

Reactions of Cyclopentadienyl-Amidinate Titanium Hydrazides with CO₂, CS₂, and Isocyanates: Ti=N_α Cycloaddition, Cycloaddition-Insertion, and Cycloaddition-NNR₂ Group Transfer Reactions

Pei Jen Tiong,[†] Ainara Nova,[‡] Laura R. Groom,[†] Andrew D. Schwarz,[†] Jonathan D. Selby,[†] A. Daniel Schofield,[†] Eric Clot,^{*,‡} and Philip Mountford^{*,†}

[†]Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K., and [‡]Institut Charles Gerhardt, Université Montpellier 2, CNRS 5253, cc 1501, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

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We report a comprehensive combined experimental and DFT investigation of the synthesis, molecular and electronic structures, and reactivity of terminal hydrazido complexes with CO₂, CS₂, isocyanates, and isothiocyanates. Reaction of Cp*Ti{MeC(NⁱPr)₂}(N^tBu) with hydrazines $R^{1}R^{2}NNH_{2}$ gave the structurally characterized series of hydrazides $Cp^{*}Ti\{MeC(N^{i}Pr)_{2}\}(NNR^{1}R^{2})$ ($R^{1} = Ph, R^{2} = Ph$ (13), Me (14); $R^{1} = R^{2} = Me$ (15)). The energetics of this imide/hydrazine exchange reaction, as well as the electronic and molecular structures of 13-15, have been evaluated by DFT and compared with those of their methyl and phenyl imido counterparts. Reaction of 13-15 with CO_2 or CS_2 gave $Ti = N_{\alpha}$ cycloaddition products of the type $Cp^*Ti\{MeC(N^1Pr)_2\}\{N(NR_2)C(E)E\}$ (R = Ph, Me; E = O, S) and, in the case of CO₂, cycloaddition-insertion products Cp*Ti{MeC- $(N^{i}Pr)_{2}$ {OC(O)N(NR₂)C(O)O}, in which 2 equivs of CO₂ had effectively inserted into Ti=N_{α}. Reaction of 13 with isocyanates and isothiocyanates also gave stable cycloaddition products. $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NPh_{2})C(NTol)O}$ reacted further with CO₂ to give a mixed cycloaddition-insertion product. The ^tBuNCO moiety in Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(N^tBu)O} could be displaced by CO_2 or TolNCO. In contrast, the reactions of 15 are dominated by cycloaddition-elimination reactions. Reaction with 'BuNCO or Ar'NCO (2 equivs) gave 'BuNCNNMe₂ or the heterocycle 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O), respectively, along with [Cp*Ti{MeC- $(N^{i}Pr)_{2}(\mu-O)]_{2}$. With TolNCO (2 equivs), Cp*Ti{MeC(N^{i}Pr)_{2}}OC(NNMe_{2})N(Tol)C(NTol)O{ was formed via a series of cycloaddition-elimination and cycloaddition-insertion steps. The energetics and mechanisms of the cycloaddition, cycloaddition-insertion, and cycloaddition-extrusion processes of various model imido and hydrazido complexes have been investigated using DFT. In the latter (metathesis) reactions, the reaction outcomes depend on a delicate balance of the relative affinities of NR or NNR₂ for the metal center or the organic fragment (CO, CS, or RNC).

Introduction

Since being established 20 years ago,¹⁻⁴ the chemistry of terminal titanium imido compounds (L)Ti=NR (R = alkyl, aryl) has advanced enormously. Much of this progress has

been charted in a series of reviews,⁵⁻¹¹ and most of the interest in this chemistry concerns reactions of the polar and unsaturated Ti=NR multiple bond itself (formally a $\sigma^2 \pi^4$ triple bond in most instances¹²⁻¹⁴), which can undergo coupling or exchange with a range of unsaturated substrates. As a development of our work in titanium imido chemistry we have become interested in exploring the apparently related hydrazido complexes (L)Ti=NNR₂. The chemistry

^{*}To whom correspondence should be addressed. Email: clot@ univ-montp2.fr (E.C.); philip.mountford@chem.ox.ac.uk (P.M.).

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Figure 1. Influence of N_{α} substituents on reaction outcomes in imido and hydrazido chemistry (top) for reactions of Ti(N_2N^{py})-(NR)(py) (R = ^tBu, NPh₂) with XylNC or PhCCMe;^{25,26} (bottom) for reactions of Cp*Ti{MeC(NⁱPr)₂}(NR) (R = ^tBu, Ar) with CO₂.²⁷⁻²⁹ Atoms derived from the original Ti=NR group are shown in red, while those originating from the organic substrate are shown in blue.

of well-defined examples of these species was hardly developed at all until relatively recently, although they had been postulated as intermediates in hydrohydrazination catalysis.^{15–21} While the first report of a terminal titanium hydrazide was in 1978,²² the first structurally characterized examples only appeared in 2004 and 2005.^{17,23} Similarly, the first fully authenticated [2 + 2] cycloaddition product of any group 4 hydrazide was reported only in 2008.²⁴

One very distinctive feature of titanium hydrazides and their zirconium congeners is their tendency to undergo facile $N_{\alpha}-N_{\beta}$ bond insertion or cleavage with substrates such as alkynes, isonitriles, CO, and heavier chalcogen sources,

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processes that are unavailable to their imido counterparts.^{24,30-35} For example, Ti(N₂N^{py})(N^tBu) reacts with XylNC and PhCCMe to form 1 and 2 (Figure 1), involving coupling or addition reactions across the Ti=N multiple bond.^{25,26} In contrast, Ti(N₂N^{py})(NNPh₂)(py) forms 3 and 4 with the same substrates. Mechanistically,^{31,32} these reactions also proceed via addition to Ti=N_α but then lead on to N_α-N_β bond scission. The latter steps formally involve reduction of the nitrogen atoms of the original Ti=N-NPh₂ linkage from 2– in Ti(N₂N^{py})(NNPh₂)(py) to 3– in the products and a corresponding net two-electron oxidation of the substrates. Accordingly, reactions of group 4 hydrazides with nonoxidizable substrates such as CO₂, isocyanates, and organic nitriles do not give N_α-N_β bond reduction and stop at Ti=N_α cycloaddition or insertion.^{24,32,36-39}

We have been trying to gain a better knowledge and understanding of the reactions of the hydrazide $M=N_{\alpha}$ bond both in general terms and in comparison with relevant imido counterparts and also as a function of different β -nitrogen groups which are known to have significant effects on molecular and electronic structure. This aspect of hydrazido chemistry is totally underdeveloped for the following reasons. First, it is only for the recently developed group 4 systems that any significant $M=N_{\alpha}$ bond reactivity is seen at all, despite studies of group 6 hydrazido complexes for many

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years.^{40,41} The more dative (donor/acceptor) nature of the group 6 M \leftarrow :N_{α} bond and reduced multiple-bond character reduces its reactivity. Second, with formally oxidizable substrates, N_{α}-N_{β} bond scission readily occurs, effectively masking the initial M=N_{α} bond reaction. Finally, with regard to comparing different N_{β}R₂ groups, there are relatively few homologous pairs or series of complexes of this type.⁴²⁻⁴⁴ A significant cause of this problem is the well-established tendency of group 4 N_{β}-dialkyl-substituted hydrazides to dimerize, forming unreactive M₂(μ ₂-NNR₂)₂ moieties.^{17,23,44}

Although we had previously reported the series of welldefined terminal hydrazides Ti(Me₂Calix)(NNR¹R²) (**5**; R¹ = R² = Ph, Me; R¹ = Ph, R² = Me) with the aim of making a comparative study of the various Ti=NNR¹R² groups, their negligible intrinsic reactivity caused this approach to fail.⁴³ To date, only one report has appeared describing comparative reactions of differently N_β-substituted M=N– NR₂ functional groups.³⁷ Here Gade et al. found rather similar [2 + 2] cycloaddition reaction chemistry between Cp*Ti(N^{XyI}N)(NNR¹R²)(L) (**6**; R¹ = R² = Ph, L = ^tBuN-H₂; R¹ = Ph, R² = Me, L = py; Xyl = 3,5-C₆H₃Me₂) and phenylallene, PhNCO, and PhNCS. Reactions of the dimethylhydrazido homologue Cp*Ti(N^{XyI}N)(NNMe₂)(L) (which has a tendency to lose L and dimerize) with these substrates was not reported.



In a renewed attempt to develop the chemistry of the hydrazide Ti= N_{α} bond, we decided to target hydrazido analogues of the tert-butyl and aryl imido complexes Cp*Ti- ${MeC(N^{i}Pr)_{2}}(NR)$. These undergo a number of different transformations of the Ti=NR bond with a wide range of nonoxidizable substrates, namely CO₂, CS₂, COS, RNCO, RNCS, PhNO, RCONH₂, and RCOR'.^{27–29,45,46} These systems, which have been studied in detail both by experiment and by DFT, are also rather sensitive to the identity of the imido N substituent, making them good candidates for developing hydrazido chemistry. For example, reaction of both $Cp*Ti{MeC(N^{i}Pr)_{2}}(N^{t}Bu)$ (7) and $Cp*Ti{MeC}$ - $(N^{1}Pr)_{2}$ (NAr) (8, Ar = Tol, 4-C₆H₄CF₃, 4-C₆H₄NMe₂, 2,6-C₆H₃Me₂) with CO₂ forms the [2 + 2] cycloaddition products 9 and 10 (Figure 1). However, while 8 reacts with further CO_2 to form the "double insertion" product 11, the tert-butyl homologue does not, giving instead ^tBuNCO

extrusion and the μ -oxo dimer $[Cp*Ti{MeC(N^1Pr)_2}(\mu-O)]_2$ (12).

In this contribution we report a comprehensive combined experimental and DFT investigation of the synthesis, structures, and reactivity of cyclopentadienyl-amidinate hydrazido complexes. A part of this work has been communicated.³⁹

Results and Discussion

Synthesis and Molecular Structures of New Titanium Hydrazido Complexes. The new hydrazido compounds Cp*Ti-{MeC(NⁱPr)₂}(NNR¹R²) (R¹ = Ph, R² = Ph (13), Me (14); $R^1 = R^2 = Me$ (15)) were prepared from Cp*Ti{MeC- $(N^{i}Pr)_{2}$ ($N^{t}Bu$) (7) and the corresponding hydrazines at room temperature according to eq 1 using the tert-butyl imide-hydrazide exchange strategy introduced by us previously.³⁶ An analogous approach had also proved successful for preparing the aryl imido complexes $Cp^*Ti\{MeC-(N^iPr)_2\}(NAr)$ (8).^{29,46} Compounds 13 and 15 were isolated as yellow or dark green solids in 83 and 67% optimized yields, respectively, while 14 (34% yield) was a very soluble green-brown, waxy material that was hard to crystallize and purify. Attempts to vary the cyclopentadienyl-amidinate supporting ligand set in a way that was successful for the analogous aryl imido systems⁴⁶ were unrewarding. Treatment of Cp*Ti{PhC(NSiMe₃)₂}(N^tBu)⁴⁷ with Ph₂NNH₂ in toluene- d_8 at room temperature or 100 °C for 3 days gave no reaction. With Me₂NNH₂, no reaction occurred at room temperature, while at higher temperatures an unknown mixture of products was formed. Reactions of Cp'Ti{PhC- $(NSiMe_3)_2$ $(N^tBu)^{46}$ (Cp' = C₅H₄Me) with Ph₂NNH₂ and PhMeNH₂ were more promising, but the products were oils and again were difficult to manipulate and purify.



