-NMe_2)(MeC(N^iPr)$_2$} (**37**), prepared from **6** and *p*-dimethylaniline.[46,47] No reaction between **34** and PhC(NTol)H occurred at room temperature in C_6D_6, but on heating to 80 °C for 19 h, 60% conversion of **37** to **10** was observed (eq 5), together with resonances attributed to the expected organic product of metathesis, namely, PhC(N-4-$C_6H_4NMe_2$)H (confirmed by a parent ion in the APCI mass spectrum).[99]



V

The imide/imine exchange of **37** with PhC(NTol)H is a rare example of this type of metathesis reaction. Although no intermediate was observed, it is likely that a species of the type **V** is involved in this reaction. Detailed mechanistic studies (beyond the range of this present work) would be required to confirm this and determine the scope of the reaction and any potential catalytic application. The slower rate of reaction of PhC(NTol)H in comparison with that of PhCOH is attributed to the increased steric bulk of the imine and the reduced electrophilicity of the imine C=N carbon.

Scheme 7. Reaction of Ti(η-C_5Me_5)(N^tBu){PhC(N^iPr_2)$_2$} (6) with Primary Amides $RCONH_2$ (R = Ph, Me(CH_2)$_4$, or ^{t}Bu



Reactions with Organic Amides $RCONH_2$. Bergman has recently reported that Cp_2ZrMe_2 reacts with certain organic primary amides $RCONH_2$ to form $[Cp_2Zr(O)]_x$ and the corresponding nitriles RCN (presumably via transient imido species of the type Cp_2Zr{NC(O)R}).[100] Apart from this zirconocene system, the only other example of an early transition metal-mediated dehydration reaction of primary amides was with $TiCl_4$ and base at 0 °C.[101] With these observations in mind, we were interested to examine the reactions of Ti(η-C_5Me_5)(N^tBu){MeC(N^iPr)$_2$} (**6**) and related compounds with selected primary amides to see if this offered a method for their conversion to nitriles.[102]

Ti(η-C_5Me_5)(N^tBu){MeC(N^iPr)$_2$} (**6**) was treated with 1.0 equiv of benzamide, hexanoamide, or trimethylacetamide on the NMR tube scale in the presence of a 1,4-dimethoxybenzene internal standard. The ^{1}H NMR spectra were monitored over 1 h and showed consumption of the amide with concomitant formation of the corresponding nitrile, as verified by comparison with authentic samples. The reactions yielded the oxo dimer **2**[23] as the dominant organometallic product. The reactions with benzamide and hexanoamide showed complete conversion within 1 h, while reaction with the sterically encumbered trimethylacetamide had achieved only 60% conversion to trimethylacetonitrile after 2 days. A likely intermediate based on Bergman's work[100] is species **VI** (Scheme 7).

Corresponding reactions were also carried out to evaluate other titanium imido and amido compounds as reagents for these

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transformations. Ti(N^{t}Bu)Cl$_2$(py)$_3$,[33] Ti(NMe$_2$)$_2$Cl$_2$,[103,104] Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py),[32] and Ti(N^{t}Bu){Me$_3$SiNC(Ph)N(CH$_2$)$_3$NMe$_2$}Cl[105] all showed ^{1}H NMR evidence for conversion of the amide starting materials to nitrile compounds, although none of these reagents facilitated complete conversion of the bulky trimethylacetamide to trimethylacetonitrile.

Conclusions

Metathesis reactions of half-sandwich titanium imido complexes combined with *tert*-butyl imide/arylamine exchange strategies provide a useful route to a family of 16-valence-electron cyclopentadienyl-amidinate derivatives. The *tert*-butyl and aryl imido complexes show significant differences in reactivity, the former reacting more slowly and being, in general, more prone to cycloaddition/elimination reactions. The aryl imido complexes can undergo single-, double-, and cross-coupling reactions with isocyanates and CO$_2$. In addition to their reactions with isocyanates, the cyclopentadienyl-amidinate complexes undergo rapid cycloaddition−elimination reactions with CS$_2$, COS, PhNO, ketones, aldehydes, and imines, although in some instances intermediates could be observed or isolated. Interestingly, the aryl imido cycloaddition products appear to show increasing stability with increasing steric crowding. Similar trends have been noted before in the reactions of CO$_2$ with certain cyclopentadienyl-amidinate *tert*-butyl imido complexes.[28]

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, 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, ^{13}C{^{1}H}, and ^{13}C NMR spectra were recorded on Varian Unity Plus 500 and Varian Mercury spectrometers. ^{1}H and ^{13}C assignments were confirmed where necessary with the use of NOE, DEPT-135, DEPT90, DEPT-45, and two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H NMR experiments. All spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls or thin films between KBr plates and were recorded on Perkin-Elmer 1600 and 1700 series spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory.

Starting Materials and Literature Preparations. The compounds Li[MeC(N^{i}Pr)$_2$],[106] Li[PhC(NSiMe$_3$)$_2$],[107] Ti(N^{t}Bu)Cl$_2$(py)$_3$, Ti(NMe$_2$)$_2$Cl$_2$, Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py), Ti(η-C$_5$H$_4$Me)(N^{t}Bu)Cl(py), Ti(η-C$_5$Me$_5$){N(Tol)C(O)O}{MeC(N^{i}Pr)$_2$} (**29**), Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$NMe$_2$)(MeC(N^{i}Pr)$_2$} (**34**), and Ti(N^{t}Bu){Me$_3$SiNC(Ph)N(CH$_2$)$_3$NMe$_2$}Cl were prepared according to previously described methods.[33,46,47,103−105,108] All other compounds and reagents were purchased and were either used without further purification or purified by standard methods.[109]

Ti(η-C$_5$Me$_5$)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (5). To a solution of 714 mg (1.94 mmol) of [Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py)] in ca. 30 mL of benzene was added 532 mg (1.97 mmol) of Li[PhC(NSiMe$_3$)$_2$] dissolved in ca. 40 mL of benzene. After 16 h, the volatiles were removed under reduced pressure and the residues were purified by tube distillation (160 °C, 3×10^{-6} Torr, 2 h) to give **5** as a dark red, waxy solid. Yield: 410 mg (41%). The compound was characterized by comparison of spectroscopic data with literature values.[30]

Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (6). To a solution of 9.48 g (0.026 mol) of Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py) in ca. 200 mL of benzene was added 3.81 g (0.026 mol) of Li[MeC(N^{i}Pr)$_2$] slurried in ca. 30 mL of benzene over a period of 30 min. After 16 h the solution was filtered, and volatiles were removed under reduced pressure to give **6** as a waxy brown solid. Yield: 10.25 g (99%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 3.56 (2 H, apparent sept, $J = 6.4$ Hz, NC*H*MeMe), 2.13 (15 H, s, C$_5$Me$_5$), 1.68 (3 H, s, MeCN$_2$), 1.10 (9 H, s, N^{t}Bu), 1.04 (6 H, d, $J = 6.4$ Hz, NCH*Me*Me), 1.01 (6 H, d, $J = 6.4$ Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 163.6 (CN$_2$), 118.9 (*C*$_5$Me$_5$), 66.0 (N*C*Me$_3$), 47.9 (N*C*HMeMe), 31.8 (NC*Me*$_3$), 25.2 (NCH*Me*Me), 24.0 (NCHMe*Me*), 11.2 (C$_5$*Me*$_5$), 9.8 (*Me*CN$_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 2722 (w), 2041 (w), 1597 (w), 1339 (s, br), 1317 (m), 1244 (s), 1213 (s), 1174 (s), 1143 (w), 1122 (m), 1057 (w), 1018 (m), 812 (m), 754 (w), 723 (m), 700 (w), 623 (m), 591 (m), 554 (s), 534 (s), 507 (w), 419 (s). Anal. Found (calc for C$_{22}$H$_{41}$N$_3$Ti): C 67.1 (66.8); H 10.4 (10.5); N 10.2 (10.6). EIMS: *m*/*z* 395 [M]$^+$, 380 [M − Me]$^+$.

Ti(η-C$_5$H$_4$Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (7). To a solution of 6.79 g (0.022 mol) of Ti(η-C$_5$H$_4$Me)(N^{t}Bu)Cl(py) in ca. 70 mL of benzene was added 5.88 g (0.022 mol) of Li[PhC(NSiMe$_3$)$_2$] dissolved in ca. 200 mL of benzene. After 16 h the solution was filtered, and the volatiles were then removed under reduced pressure to give **7** as a waxy red-brown solid. Yield: 9.34 g (93%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.16 (3 H, m, *o*-, *p*-C$_6$H$_5$), 7.03 (2 H, m, *m*-C$_6$H$_5$), 6.87 (2 H, virtual t, C$_5$*H*$_2$(β)H$_2$(α)Me), 5.80 (2 H, virtual t, C$_5$H$_2$(β)*H*$_2$(α)Me), 2.06 (3 H, s, C$_5$H$_4$*Me*), 1.17 (9 H, s, N^{t}Bu), −0.10 (18 H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 170.6 (CN$_2$), 139.7 (*i*-C$_6$H$_5$), 128.6 (*o*-C$_6$H$_5$), 128.1 (*m*-C$_6$H$_5$), 127.5 (*p*-C$_6$H$_5$), 123.0 (C$_2$(β)C$_2$(α)*C*Me), 113.1 (*C*$_2$(β)C$_2$(α)CMe), 108.8 (C$_2$(β)*C*$_2$(α)CMe), 67.0 (N*C*Me$_3$), 32.7 (NC*Me*$_3$), 14.8 (C$_2$(β)C$_2$(α)C*Me*), 2.0 (SiMe$_3$). IR (KBr plates, Nujol mull, cm^{-1}): 3061 (w), 2728 (w), 2363 (w), 1946 (w), 1614 (w, br), 1578 (w, br), 1350 (s), 1305 (m), 1248 (s), 1209 (m), 1177 (m), 1123 (m), 1073 (m), 1047 (w), 1033 (m), 1007 (s), 996 (s), 935 (w), 918 (m), 839 (s, br), 805 (w), 785 (s), 764 (s), 723 (w), 701 (m), 687 (w), 625 (m, br), 604 (m, br), 548 (s), 507 (s), 446 (m), 402 (m). Anal. Found (calc for C$_{23}$H$_{39}$N$_3$Si$_2$Ti): C 59.8 (59.8); H 8.2 (8.5); N 9.0 (9.1). EIMS: *m*/*z* 461 [M]$^+$, 446 [M − Me]$^+$.

Ti(η-C$_5$H$_4$Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (8). A 2.50 g (7.96 mmol) sample of Ti(η-C$_5$H$_4$Me)(N^{t}Bu)Cl(py) in ca. 140 mL of benzene was added to 1.18 g (7.96 mmol) of Li[MeC(N^{i}Pr)$_2$] slurried in ca. 30 mL of benzene. After 16 h, the volatiles were removed under reduced pressure, and the residue was extracted with ca. 100 mL of pentane and filtered. Volatiles were then again removed under reduced pressure to afford **8** as a red oil. Yield: 2.59 g (96%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 6.68 (2 H, virtual t, C$_5$*H*$_2$(β)H$_2$(α)Me), 5.94 (2 H, virtual t, C$_5$H$_2$(β)*H*$_2$(α)Me), 3.55 (2 H, apparent sept., $J = 6.4$ Hz, NC*H*MeMe), 1.98 (3 H, s, C$_5$H$_2$(β)-

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H$_2$(α)*Me*), 1.54 (3 H, s, MeCN$_2$), 1.11 (9 H, s, N^{t}Bu), 1.06 (6 H, d, *J* = 6.4 Hz, NCH*Me*Me), 0.87 (6 H, d, *J* = 6.4 Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 159.3 (Me*C*N$_2$), 121.8 (C$_2$(*β*)C$_2$(α)*C*Me), 112.6 (C$_2$(*β*)*C*$_2$(α)CMe), 108.5 (*C*$_2$(*β*)C$_2$(α)CMe), 66.8 (N*C*Me$_3$), 48.2 (N*C*HMeMe), 32.9 (NC*Me*$_3$), 25.9 (NCH*Me*Me), 25.7 (NCHMe*Me*), 14.2 (C$_2$(*β*)C$_2$(α)C*Me*), 10.3 (*Me*CN$_2$). IR (KBr plates, neat thin film, cm^{-1}): 2963 (s), 2931 (s), 2867 (m), 2601 (w), 2362 (w), 1489 (s, br), 1451 (s, br), 1378 (m), 1361 (m), 1336 (s), 1317 (m), 1247 (s), 1225 (s), 1210 (m), 1174 (m), 1145 (w), 1123 (m), 1091 (m), 1059 (w), 1033 (w), 986 (w), 935 (w), 842 (m), 785 (s, br), 721 (m), 621 (w), 590 (m, br), 558 (m), 534 (w), 507 (w), 470 (w). EIMS: *m/z* 339 [M]$^+$, 324 [M − Me]$^+$, 268 [M − N^{t}Bu]$^+$.