The ¹H and ¹³C NMR data for 13–15 are consistent with the C_s -symmetric half-sandwich structures depicted in eq 1. Diffraction-quality crystals of all three were grown from pentane. The molecular structures are shown in Figures 2 and 3, and selected distances and angles are given in Table 1. The compounds possess a three-legged piano-stool geometry around titanium with η^5 -C₅Me₅ and $\kappa^2 N, N'$ acetamidinate ligands. The metric parameters associated with the Cp*Ti- ${MeC(N^{i}Pr)_{2}}$ fragments are similar in all three and are comparable to those reported previously for imido compounds of the type $Cp^R Ti \{R^1 C (NR^2)_2\} (NR^3)$.^{29,46} The main point of interest is the variation in the $Ti=NNR^{1}R^{2}$ linkages as a function of the β -N substituents. One such homologous series has been structurally characterized previously, namely $Ti(Me_2Calix)(NNR^1R^2)$ (5; $R^1 = Ph, R^2 = Ph, Me; R^1 = R^2 =$ Me). Gade et al. have also structurally characterized the series $Cp^{Ti}(N^{Xyl}N)(NNR^{1}R^{2})(L)$ (6) with the same hydrazide ligands as in 13-15 and 5, but here the donor ligand L

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Figure 2. Displacement ellipsoid plots (25% probability) of (a) $Cp*Ti\{MeC(N^{1}Pr)_{2}\}(NNPh_{2})$ (13) and (b) $Cp*Ti\{MeC(N^{1}Pr)_{2}\}(NNMePh)$ (14). H atoms are omitted for clarity.



Figure 3. Displacement ellipsoid plot (20% probability) of Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (15). H atoms are omitted for clarity. Atoms carrying the suffix "A" are related to their counterparts by the symmetry operator x, y, $-z + \frac{3}{2}$).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Cp*Ti-{ $MeC(N^iPr)_2$ }(NNPh₂) (13), Cp*Ti{ $MeC(N^iPr)_2$ }(NNMePh) (14), and Cp*Ti{ $MeC(N^iPr)_2$ }(NNMe₂) (15)^{*a*}

13	14	15
2.097	2.067	2.063
1.734(2)	1.734(2)	1.723(2)
2.115(2)	2.110(2)	2.101(1)
2.099(2)	2.090(2)	
1.369(2)	1.371(3)	1.386(2)
1.409(3)	1.396(4)	1.461(2)
1.425(3)	1.460(4)	
121.4	121.1	119.5
120.8	121.8	120.8
119.6	119.7	
64.23(7)	64.44(9)	64.45(7)
163.9(1)	166.3(2)	159.5(1)
118.9(2)	118.2(2)	110.7(1)
116.7(2)	115.3(2)	110.7(1)
121.5(2)	120.8(2)	112.9(2)
	13 2.097 1.734(2) 2.115(2) 2.099(2) 1.369(2) 1.409(3) 1.425(3) 121.4 120.8 119.6 64.23(7) 163.9(1) 118.9(2) 116.7(2) 121.5(2)	13 14 2.097 2.067 1.734(2) 1.734(2) 2.115(2) 2.110(2) 2.099(2) 2.090(2) 1.369(2) 1.371(3) 1.409(3) 1.396(4) 1.425(3) 1.460(4) 121.4 121.1 120.8 121.8 119.6 119.7 64.23(7) 64.44(9) 163.9(1) 166.3(2) 118.9(2) 118.2(2) 116.7(2) 115.3(2) 121.5(2) 120.8(2)

^{*a*} Cp_{cent} is the computed Cp* ring carbon centroid. Atoms carrying the suffix "A" are related to their counterparts by the symmetry operator *x*, *y*, $-z + \frac{3}{2}$.

(py, DMAP, or none) varies in each case, making precise comparisons difficult.

In general terms, the Ti= N_{α} and N_{α} - N_{β} distances and angles subtended at N_{α} and N_{β} are comparable to those of (L)Ti=NNR¹R² complexes reported previously (R¹, R² = alkyl, aryl, H).^{48,49} The short average Ti=N_{α} bond distance of 1.730 Å and approximately linear Ti= N_{α} - N_{β} angle (average 163°) are consistent with a $\sigma^2 \pi^4$ triple bond and formally dianionic $[NNR^1R^2]^{2-}$ ligands (see below for a DFT analysis).^{23,42,50} The N_{β} atoms for the phenyl-substituted compounds 13 and 14 are planar within error (due to conjugation of the lone pair with the phenyl ring(s)),^{42,50} whereas that of 15 is pyramidal. The sum of the angles subtended at N(2) in this case is 334.3(2)°, close to that expected for formal sp³ hybridization (328.4°). The Ti= N_{α} and $N_{\alpha}-N_{\beta}$ distances for 13 and 14 are identical within error, whereas those for 15 are shorter and longer, respectively. A similar trend in $N_{\alpha} - N_{\beta}$ distance was found for the calixarene-supported compounds 5, and group 4 N_b-dialkylsubstituted hydrazides generally have longer $N_\alpha - N_\beta$ distances and pyramidal N_β atoms.^{48,49} The $N_\alpha - N_\beta$ single bond in free Me_2NNH_2 (1.436(2) Å, pyramidal NMe_2) is likewise longer than that in Ph₂NNH₂ (1.418(2) Å, planar *N*Ph₂), apparently due to N_{β} hybridization effects.^{50,51}

The Ti=N_{α} distances for 13 and 14 are equivalent within error to the value of 1.738(2) Å found for Ti=N in the aryl imide Cp*Ti{MeC(NⁱPr)₂}(N-2,6-C₆H₃Me₂), while that of 15 is significantly shorter.⁴⁶ Within the series 13–15 the Ti=N_{α} bond distances vary in the order Ti=NNPh₂ \approx Ti=NNMePh > Ti=NNMe₂, with Δ (Ti=N_{α}) = 0.011(3) Å between 15 and 13 or 14. In contrast, the corresponding distances for Ti(Me₂Calix)(NNR¹R²) (5) vary in the opposite way with Ti=NNPh₂ < Ti=NNMePh \approx Ti=NNMe₂ (1.717(2), 1.727(3), and 1.729(4) Å, respectively),⁴³ although all were longer than Ti=N in Ti(Me₂calix)(N¹Bu) (1.705(3) Å).⁵² To explore this further, we used DFT to calculate the geometries of the simplified model imido and hydrazido compounds CpTi{MeC(NMe)₂}(NR) (R = Me (1Me), Ph

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Figure 4. Model complexes used in the DFT calculations. Selected distances (Å): Ti=N = 1.688 (1Me), 1.709 (1Ph), 1.713 (1NPh₂), 1.714 (1NMePh), 1.716 (1NMe₂-planar), 1.705 (1NMe₂); $N_{\alpha}-N_{\beta} = 1.345$ (1NPh₂), 1.339 (1NMePh), 1.329 (1NMe₂-planar), 1.360 (1NMe₂).

(1Ph)) and CpTi{MeC(NMe)₂}(NNR¹R²) (R¹ = Ph, R² = Ph (1NPh₂), Me (1NMePh); R¹ = R² = Me (1NMe₂)), as illustrated in Figure 4. A further model was calculated on the basis of CpTi{MeC(NMe)₂}(NNMe₂), but this time with a constrained NNMe₂ group in which the geometry at N_{β} was forced to be planar (1NMe₂_planar). Model 1NMe₂_planar was 4.6 kcal mol⁻¹ less stable than the fully relaxed 1NMe₂. Full details of the structures are provided in the Supporting Information.

DFT Analysis of Molecular and Electronic Structures and Imide-Hydrazine Exchange Energies. The DFT trend in $Ti=N_{\alpha}$ distances ($Ti=NNPh_2 \approx Ti=NNMePh > Ti=NNMe_2$ (1)) for the model hydrazides 1NPh₂, 1NMePh, and 1NMe₂ is consistent with that observed experimentally, although the computed distances are systematically shorter due to the reduced bulk of the models. The trends in $N_{\alpha} - N_{\beta}$ distances and angles at N_{α} and N_{β} are likewise consistent. In particular, the longest $N_{\alpha}-N_{\beta}$ distance is associated with the shortest Ti= N_{α} (i.e., 1NMe₂) and vice versa. The reason for the longer $Ti=N_{\alpha}$ distance in 1NPh₂ and 1NMePh is better conjugation of the N_{β} lone pair (N_{β}-LP) with Ti=N_{α} as a result of the planarity at N_{β}. Consistent with this, on forcing the N_{β} atom of $1NMe_2$ to be planar (giving 1NMe2_planar), there was a 0.011 Å lengthening of Ti=N_{α} and a 0.031 A shortening of N_{α}-N_{β} compared to **1NMe₂**. The better conjugation of N_{β} -LP in **1NMe₂_planar** is illustrated by a 24 kcal mol⁻¹ increase in the donation of N_{β} -LP into the Ti= $N_{\alpha} \pi^*$ bond, as obtained in the NBO second-order perturbation analysis of donor-acceptor interactions. A smaller shortening of the N-Me distances (0.018 A) was also seen, attributed to the reduction in covalent radius on going from an sp³ to an sp² N_{β}.

The Ti=NPh distance in **1Ph** lies between those of **1NPh₂** and **1NMe₂**, which is slightly different from the experimental situation for Cp*Ti{MeC(NⁱPr)₂}(N-2,6-C₆H₃Me₂), but steric effects associated with 2,6-C₆H₃Me₂ could lengthen the Ti=NAr bond. The Ti=NMe distance in **1Me** was the shortest of all, consistent with previous structural comparisons of homologous pairs of titanium alkyl and aryl imido complexes.⁵³⁻⁵⁶ The longer Ti=N bond distance in **1Ph** compared to that in **1Me** is due to a π -accepting character

[Ti]=N-Me	+	PhNH ₂	>	[Ti]=N-Ph	+	MeNH ₂	∆E = -2.5
[Ti]=N-Me	+	Ph ₂ NNH ₂		[Ti]=N-NPh2	+	MeNH ₂	∆E = -5.1
[Ti]=N-Me	+	PhMeNNH ₂		[Ti]=N-NMePh	+	MeNH ₂	∆E = -4.7
[Ti]=N-Me	+	Me ₂ NNH ₂		[Ti]=N-NMe2	+	MeNH ₂	∆E = -4.0

Figure 5. DFT computed electronic energies (kcal mol^{-1}) for the isodesmic reactions illustrated. [Ti] represents CpTi{MeC-(NMe)₂}.

of the Ph group, as illustrated by the larger donation (by 14 kcal mol⁻¹) from Ti=N π to π^* on Ph compared to the reverse donation from π on Ph toward Ti=N π^* . Such electron transfer interactions are absent in **1Me**.

Overall, the experimental and DFT results show that while alkyl imides should have the shortest $Ti=N_{\alpha}$ bonds, those for aryl imide and alkyl or aryl hydrazide ligands are more similar to each other. With respect to the $Ti=NNR_2$ systems, the geometry at N_{β} has the greatest influence on the $Ti=N_{\alpha}$ and $N_{\alpha}-N_{\beta}$ bond lengths. For a planar N_{β} the different substituents have a smaller but noticeable (for the DFT models) effect on the $Ti=N_{\alpha}$ and $N_{\alpha}-N_{\beta}$ distances.

As mentioned, compounds 13–15 were prepared from 7 and the appropriate hydrazine using an exchange strategy well established previously for aryl imido complexes. To gain additional insights into the underlying energetics of these reactions (which experimentally all proceed to completion), we computed the energies of the isodesmic processes in Figure 5 using the model systems in Figure 4. The *tert* butyl imide—hydrazine exchange reactions are all somewhat more favorable than those with PhNH₂. Ph₂NNH₂ provides the most energetically favorable exchange reaction, but there is little difference between the three hydrazines studied.

We have also compared the computed electronic structures of the Ti=NR and Ti=NNR₂ linkages for the model systems **1Me** through **1NMe₂**. The electronic structures of titanium imido compounds have been studied in detail,^{9,12–14,57–60} and a number of DFT investigations of the bonding in hydrazides have also been reported.^{23,42,50,61–63} There has been one DFT report comparing the electronic structure of

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Figure 6. Isosurfaces and energies of the π_v MOs of CpTi{MeC(NMe)₂}(NR) (R = Me (1Me), Ph (1Ph), NPh₂ (1NPh₂), NMePh (1NMePh), NMe₂ (1NMe₂ (top right) or 1NMe₂-planar (bottom right)).