Ti(*η*-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (9). ArNH$_2$ (1.4 mL, 1.37 g, 0.011 mol) was added to a solution of 4.53 g (0.011 mol) of Ti(*η*-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$] (**6**) in ca. 100 mL of pentane to give a green solution. After 16 h the volatiles were removed under reduced pressure. The residue was extracted with ca. 50 mL of dichloromethane and filtered, and the volatiles were removed under reduced pressure to leave an oily green solid. Trituration with pentane afforded **9** as a green powder. Yield: 4.62 g (95%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) *δ*: 7.02 (2 H, d, *J* = 7.3 Hz, *m*-aryl), 6.73 (1 H, t, *J* = 7.3 Hz, *p*-aryl), 3.56 (2 H, apparent sept., *J* = 6.4 Hz, NC*H*MeMe), 2.30 (6 H, s, N-2,6-C$_6$H$_3$*Me*$_2$), 1.98 (15 H, s, C$_5$Me$_5$), 1.67 (3 H, s, MeCN$_2$), 1.07 (6 H, d, *J* = 6.4 Hz, NCH*Me*Me), 1.00 (6 H, d, *J* = 6.4 Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 164.1 (CN$_2$), 158.5 (*i*-aryl), 131.5 (*o*-aryl), 127.6 (*m*-aryl), 120.7 (*p*-aryl), 118.9 (*C*$_5$Me$_5$), 49.1 (N*C*HMeMe), 25.9 (NCHMe*Me*), 25.1 (NCH*Me*Me), 20.7 (C$_6$H$_3$-*Me*$_2$), 12.5 (*Me*CN$_2$), 12.3 (C$_5$*Me*$_5$). IR (KBr disks, Nujol mull, cm^{-1}): 2720 (w), 2595 (w), 2046(w), 1892 (w), 1838 (w), 1785 (w), 1653 (w), 1623 (w), 1587 (m), 1407 (s), 1364 (s), 1334 (s), 1310(s), 1295 (s), 1216 (s), 1174 (m), 1157 (w), 1139 (w), 1121 (m), 1096 (m), 1055 (w), 1014 (m, br), 973 (m), 959 (m), 914 (w), 894 (w), 873 (w), 815 (s), 760 (s), 743 (m), 723 (m), 618 (m), 589 (m), 574 (w), 565 (m), 547 (w), 445 (s). Anal. Found (calc for C$_{26}$H$_{41}$N$_3$Ti): C 70.0 (70.4); H 9.3 (9.3); N 9.4 (9.5). EIMS: *m/z* 443 [M]$^+$.

Ti(*η*-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (10). A 676 mg (1.72 mmol) sample of Ti(*η*-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**6**) and 186 mg (1.73 mmol) of TolNH$_2$ were dissolved in ca. 40 mL of benzene. After 16 h the volatiles were removed under reduced pressure, and the product was isolated as a green solid, which was further purified by tube distillation (170 °C, 2 × 10^{-5} Torr, 4 h) to give **10** as a green solid. Yield: 170 mg (50%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) *δ*: 6.93 (2 H, d, *J* = 7.9 Hz, *m*-(N-4-C$_6$H$_4$Me)), 6.74 (2 H, d, *J* = 7.9 Hz, *o*-(N-4-C$_6$H$_4$Me)), 3.54 (2 H, apparent sept., *J* = 6.3 Hz, NC*H*MeMe), 2.13 (3 H, s, N-4-C$_6$H$_4$*Me*), 2.07 (15 H, s, C$_5$Me$_5$), 1.51 (3 H, s, MeCN$_2$), 1.10 (6 H, d, *J* = 6.3 Hz, NCH*Me*Me), 0.97 (6 H, d, *J* = 6.3 Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 163.6 (CN$_2$), 158.9 (*i*-N-4-C$_6$H$_4$-Me), 129.0 (*m*-N-4-C$_6$H$_4$Me), 127.9 (*p*-N-4-C$_6$H$_4$Me), 123.2 (*o*-N-4-C$_6$H$_4$Me), 120.6 (*C*$_5$Me$_5$), 49.3 (N*C*HMeMe), 26.2 (NCHMe*Me*), 25.3 (NCH*Me*Me), 21.1 (N-4-C$_6$H$_4$*Me*), 12.3 (C$_5$*Me*$_5$), 11.6 (*Me*CN$_2$). IR (KBr plates, Nujol mull, cm^{-1}): 2958 (s), 1871 (w), 1655 (w), 1599 (m), 1490 (s), 1315 (s, br), 1261 (s), 1212 (s, br), 1171 (m), 1141 (w), 1120 (w), 1099 (w, br), 1019 (s), 964 (m), 817 (s, br), 723 (w), 656 (m), 625 (w), 607 (w), 557 (w), 526 (w), 589 (m), 440 (m, br). Anal. Found (calc for C$_{25}$H$_{39}$N$_3$Ti): C 69.9 (69.9) H 9.2 (9.2) N 9.3 (9.8). EIMS: *m/z* 429 [M]$^+$.

[Ti(*η*-C$_5$Me$_5$)(*μ*-S){PhC(NSiMe$_3$)$_2$}]$_2$ (11). A 115 mg (0.22 mmol) sample of Ti(*η*-C$_5$Me$_5$)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**5**) was dissolved in ca. 15 mL of benzene, and to this was added an excess (0.40 mL, 6.65 mmol) of CS$_2$. After 10 days compound **11** was isolated as red crystals. Yield: 71 mg (68%). IR (KBr plates, Nujol mull): 2726 (w), 1456 (s, br), 1259 (m), 1244 (s), 1160 (w), 1095 (m, br), 1020 (m, br), 1002 (w), 983 (s), 920 (w), 835 (s, br), 781 (w), 761 (m), 722 (m, br), 681 (w, br), 627 (w), 609 (w), 598 (w), 500 (m), 413 (m) cm^{-1}. Anal. Found (calc for C$_{46}$H$_{76}$N$_4$S$_2$Si$_4$Ti$_2$): C 57.7 (57.7); H 7.5 (8.0); N 5.7 (5.9). EIMS: *m/z* = 821, [M − C$_5$Me$_5$]$^+$, *m/z* = 789 [M − C$_5$Me$_5$ − S]$^+$.

[Ti(*η*-C$_5$Me$_5$)(*μ*-S){MeC(N^{i}Pr)$_2$}]$_2$ (12). A 305 mg (0.69 mmol) sample of Ti(*η*-C$_5$Me$_5$)(N^{t}Bu)(MeC(N^{i}Pr)$_2$} (**6**) was dissolved in ca. 15 mL of benzene. The vessel was freeze−pump−thawed three times and back-filled with COS at a pressure of 500 mmHg, and the mixture was stirred for 18 h. Volatiles were removed under reduced pressure, and the residues extracted with ca. 10 mL of benzene. This was layered with ca. 15 mL of pentane to afford **12** as red-brown crystals. Yield: 55 mg (22%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) *δ*: 3.59 (4 H, apparent sept, *J* = 6.6 Hz, NC*H*MeMe), 2.28 (30 H, s, C$_5$*Me*$_5$), 1.81 (6 H, s, *Me*CN$_2$), 1.32 (12 H, d, *J* = 6.6 Hz, NCH*Me*Me), 1.26 (12 H, d, *J* = 6.6 Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 167.2 (Me*C*N$_2$), 125.7 (*C*$_5$Me$_5$), 49.6 (N*C*HMeMe), 25.7 (NCHMe*Me*), 24.8 (NCH*Me*Me), 15.5 (*Me*CN$_2$), 14.8 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull): 2721 (w), 1645 (w), 1558 (w), 1329 (s), 1296 (m), 1262 (m), 1206 (s), 1190 (s), 1169 (m), 1143 (m), 1114 (m), 1019 (m), 808 (m), 795 (m), 768 (w), 723 (w), 675 (w), 629 (w), 571 (w), 548 (w), 414 (s) cm^{-1}. Anal. Found (calc for C$_{36}$H$_{64}$N$_4$S$_2$Ti$_2$): C 60.7 (60.7); H 9.1 (9.1); N 7.5 (7.9). EIMS: *m/z* = 712 [M]$^+$, *m/z* = 356 [$^1/_2$M]$^+$.

[Ti(*η*-C$_5$H$_4$Me)(*μ*-S){PhC(NSiMe$_3$)$_2$}]$_2$ (13). A 103 mg (0.22 mmol) sample of Ti(*η*-C$_5$H$_4$Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**7**) was dissolved in ca. 10 mL of benzene, and to this was added an excess (0.40 mL, 6.65 mmol) of CS$_2$. Volatiles were removed under reduced pressure after 5 days. The residues were extracted into a minimum amount of pentane and cooled to −30 °C to afford **13** as a brown powder. Yield: 15 mg (16%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) *δ*: 7.59 (2 H, d, *J* = 6.8 Hz, *o*-C$_6$H$_5$), 7.05 (6 H, m, *m*-, *p*-C$_6$H$_5$), 6.86 (2 H, d, *J* = 6.8 Hz, *o*-C$_6$H$_5$), 6.80 (4 H, virtual triplet, *J* = 2.7 Hz, C$_5$*H*$_2$(*β*)H$_2$(α)Me), 6.35 (4 H, virtual triplet, *J* = 2.7 Hz C$_5$H$_2$(*β*)*H*$_2$(α)Me), 2.70 (6 H, s, C$_5$H$_2$(*β*)H$_2$(α)*Me*), 0.01 (18 H, s, Si*Me*$_3$. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 175.2 (C$_6$H$_5$*C*N$_2$), 139.9 (*i*-C$_6$H$_5$CN$_2$), 128.7 (*o*-C$_6$H$_5$CN$_2$), 128.6 (*m*-C$_6$H$_5$-CN$_2$), 128.3 (*p*-C$_6$H$_5$CN$_2$), 126.5 (C$_2$(*β*)C$_2$(α)*C*Me), 116.1 (*C*$_2$(*β*)-C$_2$(α)CMe), 114.9 (C$_2$(*β*)*C*$_2$(α)CMe), 18.3 (C$_2$(*β*)C$_2$(α)C*Me*), 3.06 (Si*Me*$_3$). IR (KBr plates, Nujol mull): 2726 (w), 2044 (w), 1600 (w), 1499 (m), 1244(s), 1170 (m), 1071 (w), 1055 (w), 1041 (w), 1031 (w), 1002 (m), 983 (s), 917 (m), 838 (s, br), 803 (s), 783 (m), 760 (s), 737 (m), 721 (s), 679 (w), 607 (w, br), 504 (s), 417 (s) cm^{-1}. Anal. Found (calc for C$_{38}$H$_{60}$N$_4$S$_2$Si$_4$Ti$_2$): C 57.3 (57.3), H 7.5 (7.6), N 7.0 (7.0). EIMS: *m/z* = 844 [M]$^+$, *m/z* = 422 [$^1/_2$ M]$^+$.

[Ti(*η*-C$_5$H$_4$Me)(*μ*-S){MeC(N^{i}Pr)$_2$}]$_2$ (14). Ti(*η*-C$_5$H$_4$Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**8**) (85 mg, 0.25 mmol) was dissolved in ca. 10 mL of pentane, and to this was added an excess (0.40 mL, 6.65 mmol) of CS$_2$. After 3 days, the supernatant was filtered away from brown crystalline needles that had formed (25 mg, 33% yield). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): 6.57 (4 H, virtual t, C$_5$*H*$_2$(*β*)-H$_2$(α)Me), 6.39 (4 H, virtual t, C$_5$H$_2$(*β*)*H*$_2$(α)Me), 3.45 (4 H, apparent sept, *J* = 6.6 Hz, NC*H*MeMe), 2.59 (6 H, s, C$_5$H$_2$(*β*)H$_2$-(α)*Me*), 1.55 (6 H, s, *Me*CN$_2$), 1.38 (12 H, d, *J* = 6.6 Hz, NCH*Me*Me), 1.12 (12 H, d, *J* = 6.6 Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) *δ*: 166.3 (Me*C*N$_2$), 127.4 (C$_2$-(*β*)C$_2$(α)*C*Me), 115.1 (C$_2$(*β*)*C*$_2$(α)CMe), 114.3 (*C*$_2$(*β*)C$_2$(α)CMe), 49.7 (N*C*HMeMe), 24.9 (NCH*Me*Me), 23.6 (NCHMe*Me*), 18.2 (C$_2$-(*β*)C$_2$(α)C*Me*), 9.99 (*Me*CN$_2$). IR (KBr plates, Nujol mull): 1340 (m), 1313 (w), 1261 (m), 1210 (w), 1173 (w), 1069 (w), 1038 (w), 935 (w), 859 (w), 804 (m), 723 (w), 684 (w) cm^{-1}. EIMS: *m/z* = 600 [M]$^+$. A satisfactory elemental analysis could not be obtained.

[Ti(*η*-C$_5$Me$_5$)(*μ*-S){N(^{i}Pr)C(Me)N(^{i}Pr)C(S)S}]$_2$ (18). A 127 mg (0.32 mmol) sample of Ti(*η*-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**6**) was dissolved in ca. 10 mL of benzene, and an excess (0.40 mL, 6.65 mmol) of CS$_2$ was added. After 10 days, volatiles were removed under reduced pressure and the residue was extracted into ca. 40

mL of pentane. Evaporation of the volatiles afforded **18** as an olive-brown powder. Yield: 110 mg (80%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K) δ: 5.19 (4 H, apparent sept, $J = 6.8$ Hz, CNC*H*Me$_2$), 3.38 (4 H, apparent sept, $J = 6.6$ Hz, TiNC*H*Me$_2$), 2.39 (30 H, s, C$_5$*Me*$_5$), 1.98 (6 H, s, *Me*CN$_2$, 1.25, 6 H, d, CNCH*Me*Me), 1.17 (6 H, d, CNCHMe*Me*), 1.06 (12 H, d, $J = 6.6$ Hz, TiNCH*MeMe*). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 298K) δ: 202.3 (*C*(S)S), 154.1 (Me*C*N$_2$), 127.0 (*C*$_5$Me$_5$), 53.4 (CN*C*HMeMe), 51.7 (TiN*C*HMeMe), 23.2 (TiNCH*MeMe*), 20.7 (CNCH*MeMe*), 20.1 (*Me*CN$_2$), 14.6 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull): 2955 (s), 2726 (w), 1398 (m), 1357 (s), 1343 (w), 1315 (w), 1261 (w), 1227 (m, br), 1169 (w), 1147 (m), 1123 (w), 1110 (w, br), 1063 (w), 1020 (w), 962 (w), 864 (w), 804 (w, br), 723 (m, br), 667 (w), 605 (w), 521 (w), 496 (w), 433 (m, br), 404 (m) cm^{-1}. Anal. Found (calc for $C_{38}H_{64}N_4S_6Ti_2$): C 52.6 (52.8); H 9.3 (7.5); N 6.0 (6.5) S 23.5 (22.2). EIMS: *m*/*z* = 864 [M]$^+$.

NMR Tube Scale Reactions of 5, 6, 7, and 8 with COS. The general procedure was as follows. About 0.02 mmol of the imido compound was dissolved in 0.6 mL of C_6D_6. The solution was freeze−pump−thawed three times and then back-filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^{1}H NMR spectroscopy, and the products were identified by comparison with authentic samples. The reaction of **6** with COS to form **12** was also performed on a preparative scale.

Ti(η-C$_5$Me$_5$){N(Ar)C(S)S}{MeC(N^{i}Pr)$_2$} (19). A 244 mg (0.55 mmol) sample of Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (**9**) was dissolved in ca. 20 mL of pentane to give a dark green solution, and to this was added an excess (0.40 mL, 6.65 mmol) of CS$_2$. After 6 h the volatiles were removed under reduced pressure to afford the product as a very fine black powder. Yield: 170 mg (60%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K) δ: 7.02−7.00 (3 H, m, *m*-, *p*-2,6-C$_6$H$_3$Me$_2$), 3.08 (1 H, apparent sept, $J = 6.6$ Hz, NC*H*$_a$MeMe), 3.07 (1 H, apparent sept, $J = 6.6$ Hz, NC*H*$_b$MeMe), 2.23 (3 H, s, 2,6-C$_6$H$_3$*Me*Me), 2.12 (3 H, s, 2,6-C$_6$H$_3$Me*Me*), 1.85 (15 H, s, C$_5$*Me*$_5$), 1.45 (3 H, s, *Me*CN$_2$), 0.98 (3 H, d, $J = 6.6$ Hz, NCH$_a$*Me*Me), 0.91 (3 H, d, $J = 6.6$ Hz, NCH$_a$Me*Me*), 0.72 (3 H, d, $J = 6.6$ Hz, NCH$_b$*Me*Me), 0.34 (3 H, d, $J = 6.6$ Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K) δ: 201.8 (S*C*S), 169.2 (Me*C*N$_2$), 148.2 (*i*- 2,6-C$_6$H$_3$Me$_2$), 135.1 (*o*- 2,6-C$_6$H$_3$Me$_2$), 134.1 (*o*-2,6-C$_6$H$_3$Me$_2$), 133.3 (*m*-2,6-C$_6$H$_3$Me$_2$), 130.3 (*C*$_5$Me$_5$), 125.7 (*m*-2,6-C$_6$H$_3$Me$_2$), 125.4 (*p*-2,6-C$_6$H$_3$Me$_2$), 52.5 (NC*H*$_b$MeMe), 49.7 (NC*H*$_a$MeMe), 26.0 (NCH$_b$*Me*Me), 24.5 (NCH$_a$Me*Me*), 23.7 (NCH$_b$Me*Me*), 23.1 (NCH$_a$*Me*Me), 19.3 (2,6-C$_6$H$_3$*Me*Me), 19.0 (2,6-C$_6$H$_3$Me*Me*), 14.8 (*Me*CN$_2$), 13.6 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull): 2721 (w), 2589 (w), 2364 (w), 1903 (w), 1762 (w), 1653 (w, br), 1623 (w), 1590 (w), 1563 (w, br), 1403 (s), 1344 (s), 1324 (s), 1296 (s), 1252 (s), 1198 (s), 1177 (s), 1125 (m), 1093 (s), 1055 (m), 1007 (s, br), 954 (w), 921 (w), 821 (s), 793 (s), 764 (s), 757 (s), 723 (m), 702 (m), 677 (m), 628 (w), 616 (w), 598 (w), 580 (w), 556 (m), 519 (m), 480 (w), 437 (s), 422 (s) cm^{-1}. Anal. Found (calc for $C_{27}H_{41}N_3S_2Ti$): C 62.3 (62.4); H 8.3 (8.0); N 8.0 (8.1).

Ti(η-C$_5$Me$_5$){N(Ar)C(O)S}{MeC(N^{i}Pr)$_2$} (20). In an ampule equipped with a Young's Teflon valve 277 mg (0.63 mmol) of Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (**9**) was dissolved in ca. 20 mL of benzene to give a dark green solution. The vessel was freeze−pump−thawed three times and back-filled with COS at a pressure of 500 mmHg. The solution was shaken for 5 min, after which time a color change to dark red had occurred. Volatiles were removed under reduced pressure to afford **20** as a black-brown solid. Yield: 220 mg (70%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K) δ: 7.03 (1 H, m, *p*-2,6-C$_6$H$_3$Me$_2$), 6.99 (2 H, m, *m*-2,6-C$_6$H$_3$Me$_2$), 3.25 (1 H, apparent sept, NC*H*$_a$MeMe), 2.97 (1 H, apparent sept, NC*H*$_b$MeMe), 2.32 (3 H, s, 2,6-C$_6$H$_3$*Me*Me), 1.98 (3 H, s, 2,6-C$_6$H$_3$Me*Me*), 1.92 (15 H, s, C$_5$*Me*$_5$), 1.36 (3 H, s, *Me*CN$_2$), 1.06 (3 H, d, $J = 6.6$ Hz, NCH$_a$*Me*Me), 1.03 (3H, d, $J = 6.6$ Hz, NCH$_a$Me*Me*), 0.76 (3H, d, $J = 6.4$ Hz, NCH$_b$*Me*Me), 0.43 (3H, d, $J = 6.4$ Hz), NCH$_b$Me*Me*. ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K) δ: 195.8 (S*C*O), 169.4 (Me*C*N$_2$), 146.7 (*i*-2,6-C$_6$H$_3$Me$_2$), 133.6 (*o*-2,6-C$_6$H$_3$Me$_2$), 133.3 (*o*-2,6-C$_6$H$_3$Me$_2$**)**, 130.6 (*m*-2,6-C$_6$H$_3$Me$_2$), 128.5 (*m*-2,6-C$_6$H$_3$Me$_2$), 125.7 (*C*$_5$Me$_5$), 51.8 (N*C*H$_a$MeMe), 49.9 (N*C*H$_b$MeMe), 26.5 (NCH$_b$*Me*Me), 25.2 (NCH$_a$Me*Me*), 24.5 (NCH$_a$*Me*Me), 24.1 (NCH$_b$Me*Me*), 20.0 (2,6-C$_6$H$_3$*Me*Me), 19.6 (2,6-C$_6$H$_3$Me*Me*), 14.1 (*Me*CN$_2$), 13.5 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull): 2724 (w), 2363 (w), 2274 (w), 1832 (w), 1718 (w), 1672 (m), 1648 (w), 1616 (s), 1581 (m, br), 1494 (m), 1403 (m), 1319 (s, br), 1253 (m), 1232 (s), 1205 (s), 1114 (w), 1094 (w), 1061 (w), 1011 (m, br), 956 (w), 938 (s), 883 (w), 819 (m), 790 (m), 763 (m), 724 (m), 698 (w), 676 (w), 631 (w), 581 (m), 550 (w), 491 (w), 447 (m), 417 (m), 402 (m) cm^{-1}. Anal. Found (calc for $C_{27}H_{41}N_3OSTi$): C 64.5 (64.4); H 8.3 (8.2); N 8.1 (8.3); S 7.6 (6.4).

NMR Tube Scale Reaction of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (10) with COS. A 22.5 mg (0.05 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 mL of C_6D_6. The solution was freeze−pump−thawed (× 3), and the headspace filled with COS at a pressure of 500 mmHg. The reaction was monitored using ^{1}H NMR spectroscopy.

NMR Tube Scale Reaction of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (10) with CS$_2$. A 22.5 mg (0.05 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 mL of C_6D_6. To this was added a few drops (excess) CS$_2$. A color change from green to brown occurred within 5 min. The reaction was monitored by ^{1}H NMR spectroscopy.