Ti=NMe, Ti=NPh, and Ti=NNPh₂ ligands within the same supporting ligand framework, namely Ti{HC(pz)₃}(NR)Cl₂ as models for real systems of the type Ti{HC(Me₂pz)₃}-(NR)Cl₂.^{23,64-67} The effects of varying the N_{β} substituents or geometry were not assessed.

All six model systems, **1Me** through **1NMe**₂ and **1NMe**₂– **planar**, have a formal Ti=N_{α} triple bond containing two principal d_{π}-p_{π} molecular orbitals which form or contribute to the three highest MOs of the complexes (see the Supporting Information for further details). One MO (denoted π_v) lies in the molecular mirror plane, and the other lies perpendicular to it (π_h). The π_h energies are relatively insensitive to the N_{α} substituents and vary nonsystematically due to different degrees of mixing with the out-of-phase 2p_{π} contribution of amidinate N atoms. The π_v MOs do not mix significantly with the supporting ligand orbitals and also interact with the N_{α} substituent (Ph, NR₂) orbitals. The π_v MOs for the six models are depicted in Figure 6 along with their energies.

In comparison to CpTi{MeC(NMe)₂}(NMe) (**1Me**), the phenyl substituent in **1Ph** leads to a destabilization of π_v by +0.49 eV due to a π^* antibonding interaction with one of the occupied ring MOs. This value is within the ranges determined previously by DFT and/or photoelectron spectroscopy.^{14,23} As expected, ^{23,42,50,62,63} introduction of NNPh₂ in **1NPh₂** gives a larger destabilization (+1.23 eV) due to the N_β atom lone pair. The π_v MO in **1NMePh** is slightly more destabilized compared to **1NPh₂** (+0.1 eV), and that in **1NMe₂_planar** is the least stable (+0.46 eV, cf. **1NPh₂**; +1.69 eV, cf. **1Me**). Allowing **1NMe₂_planar** to relax to **1NMe₂** stabilizes π_v by 0.52 eV. The destabilization along the series **1NPh₂**, **1NMePh**, **1NMe₂_planar** follows the reduction in delocalization of the N_β lone pair by the phenyl ring(s) and tracks the changes in Ti=N_α and N_α-N_β noted above. The eventual similarity in energy of π_v (average 4.23, range 0.16 eV) for **1NPh₂**, **1NMePh**, and **1NMe₂** arises from two different means of stabilization: conjugation with the N_{β} -phenyl group(s) or N_{β} pyramidalization.

Reactions of $Cp*Ti{MeC(N^iPr)_2}(NNR_2)$ (R = Ph (13), Me (15)) with CO₂ and CS₂. We found that the reactions of 13 or 15 with CO2 and CS2 were rather similar, and so we discuss the two systems alongside each other below. In contrast, their reactions with isocyanates and isothiocyanates differed significantly, depending upon the β -NR₂ group. These are discussed later on. We also carried out representative preparative and/or NMR tube scale reactions of Cp*Ti{MeC- $(N^{1}Pr)_{2}$ (NNMePh) (14) with CO₂ and CS₂, as described in the Supporting Information. The reaction outcomes were analogous to those for 13. For this reason, and the difficulties in obtaining synthetically useful quantities of 14, we focus hereafter on 13 and 15. The reactions of 13 and 15 with CO₂ and CS₂ are summarized in Scheme 1. DFT studies of these reactions, varying both the Ti=NR group (Ph, NPh₂, NMe₂) and the substrate (CO2, CS2, MeNCO), are discussed later on

When the reactions of 13 and 15 with CO_2 (excess, 1.1 atm pressure) were followed by ¹H NMR in C_6D_6 , the firstformed intermediates $Cp*Ti\{MeC(N^iPr)_2\}\{N(NR_2)C(O)O\}$ (R = Ph (16), Me (17)) were immediately observed. These subsequently converted into the final products $Cp*Ti\{MeC-(N^iPr)_2\}\{OC(O)N(NR_2)C(O)O\}$ (R = Ph (18), Me (19)). Under identical conditions, the reaction of 16 with CO_2 was noticeably slower than that of 17. Compounds 16 and 17 were prepared on a preparative scale in ca. 60% isolated yield by reaction of 13 and 15 with an excess of CO_2 at -78 °C for 5 min. Compounds 18 and 19 were obtained in ca. 70% yield after more extended reaction times at room temperature (Scheme 1).

The solution ¹H and ¹³C NMR data for **16** and **17** are consistent with the C_1 -symmetric N,O-bound carbamate-type [2 + 2] cycloaddition products shown in Scheme 1. For example, the ¹H NMR spectrum of **16** shows two apparent septets for the inequivalent isopropyl methine hydrogens, and four doublets for the two pairs of diastereotopic methyl groups of these substituents. The IR spectra showed bands at 1684 (**16**) and 1667 cm⁻¹ (**17**) attributed to ν (C=O) of the carbamate ligands. The corresponding absorption for Ti-(Me₄taa){N(NPh₂)C(O)O} (formed from Ti(Me₄taa)(NNPh₂) and CO₂; H₂Me₄taa = tetramethyldibenzotetraaza[14]annulene)

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Figure 7. Displacement ellipsoid plot (20% probability) of (a) $Cp^{Ti}{MeC(N^{i}Pr)_{2}}{OC(O)N(NPh_{2})C(O)O}$ (18) and (b) $Cp^{Ti}{MeC(N^{i}Pr)_{2}}{OC(O)N(NMe_{2})C(O)O}$ (19). H atoms omitted for clarity.



Scheme 1. Reactions of $Cp*Ti{MeC(N'Pr)_2}(NNR_2)$ (R = Ph (13), Me (15)) with CO₂ and CS₂

appears at 1685 cm⁻¹;³⁶ those for imide-derived Cp*Ti{MeC (NⁱPr)₂}{N(R)C(O)O} (R = ^tBu, aryl) are observed between 1672 and 1655 cm⁻¹.²⁹ Compounds **16** and **17** are the second reported [2 + 2] cycloaddition products formed between CO₂ and a transition-metal hydrazide. Like the aryl imido derived carbamate **10** (Figure 1) they are stable in solution for days at room temperature and do not eliminate the corresponding aminoisocyanates R₂NNCO.

The NMR spectra for **18** and **19** indicate C_s -symmetric products, and their IR spectra show two strong bands at 1715 and 1676 cm⁻¹ and at 1702 and 1655 cm⁻¹, respectively, consistent with the incorporation of a second CO₂ molecule. Since the ¹³C spectra show only one C = O resonance (δ 157.2 ppm), these bands are attributed to the symmetric and antisymmetric ν (C=O) modes of a dicarboxylate OC(O)N-(NR₂)C(O)O ligand. The corresponding absorptions for the imido-derived compounds **11** (Figure 1) appear between 1704 and 1694 cm⁻¹ and between 1658 and 1651 cm⁻¹. Diffraction-quality crystals of both **18** and **19** were grown by slow evaporation of a diethyl ether solution. The molecular structures are shown in Figure 7, and selected distances and angles are given in Table 2. These confirm that two molecules of CO₂ have been effectively inserted into the Ti=N_{α} bonds of **13** and **15**. The X-ray structure of the homologous Cp*Ti{MeC(NⁱPr)₂}{OC(O)N(NMePh)C-(O)O}, derived from **14**, is given in the Supporting Information. The distances and angles within the new dicarboxylate ligands are analogous to those reported for **11**.²⁹ The atoms of the {TiOC(O)N(N)C(O)O} moieties are approximately coplanar. For **18** the maximum displacement from the least squares plane is 0.20 Å, and for **19** it is 0.14 Å. The N_{α}-N_{β} distance for **18** is 0.020(4) Å shorter than for **19**, reflecting the different N_{β} hybridization. The β -NR₂ groups are effectively "locked" between the two adjacent C=O groups, consistent with the NMR data, which find two chemically inequivalent N_{β} substituents.

The net "double insertion" of two CO₂ molecules into the Ti= N_{α} bonds of 13–15 is a new transformation for a metal hydrazido compound (mechanistically, a sequential

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cycloaddition-insertion process). This is also a very unusual process in imido chemistry, having been observed for either two CO₂ or two isocyanates "inserting" into the Ti=NAr of **8** or two alkynes into the Ir=N^tBu bond of Cp*Ir(N^tBu).^{29,46,68} We have previously reported mechanistic studies of this process in the case of **11**. Very recently we reported another Ti=N_α bond "insertion": namely, the reaction of Ti(N₂N^{Me})(NNPh₂)(py) (N₂N^{Me} = MeN(CH₂CH₂NSiMe₃)₂) with fluorinated benzonitriles to give the hydrazonamide complexes Ti(N₂N^{Me})-{NC(Ar^F)NNPh₂}(py) (Ar^F = 2,6-C₆H₃F₂, C₆F₅).³² This reaction proceeds via a [2 + 2] cycloaddition followed by reverse cycloaddition in the opposite sense.

Reaction of 13 or 15 with an excess of CS₂ for 16 h at room temperature afforded the dark brown thiocarbamates Cp*Ti{MeC(NⁱPr)₂}{N(NR₂)C(S)S} (R = Ph (20), Me (21)) in reasonable yields. The ¹H and ¹³C NMR data are consistent with the C_1 -symmetric structures illustrated in Scheme 1. An analogous product was formed with 14 (see the Supporting Information). Longer reaction times did not lead to "double-insertion" analogues of 18 and 19. However, whereas 20 and 21 are stable in solution for days, the corresponding cycloaddition products formed from the imido analogues Cp*Ti{MeC(NⁱPr)₂}(NR) (R = ^tBu (7), Ar (8)) all eliminate RNCS, forming [Cp*Ti{MeC(NⁱPr)₂} $(\mu$ -S)]₂.

Since CO₂ inserts into the Ti-N bond of **16** to form **18**, we attempted the corresponding reaction of CS₂ with **16** with the hope of forming a mixed CO₂/CS₂ "double insertion" product. Surprisingly, this led to **20** (major product, ca. 80%) along with **18** after 16 h in C₆D₆ (eq 2). Compound **18** is presumably formed by reaction of **16** with displaced CO₂. In contrast, exposure of **20** to an excess of CO₂ (1.1 atm) for several days gave no reaction. Given the established reversibility of heterocumulene addition to the Ti=NR bonds of **7** and **8** and other reactions discussed below, eq 2 probably proceeds via a dissociative mechanism transiently forming **13**. Overall these results suggest that [2 + 2] cycloaddition of CS₂ to the Ti=NNPh₂ bond of **13** is thermodynamically preferred to addition of CO₂.



To gain additional insight into the different intrinsic reactivity patterns of phenyl imido and hydrazido complexes, we carried out DFT studies of various reaction pathways. Figure 8 shows the computed reaction profile for CpTi{MeC(NMe)₂}(NNMe₂) (**1NMe**₂) with the three model substrates CO₂, CS₂, and MeNCO (see below for

Table 2. Selected Distances (Å) and Angles (deg) for Cp*Ti-{ $MeC(N^iPr)_2$ }{ $OC(O)N(NPh_2)C(O)O$ } (18) and Cp*Ti{ $MeC-(N^iPr)_2$ }{ $OC(O)N(NMe_2)C(O)O$ } (19)^{*a*}

param	18	19
Ti(1)-Cp _{cent}	2.051	2.053
Ti(1) - O(1)	1.9367(19)	1.9018(18)
Ti(1) - O(3)	1.9512(18)	1.9460(18)
Ti(1) - N(3)	2.059(2)	2.073(2)
Ti(1) - N(4)	2.090(2)	2.123(2)
C(1) - O(2)	1.206(3)	1.209(3)
C(2) - O(4)	1.218(3)	1.213(3)
N(1) - N(2)	1.394(3)	1.414(3)
Cp_{cent} -Ti(1)-N(3)	117.3	120.1
Cp_{cent} -Ti(1)-N(4)	111.9	114.3
Cp_{cent} -Ti(1)-O(1)	114.3	114.5
Cp_{cent} -Ti(1)-O(3)	109.5	108.7
N(3) - Ti(1) - N(4)	64.14(9)	63.79(9)
O(1) - Ti(1) - O(3)	82.99(8)	82.63(7)
Ti(1) - O(1) - C(1)	134.43(17)	136.84(16)
Ti(1) - O(3) - C(2)	131.98(16)	136.68(17)
C(1) - N(1) - C(2)	128.3(2)	126.6(2)

^{*a*}Cp_{cent} is the computed Cp* ring carbon centroid.

the corresponding experimental systems), comparing cycloaddition, cycloaddition-insertion, and cycloaddition-extrusion possibilities. Examples of all three pathways have been found for the hydrazides 13–15 (Scheme 1 and below) and previously for the imido complexes 7 and 8.^{28,29,46} Figure 9 compares these same three reaction outcomes for CO₂ with CpTi{MeC(NMe)₂}(NR), where R = Ph (1Ph), NPh₂ (1NPh₂), NMe₂ (1NMe₂).