NMR Tube Scale Reaction of Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (6) with *tert*-Butyl Isocyanate. A 9.9 mg (0.03 mmol) sample of Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**6**) was dissolved in 0.6 mL of C_6D_6, and to this was added 3.0 μL (3 mg, 0.03 mmol) of *tert*-butyl isocyanate via microliter syringe. The reaction was monitored by ^{1}H NMR spectroscopy. Complete conversion to *trans*-[Ti(η-C$_5$Me$_5$)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ and 1,3-di-*tert*-butyl carbodiimide was observed after 25 days. A corresponding procedure was used to examine the reactivity of **5**, **7**, and **8** with *tert*-butyl isocyanate.

Ti(η-C$_5$Me$_5$){N(Ar)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$} (21). A 163 mg (0.37 mmol) sample of [Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$}] was dissolved in ca. 10 mL of benzene to give a dark green solution. To this was added 45 μL (39.1 mg, 0.39 mmol) of *tert*-butyl isocyanate via microliter syringe. After 4 h, all volatiles were removed under reduced pressure, and the residue was triturated with ca. 5 mL of pentane to afford the product as a sticky brown solid. Yield: 55 mg (27%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K) δ: 6.98 (1 H, d, $J = 7.3$ Hz, *m*-2,6-C$_6$H$_3$Me$_2$), 6.94 (1 H, d, $J = 7.3$ Hz, *m*-2,6-C$_6$H$_3$Me$_2$), 6.88 (1 H, t, $J = 7.3$ Hz, *p*-2,6-C$_6$H$_3$Me$_2$), 3.32 (1 H, apparent sept, $J = 6.4$ Hz, NC*H*$_a$MeMe), 3.14 (1 H, apparent sept, $J = 6.4$ Hz, NC*H*$_b$MeMe), 2.32 (3 H, s, 2,6-C$_6$H$_3$*Me*Me), 1.99 (3 H, s, 2,6-C$_6$H$_3$Me*Me*), 1.97 (15 H, s, C$_5$Me$_5$), 1.66 (9 H, s, ^{t}Bu), 1.44 (3 H, s, MeCN$_2$), 1.15 (3 H, d, $J = 6.4$ Hz, NCH$_a$*Me*Me), 0.99 (3 H, d, $J = 6.4$ Hz, NCH$_b$Me*Me*), 0.78 (3 H, d, $J = 6.4$ Hz, NCH$_b$*Me*Me), 0.50 (3 H, d, $J = 6.4$ Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K) δ: 166.9 (CN$_2$), 152.5 (OCN), 148.8 (*i*-2,6-C$_6$H$_3$Me$_2$), 133.6 (*o*-2,6-C$_6$H$_3$Me$_2$), 133.0 (*o*-2,6-C$_6$H$_3$Me$_2$), 127.4 (C$_5$Me$_5$), 127.6 (*m*-2,6-C$_6$H$_3$Me$_2$), 124.1 (*p*-2,6-C$_6$H$_3$Me$_2$), 51.9 (NC*H*$_a$MeMe), 49.7 (NC*H*$_b$MeMe), 32.9 (NC*Me*$_3$), 25.5 (NCH$_b$*Me*Me, NCH$_a$Me*Me* (br)), 24.2 (NCH$_a$*Me*Me, NCH$_b$Me*Me* (br)), 19.6 (2,6-C$_6$H$_3$*Me*$_2$), 13.5 (*Me*CN$_2$), 12.8 (C$_5$*Me*$_5$). N*C*Me$_3$ resonance not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2957 (s), 2721 (w), 2602 (w), 2359 (w), 2140 (m), 1904 (w), 1652 (m), 1610 (m, br), 1549 (m), 1366 (m), 1349 (w), 1334 (m), 1313 (w), 1284 (m), 1262 (w), 1250 (w), 1232 (w), 1206 (s, br), 1174 (m, br), 1138 (w), 1123 (w), 1097 (w), 1049 (m), 1017 (m), 955 (w), 940 (w), 919 (w), 860 (w), 792 (m), 764 (m), 732 (w), 634 (m, br), 610 (w), 594 (w), 558 (w), 529 (w), 499 (m), 477 (m), 423 (w).

NMR Scale Reaction of Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} (10) with *tert*-Butyl Isocyanate. Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} (**10**) (13.2 mg, 0.03 mmol) was dissolved in 0.6 mL of C$_6$D$_6$, and to this was added 3.5 μL (3.0 mg, 0.03 mmol) of *tert*-butyl isocyanate via microliter syringe. The reaction was monitored using ^{1}H NMR spectroscopy. A color change from green to dark red was observed after ca. 10 min. Complete conversion of the starting materials to *trans*-[Ti(η-C$_5$Me$_5$)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ and *N*-*tert*-butyl-*N′*-*p*-tolyl carbodiimide was observed after 16 h.

Ti(η-C$_5$Me$_5$){N(Ar)C(NAr)O}{MeC(N^{i}Pr)$_2$} (22). Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (273 mg, 0.62 mmol) was dissolved in ca. 15 mL of benzene. To this was added 86 μL (84.6 mg, 0.62 mmol) of 2,6-dimethylphenyl isocyanate via microliter syringe, and the solution was stirred for 21 h. Volatiles were then removed under reduced pressure to afford the product as a brown solid. Yield: 308 mg (84%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.24 (2 H, d, *J* = 7.6 Hz, *m*-N$_b$-2,6-C$_6$H$_3$Me$_2$), 7.09 (1 H, m, *m*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 7.04 (1 H, m, *m*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 7.00 (2 H, t, *J* = 7.6 Hz, *p*-N$_b$-2,6-C$_6$H$_3$Me$_2$, *p*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 3.20 (1 H, apparent sept, *J* = 6.4 Hz, NC*H*$_a$MeMe), 3.17 (1 H, apparent sept, *J* = 6.4 Hz, NC*H*$_b$MeMe), 2.50 (6 H, s, N$_b$-2,6-C$_6$H$_3$*Me*$_2$), 2.40 (3 H, s, N$_a$-2,6-C$_6$H$_3$*Me*Me), 2.07 (3 H, s, N$_a$-2,6-C$_6$H$_3$Me*Me*), 1.83 (15 H, s, C$_5$Me$_5$), 1.41 (3 H, s, MeCN$_2$), 0.93 (3 H, d, *J* = 6.4 Hz, NCH$_a$*Me*Me), 0.92 (3 H, d, *J* = 6.4 Hz, NCH$_a$Me*Me*), 0.75 (3 H, d, *J* = 6.4 Hz, NCH$_b$*Me*Me), 0.55 (3 H, d, *J* = 6.4 Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 166.3 (CN$_2$), 153.3 (OCN), 148.3 (*i*-2,6-C$_6$H$_3$Me$_2$), 148.2 (*i*-2,6-C$_6$H$_3$Me$_2$), 134.0 (*o*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 133.5 (*o*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 130.1 (*o*-N$_b$-2,6-C$_6$H$_3$Me$_2$), 128.4 (*p*-N$_b$-2,6-C$_6$H$_3$Me$_2$), 128.3 (*p*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 127.7 (*m*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 127.6 (*m*-N$_a$-2,6-C$_6$H$_3$Me$_2$), 124.6 (*C*$_5$Me$_5$), 121.0 (*m*-N$_b$-2,6-C$_6$H$_3$Me$_2$), 49.6 (N*C*H$_a$MeMe), 48.8 (N*C*H$_a$MeMe), 25.1 (NCH$_b$*Me*Me), 24.9 (NCH$_a$Me*Me*), 24.6 (NCH$_b$*Me*Me), 24.1 (NCH$_b$Me*Me*), 20.4 (N$_b$-2,6-C$_6$H$_3$*Me*$_2$), 19.6 (N$_a$-2,6-C$_6$H$_3$*Me*Me), 19.2 (N$_a$-2,6-C$_6$H$_3$Me*Me*), 14.0 (*Me*CN$_2$), 12.9 C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2722 (w), 1610 (s), 1580 (s), 1495 (m), 1404 (w), 1338 (w), 1316 (m), 1302 (m), 1259 (w), 1226 (w), 1210 (m), 1192 (w), 1168 (w), 1114 (w), 1094 (w), 995 (m), 925 (m), 819 (w), 789 (w), 761 (m), 725 (m), 708 (w), 588 (w), 559 (w), 498 (w), 456 (m), 442 (m). Anal. Found (calc for C$_{35}$H$_{50}$N$_4$OTi): C 71.2 (71.2); H 8.2 (8.5); N 9.4 (9.5). EIMS: *m*/*z* 591 [M]$^+$, 575 [M − Me]$^+$, 545 [M − 3Me]$^+$.

Ti(η-C$_5$Me$_5$){N(Ar)C(NTol)O}{MeC(N^{i}Pr)$_2$} (23). Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (565 mg, 1.28 mmol) was dissolved in ca. 40 mL of pentane, to which was added 161 μL (170 mg, 1.28 mmol) of *p*-tolyl isocyanate via microliter syringe, and the resulting solution was stirred for 18 h. A crop of dark brown crystals (362 mg, 49% yield) was isolated from the mother liquor. The remaining solution had all volatiles removed under reduced pressure to afford a further 262 mg (36% yield) of product as a brown powder. Total yield: 624 mg (85%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.66 (2 H, d, *J* = 8.2 Hz, *o*-4-C$_6$H$_4$Me), 7.14 (2 H, d, *J* = 8.2 Hz, *m*-4-C$_6$H$_4$Me), 7.04 (1 H, d, *J* = 7.2 Hz, *o*-2,6-C$_6$H$_3$Me$_2$), 6.99 (1 H, d, *J* = 7.2 Hz, *o*-2,6-C$_6$H$_3$Me$_2$), 6.95 (1 H, t, *J* = 7.2 Hz, *p*-2,6-C$_6$H$_3$Me$_2$), 3.26 (1 H, apparent sept, *J* = 6.6 Hz, NC*H*$_a$MeMe), 3.09 (1 H, apparent sept, *J* = 6.4 Hz, NC*H*$_b$MeMe), 2.37 (3 H, s, 4-C$_6$H$_4$*Me*), 2.21 (3 H, s, 2,6-C$_6$H$_3$*Me*Me), 2.02 (3 H, s, 2,6-C$_6$H$_3$Me*Me*), 1.96 (15 H, s, C$_5$*Me*$_5$), 1.43 (3 H, s, *Me*CN$_2$), 1.07 (3 H, d, *J* = 6.6 Hz, NCH$_a$*Me*Me), 0.97 (3 H, d, *J* = 6.6 Hz, NCH$_a$Me*Me*), 0.84 (3 H, d, *J* = 6.4 Hz, NCH$_b$*Me*Me), 0.56 (3 H, d, *J* = 6.4 Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 167.9 (CN$_2$), 154.9 (OCN), 148.3 (*i*-NAr), 147.9 (*i*-NAr), 133.7 (*o*-2,6-C$_6$H$_3$Me$_2$), 133.4 (*o*-2,6-C$_6$H$_3$Me$_2$), 129.4 (*p*-4-C$_6$H$_4$Me), 129.0 (*m*-4-C$_6$H$_4$Me), 128.6 (*m*-2,6-C$_6$H$_3$Me$_2$), 128.3 (*m*-2,6-C$_6$H$_3$Me$_2$), 128.1 (*C*$_5$Me$_5$), 125.6 (*o*-4-C$_6$H$_4$Me), 124.5 (*p*-2,6-C$_6$H$_3$Me$_2$), 50.3 (N*C*H$_a$MeMe), 49.3 (N*C*H$_b$MeMe), 25.9 (NCH$_b$*Me*Me), 24.8 (NCH$_a$Me*Me*), 24.2 (NCH$_a$*Me*Me), 24.0 (NCH$_b$Me*Me*), 21.0 (2,6-C$_6$H$_3$*Me*Me), 19.7 (4-C$_6$H$_4$*Me*), 19.4 (2,6-C$_6$H$_3$Me*Me*), 13.6 (*Me*CN$_2$), 13.0 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2727 (w), 1655 (w), 1615 (w), 1595 (m), 1576 (s), 1504 (s), 1410 (m), 1338 (m), 1311 (m), 1295 (m), 1247 (m), 1208 (m), 1170 (w), 1118 (w), 1069 (w), 996 (w), 927 (w), 847 (w), 811 (w), 787 (w), 757 (w), 724 (w), 631 (w), 592 (w), 550 (w), 537 (w), 522 (w), 499 (w).

Ti(η-C$_5$Me$_5$){N(Tol)C(NAr)O}{MeC(N^{i}Pr)$_2$} (24). A 234 mg (0.55 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} was dissolved in ca. 20 mL of pentane. To this was added 76 μL (75 mg, 0.55 mmol) of 2,6-dimethylphenyl isocyanate. The solution was stirred and then stood for 18 h at −30 °C. The supernatant was then decanted off, and the residue was desolvated under reduced pressure to afford a brown powder. Yield: 210 mg (67%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.57 (2 H, d, *J* = 8.2 Hz, *m*-4-C$_6$H$_4$Me), 7.23 (2 H, d, *J* = 7.6 Hz, *m*-2,6-C$_6$H$_3$Me$_2$), 7.09 (2 H, d, *J* = 8.2 Hz, *o*-4-C$_6$H$_4$Me), 6.99 (1 H, t, *J* = 7.6 Hz, *p*-2,6-C$_6$H$_3$Me$_2$), 3.61 (1 H, s (br), NC*H*$_a$MeMe), 3.25 (1 H, s (br), NC*H*$_b$MeMe), 2.51 (6 H, s, 2,6-C$_6$H$_3$*Me*$_2$), 2.19 (3 H, s, 4-C$_6$H$_4$*Me*), 1.91 (15 H, s, C$_5$Me$_5$), 1.42 (3 H, s, MeCN$_2$), 0.95 (6 H, s (br), NCH$_{a,b}$*Me*Me), 0.87 (3 H, s (br), NCH$_b$Me*Me*), 0.61 (3 H, s (br), NCH$_a$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 167.3 (CN$_2$), 150.1 (OCN), 148.2 (*i*-NAr), 146.7 (*i*-NAr), 130.7 (*o*-4-C$_6$H$_4$Me), 130.2 (*o*-4-C$_6$H$_4$Me), 128.7 (*p*-4-C$_6$H$_4$Me), 128.6 (*m*-2,6-C$_6$H$_3$Me$_2$), 127.6 (*o*-2,6-C$_6$H$_3$Me$_2$), 123.4 (*m*-4-C$_6$H$_4$Me), 123.3 (*m*-4-C$_6$H$_4$Me), 121.0 (*p*-2,6-C$_6$H$_3$Me$_2$), 49.8 (N*C*H$_b$MeMe), 49.4 (N*C*H$_a$MeMe), 24.6 (NCH$_b$Me*Me*), 23.9 (NCH$_{a,b}$*Me*Me), 23.6 (NCH$_a$Me*Me*), 21.0 (4-C$_6$H$_4$*Me*), 19.8 (2,6-C$_6$H$_3$*Me*$_2$), 15.4 (*Me*CN$_2$), 12.6 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2957 (s), 2721 (w), 2670 (w), 1883 (w), 1732 (w), 1616 (s), 1582 (s), 1507 (s), 1350 (m), 1326 (s), 1257 (m), 1228 (m), 1214 (m), 1181 (w), 1169 (w), 1158 (w), 1144 (w), 1118 (w), 1106 (w), 1094 (w), 1076 (w), 1019 (w), 990 (m), 932 (w), 920 (m), 820 (m), 803 (m), 791 (w), 773 (w), 753 (m), 728 (m), 716 (m), 655 (w), 619 (w), 610 (w), 580 (w), 556 (w), 517 (w). Anal. Found (calc for C$_{34}$H$_{48}$N$_4$OTi): C 70.7 (70.8); H 8.9 (8.4); N 9.3 (9.7).

Ti(η-C$_5$Me$_5$){N(Tol)C(NTol)O}{MeC(N^{i}Pr)$_2$} (25). A 437 mg (1.02 mmol) sample of [Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$}] was dissolved in ca. 25 mL of benzene, to which was added 131 μL (138 mg, 1.02 mmol) of *p*-tolyl isocyanate. The resulting red solution was stirred for 30 min, after which volatiles were removed under reduced pressure. The residue was extracted with ca. 40 mL of pentane and cooled to −30 °C. Brown crystals (235 mg, 41% yield) were removed from the supernatant, which then had all volatiles removed under reduced pressure to afford a further 66 mg of product as a brown powder. Total yield: 301 mg (53%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.81 (2 H, d, *J* = 8.3 Hz, *o*-N$_b$-4-C$_6$H$_4$Me), 7.41 (2 H, d, *J* = 8.3 Hz, *o*-N$_a$-4-C$_6$H$_4$Me), 7.22 (2 H, d, *J* = 8.3 Hz, *m*-N$_b$-4-C$_6$H$_4$Me), 7.06 (2 H, d, *J* = 8.3 Hz, *m*-N$_a$-4-C$_6$H$_4$Me), 3.61 (1 H, sept, *J* = 6.8 Hz, NC*H*$_a$MeMe), 3.26 (1 H, sept, *J* = 6.6 Hz, NC*H*$_b$MeMe), 2.21 (3 H, s, N$_b$-4-C$_6$H$_4$*Me*), 2.17 (3 H, s, N$_a$-4-C$_6$H$_4$*Me*), 1.94 (15 H, s, C$_5$Me$_5$), 1.36 (3 H, s, MeCN$_2$), 1.05 (3 H, d, *J* = 6.6 Hz, NCH$_b$*Me*Me), 1.00 (3 H, d, *J* = 6.6 Hz, NCH$_b$Me*Me*), 0.92 (3 H, d, *J* = 6.8 Hz, NCH$_a$*Me*Me), 0.66 (3 H, d, *J* = 6.8 Hz, NCH$_a$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 169.1 (CN$_2$), 153.5 (OCN), 148.1 (*i*-N-4-C$_6$H$_4$Me), 146.5 (*i*-N-4-C$_6$H$_4$Me), 131.2 (*p*-N-4-C$_6$H$_4$Me), 129.5 (*p*-N-4-C$_6$H$_4$Me), 129.2 (*m*-N$_b$-4-C$_6$H$_4$Me), 128.7 (*m*-N$_a$-4-C$_6$H$_4$Me), 128.5 (*C*$_5$Me$_5$), 125.7 (*o*-N$_b$-4-C$_6$H$_4$Me), 123.7 (*o*-N$_a$-4-C$_6$H$_4$Me), 50.3 (N*C*H$_b$MeMe), 49.4 (N*C*H$_a$MeMe), 24.3 (NCH$_a$*MeMe*), 23.9 (NCH$_b$*MeMe*), 21.1 (N-4-C$_6$H$_4$*Me*), 21.1 (N-4-C$_6$H$_4$*Me*), 14.6 (*Me*CN$_2$), 12.6 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2727 (w), 2360 (w), 2342 (w), 1886 (w), 1609 (m), 1569 (s), 1500 (s), 1338 (s), 1322 (s), 1245 (m), 1208 (s), 1127 (m), 1107 (m), 1076 (w), 1018 (w), 996 (m), 918 (s), 817 (s), 785 (m), 724 (m), 698 (w), 681 (w), 642 (w), 620 (w), 611 (w), 578 (w), 544 (w), 515 (m), 487 (m), 440 (m), 408 (m). Anal. Found (calc for C$_{33}$H$_{46}$N$_4$OTi): C 70.3 (70.5); H 8.4 (8.2); N 9.9 (10.0). MS (F.I.): *m*/*z* 562 [M]$^+$.

Ti(η-C$_5$Me$_5$){OC(NTol)N(Tol)C(NTol)O}{MeC(N^{i}Pr)$_2$} (26). Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (204 mg, 0.48 mmol) was dissolved in ca. 20 mL of benzene to give a dark green solution. To this was added 120 μL (127 mg, 0.99 mmol) of *p*-tolyl isocyanate via microliter syringe. The solution was observed to turn brown and was stirred for 16 h. Volatiles were then removed under reduced pressure to afford an oily red product. This was triturated with pentane to yield a very static sensitive, dark brown solid. Yield: 171 mg (51%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.61 (2 H, d, $J = 8.6$ Hz, *o*-N$_b$-4-C$_6$H$_4$Me), 7.16 (4 H, d, $J = 8.6$ Hz, *o*-N$_a$-4-C$_6$H$_4$Me), 7.10 (2 H, d, $J = 8.6$ Hz, *m*-N$_b$-4-C$_6$H$_4$Me), 7.02 (4 H, d, $J = 8.6$ Hz, *m*-N$_a$-4-C$_6$H$_4$Me), 3.43 (2 H, apparent sept, $J = 7.1$ Hz, NC*H*MeMe), 2.17 (6 H, s, N$_a$-4-C$_6$H$_4$*Me*), 2.05 (3 H, s, N$_b$-4-C$_6$H$_4$*Me*), 1.85 (15 H, s, C$_5$Me$_5$), 1.44 (3 H, s, MeCN$_2$), 0.91 (6 H, d, $J = 7.1$ Hz, NCH*Me*Me), 0.83 (6 H, d, $J = 6.8$ Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 169.5 (CN$_2$), 153.1 (*i*-N$_a$-4-C$_6$H$_4$Me), 147.7 (*p*-N$_a$-4-C$_6$H$_4$Me), 142.2 (*i*-N$_b$-4-C$_6$H$_4$Me), 135.2 (*p*-N$_b$-4-C$_6$H$_4$Me), 130.0 (*o*-N$_b$-4-C$_6$H$_4$Me), 129.7 (*m*-N$_b$-4-C$_6$H$_4$Me), 129.4 (*m*-N$_a$-4-C$_6$H$_4$Me), 128.6 (*o*-N$_a$-4-C$_6$H$_4$Me), 124.3 (*C*$_5$Me$_5$), 49.5 (N*C*HMeMe), 23.9 (NCH*Me*Me), 23.5 (NCHMe*Me*), 21.1 (N$_b$-4-C$_6$H$_4$*Me*), 21.0 (N$_a$-4-C$_6$H$_4$*Me*), 16.4 (*Me*CN$_2$), 12.31 (C$_5$*Me*$_5$). OC(N)(N) resonance not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w). Anal. Found (calc for C$_{41}$H$_{53}$N$_5$O$_2$Ti): C 70.8 (70.8); H 7.8 (7.7); N 9.7 (10.1).