Figure 8 predicts that, in the absence of significant steric repulsions, [2 + 2] cycloaddition products of the type 2NMe₂Z should be stable for all three substrates, with those formed from CS2 being the most thermodynamically stable by 2.8 kcal mol⁻¹. This is consistent with eq 2. "Double insertion" products modeled by 3NMe2 Z are thermodynamically stable with regard to the cycloaddition products for CO₂ and MeNCO but unstable in the case of CS₂, again consistent with experiment. In contrast to 3NMe2_O and **3NMe₂N**, where the {Ti(OC)₂(N_{α})} ring is almost planar, as in the crystal structures of 18 and 19 (Figure 7), 3NMe₂ S is puckered (see Table S5 in the Supporting Information). This prevents electron donation from the sulfur LP to the metal, destabilizing the overall molecule. With CO₂ and MeNCO, the activation barrier required for the second insertion is around 14 kcal mol⁻¹ higher than for the first one, explaining the higher temperatures and reaction times normally required for the second insertion reaction. The barrier to extrusion from 2NMe2_Z forming 4_X and Me2NNCO or Me₂NNCNMe is comparable to that for CO₂ or MeNCO insertion in the case of 2NMe2_O and 2NMe2_NMe, but the elimination products are +7.6 and +9.9 kcal mol⁻¹ less stable thermodynamically. On the other hand, Me₂NNCS elimination from 2NMe2_S is only slightly thermodynamically unfavorable $(+1.6 \text{ kcal mol}^{-1})$, showing the possibility for extrusion in the latter case. Interestingly, while both 2NMe₂O and 2NMe₂S are stable to extrusion, loss of CO_2 is the kinetically most accessible and thermodynaically least unfavorable option for 2NMe₂O, whereas for 2NMe₂ S, Me₂NNCS extrusion is the least unfavored option and is slightly kinetically preferred.

Figure 9 compares the reaction profiles of the three model systems **1Ph**, **1NMe**₂, and **1NPh**₂ with CO₂ as a representative substrate. We have reported the profile for **1Ph** (and that of the



Figure 8. Simplified Gibbs free energy diagram (kcal mol⁻¹) at 298 K for the cycloaddition–insertion and cycloaddition–extrusion reactions of CpTi{MeC(NMe)₂}(NNMe₂) (1NMe₂) with CO₂, CS₂, and MeNCO. Note that Z = O, S in the case of CO₂ and CS₂, respectively, and Z = N in the case of MeNCO. Some intermediates with CS₂ and MeNCO have been omitted to facilitate the comparison between the various substrates (see Figure 13 and Figure S2 in the Supporting Information).



Figure 9. Gibbs free energy diagram (kcal mol⁻¹) at 298 K for the CO_2 cycloaddition and second CO_2 insertion (solid lines) or isocyanate extrusion (dotted lines) for the phenyl imido complex **1Ph** (black lines) and its hydrazide analogues **1NPh₂** (blue lines) and **1NMe₂** (red lines).

tert-butyl analogue CpTi{MeC(NMe)₂}(N^tBu) (1^tBu)) recently as part of our detailed study of the reactions of imido complexes **7** and **8** with CO₂.²⁹ Here we are mainly interested in comparing the differences between hydrazides and imides, and the effect of the N_{β} substituents.

The cycloaddition products **2R_O** are of similar energies for all three systems, with addition to $Ti=NNMe_2$ being the most favorable. A low activation barrier is found for all cases, although that for **1Ph** is somewhat higher than for the hydrazido systems, which are effectively identical. The activation barrier for CO_2 insertion to form $3R_0$ is significantly higher for $2NPh_2$ (30.6 kcal mol⁻¹) than for the others, consistent with the extended reaction times needed to form 18 experimentally. Thermodynamically, insertion is most favored for the hydrazide-derived systems than for $2Ph_0$. As for $2R_0$ hydrazide-derived systems, the most stable $3R_0$ complex appears to be for $R = NMe_2$.



Scheme 2. Reaction of $Cp^{Ti}{MeC(N^iPr)_2}{N(NPh_2)C(O)O}$ (16) with $Cp^{Ti}{MeC(N^iPr)_2}(NTol)$ (23)

With regard to extrusion of RNCO from 2R_O, the activation barriers increase in the order $R = Ph < NMe_2$ < NPh₂. In all cases the process is unfavorable but is least prohibited for R = Ph and most disfavored for $R = NPh_2$. Figure 9 suggests that CO₂ loss from the **2R_O** hydrazidederived systems is less unfavorable both kinetically and thermodynamically than RNCO elimination. In contrast, CO₂ and PhNCO elimination from **2Ph O** appear to be equally kinetically feasible and thermodynamically disfavored by a similar amount. We have previously shown that the TolNCO moiety in Cp*Ti{MeC(NⁱPr)₂}{N(Tol)C(O)O} (22) can be sequestered by added Ti(Me4taa)(O) as an isocyanate trap.²⁹ A comparison of Figures 8 and 9 offers an explanation for the stability of the CS₂ cycloaddition products $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NR_{2})C(S)S}$ (20 and 21), while the imido-derived analogues all eliminate RNCS. The previously reported profile for 1^tBu was similar to that for 1Ph, but the barrier to CO₂ insertion from 2^tBu_O was very high, while ^tBuNCO extrusion became thermodynamically favorable by -2.3 kcal mol⁻¹ due to steric repulsions.

We carried out additional NMR tube scale reactions as a probe of Figures 8 and 9. Reaction of $Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}-\{N(NPh_{2})C(O)O\}$ (16) with $Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}(NNMe_{2})$ (15) in C₆D₆ gave immediate conversion to $Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}\{N(NMe_{2})C(O)O\}$ (17) and $Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}-(NNPh_{2})$ (13). This is consistent with the low computed barrier to CO₂ extrusion from **2R_O** and more thermodynamically favorable cycloaddition of CO₂ to Ti=NNMe₂. However, the corresponding reaction of 16 with the tolyl imide Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}(NTol) (23) gave the unexpected outcome summarized in Scheme 2 after heating at 60 °C (negligible reaction was observed at room temperature). The potential products $Cp^{Ti}\{MeC(N^{i}Pr)_{2}\}\{N(Tol)C(O)O\}$

(22⁴⁶) and 13 were not observed, and instead the μ -oxo dimer 12^{29,46} and the new compound Cp*Ti{MeC(NⁱPr)₂}{N-(NPh₂)C(NTol)O} (24) were formed immediately in quantitative yield. Compound 24 can be prepared independently from 13 and TolNCO and is discussed later on.

Given that 24 can be formed from 13 and TolNCO, a likely mechanism accounting for the formation of 12 and 24 is initial extrusion of CO₂ from 16 to form 22, which is not observed but is known to release TolNCO in the presence of a suitable trap (see above²⁹). Trapping of the TolNCO released from 22 by 13 would lead to 24 and monomeric Cp*Ti{MeC(NⁱPr)₂}(O), which is unstable to dimerization, forming 12. Consistent with this, we found that an independently prepared sample of 22 reacted immediately with 13 in C₆D₆, forming 24 and 12 in quantitative yield.

In contrast to the facile transfer of CO₂ from **16** to **15**, there was no reaction between Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C-(S)S} (**20**) and **15** at room temperature. Heating to 60 °C gave decomposition to a mixture containing the previously reported⁴⁶ μ -sulfido dimer [Cp*Ti{MeC(NⁱPr)₂}(μ -S)]₂ (**25**) and a number of unknown products. Although this could mean that addition of CS₂ to Ti=NNPh₂ is thermodynamically more favorable than addition to Ti=NNMe₂, it could also represent a kinetic limitation, since the computed barrier for CS₂ extrusion from **2NMe₂S** (25.4 kcal mol⁻¹) is significantly higher than for CO₂ extrusion from **2NMe₂O** (18.3 kcal mol⁻¹).

The corresponding reaction starting from **21** and **13** as a further attempt to test experimentally the thermodynamic preferences for CS₂ binding gave $[Cp*Ti\{MeC(N^iPr)_2\}(\mu-S)]_2$ (**25**) and a new compound formulated as $Cp*Ti\{MeC(N^iPr)_2\}\{N(NPh_2)C(NNMe_2)S\}$ (**26**) on the basis of its ¹H and ¹³C NMR spectra (eq 3). Compound **26** is the cycloaddition product of **13** and Me₂NNCS and is the analogue of the fully characterized compounds $Cp*Ti\{MeC(N^iPr)_2\}\{N(NPh_2)C(NAr)S\}$ (Ar = Tol, Ar' (2,6-C₆H₃ⁱPr₂)) prepared from **13** and ArNCS (see below). The formation of **26** is consistent with the DFT prediction (Figure 8) that Me₂NNCS extrusion from **2NMe₂_S** is thermodynamically less disfavored than CS₂ extrusion while being equally kinetically accessible.



Reactions of Cp*Ti{MeC(NⁱPr)₂}(NNPh₂) (13) with Isocyanates and Isothiocyanates. The reactions of Cp*Ti{MeC-(NⁱPr)₂}(NNPh₂) (13) and Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (15) with isocyanates differ significantly, depending on the individual β -NR₂ group, and are described in turn. Scheme 3 summarizes the reactions of 13 with selected isocyanates and isothiocyanates.

Scheme 3. Reactions of Cp*Ti{MeC(NⁱPr)₂}(NNPh₂) (13) with Isocyanates, Isothiocyanates, and CO_2^{a}



 a Ar' = 2,6-C₆H₃ⁱPr₂.

Reaction of 13 with TolNCO or Ar'NCO at room temperature in benzene gave the C_1 -symmetric ureate-type cycloaddition products $Cp*Ti{MeC(N^{1}Pr)_{2}}{N(NPh_{2})C}$ (NAr)O (Ar = Tol (24), Ar' (27)) as dark brown solids in ca. 70% isolated yield. The corresponding reactions with $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NPh_{2})C}$ ArNCS afforded (NAr)S (Ar = Tol (28), Ar' (29)) as dark green solids in slightly lower yields (ca. 50%), although the corresponding NMR tube scale experiments for both ArNCO and ArNCS were effectively quantitative. Diffractionquality crystals of 27 and 29 were grown by slow cooling of a hexane solution, and the molecular structures and selected distances and angles are shown in Figure 10 and Table 3.

Figure 10 confirms the four-legged piano-stool geometries around titanium and the κ^2 N,O and κ^2 N,S coordination modes for the $N(NPh_2)C(NAr)E$ ligands (E = O, S). The NMR spectra for 24 and 27-29 are consistent with the proposed structures. No signals for other isomers of 24 and 27-29 (e.g., with a $\kappa^2 N$, N'-N(NPh₂)C(E)NAr moiety) were observed in the NMR tube scale experiments or crude reaction products. Although they have not been crystallographically authenticated, the tolvl-substituted analogues Cp*Ti{MeC(NⁱPr)₂}{N-(NPh₂)C(NTol)E} (24 and 28) appear to have analogous structures. For example, very similar ν (C=N) bands for 24 and 27 were observed at 1619 and 1622 cm⁻¹, respectively, which are also comparable to those for the imido-derived products $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(Ar^{1})C(NAr^{2})O}$ (Ar¹, Ar² = Tol, 2,6-C₆H₃Me₂, ν (C=N) 1609–1615 cm⁻¹), which possess κ^2 N,O-bound N(Ar¹)C(NAr²)O groups. In contrast, the IR spectrum of $Ti(Me_4taa)$ {N(NPh₂)C(O)NTol}, possessing a $\kappa^2 N, N' - N(NPh_2)C(O)NTol ligand, features a \nu(C=O) band at$ 1656 cm^{-1}

The metric parameters for the Cp*Ti{MeC(N'Pr)₂} moiety in **27** and **29** are within the expected ranges, and those for the N(NPh₂)C(NAr')E ligands are comparable to the same groups recently reported in Ti(N₂N^{Me}){N(NPh₂)C(NAr')E}(L) (L = py, E = O; L = none, E = S) which also feature κ^2 N,O or κ^2 N, S coordination.³² Interestingly, Gade et al. found that Cp*Ti-(N^{Xyl}N)(NNRPh)(L) (6; R = Ph, Me, L = ^tBuNH₂, py) reacts with PhNCO or PhNCS to give a mixture of isomers possessing either a κ^2 N,E or κ^2 N,N' ureate ligand.³⁷ An example of each type was crystallographically characterized.