Ti(η-C$_5$Me$_5$){OC(NTol)N(Tol)C(NAr)O}{MeC(N^{i}Pr)$_2$} (27). A 83.6 mg (0.15 mmol) sample of Ti(η-C$_5$Me$_5$){N(Tol)C(NAr)O}{MeC(N^{i}Pr)$_2$} was dissolved in a solution of 19.3 mg (0.15 mmol) of *p*-tolyl isocyanate in ca. 5 mL of benzene to give a ruby solution. After 30 min, volatiles were removed under reduced pressure, and the final 1 mL of benzene was triturated with ca. 5 mL of pentane. All remaining volatiles were removed under reduced pressure to afford the product as a light brown powder. Yield: 84.3 mg (82%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.61 (2 H, d, $J = 8.1$ Hz, *o*-N$_b$-C$_6$H$_4$Me), 7.15−7.13 (4 H, m, *o*-N$_a$-C$_6$H$_4$Me, *m*-N$_a$-C$_6$H$_4$Me), 7.04 (2 H, d, $J = 8.1$ Hz, *m*-N$_b$-C$_6$H$_4$Me), 7.02 (1 H, m, *m*-2,6-C$_6$H$_3$Me$_2$), 6.94 (1 H, m, *m*-2,6-C$_6$H$_3$Me$_2$), 6.86 (1 H, t, $J = 7.5$ Hz, *p*-2,6-C$_6$H$_3$Me$_2$), 3.50 (1 H, apparent sept, $J = 6.7$ Hz, NC*H*$_a$MeMe), 3.05 (1 H, apparent sept, $J = 6.7$ Hz, NC*H*$_b$MeMe), 2.35 (3 H, s (br), 2,6-C$_6$H$_3$*Me*Me), 2.23 (3 H, s, N$_a$-C$_6$H$_4$*Me*), 2.14 (3 H, s, N$_b$-C$_6$H$_4$*Me*), 2.07 (3 H, s (br), 2,6-C$_6$H$_3$Me*Me*), 1.85 (15 H, s, C$_5$Me$_5$), 1.51 (3 H, s, MeCN$_2$), 1.06 (3 H, d, $J = 6.8$ Hz, NCH$_a$*Me*Me), 1.01 (3 H, d, $J = 6.8$ Hz, NCH$_a$Me*Me*), 0.91 (3 H, d, $J = 6.1$ Hz, NCH$_b$*Me*Me), 0.61 (3 H, d, $J = 6.1$ Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 168.9 (CN$_2$), 153.4 (*i*-N$_a$-C$_6$H$_4$Me), 150.7 (*i*-2,6-C$_6$H$_3$Me$_2$), 148.2 (*o*-2,6-C$_6$H$_3$Me$_2$), 147.9 (*p*-N$_a$-C$_6$H$_4$Me), 142.6 (*p*-N$_b$-C$_6$H$_4$Me), 135.3 (*i*-N$_b$-C$_6$H$_4$Me), 130.7 (*o*-N$_b$-C$_6$H$_4$Me), 129.9 (*C*$_5$Me$_5$), 129.6 (*o*-2,6-C$_6$H$_3$Me$_2$), 129.4 (*m*-N$_b$-C$_6$H$_4$Me), 128.9 (*m*-N$_a$-C$_6$H$_4$Me), 128.3 (*m*-2,6-C$_6$H$_3$Me$_2$), 127.9 (*m*-2,6-C$_6$H$_3$Me$_2$), 124.2 (*o*-N$_a$-C$_6$H$_4$Me), 121.1 (*p*-2,6-C$_6$H$_3$Me$_2$), 50.5 (NC*H*$_a$MeMe), 50.3 (NC*H*$_b$MeMe), 26.4 (NCH$_b$*Me*Me), 23.7 (NCH$_a$*Me*Me), 23.6 (NCH$_a$Me*Me*), 22.5 (NCH$_b$Me*Me*), 21.2 (N$_b$-C$_6$H$_4$*Me*), 21.1 (N$_a$-C$_6$H$_4$*Me*), 19.1 (2,6-C$_6$H$_3$*Me*Me), 19.1 (2,6-C$_6$H$_3$Me*Me*), 14.0 (*Me*CN$_2$), 12.7 (C$_5$*Me*$_5$). O*C*(N)(N) resonances not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2725 (w), 2360 (w), 2273 (w), 1637 (m), 1614 (m), 1597 (m), 1581 (s), 1507 (m), 1311 (m), 1261 (m), 1252 (m), 1202 (s), 1171 (w), 1127 (w), 1103 (w), 1070 (m), 1031 (w), 997 (m), 931 (w), 875 (w), 848 (w), 811 (w), 785 (w), 759 (w), 729 (m), 678 (w), 659 (w), 604 (w), 586 (w), 566 (w), 541 (w), 520 (w), 475 (m), 446 (m). Anal. Found (calc for C$_{42}$H$_{55}$N$_5$O$_2$Ti): C 71.3 (71.1); H 7.6 (7.8); N 9.1 (9.9).

Ti(η-C$_5$Me$_5$){OC(O)N(Tol)C(NTol)O}{MeC(N^{i}Pr)$_2$} (28). Ti(η-C$_5$Me$_5$){N(Tol)C(O)O}{MeC(N^{i}Pr)$_2$} (**29**) (103 mg, 0.22 mmol) was dissolved in ca. 15 mL of benzene to give a deep red solution. To this was added 28.9 mg (0.22 mmol) of *p*-tolyl isocyanate in ca. 5 mL of benzene to give a lighter red solution. After 10 min, all volatiles were removed under reduced pressure, and the resulting dark red oily solid was triturated with ca. 10 mL of pentane. The product was afforded as a red-brown powder. Yield: 73 mg (55%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.51 (2 H, d, $J = 8.0$ Hz, *o*-N$_a$-4-C$_6$H$_4$Me), 7.08 (2 H, d, $J = 8.1$ Hz, *o*-N$_b$-4-C$_6$H$_4$Me), 7.06* (2 H, d, $J = 8.0$ Hz, *m*-N$_a$-4-C$_6$H$_4$Me), 7.02 (2 H, d, $J = 8.1$ Hz, *m*-N$_b$-4-C$_6$H$_4$Me), 3.47 (1 H, apparent sept, $J = 6.9$ Hz, NC*H*$_a$MeMe), 3.38 (1 H, apparent sept, $J = 6.9$ Hz, NC*H*$_b$MeMe), 2.17 (3 H, s, N$_b$-4-C$_6$H$_4$*Me*), 2.05 (3 H, s, N$_a$-4-C$_6$H$_4$*Me*), 1.89 (15 H, s, C$_5$Me$_5$), 1.36 (3 H, s, MeCN$_2$), 1.10 (3 H, d, $J = 6.8$ Hz, NCH$_a$*Me*Me), 1.09 (3 H, d, $J = 6.8$ Hz, NCH$_a$Me*Me*), 0.89 (3 H, d, $J = 6.8$ Hz, NCH$_b$*Me*Me), 0.86* (3 H, d, $J = 6.8$ Hz, NCH$_b$*Me*Me) (* indicates cross-peak in NOESY experiment). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 169.5 (CN$_2$), 154.3 (OCO), 153.5 (*i*-N$_a$-4-C$_6$H$_4$Me), 147.5 (*p*-N$_a$-4-C$_6$H$_4$Me), 140.7 (*p*-N$_b$-4-C$_6$H$_4$Me), 135.7 (*i*-N$_b$-4-C$_6$H$_4$Me), 130.4 (*C*$_5$Me$_5$), 129.6 (*m*-N$_a$-4-C$_6$H$_4$Me), 129.4 (*o*-N$_b$-4-C$_6$H$_4$Me), 127.5 (*m*-N$_b$-4-C$_6$H$_4$Me), 123.9 (*o*-N$_a$-4-C$_6$H$_4$Me), 50.3 (N*C*H$_a$MeMe), 49.9 (N*C*H$_b$MeMe), 24.3 (NCH$_a$*Me*Me), 23.9 (NCH$_b$*Me*Me), 23.7 (NCH$_{a,b}$Me*Me*), 21.1 (N$_a$-4-C$_6$H$_4$*Me*), 21.0 (N$_b$-4-C$_6$H$_4$*Me*), 14.9 (*Me*CN$_2$), 12.5 (C$_5$*Me*$_5$). OC(N)(N) resonance not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2955 (s), 2726 (w), 2272 (w), 1681 (m), 1618 (m), 1592 (m, br), 1507 (m), 1408 (w), 1258 (w), 1206 (w), 1183 (w), 1103 (w), 1068 (w), 1024 (w), 1001 (m), 933 (w), 883 (w), 859 (w), 812 (m), 788 (m), 736 (w), 723 (w), 680 (w), 643 (w), 604 (w), 587 (w), 545 (w), 533 (w), 474 (w), 445 (w). Anal. Found (calc for C$_{34}$H$_{46}$N$_4$O$_3$Ti): C 67.2 (67.2); H 8.1 (7.6); N 8.5 (9.2).

Ti(η-C$_5$Me$_5$){OC(O)N(Tol)C(NAr)O}{MeC(N^{i}Pr)$_2$} (30). A 44.5 mg (0.09 mmol) sample of Ti(η-C$_5$Me$_5$){N(Tol)C(O)O}{MeC(N^{i}Pr)$_2$} was dissolved in ca. 5 mL of benzene. To this was added a solution of 13.8 mg (0.09 mmol) of 2,6-dimethylphenyl isocyanate in ca. 1 mL of benzene. After 18 h, volatiles were removed under reduced pressure, and the final 0.5 mL of benzene was triturated with ca. 2 mL of pentane. All remaining volatiles were removed under reduced pressure to afford the product as a dark red solid. Yield: 38 mg (65%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.53 (2 H, d, $J = 8.1$ Hz, *o*-4-C$_6$H$_4$Me), 7.13 (2 H, d, $J = 8.1$ Hz, *m*-4-C$_6$H$_4$Me), 7.03 (1 H, d (br), $J = 7.1$ Hz, *m*-2,6-C$_6$H$_3$Me$_2$), 6.93 (1 H, d (br), $J = 7.1$ Hz, *m*-2,6-C$_6$H$_3$Me$_2$), 6.87 (1 H, t, $J = 7.1$ Hz, *p*-2,6-C$_6$H$_3$Me$_2$), 3.37 (1 H, apparent sept, $J = 6.6$ Hz, NC*H*$_a$MeMe), 3.02 (1 H, apparent sept, $J = 6.6$ Hz, NC*H*$_b$MeMe), 2.29 (3 H, s (br), 2,6-C$_6$H$_3$*Me*Me), 2.11 (3 H, s, C$_6$H$_4$*Me*), 1.99 (3 H, s (br), 2,6-C$_6$H$_3$Me*Me*), 1.94 (15 H, s, C$_5$Me$_5$), 1.39 (3 H, s, MeCN$_2$), 1.15 (3 H, d, $J = 6.6$ Hz, NCH$_a$*Me*Me), 1.08 (3 H, d, $J = 6.6$ Hz, NCH$_a$Me*Me*), 0.85 (3 H, d, $J = 6.5$ Hz, NCH$_b$*Me*Me), 0.58 (3 H, d, $J = 6.5$ Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 169.1 (CN$_2$), 154.2 (OCO), 151.2 (*i*-2,6-C$_6$H$_3$Me$_2$), 147.5 (*o*-2,6-C$_6$H$_3$Me$_2$), 140.8 (*i*-4-C$_6$H$_4$Me), 135.9 (*p*-4-C$_6$H$_4$Me), 131.1 (*C*$_5$Me$_5$), 129.5 (*o*-4-C$_6$H$_4$Me), 129.4 (*m*-4-C$_6$H$_4$Me), 128.9 (*m*-2,6-C$_6$H$_3$Me$_2$), 125.5 (*m*-2,6-C$_6$H$_3$Me$_2$), 121.3 (*p*-2,6-C$_6$H$_3$Me$_2$), 51.5 (N*C*H$_a$MeMe), 51.0 (N*C*H$_b$MeMe), 26.9 (NCH$_b$*Me*Me), 24.2 (NCH$_a$Me*Me*), 24.1 (NCH$_a$*Me*Me), 23.4 (NCH$_b$Me*Me*), 21.5 (4-C$_6$H$_4$*Me*), 19.5 (2,6-C$_6$H$_3$*Me*Me), 19.3 (2,6-C$_6$H$_3$Me*Me*), 13.4 (C$_5$*Me*$_5$), 13.3 (*Me*CN$_2$). OC(N)(N) resonance not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2926 (s), 2725 (w), 1680 (s), 1620 (s), 1587 (s), 1514 (m, sh), 1313 (m), 1243 (m), 1203 (m), 1184 (m), 1105 (w), 1083 (w), 1025 (w), 1001 (s), 932 (w), 919 (w), 876 (w), 857 (w), 819 (m, br), 795 (m), 773 (m), 733 (w), 678 (w), 605 (w), 587 (w), 567 (w), 537 (w), 523 (w), 481 (w), 410 (w). Anal. Found (calc for C$_{35}$H$_{48}$N$_4$O$_3$Ti): C 67.7 (67.3); H 7.8 (7.8); N 9.0 (8.6).