To probe further the coordination mode preferences in **24** and **27**, we calculated the DFT energies of the model complexes CpTi{MeC(NMe)₂}{ $\kappa N, O$ -N(NPh₂)C(NPh)O} ($\kappa N, O$ -2Ph_N) and CpTi{MeC(NMe)₂{ $\kappa N, N'$ -N-(NPh₂)C(O)NPh} ($\kappa N, N'$ -2Ph_N). Isomer $\kappa N, N'$ -2Ph_N was found to be more stable, but by only 1 kcal mol⁻¹. Thus, as found in related systems, the N, N'-ureate systems appear to be electronically preferred, but steric factors can easily overturn this.^{32,46}



Reaction of 13 with ^tBuNCO gave Cp*Ti{MeC(NⁱPr)₂}-{N(NPh₂)C(N^tBu)O} (30; Scheme 3). While 30 slowly eliminates ^tBuNCNNPh₂, forming the oxo dimer 12 (ca. 30% after 4 days at room temperature), it is significantly more stable than the corresponding products formed from Cp*Ti-{MeC(NⁱPr)₂}(NR) (R = ^tBu (7), Tol (23)) which quantitatively eliminate ^tBuNCNR within 2–3 h.⁴⁶ These observations are consistent with the DFT calculations in Figure 9 for the cycloaddition–isocyanate extrusion reactions of 1Ph and 1NPh₂ with CO₂.

We previously found that the imide-isocyanate cycload- $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(Tol)C(NTol)O}$ species dition could form "double insertion" products on reaction with CO_2 or ArNCO (Ar = Tol, 2,6-C₆H₃Me₂). In a similar manner, $Cp*Ti{MeC(N^{1}Pr)_{2}}{N(Tol)C(O)O}$ (22) inserted ArNCO into the Ti-N(Tol) bond to also give a crosscoupled derivative.⁴⁶ In contrast, treatment of Cp*Ti{MeC- $(N^{i}Pr)_{2}$ { $N(NPh_{2})C(NTol)O$ } (24) with further TolNCO either at room temperature or at 60 °C gave no reaction. The corresponding reaction of 24 with CO₂ successfully but slowly (4 days) formed the mixed TolNCO/CO₂ "double insertion" product $Cp*Ti{MeC(N^{i}Pr)_{2}}{OC(NTol)N (NPh_2)C(O)O$ (31). The IR spectrum of 31 shows strong bands at 1699 and 1628 cm⁻¹ attributed to ν (C=O) and ν (C=N), consistent with the proposed structure.⁴⁶ No reaction was observed between the bulkier 27 and CO₂. Compound 31 is the analogue of the structurally authenticated $Cp*Ti{MeC(N^{1}Pr)_{2}}{OC(O)N(NPh_{2})C(O)O}$ (18). Surprisingly, an attempt to form 31 by reaction of Cp*Ti{MeC- $(N^{i}Pr)_{2}$ { $N(NPh_{2})C(O)O$ } (16) with TolNCO gave a mixture of 24, 31, 18, and unreacted 16.

Reaction of the bulkier $Cp*Ti\{MeC(N^iPr)_2\}\{N(NPh_2)C-(N^tBu)O\}$ (30) with CO_2 in C_6D_6 slowly led to ^tBuNCO extrusion and formation of 18 (Scheme 3). This reaction



Figure 10. Displacement ellipsoid plots (25% probability) of (a) $Cp*Ti\{MeC(N'Pr)_2\}\{N(NPh_2)C(NAr')O\}$ (27) and (b) $Cp*Ti\{MeC(N'Pr)_2\}\{N(NPh_2)C(NAr')S\}$ (29). H atoms are omitted for clarity.

 $\label{eq:table_transform} \begin{array}{l} Table 3. Selected Bond Lengths (Å) and Angles (deg) for Cp*Ti- \\ \{MeC(N^iPr)_2\}\{N(NPh_2)C(NAr')O\} \mbox{ (27) and } Cp*Ti\{MeC- \\ (N^iPr)_2\}\{N(NPh_2)C(NAr')S\} \mbox{ (29)}^a \end{array}$

		·
param ^b	27	29
Ti(1)-Cp _{cent}	2.065	2.075
Ti(1) - N(1)	2.000(15)	2.0335(18)
Ti(1)-E(1)	2.0060(14)	2.4512(8)
Ti(1) - N(3)	2.1498(17)	2.171(3)
Ti(1) - N(4)	2.0526(18)	2.050(2)
N(1) - N(2)	1.400(2)	1.416(3)
C(13) - N(5)	1.286(3)	1.273(3)
E(1) - C(13)	1.337(2)	1.769(2)
Cp_{cent} -Ti(1)-N(1)	126.4	128.3
Cp_{cent} -Ti(1)-E(1)	110.5	107.8
Cp_{cent} -Ti(1)-N(3)	112.3	111.9
Cp_{cent} -Ti(1)-N(4)	119.0	119.6
N(3) - Ti(1) - N(4)	63.46(7)	62.63(10)
N(1) - Ti(1) - E(1)	65.60(6)	67.98(6)
Ti(1) - N(1) - C(13)	93.31(11)	105.94(14)
Ti(1) - E(1) - C(13)	94.72(11)	80.08(8)
N(1) - C(13) - E(1)	105.50(15)	105.58(15)

^{*a*} Cp_{cent} is the computed Cp* ring carbon centroid. ^{*b*} E = O, S for 27 and 29, respectively.

most likely proceeds via elimination of the isocyanate to form **13**. The reaction of pure **13** with CO₂ to form **18** is faster than the reaction with **30**, explaining why the cycloaddition intermediate **16** is not observed in the reaction of **30**. Addition of TolNCO to **30** also led to loss of ^tBuNCO, immediately forming **24**. Reaction of Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (**15**) with **30** in C₆D₆ gave quantitative formation of **13**, the μ -oxo compound **12**, and ^tBuNCONMe₂, consistent with the reactions of **15** with ^tBuNCO and Ar'NCO described below (Scheme 4).

As mentioned, the reaction of **24** with CO₂ to form **31** requires 4 days for completion (with NMR monitoring), whereas the corresponding reaction for Cp*Ti{MeC- $(N^{i}Pr)_{2}$ {N(Tol)C(NTol)O} under comparable conditions was complete within 10 min.⁴⁶ These differences are again consistent with Figure 9 by analogy with the significantly higher TS for **2NPh₂O** + CO₂ \rightarrow **3NPh₂O** compared to **2Ph_O** + CO₂ \rightarrow **3Ph_O**.

Reactions of Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (15) with Isocyanates. In contrast to the relatively well-behaved cycloaddition chemistry of 13 with RNCO and RNCS, the reactions

Scheme 4. Reactions of $Cp^{*}Ti\{MeC(N^{i}Pr)_{2}\}(NNMe_{2})$ (15) with Isocyanates^{*a*}



of 15 with these substrates are dominated by cycloaddition-extrusion processes. The reactions of 15 with isocyanates are shown in Scheme 4. Initial studies of the corresponding reactions with isothiocyanates led to unstable complexes and/or mixtures and were not pursued further.

Reaction of **15** with ^tBuNCO in C₆D₆ gave quantitative conversion to the μ -oxo compound **12** and the previously reported^{69,70} *N*-(dimethylamino)carbodiimide ^tBuNCNNMe₂ (**32**). Amidocarbodiimides are not stable and are known

⁽⁷⁰⁾ Sarker, S.; Cooley, J. H.; Willett, R. D.; Rheingold, A. L. J. Org. Chem. 1995, 60, 476.

to dimerize. In the case of **32**, the heterocyclic product 1,2,4-N(Me)₂NC(N^tBu)N(^tBu)C(NNMe₂) (**33**) has been crystallographically characterized.⁷⁰ The instability of the presumed cycloaddition intermediate Cp*Ti{MeC-(NⁱPr)₂}{N(NMe₂)C(N^tBu)O} to extrusion contrasts strongly with that of **30** and is reminiscent of the corresponding reactions of Cp*Ti{MeC(NⁱPr)₂}(NR) (R = ^tBu (7), Tol (**23**)) mentioned above. The outcomes of these reactions are consistent with the DFT calculations in Figure 9 for extrusion of RNCO from **2R_O**, which become progressively more favored (both kinetically and thermodynamically) in the order R = Ph > NMe₂ > NPh₂.



The stoichiometric reaction of **15** with Ar'NCO gave a mixture of products and unreacted starting hydrazide. Conducting the reaction at 60 °C and with 2 equiv of Ar'NCO gave **12** and 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O) (**34**). When it was conducted on the NMR tube scale in C₆D₆, the conversion of **15** to the products was near-quantitative. On scale-up, the white solid **34** could only be isolated in analytically pure form by high vacuum (5 × 10⁻⁶ mbar) tube sublimation, leading to an overall yield of 15%.

Diffraction-quality crystals of 34 were grown from a concentrated hexane solution at -4 °C. The molecular structure is shown in Figure 11, and selected distances and angles are given in Table S1 of the Supporting Information. These are all within normal ranges⁷¹ and comparable to those of 33.70 Compound 34 is the apparent product of coupling between Ar'NCO and Ar'NCNNMe2, which is not observed in the reaction mixture but is analogous to ^tBuNCNNMe₂ formed in the reaction of **15** with ^tBuNCO. Carbodiimide Ar'NCNNMe2 is probably formed by extrusion from the likely intermediate $Cp*Ti\{MeC(N^{1}Pr)_{2}\}$ $\{N(NMe_2)C(NAr')O\}$ (34_int), the analogue of the crystallographically characterized 27 (Figure 10). The incorporation of both an Ar'NCO and Ar'NC fragment into 34 accounts for the 1:2 stoichiometry required for this reaction.

The reaction of **15** with TolNCO also required 2 equiv of the isocyanate for complete reaction (Scheme 4). However, in this case the single reaction product was the "doubleinsertion" compound Cp*Ti{MeC(NⁱPr)₂}{OC(NNMe₂)N-(Tol)C(NTol)O} (**35**), isolated in 76% yield. Compound **35** has been crystallographically characterized, and the molecular structure is shown in Figure 12. Selected distances and angles are given in Table 4 and are within the expected ranges. The ¹H and ¹³C NMR spectra of **35** show two sets of *p*-tolyl group resonances and two inequivalent isopropyl groups for the MeC(NⁱPr)₂ ligand. The IR spectrum shows two ν (C=N) bands at 1619 and 1599 cm⁻¹. Surprisingly, the





Figure 11. Displacement ellipsoid plot (20% probability) of 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O) (34). H atoms are omitted for clarity.



Figure 12. Displacement ellipsoid plot (20% probability) of $Cp*Ti\{MeC(N^iPr)_2\}\{OC(NNMe_2)N(Tol)C(NTol)O\}$ (35). H atoms are omitted for clarity.