Ti(η-C$_5$Me$_5$){N(Ar)C(NTol)N(Tol)}{MeC(N^{i}Pr)$_2$} (31). Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (46.5 mg, 0.11 mmol) was dissolved in 0.6 mL of C$_6$D$_6$. To this was added 23.4 mg (0.15 mmol) of 1,3-di-*p*-tolyl carbodiimide, and the reaction was monitored using ^{1}H NMR spectroscopy. Complete formation of product was observed after 24 h. Removal of all volatiles and trituration with ca. 2 mL of pentane afforded the product as a dark brown powder. Yield: 50.2 mg (72%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.41 (2 H, d (br), *m*-N$_a$-4-C$_6$H$_4$Me), 7.01 (2 H, d, *o*-N$_a$-4-C$_6$H$_4$-Me), 6.79 (1 H, m, *p*-N-2,6-Me$_2$C$_6$H$_3$), 6.72 (2 H, d, *m*-N$_b$-4-C$_6$H$_4$-Me), 6.67 (2 H, m, *m*-N-2,6-Me$_2$C$_6$H$_3$), 6.62 (2 H, d, *o*-N$_b$-4-C$_6$H$_4$Me), 3.89 (1 H, apparent sept, NC*H*$_a$MeMe), 3.11 (1 H, apparent sept, NC*H*$_b$MeMe), 2.26 (3 H, s, N$_a$-4-C$_6$H$_4$*Me*), 2.19 (6 H, s, N-2,6-C$_6$H$_3$*Me*$_2$), 2.07 (3 H, s, N$_b$-4-C$_6$H$_4$*Me*), 1.81 (15 H, s, C$_5$Me$_5$), 1.56 (3 H, s, MeCN$_2$), 1.15 (3 H, d, $J = 6.8$ Hz, NCH$_a$*Me*Me), 1.06 (3 H, d, $J = 6.8$ Hz, NCH$_a$Me*Me*), 0.89 (3 H, d, $J = 6.8$ Hz, NCH$_b$*Me*Me), 0.31 (3 H, s (br), NCH$_b$Me*Me*). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 166.6 (Me*C*N$_2$), 149.9 (*o*-2,6-Me$_2$C$_6$H$_3$), 149.0 (*i*-N$_a$-4-C$_6$H$_4$Me), 147.9 (*m*-,*p*-2,6-Me$_2$C$_6$H$_3$), 133.6 (*o*-2,6-Me$_2$C$_6$H$_3$), 131.4 (*p*-N$_a$-4-C$_6$H$_4$Me), 128.4 (*m*-N$_a$-4-C$_6$H$_4$Me), 128.3 (*i*-N$_b$-4-C$_6$H$_4$Me), 128.1 (*o*-N$_a$-4-C$_6$H$_4$Me), 127.4 (*p*-N$_b$-4-C$_6$H$_4$Me), 127.2 (*o*-N$_b$-4-C$_6$H$_4$Me), 126.8 (*C*$_5$Me$_5$), 121.1 (*m*-N$_b$-4-C$_6$H$_4$Me), 50.1 (N*C*H$_a$MeMe), 49.0 (N*C*H$_b$MeMe), 24.8 (NCH$_b$*Me*Me), 24.7 (NCH$_a$Me*Me*), 23.9 (NCH$_b$Me*Me*), 23.0 (NCH$_a$-*Me*Me), 21.0 (N$_b$-4-C$_6$H$_4$*Me*), 20.9 (2,6-C$_6$H$_3$*Me*Me), 20.4 (N$_a$-4-C$_6$H$_4$*Me*), 19.5 (2,6-C$_6$H$_3$Me*Me*), 18.6 (*Me*CN$_2$), 12.8 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w). Anal. Found (calc for C$_{41}$H$_{55}$N$_5$Ti): C 72.7 (74.0); H 8.6 (8.3); N 10.2 (10.5).

Ti(η-C$_5$Me$_5$){N(Tol)C(NTol)N(Tol)}{MeC(N^{i}Pr)$_2$} (32). A 19.0 mg (0.04 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} was dissolved in 0.6 mL of C$_6$D$_6$. To this was added 9.8 mg (0.04 mmol) of 1,3-di-*p*-tolyl carbodiimide, resulting in an immediate color change from dark green to dark brown. The reaction was monitored using ^{1}H NMR spectroscopy and was found to go to completion after 1 h. Removal of all volatiles under reduced pressure and trituration with pentane afforded the product as a brown powder. Yield: 21 mg (73%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K) δ: 7.24 (4 H, d (br), *m*-N$_a$-4-C$_6$H$_4$Me), 6.97 (2 H, d, $J = 8.3$ Hz, *m*-N$_b$-4-C$_6$H$_4$Me), 6.92 (4 H, d, $J = 7.8$ Hz, *o*-N$_a$-4-C$_6$H$_4$-Me), 6.85 (2 H, d, $J = 8.3$ Hz, *o*-N$_b$-4-C$_6$H$_4$Me), 3.69 (2 H, apparent sept, $J = 7.1$ Hz, NC*H*MeMe), 2.11 (6 H, s, N$_a$-4-C$_6$H$_4$*Me*), 2.02 (3 H, s, N$_b$-4-C$_6$H$_4$*Me*), 1.87 (15 H, s, C$_5$Me$_5$), 1.54 (3 H, s, MeCN$_2$), 1.02 (6 H, d, $J = 7.1$ Hz, NCH*Me*Me), 0.73 (6H, d, $J = 7.1$ Hz, NCHMe*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K) δ: 173.6 (N$_2$CN), 166.6 (Me*C*N$_2$), 149.7 (*i*-N$_b$-4-C$_6$H$_4$Me), 148.3 (*p*-N$_b$-4-C$_6$H$_4$Me), 147.6 (*i*-N$_a$-4-C$_6$H$_4$Me), 130.1 (*p*-N$_a$-4-C$_6$H$_4$Me), 128.6 (*o*-N$_b$-4-C$_6$H$_4$Me), 128.3 (*o*-N$_a$-4-C$_6$H$_4$Me), 127.7 (*C*$_5$Me$_5$), 123.8 (*m*-N$_a$-4-C$_6$H$_4$Me), 122.6 (*m*-N$_b$-4-C$_6$H$_4$Me), 49.3 (N*C*H-MeMe), 24.1 (NCH*Me*Me), 23.1 (NCHMe*Me*), 20.9 (N$_a$-4-C$_6$H$_4$*Me*), 20.9 (N$_b$-4-C$_6$H$_4$*Me*), 18.8 (*Me*CN$_2$), 12.7 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 2728 (w), 2671 (w), 1882 (w), 1733 (w), 1655 (s), 1609 (m), 1572 (m), 1538 (s), 1505 (s), 1292 (m, br), 1209 (w), 1145 (w), 1107 (w), 1072 (w), 1021 (w), 998 (w), 946 (m), 891 (w), 813 (s), 791 (m), 723 (m), 670 (w), 638 (w), 616 (w), 584 (w), 549 (w), 519 (w), 442 (w), 417 (w), 407 (w). Anal. Found (calc for C$_{40}$H$_{53}$N$_5$Ti): C 73.1 (73.7); H 8.7 (8.2); N 10.8 (10.8).

Reaction of Ti(η-C$_5$Me$_5$)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (5) with Nitrosobenzene. A 740 mg (1.43 mmol) sample of Ti(η-C$_5$Me$_5$)-(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**5**) was dissolved in ca. 30 mL of pentane, and to this was added a solution of 155 mg (1.45 mmol) of nitrosobenzene dissolved in ca. 15 mL of pentane. The reaction was stirred for 16 h, after which a fine yellow precipitate was observed. The supernatant was decanted off and the residue washed with ca. 20 mL of pentane, to afford the product **15** as an insoluble yellow powder (350 mg, 76% yield). The corresponding reaction of **6** with nitrosobenzene was monitored by ^{1}H NMR spectroscopy and found to yield the corresponding dimeric oxo product **2**.

NMR Tube Scale Reaction of Ti(η-C$_5$Me$_5$)(NAr){MeC-(N^{i}Pr)$_2$} (9) with Nitrosobenzene. A 16.0 mg (0.04 mmol) sample of Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (**9**) was dissolved in 0.6 mL of C$_6$D$_6$. To this was added 3.9 mg (0.04 mmol) of nitrosobenzene, resulting in an immediate color change from green to orange. The reaction was monitored using ^{1}H NMR spectroscopy, and the ^{1}H NMR spectrum was found to contain resonances attributable to the dimeric oxo compound **2** and ^{t}BuN=NAr. A corresponding reaction was also carried out for Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (**10**).

Ti(η-C$_5$Me$_5$){N(Tol)C(Ph)$_2$O}{MeC(N^{i}Pr)$_2$} (33). A 7.0 mg (0.02 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (**10**), 3.0 mg (0.02 mmol) of benzophenone, and 1.9 mg (0.01 mmol) of 1,4-dimethoxybenzene (internal standard) were dissolved in 592 mg of toluene-*d*$_8$. The reaction was monitored using ^{1}H NMR spectroscopy in the temperature range 16 to −40 °C. Upon cooling of the solution to −40 °C, Ti(η-C$_5$Me$_5$){N(Tol)C(Ph)$_2$O}{MeC(N^i-Pr)$_2$} (**33**) was afforded in ca. 100% yield by ^{1}H NMR spectroscopy. ^{1}H NMR (toluene-*d*$_8$, 500.0 MHz, 233 K) δ: 8.05−8.03 (2 H, m, *o*-4-C$_6$H$_4$Me), 7.70 (2 H, d, $J = 7.6$ Hz, *o*-C$_6$H$_5$ (a)), 7.37−7.35 (2 H, m, *o*-C$_6$H$_5$ (b)), 7.21−7.19 (2 H, m, *m*-4-C$_6$H$_4$Me), 7.13 (1 H, t, $J = 7.6$ Hz, *p*-C$_6$H$_5$ (a)), 7.10−7.07 (3 H, m, *m*-, *p*-C$_6$H$_5$ (b)), 7.05−7.01 (2 H, m, *m*-C$_6$H$_5$ (a)), 4.14 (1 H, apparent sept, $J = 7.0$ Hz, NC*H*$_a$MeMe), 3.55 (1 H, apparent sept, $J = 7.0$ Hz, NC*H*$_b$-MeMe), 2.16 (3 H, s, 4-C$_6$H$_4$*Me*), 1.95 (15 H, s, C$_5$Me$_5$), 1.67 (3 H, s, MeCN$_2$), 1.30 (3 H, d, $J = 7.0$ Hz, NCH$_a$*Me*Me), 1.19 (3 H, d, $J = 7.0$ Hz, NCH$_b$*Me*Me), 0.96 (3 H, d, $J = 7.0$ Hz, NCH$_b$-Me*Me*), 0.72 (3 H, d, $J = 7.0$ Hz, NCH$_a$Me*Me*).

Ti(η-C$_5$Me$_5$){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (34). Ti(η-C$_5$-Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**6**) (20.4 mg, 0.05 mmol) was dissolved in 0.6 mL of C$_6$D$_6$, and to this was added 5.0 μL (5.2 mg, 0.05 mmol) of benzaldehyde via microliter syringe. After 5 min, [Ti-(η-C$_5$Me$_5$){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$}] (**34**) was afforded in ca. 100% yield by ^{1}H NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 289 K) δ: 7.39 (2 H, d, $J = 7.1$ Hz, *o*-C$_6$H$_5$), 7.20−7.08 (3 H, m, *m*-, *p*-C$_6$H$_5$), 6.01 (1 H, s, OC(H)), 3.90 (1 H, apparent sept, $J = 6.8$ Hz, NC*H*$_a$MeMe), 3.58 (1 H, apparent sept, $J = 6.8$ Hz, NC*H*$_b$MeMe), 2.01 (15 H, s, C$_5$Me$_5$), 1.73 (3 H, s, MeCN$_2$), 1.31 (3 H, d, $J = 6.8$ Hz, NCH$_a$*Me*Me), 1.24 (3 H, d, $J = 6.8$ Hz, NCH$_a$-Me*Me*), 1.12 (3 H, d, $J = 6.8$ Hz, NCH$_b$*Me*Me), 1.09 (9 H, s, ^{t}Bu), 1.01 (3 H, d, $J = 6.5$ Hz, NCH$_b$Me*Me*).

Ti(η-C$_5$Me$_5$){N(Tol)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (35a/35b). A 7.5 mg (0.02 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (**10**) was dissolved in 0.6 mL of C$_6$D$_6$. To this was added 1.8 μL (1.9 mg, 0.02 mmol) of benzaldehyde via microliter syringe, and the reaction was monitored using ^{1}H NMR spectroscopy. Complete conversion of the starting materials to form the product, presumed to be **35a**, was observed after 5 min. This compound was found to interconvert to another product, presumed to be **35b**, with a half-life of ca. 15 min. Decomposition of this compound to the oxo species [Ti(η-C$_5$Me$_5$)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**2**) prevented isolation and full characterization of the species. **35a**: ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 289 K) δ: 7.40 (2 H, d, $J = 6.8$ Hz, *o*-C$_6$H$_5$), 7.15−7.10 (3 H, m, *m*-, *p*-C$_6$H$_5$), 6.93 (2 H, d, $J = 8.5$ Hz, *o*-4-C$_6$H$_4$Me), 6.65 (2 H, d, $J = 8.5$ Hz, *m*-4-C$_6$H$_4$Me), 6.18 (1 H, s, OC(H)), 4.14 (1 H, apparent sept, $J = 7.0$ Hz, NC*H*$_a$MeMe), 3.54 (1 H, apparent sept, $J = 7.0$ Hz, NC*H*$_b$MeMe), 2.13 (3 H, s, 4-C$_6$H$_4$*Me*), 1.97 (15 H, s, C$_5$*Me*$_5$), 1.58 (3 H, s, *Me*CN$_2$), 1.25 (3 H, d, $J = 7.1$ Hz, NCH$_a$*Me*Me), 1.12 (3 H, d, $J = 6.6$ Hz, NCH$_b$*Me*Me), 0.93 (3 H, d, $J = 7.0$ Hz, NCH$_a$Me*Me*), 0.81 (3 H, d, $J = 6.8$ Hz, NCH$_b$-Me*Me*). **35b**: ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 289 K) δ: 7.22 (2 H, m, *o*-C$_6$H$_5$), 7.15−7.10 (3 H, m, *m*-,*p*-C$_6$H$_5$), 6.84 (2 H, d, $J = 8.5$

Table 4. X-ray Data Collection and Processing Parameters for Ti(η-C$_5$Me$_5$)(NAr){MeC(N^{i}Pr)$_2$} (9), [Ti(η-C$_5$Me$_5$)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (11), [Ti(η-C$_5$H$_4$Me)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (13), and Ti(η-C$_5$Me$_5$){N(Ar)C(NR)O}{MeC(N^{i}Pr)$_2$} (R = Ar (22) or Tol (23))

	9	11	13	22	23
empirical formula	$C_{26}H_{41}N_3Ti$	$C_{46}H_{76}N_4S_2Si_4Ti_2$	$C_{38}H_{60}N_4S_2Si_4Ti_2$	$C_{35}N_{50}N_4O_1Ti_1$	$C_{34}H_{48}N_4O_1Ti_1$
fw	443.53	957.4	845.18	590.71	575.68
temp/K	150	150	175	150	150
wavelength/Å	0.71073	0.71073	0.71069	0.71073	0.71073
space group	$I4_1cd$	$C2/m$	$P\bar{1}$	$P21/c$	$P\bar{1}$
a/Å	20.5223(4)	20.5239(8)	9.416(1)	19.0867(9)	9.5758(3)
b/Å	20.5223(4)	14.2637(7)	10.684(2)	9.8270(4)	9.9197(3)
c/Å	24.3873(6)	10.5071(4)	12.409(2)	17.7637(7)	17.2651(6)
α/deg	90	90	93.934(6)	90	82.229(1)
β/deg	90	104.031(3)	94.552(8)	93.316(2)	78.344(1)
γ/deg	90	90	115.495(8)	90	84.112(1)
V/Å^3	10271.1	2984.2	1115.9	3326.3(2)	1586.63(9)
Z	16	2	1	4	2
d(calcd)/Mg·m^{-3}	1.15	1.07	1.26	1.18	1.20
abs coeff/mm^{-1}	0.35	0.44	0.58	0.29	0.30
R indices R_1, R_w	$R_1 = 0.0396$	$R_1 = 0.0744$	0.0636	$R_1 = 0.0591$	0.0890
$[I > 3\sigma(I)]^a$	$R_w = 0.0418$	$R_w = 0.0900$	0.0534	$R_w = 0.0608$	0.0919

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|^2\}}$.

Hz, *o*-4-C$_6$H$_4$Me), 6.67 (2 H, d, J = 8.5 Hz, *m*-4-C$_6$H$_4$Me), 6.24 (1 H, s, OC(H)), 3.30 (1 H, apparent sept, J = 6.4 Hz, NCH_aMeMe), 3.25 (1 H, apparent sept, J = 6.4 Hz, NCH_bMeMe), 2.10 (3 H, s, 4-C$_6$H$_4$*Me*), 2.04 (15 H, s, C$_5$Me$_5$), 1.65 (3 H, d, J = 6.7 Hz, NCH$_a$*Me*Me), 1.14 (3 H, d, J = 6.7 Hz, NCH$_a$Me*Me*), 1.12 (3 H, s, MeCN$_2$), 1.04 (3 H, d, J = 6.6 Hz, NCH$_b$*Me*Me), 0.85 (3 H, d, J = 6.4 Hz, NCH$_b$Me*Me*).

Ti(η-C$_5$Me$_5$){N(Tol)C(Ph)(Me)O}{MeC(N^{i}Pr)$_2$} (36). A 182 mg (0.43 mmol) sample of Ti(η-C$_5$Me$_5$)(NTol){MeC(N^{i}Pr)$_2$} (**10**) was dissolved in ca. 5 mL of benzene. To this was added a solution of 49.6 μL (51.1 mg, 0.43 mmol) of acetophenone in ca. 5 mL of benzene to afford a dark brown solution. After 15 min all volatiles were removed under reduced pressure, and the residue was triturated with ca. 5 mL of pentane to afford the product as a dark brown wax. Yield: 132 mg (57%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 289 K) δ: 7.37 (2 H, d, J = 8.1 Hz, *o*-C$_6$H$_5$), 7.18−7.13 (1 H, m, *p*-C$_6$H$_5$), 7.08 (2 H, m, *m*-C$_6$H$_5$), 6.89 (2 H, d, J = 8.1 Hz, *o*-4-C$_6$H$_4$Me), 6.53 (2 H, d, J = 8.1 Hz, *m*-4-C$_6$H$_4$Me), 6.18 (1 H, s, OC(H)), 4.10 (1 H, apparent sept, J = 6.7 Hz, NCH_aMeMe), 3.10 (1 H, apparent sept, J = 6.7 Hz, NCH_bMeMe), 2.14 (3 H, s, 4-C$_6$H$_4$*Me*), 2.06 (15 H, s, C$_5$Me$_5$), 2.05 (3 H, s, OCMe), 1.53 (3 H, s, MeCN$_2$), 1.25 (3 H, d, J = 6.7 Hz, NCH$_a$*Me*Me), 1.12 (3 H, d, J = 6.7 Hz, NCH$_a$Me*Me*), 0.93 (3 H, d, J = 6.7 Hz, NCH$_b$*Me*Me), 0.81 (3 H, d, J = 6.7 Hz, NCH$_b$Me*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 289 K) δ: 164.3 (CN$_2$), 148.6 (*i*-/*p*-4-C$_6$H$_4$Me), 148.1 (*p*-/*i*-4-C$_6$H$_4$-Me), 128.9 (*o*-4-C$_6$H$_4$Me), 128.5 (*i*-C$_6$H$_5$), 128.4 (*p*-C$_6$H$_5$), 127.6 (*o*-C$_6$H$_5$), 127.1 (*m*-C$_6$H$_5$), 124.3 (*C*$_5$Me$_5$), 118.4 (*m*-4-C$_6$H$_4$Me), 84.1 (O*C*Me), 49.1 (N*C*H$_b$MeMe), 48.2 (N*C*H$_a$MeMe), 25.4 (OC*Me*), 24.5 (NCH$_b$Me*Me*), 24.4 (NCH$_a$*Me*Me), 23.6 (NCH$_b$-*Me*Me), 23.2 (NCH$_a$Me*Me*), 20.7 (4-C$_6$H$_4$*Me*), 16.6 (*Me*CN$_2$), 12.4 (C$_5$*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 1654 (m), 1636 (m), 1610 (m), 1578 (w), 1505 (s), 1311 (m), 1288 (m), 1262 (m), 1206 (w), 1171 (w), 1115 (m), 1088 (m), 1071 (m), 1027 (m), 914 (w), 899 (w), 841(w), 792 (m), 763 (w), 735 (w), 723 (w), 697 (w), 669 (w), 655 (w), 628 (w), 610 (w), 594 (w), 572 (w), 527 (w), 498 (w), 435 (w), 402 (w).

NMR Tube Scale Reactions of Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (6) with Benzamide, Hexanoamide, and Trimethylacetamide. Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**6**) (10.1 mg, 5.1 × 10^{-5} mol) was dissolved in CD$_2$Cl$_2$ (0.6 mL), and the resulting red solution was used to dissolve 1.5 equiv of dimethoxybenzene (5.6 mg, 7.7 × 10^{-5} mol) and 1.0 equiv of benzamide (3.7 mg, 5.1 × 10^{-5} mol). The mixture was transferred to an NMR tube equipped with a J. Young Teflon valve, and the ^{1}H NMR spectrum was recorded over 24 h. Anolgous procedures were followed for screening reactions with other metal compounds and hexanoamide and trimethylacetamide.

Crystal Structure Determinations of Ti(η-C$_5$Me$_5$)(N-2,6-C$_6$H$_3$Me$_2$){MeC(N^{i}Pr)$_2$} (9), [Ti(η-C$_5$Me$_5$)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (11), [Ti(η-C$_5$H$_4$Me)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (13), and Ti(η-C$_5$Me$_5$){N(Ar)C(NR)O}{MeC(N^{i}Pr)$_2$} (R = Ar (22) or Tol (23)). Crystal data collection and processing parameters are given in Table 4. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 or 175 K in a stream of cold N$_2$ using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using either an Enraf-Nonius DIP2000 or KappaCCD diffractometer. Intensity data were processed using the DENZO package.[110] The structures were solved with SIR92,[111] and subsequent full-matrix least-squares refinements were carried out using CRYSTALS.[112] For **9** the choice of space group as *C*2/*m* over the possible non-centrosymmetric alternatives was favored by examination of the normalized structure factors with the expected values and by the satisfactory refinement in *C*2/*m*. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were placed in calculated positions. A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for the eight structures has been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

Computational Details. All calculations were performed with the Gaussian 98 set of programs[113] within the framework of hybrid DFT (B3PW91).[114,115] The Ti atom was represented with the small core RECP from the Stuttgart's group and the associated basis set.[116] The remaining atoms (C, H, N, O) were represented by a 6-31G-(d,p) basis set.[117] The nature of the extrema located after geometry

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optimization without any symmetry constraint has been determined by analytic calculations of the vibrational frequencies.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations and further details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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