Table 4. Selected Distances (Å) and Angles (deg) for Cp*Ti-{MeC(NⁱPr)₂}{OC(NNMe₂)N(Tol)C(NTol)O} $(35)^{a}$

Ti(1)-Cp _{cent}	2.067	Ti(1)-O(2)	1.9359(17)
Ti(1) - N(3)	2.108(2)	N(5) - C(5)	1.455(3)
Ti(1) - N(4)	2.077(2)	C(3) - N(1)	1.289(3)
Ti(1) - O(1)	1.9065(17)	C(4) - N(6)	1.288(3)
N(1)-N(2)	1.457(3)		
Cp_{cent} -Ti(1)-N(3)	110.9	Cp _{cent} -Ti(1)-N(4)	114.6
Cp_{cent} -Ti(1)-O(1)	116.1	Cp_{cent} -Ti(1)-O(2)	111.0
N(3) - Ti(1) - N(4)	63.54(8)	O(1) - Ti(1) - O(2)	83.63(7)
Ti(1) - O(1) - C(3)	134.38(15)	Ti(1) - O(2) - C(4)	135.27(15)
C(3) - N(5) - C(4)	124.5(2)		

^{*a*}Cp_{cent} is the computed Cp* ring carbon centroid.

product is not the *C_s*-symmetric Cp*Ti{MeC(N¹Pr)₂} {OC(NTol)N(NNMe₂)C(NTol)O} (**35_alt**) which would be expected on the basis of the reactions of Cp*Ti{MeC(NⁱPr)₂}(NTol) with 2 equiv of TolNCO or Cp*Ti{MeC-(NⁱPr)₂}(NNR₂) with an excess of CO₂. The presence of both an exocyclic C=NTol and C=NNMe₂ moiety suggests that at least one rearrangement must have taken place between the likely intermediate Cp*Ti{MeC(NⁱPr)₂}{N(NMe₂)}



Figure 13. DFT mechanism for the formation of $CpTi\{MeC(NMe_2)\}\{OC(NNMe_2)N(Me)C(NMe)O\}$ (**3NMe₂N**'). Gibbs free energies (298 K) are expressed in kcal mol⁻¹ relative to **1NMe₂** + 2 MeNCO. The "first" MeNCO is colored blue and the "second" in red for clarity. All energies are shown in boxes; the values labeled \ddagger are transition states.

C(NAr)O} (**35_int**, the analogue of **24**) and the final product **35**.



We have used DFT to study the mechanism of formation of **35** using the model system CpTi{MeC(NMe)₂}(NNMe₂) (**1NMe**₂) and MeNCO (Figure 13). A part of this mechanism was already included in Figure 8. Addition of MeNCO forms **2NMe**₂_N with a κN ,O-ureate ligand. Insertion of MeNCO into the Ti-N(NMe₂) bond of **2NMe**₂_N forms the symmetric "double insertion" product **3NMe**₂_N in a slightly exergonic process ($\Delta G = -2.2 \text{ kcal mol}^{-1}$). The TS for this process lies 27.2 kcal mol⁻¹ above **2NMe**₂_N. A more accessible second MeNCO insertion was found via the alternative N,O coordination isomer 2NMe2_N', with an exocyclic C=NNMe2 group. Direct rearrangement of 2NMe2_N to 2NMe2_N' by effective rotation about the O-CN₂ bond has a prohibitively high TS of +36.5 kcal mol⁻¹ relative to 2NMe₂N. However, extrusion of MeNCNNMe₂ from 2NMe₂N to form 4_O, followed by recoordination and cycloaddition, presents an alternative route to 2NMe2_N'. Relative to 2NMe2_N, the highest TS along this route is $23.5 \text{ kcal mol}^{-1}$ (between $2NMe_2N_{int'}$ and $2NMe_2N'$, which is lower than the 27.2 kcal mol⁻¹ between **2NMe₂**N and **3NMe₂**N. Insertion of MeNCO into the Ti-N(Me) of 2NMe2_N' forms the desired isomer $3NMe_2N'$ (a model of 35) with an activation free energy barrier of +20.7 kcal mol⁻¹ relative to $2NMe_2N'$. Note that $3NMe_2N'$ is -3.1 kcal mol⁻¹ more stable than the more symmetrical isomer 3NMe₂N and so represents both the thermodynamic and kinetically favored product.

In principle, this model mechanism could apply to TolN-CO, ^tBuNCO, or Ar'NCO, whereas in practice different outcomes are found for each isocyanate. These reflect the different steric bulk of each of the isocyanates and their



Figure 14. Energy decomposition scheme for selected isodesmic multiple bond exchange reactions of CpTi{MeC(NMe)₂}(NR) (R = Me, Ph, NPh₂, NMe₂) with heterocumulenes and computed bond dissociation energies (ΔE , kcal mol⁻¹). All species are spin state singlets except for the fragments CpTi{MeC(NMe)₂}, X, NMe, and NPh, which are spin triplets. $\Delta E_{exch} = \Delta E_1 + \Delta E_2 - \Delta E_3 - \Delta E_4$.

relative rates of RNCNNMe₂ being trapped back by $Cp*Ti\{MeC(N^{i}Pr)_{2}\}(O)$ (seen for R = Tol), free RNCO in the reaction mixture (R = Ar'), or not at all ($R' = {}^{t}Bu$).

Further Thermodynamic Considerations. Although many reactions of Cp*Ti{MeC(N¹Pr)₂}(NR) (R = ^tBu (7), Tol (23), NNPh₂ (13), NNMe₂ (15)) and their homologues with heterocumulenes can result in isolable cycloaddition or "double-insertion" products, there is also a propensity to undergo an overall cycloaddition/extrusion process whereby the "NR" group is transferred to an organic fragment, itself being replaced by O or S. We have shown previously, through DFT and experimental studies, that increased steric bulk of the cyclopentadienyl-amidinate ligand set can kinetically stabilize cycloaddition products toward extrusion. We also showed that the steric demands of the ^tBu group in tert-butyl imido complexes leads to extrusion becoming thermodynamically more favorable.29,46 The DFT computed reaction of the model imido complex CpTi{MeC- $(NMe)_2$ (NMe) (1Me) with CO₂ to form CpTi{Me $C(NMe)_2$ {O) (**4_O**) and MeNCO was found to be 5.7 kcal mol⁻¹ more favorable (in terms of ΔE) than the corresponding reaction of **1Ph** with CO₂ to form PhNCO, showing a clear underlying preference for NR group transfer to CO in the case of NMe compared to NPh.

In this contribution, we have extended the experimental and DFT information for this type of reactivity to include NNMe₂ and NNPh₂ ligands for the three main substrate classes (CO₂, CS₂, and isocyanates) studied previously with the imido complexes 7 and 23. Overall, as demonstrated by experiment and DFT (cf. Figure 9), the tendency to transfer an imido or hydrazido group from titanium to an organic fragment (CO, CS, CNR) appears to increase in the order NNPh₂ < NNMe₂ < NTol (< N^tBu). Additionally, taking into account the new results above and those described previously for 7 and 23, the imido or hydrazide group exchange occurs more readily with CS₂ than with isocyanates, which in turn are less likely than CO₂ to give an overall metathesis reaction (cf. Figure 8). To gain further insight into the underlying factors in these metathesis processes, we have analyzed the model thermodynamic cycle in Figure 14, in which Ti=NR of **1Me**, **1Ph**, **1NPh**₂, or **1NMe**₂ exchanges with C=X (X = O, S) of CO₂, MeNCO, or CS₂. The overall energy of this exchange (ΔE_{exch}) can be expressed as the sum of four stepwise ond dissociation energies (BDEs) or the reverse processes: ΔE_1 (Ti=NR homolysis), ΔE_2 (substrate C=X homolysis), $-\Delta E_3$ (Ti=X formation), and $-\Delta E_4$ (product C=NR

bond formation). This allows us to assess the effects of the relative affinities of the metal and organic fragment for the NR or X groups and their overall impact on ΔE_{exch} .⁷²

The computed BDEs for the hydrazides $1NMe_2$ and $1NNPh_2$ (entries 1 and 2) are between 23.9 and 33.1 kcal mol⁻¹ less than for the imides **1Ph** and **1Me** (entries 3 and 4). The Ti=NNMe₂ BDE is somewhat less than that of Ti=NNPh₂ (8.7 kcal mol⁻¹). The bond energies of Ti=O and Ti=S (entries 8 and 9) are both greater than those of any of the Ti=NR systems. Therefore, in terms of titanium–ligand bond strengths, the metathesis reaction is always favorable, and more so for the hydrazides than the imides and for oxide than sulfide bond formation. However, the experimental results reported above and previously,^{29,46} along with Figures 8 and 9, are not consistent with these expectations based on titanium–ligand bond strengths alone. The substrate and product bond energies also play a key role.

Comparison of entries 1-4 (Ti=NR BDEs) with entries 10-13 (OC=NR BDEs) or 14-17 (SC=NR BDEs) show that these all increase in the order $NR = NNMe_2 < NNPh_2$ < NPh < NMe. However, the magnitudes of the changes (i.e., the relative affinities of NR for Ti, CO, or CS) differ, and this accounts for the different propensities for Ti=NR/C=O or C=S metathesis in the real systems. Consider, for example, the reactions with CO₂. Although the BDE for OC=NNPh₂ (entry 11) is 2.8 kcal mol⁻¹ greater than for OC=NNMe₂ (entry 10), that for $Ti=NNPh_2$ is 8.7 kcal mol⁻¹ greater than that for Ti=NNMe2. Overall, therefore, exchange of Ti=NNR₂ and OC=O forming Ti=O and OC=NNR₂ is 5.9 kcal mol⁻¹ more favorable for NNR₂ = NNMe₂. Likewise, exchange between Ti=NNR₂ and MeNC=O forming Ti=O and MeNC=NNR₂ is 4.0 kcal mol⁻¹ more favorable for $NNR_2 = NNMe_2$ (compare entries 1, 2 and 18, 19), which is consistent with experimental trends.

On comparison of phenyl imido and hydrazido systems, entries 2 and 3 show that the Ti=NPh BDE is 23.9 kcal mol⁻¹ greater than for Ti=NNPh₂, whereas NPh transfer reactions are more favored. This is explained by comparing the BDEs for OC=NNPh₂ and OC=NPh (entries 11 and 12), which are greater by 35.6 kcal mol⁻¹ for NPh. Thus, Ti=NPh/OC=O metathesis is favored by 11.7 kcal mol⁻¹ compared to Ti=NNPh₂ because of the greater affinity of NPh for CO. Similarly, Ti=NPh/SC=S metathesis is favored by 9.8 kcal mol⁻¹ compared to the same process for Ti=NNPh₂ (compare entries 2, 3 and 15, 16), again consistent with experimental observations of ready formation of sulfide products in the reactions of aryl imido compounds with CS₂ but stable cycloaddition products with **13** and **15**. Finally, it should be noted that the calculated energy for Ti=NNMe₂ + CO₂ → Ti=O + OCNNMe₂ (8.4 kcal mol⁻¹) is significantly higher than the corresponding process for MeNCO forming MeNCNNMe₂ (2.7 kcal mol⁻¹), consistent with the observed behavior of the real system **15** with CO₂ and isocyanates.

Conclusions

The cyclopentadienyl–amidinate complexes Cp*Ti-{MeC(NⁱPr)₂}(NNR¹R²) (R¹ = Ph, R² = Ph (13), Me (14); R¹ = R² = Me (15)) have allowed a detailed combined experimental and DFT study of terminal titanium hydrazido complexes as a function of the N_β substituents. Compounds 13–15 permitted the second crystallographic comparison of a series of this type. DFT studies of the model analogues CpTi{MeC(NMe)₂}(NNR¹R²) confirmed the overall structural trends and an explanation in terms of the effects of the N_β lone pair. A comparison with the corresponding model imido complexes CpTi{MeC(NMe)₂}(NR) (R = Me, Ph) completed the bonding picture.

Compounds 13 and 15 can have different reactivities at the Ti= N_{α} bond (cycloaddition, cycloaddition-insertion, cycloaddition-elimination), depending on the N_β substituents and the substrates in question. With CO_2 and CS_2 , the chemistry is generally rather similar, and reaction products of the type seen previously with imido compounds Cp*Ti-{MeC(NⁱPr)₂}(NR) (R = ^tBu (7), Tol (23)) were observed. The cycloaddition products formed with the hydrazides were, however, more stable with regard to extrusion reactions. In the reactions of 13 and 15 with ^tBuNCO, TolNCO, and Ar'NCO there was a more clear-cut difference in reactions. The diphenyl hydrazido compound 13 formed quite stable cycloaddition products, which in the case of Cp*Ti- ${MeC(N^{1}Pr)_{2}}{N(NPh_{2})C(NTol)O}$ reacted further with CO₂ to give a mixed cycloaddition-insertion product. With 15 the chemistry was more dominated by cycloadditionelimination reactions. Reaction with ^tBuNCO or Ar'NCO (2 equiv) gave ^tBuNCNNMe₂ or the heterocycle 1,2,4-N- $(Me)_2NC(NAr')N(Ar')C(O)$, respectively, along with $[Cp*Ti\{MeC(N^iPr)_2\}(\mu-O)]_2$. With TolNCO (2 equiv), $Cp*Ti{MeC(N^{1}Pr)_{2}}{OC(NNMe_{2})N(Tol)C(NTol)O}$ was formed via a series of cycloaddition-elimination and cycloaddition-insertion steps.

The energetics and mechanisms of the cycloaddition, cycloaddition–insertion, and cycloaddition–extrusion processes of various model imido and hydrazido complexes were investigated using DFT. In the latter (metathesis) reactions, the reaction outcomes depend on a delicate balance of the relative affinities of NR or NNR₂ for the metal center or the organic fragment (CO, CS, or RNC).

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent.⁷³ Deuterated solvents were refluxed over the appropriate drying agent, distilled, 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. ¹H and ¹³C-{¹H} NMR spectra were recorded on Varian Mercury-VX 300

⁽⁷²⁾ Note that Figure 14 presents electronic energies using $6-311++G^{**}$ basis sets, whereas Figures 8 and 9 present Gibbs free energies using a $6-31G^{**}$ basis set.

⁽⁷³⁾ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

and Varian Unity Plus 500 spectrometers and referenced internally to residual protio solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane (δ 0 ppm). Assignments were confirmed as necessary with the use of DEPT-135, DEPT-90, and two-dimensional ¹H⁻¹H and ¹³C⁻¹H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 ESP FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

Starting Materials. Cp*Ti{ $MeC(N^iPr)_2$ } (N^tBu) (7),⁴⁶ Cp*Ti-{ $MeC(N^iPr)_2$ }(NTol) (23),⁴⁶ and Cp*Ti{ $MeC(N^iPr)_2$ }(N(Tol)C-(O)O} (22)⁴⁶ were prepared according to the literature methods. 1,1-Diphenylhydrazine was obtained from Sigma-Aldrich as the hydrogen chloride salt, from which the free hydrazine was obtained by basification, drying, and removal of residual solvent, followed by distillation under inert atmospheric conditions. 1,1-Dimethyl-hydrazine and 1-methyl-1-phenylhydrazine and pyridine were dried over freshly ground CaH₂ and distilled before use. Other reagents were obtained commercially and used as received.

Representative syntheses and associated characterization data are listed below. Details of the remaining syntheses, NMR spectra, and characterization data are given in the Supporting Information.

 $Cp*Ti{MeC(N^{i}Pr)_{2}}(NNPh_{2})$ (13). To a stirred red solution of Cp*Ti{MeC(N¹Pr)₂}(N¹Bu) (7; 1.70 g, 4.30 mmol) in benzene (10 mL) was added Ph₂NNH₂ (0.140 g, 0.760 mmol) in benzene (10 mL). The solution darkened, and after 16 h the volatiles were removed under reduced pressure. The resultant solid was extracted into pentane $(3 \times 10 \text{ mL})$ and filtered, and the volatiles were removed under reduced pressure to give 13 as a dark yellow solid. Yield: 1.81 g (83%). Diffraction-quality crystals were grown by slow cooling of a saturated pentane solution. ¹H NMR (C_6D_6 , 299.9 MHz, 293 K): δ 7.22 (4 H, d, 3J = 8.8 Hz, $o-C_6H_5$), 7.13 (4 H, dd, ${}^{3}J = 7.5$ and 8.8 Hz, $m-C_6H_5$), 6.81 (2 H, t, ${}^{3}J = 7.5$ Hz, *p*-C₆H₅), 3.60 (2 H, app sept, app ${}^{3}J = 6.3$ Hz, NCHMeMe), 1.99 (15 H, s, C₅Me₅), 1.65 (3 H, s, MeCN₂), 1.04 $(6 \text{ H}, d, {}^{3}J = 6.3 \text{ Hz}, \text{ NCH}Me\text{Me}), 1.03 (6 \text{ H}, d, {}^{3}J = 6.3,$ NCHMeMe). ¹³C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 160.7 $(MeCN_2)$, 147.1 $(i-C_6H_5)$, 129.1 $(m-C_6H_5)$, 122.0 $(p-C_6H_5)$, 120.6 (o-C₆H₅), 120.0 (C₅Me₅), 49.5 (NCHMeMe), 26.8 (NCHMeMe), 25.8 (NCHMeMe), 12.7 (C₅Me₅), 12.3 (MeCN₂). IR (NaCl plates, Nujol mull, cm⁻¹): v 1595 (m), 1586 (m), 1488 (s), 1465 (s), 1417 (w), 1378 (m), 1364 (s), 1340 (w), 1320 (w), 1295 (w), 1277 (w), 1254 (w), 1215 (m), 1169 (m), 1148 (w), 1119 (w), 1070 (w), 1026 (w), 992 (w), 839 (w), 812 (w), 792 (w), 751 (w), 741 (s), 701 (w), 693 (s), 666 (w), 631 (m). Anal. Found (calcd for C₃₀H₄₂N₄Ti): C, 71.0 (71.1); H, 8.3 (8.4); N, 11.0 (11.1).

 $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NPh_{2})C(O)O}$ (16). A solution of $Cp*Ti{MeC(N^{1}Pr)_{2}(NNPh_{2}) (13; 0.300 g, 0.590 mmol) in$ toluene (20 mL) was freeze-pump-thawed three times. The solution was then exposed to CO2 at a pressure of ca. 1.1 atm at -78 °C. Immediately after the color changed from dark yellow to dark brown, the excess CO_2 and the other volatiles were removed under reduced pressure to afford 16 as a dark brown solid. The resultant dark brown solid was washed with cold pentane (3×5 mL), filtered, and dried in vacuo. Yield: 0.175 g (54%). ¹H NMR (C₇D₈, 499.9 MHz, 293 K): δ 7.51 (2 H, d, ³J = 7.0 Hz, o_a -C₆H₅), 7.19 (2 H, m, m_a -C₆H₅), 6.95 (4 H, m, overlapping o_b -C₆H₅ and m_b -C₆H₅), 6.91 (1 H, t, ${}^3J = 7.0$ Hz, p_a - C_6H_5), 6.73 (1 H, t, ${}^{3}J = 7.0$ Hz, p_b - C_6H_5), 3.31 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 2.83 (1 H, app sept, app ${}^{3}J =$ 6.5 Hz, NC H_b MeMe), 1.95 (15 H, s, C₅Me₅), 1.46 (3 H, s, MeCN₂), 1.16 (3 H, d, ³J = 6.5 Hz, NCH_aMeMe), 1.11 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 1.09 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_a*Me*Me), 0.93 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_b*Me*Me). ${}^{13}C$ -{¹H} NMR (C₇D₈, 125.7 MHz, 293 K): δ 170.3 (MeCN₂), 160.6

(OC(O)N), 147.9 (i_a -C₆H₅), 147.9 (i_b -C₆H₅), 130.4 (C_5 Me₅), 128.5 (m_a -C₆H₅, m_b -C₆H₅), 122.8 (p_a -C₆H₅), 122.4 (o_a -C₆H₅), 119.6 (p_b -C₆H₅), 117.0 (o_b -C₆H₅), 51.2 (NCH_aMeMe), 50.2 (NCH_bMeMe), 26.3 (NCH_bMeMe), 24.6 (NCH_bMeMe), 24.2 (NCH_aMeMe), 24.1 (NCH_aMeMe), 12.9 (C_5Me_5), 12.6 ($MeCN_2$). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1684 (s), 1589 (m), 1492 (s), 1338 (m), 1206 (w), 1026 (w), 744 (m), 691 (m). EI-MS: m/z 233 [M - C₅Me₅ - N(NPh₂)]⁺ (30%), Anal. Found (calcd for C₃₁H₄₂N₄O₂Ti): C, 67.61 (67.63); H, 7.78 (7.69); N, 10.11 (10.18).

 $Cp*Ti\{MeC(N^{i}Pr)_{2}\}\{OC(O)N(NPh_{2})C(O)O\}$ (18). A solution of $Cp*Ti{MeC(N^{1}Pr)_{2}}(NNPh_{2})$ (13; 0.300 g, 0.590 mmol) in toluene (20 mL) was freeze-pump-thawed three times. The solution was then exposed to \overline{CO}_2 at a pressure of ca. 1.1 atm at room temperature. An immediate color change from dark yellow to dark brown was observed. After 3 days, excess CO₂ and the other volatiles were removed under reduced pressure to afford 18 as a dark brown solid. The resultant dark brown solid was washed with cold pentane $(3 \times 5 \text{ mL})$, filtered, and dried in vacuo. Yield: 0.247 g (70%). Diffraction-quality crystals were grown by slow evaporation of an ether solution. ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.88 (2 H, d, ³J = 7.2 Hz, o_a -C₆H₅), 7.27 (2H, m, *o*_b-C₆H₅), 7.24 (2 H, m, *m*_a-C₆H₅), 7.09 (2 H, m, m_b -C₆H₅), 6.98 (1 H, t, 3J = 7.2 Hz, p_b -C₆H₅), 6.78 (1 H, t, 3J 7.2 Hz, p_a -C₆H₅), 3.42 (2 H, app sept, app ${}^{3}J = 6.6$ Hz, NCHMeMe), 1.87 (15 H, s, C₅Me₅), 1.39 (3 H, s, MeCN₂), 1.05 (12 H, overlapping 2 × d, ${}^{3}J = 6.6$ Hz, NCH*MeM*e, NCHMe*M*e). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 75.4 MHz, 293 K): δ 169.5 (MeCN₂), 152.7 (OC(O)N), 146.7 (*i*_b-C₆H₅), 146.0 (*i*_a-C₆H₅), 131.6 (C₅Me₅), 129.2 (*m*_a-C₆H₅), 129.0 (*m*_b-C₆H₅), 123.9 (p_a-C₆H₅), 123.5 (o_a-C₆H₅), 120.9 (p_b-C₆H₅), 117.4 (o_b-C₆H₅), 50.6 (NCHMeMe), 24.1 (NCHMeMe), 23.5 (NCHMeMe), 14.3 (MeCN₂), 12.7 (C₅Me₅). IR (NaCl plates, Nujol mull, cm⁻¹): ν 2205 (w), 1715 (s), 1676 (s), 1590 (m), 1496 (s), 1365 (s), 1330 (s), 1209 (m), 1174 (m), 1122 (m), 1030 (w), 925 (w), 794 (m), 745 (m), 691 (m), 671 (w), 623 (w). EI-MS: m/z 459 $[M - C_5Me_5]^+$ (10%), 426 $[M - NPh_2]^+$ (10%). Anal. Found (calcd for C₃₂H₄₂N₄O₄Ti): C, 64.58 (64.64); H, 7.14 (7.12); N, 9.37 (9.42).

NMR Tube Scale Reaction of Cp*Ti{MeC(NⁱPr)₂}{N-(NPh₂)C(O)O} (16) with CO₂. A 10.0 mg portion (0.018 mmol) of Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(O)O} (16) was dissolved in C₆D₆ (0.6 mL), and and the solution was freeze–pump–thawed three times. The solution was then exposed to CO₂ at a pressure of ca. 1.1 atm at room temperature. The reaction was monitored by ¹H NMR spectroscopy. The ¹H NMR spectrum recorded after 3 days showed quantitative formation of Cp*Ti{MeC-(NⁱPr)₂}{OC(O)N(NPh₂)C(O)O} (18).

 $Cp*Ti\{MeC(N^iPr)_2\}\{N(NPh_2)C(S)S\} (20). \text{ To a solution of }$ $Cp*Ti{MeC(N^{1}Pr)_{2}}(NNPh_{2})$ (13, 0.300 g, 0.590 mmol) in benzene (20 mL) was added an excess of CS₂ (0.107 mL, 1.78 mmol), all at room temperature. The resulting dark brown solution was stirred for 16 h. Volatiles were then removed under reduced pressure to afford 20 as a dark brown solid. The resultant dark brown solid was washed with cold pentane (3 \times 5 mL), filtered, and dried in vacuo. Yield: 0.245 g (71%). 1 H NMR (C₇D₈, 499.9 MHz, 263 K): δ 7.47 (4 H, d, ³J = 6.5 Hz, o- C_6H_5), 7.18 (4 H, t, ${}^{3}J = 6.5$ Hz, m- C_6H_5), 6.90 (2 H, t, ${}^{3}J = 6.5$ Hz, p-C₆H₅), 3.34 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 3.17 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 1.91 (15 H, s, C₅Me₅), 1.46 (3 H, s, MeCN₂), 1.10 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 1.04 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 0.90 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 0.86 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe). ${}^{13}C{}^{1}H$ NMR (C₇D₈, 125.7 MHz, 263 K): δ 166.3 (MeCN₂), 149.1 (overlapping *i*-C₆H₅ and SC(S)N), 131.0 (C₅Me₅), 128.6 (m-C₆H₅), 121.6 (overlapping o- and p-C₆H₅), 50.9 (overlapping NCH_aMeMe and NCH_bMeMe), 24.7 (NCH_aMeMe), 24.2 (overlapping NCH_aMeMe and NCH_bMeMe), 24.0 (NCH_bMeMe), 13.8 $(C_5 M e_5)$, 13.3 (MeCN₂). IR (NaCl plates, Nujol mull, cm⁻¹): v 1587 (s), 1491 (s), 1401 (m), 1333 (m), 1310 (m), 1276 (m), 1203

(s), 750 (m), 603 (m). EI-MS: m/z 279 $[M - C_5Me_5 - NPh_2]^+$ (10%). Anal. Found (calcd for $C_{31}H_{42}N_4S_2Ti$): C, 63.88 (63.90); H, 7.40 (7.27); N, 9.55 (9.62).

NMR Tube Scale Reaction of Cp*Ti{MeC(NⁱPr)₂}(NNPh₂) (13) with $Cp*Ti\{MeC(N^{1}Pr)_{2}\}\{N(NMe_{2})C(S)S\}$ (21). To a solution of Cp*Ti{MeC(NⁱPr)₂}{N(NMe₂)C(S)S} (21; 0.012 g, 0.026 mmol) in C_6D_6 (0.3 mL) in an NMR tube equipped with a J. Young Teflon valve was added Cp*Ti{MeC(NⁱPr)₂}-(NNPh₂) (13; 0.013 g, 0.026 mmol) in C₆D₆ (0.3 mL) at room temperature. The reaction was monitored by ¹H NMR spectroscopy. $[Cp*Ti{MeC(N^{1}Pr)_{2}}(\mu-S)]_{2}$ (25) and $Cp*Ti{MeC (N^{1}Pr)_{2}$ { $N(NPh_{2})C(NNMe_{2})S$ } (26) were formed quantitatively after 4 days. 26 was characterized by ¹H NMR spectroscopy. ¹H NMR data (C₆D₆, 499.9 MHz, 293 K): δ 7.52 (1 H, d, ³J = 7.5 Hz, o_a -C₆H₅), 7.30 (1 H, d, ³J = 7.5 Hz, o_b -C₆H₅), 7.21 (2 H, app t, app ${}^{3}J = 7.5$ Hz, m_{a} -C₆H₅), 7.10 (2 H, app t, app ${}^{3}J = 7.5$ Hz, m_{b} -C₆H₅), 6.88 (2 H, t, ${}^{3}J = 7.5$ Hz, p_{a} -C₆H₅), 6.79 (2 H, t, ${}^{3}J = 7.5$ Hz, p_{b} -C₆H₅), 3.29 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 2.97 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 2.51 (6 H, s, NNMe₂), 1.96 (15 H, s, C₅Me₅), 1.50 (3 H, s, MeCN₂), 1.20 (6 H, overlapping $2 \times d$, ${}^{3}J = 6.5$ Hz, overlapping NCH_aMeMe and NCH_bMeMe), 1.17 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 0.83 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 293 K): δ 168.7 (MeCN₂), 156.0 (SC(N)N), 147.4 (*i*_a-C₆H₅) 147.4 (*i*_b-C₆H₅), 129.2 (C₅Me₅), 128.3 (ma-C6H5), 128.1 (mb-C6H5), 121.7 (pa-C6H5), 121.3 (oa-C₆H₅), 119.4 (*p*_b-C₆H₅), 117.7 (*o*_b-C₆H₅), 51.6 (NCH_aMeMe), 49.4 (NCH_bMeMe), 48.7 (NNMe₂), 26.3 (NCH_bMeMe), 25.5 (NCH_bMeMe), 24.6 (NCH_aMeMe), 23.5 (NCH_aMeMe), 14.2 (MeCN₂), 13.5 (C₅Me₅).

 $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NPh_{2})C(NTol)O}$ (24). To a solution of Cp*Ti{MeC(N¹Pr)₂}(NNPh₂) (13; 0.400 g, 0.790 mmol) in benzene (20 mL) was added p-TolNCO (0.100 mL, 0.790 mmol), all at room temperature. An immediate color change from dark yellow to dark brown was observed. After 16 h, the volatiles were removed under reduced pressure to afford 24 as a dark brown solid. The resultant dark brown solid was washed with cold pentane (3 \times 5 mL), filtered, and dried in vacuo. Yield: 0.342 g (68%). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.71 (2 H, d, ${}^{3}J = 7.5$ Hz, o_{a} -C₆H₅), 7.65 (2 H, d, ${}^{3}J = 7.5$ Hz, o-C₆H₄Me), 7.20 (2 H, t, ${}^{3}J = 7.5$ Hz, m_{a} -C₆H₅), 7.10 (4 H, m, overlapping $o_{\rm b}$ -C₆H₅ and *m*-C₆H₄Me), 7.02 (2 H, t, ³J = 7.5 Hz, $m_{\rm b}$ -C₆H₅), 6.90 (1 H, t, ${}^{3}J = 7.5$ Hz, p_{a} -C₆H₅), 6.74 (1 H, t, ${}^{3}J = 7.5$ Hz, p_{b} - C_6H_5), 3.29 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NC H_a MeMe), 2.82 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 2.18 (3 H, s, C₆H₄Me), 1.96 (15 H, s, C₅Me₅), 1.40 (3 H, s, MeCN₂), 1.17 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 1.11 (6 H, overlapping 2 × d, ${}^{3}J = 6.5$ Hz, overlapping NCH_aMeMe and NCH_aMeMe), 0.93 $(3 \text{ H}, \text{d}, {}^{3}J = 6.5 \text{ Hz}, \text{NCH}_{b}\text{Me}Me). {}^{13}\text{C}\{{}^{1}\text{H}\} \text{ NMR} (\text{C}_{6}\text{D}_{6}, 75.4 \text{ Hz})$ MHz, 293 K): & 169.4 (MeCN2), 155.9 (OC(N)N), 147.7 (overlapping i_a -C₆H₅ and i_b -C₆H₅), 147.2 (*i*-C₆H₄Me), 129.7 $(p-C_6H_4Me)$, 129.6 (C_5Me_5) , 129.0 $(m-C_6H_4Me)$, 128.7 $(m_a-C_6H_4Me)$ C_6H_5), 128.4 (m_b - C_6H_5), 125.8 (o- C_6H_4Me), 122.41 (p_a - C_6H_5), 122.2 $(o_a-C_6H_5)$, 119.3 $(p_b-C_6H_5)$, 117.2 $(o_b-C_6H_5)$, 50.9 (NCH_aMeMe), 49.9 (NCH_bMeMe), 26.3 (NCH_bMeMe), 24.8 (NCH_bMeMe), 24.4 (NCH_aMeMe), 24.2 (NCH_aMeMe), 21.0 (C₆H₄Me), 12.9 (C₅Me₅), 12.7 (MeCN₂). IR (NaCl plates, Nujol mull, cm⁻¹): v 1619 (m), 1587 (s), 1491 (s), 1336 (m), 1315 (m), 1206 (m), 1173 (w), 1124 (w), 1027 (w), 982 (w), 811 (w), 743 (m), 691 (w). EI-MS: m/z 506 $[M - OC(NTol)]^+$ (20%). A satisfactory elemental analysis could not be obtained.

 $Cp*Ti{MeC(N^iPr)_2}{N(NPh_2)C(NTol)S}$ (28). To a solution of Cp*Ti{MeC(NⁱPr)_2}(NNPh_2) (13; 0.300 g, 0.590 mmol) in benzene (15 mL) was added *p*-TolNCS (88.0 mg, 0.590 mmol) in benzene (15 mL), all at room temperature. The resulting dark green solution was stirred for 16 h. Volatiles were then removed under reduced pressure to afford 28 as a dark green solid. The resultant dark green solid was washed with cold pentane (3 × 5 mL), filtered, and dried in vacuo. Yield: 0.210 g (54%). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.57 (2 H, d, ³J = 7.5 Hz, o_a - C_6H_5), 7.36 (2 H, d, ${}^{3}J = 7.5$ Hz, o_b - C_6H_5), 7.21 (2H, t, ${}^{3}J = 7.5$ Hz, ma-C6H5), 7.12 (4 H, m, overlapping mb-C6H5 and m- C_6H_4Me), 6.97 (2 H, d, ${}^3J = 8.4$ Hz, $o-C_6H_4Me$), 6.89 (1 H, t, ${}^{3}J = 7.5 \text{ Hz}, p_{a}\text{-}C_{6}\text{H}_{5}), 6.79 (1 \text{ H}, \text{t}, {}^{3}J = 7.5 \text{ Hz}, p_{b}\text{-}C_{6}\text{H}_{5}), 3.25$ (1 H, app sept, app ${}^{3}J = 6.6$ Hz, NCH_aMeMe), 2.98 (1 H, app sept, app ${}^{3}J = 6.6$ Hz, NCH_bMeMe), 2.08 (3 H, s, C₆H₄Me), 1.94 (15 H, s, C₅Me₅), 1.51 (3 H, s, MeCN₂), 1.21 (6 H, over-lapping 2 × d, ${}^{3}J = 6.6$ Hz, overlapping NCH_aMeMe and $NCH_bMeMe)$, 1.10 (3 H, d, ${}^{3}J = 6.6$ Hz, $NCH_aMeMe)$, 0.97 (3) H, d, ${}^{3}J = 6.6$ Hz, NCH_bMeMe). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 75.4 MHz, 293 K): δ 169.1 (MeCN₂), 154.7 (SC(N)N), 147.5 (overlapping i_a -C₆H₅, i_b -C₆H₅ and i-C₆H₄Me), 130.9 (p- C_6H_4Me), 129.8 (C_5Me_5), 129.0 ($o-C_6H_4Me$), 128.5 ($m_a C_6H_5$), 123.7 (overlapping *m*- C_6H_4 Me and *m*_b- C_6H_5), 121.9 $(p_a-C_6H_5)$, 121.4 $(o_a-C_6H_5)$, 119.5 $(p_b-C_6H_5)$, 117.7 $(o_b-C_6H_5)$, 51.9 (NCH_aMeMe), 49.6 (NCH_bMeMe), 26.3 (NCH_bMeMe), 25.5 (NCH_bMeMe), 24.6 (NCH_aMeMe), 23.5 (NCH_aMeMe), 20.9 (C_6H_4Me), 14.2 ($MeCN_2$), 13.6 (C_5Me_5). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1577 (s), 1490 (s), 1412 (m), 1327 (m), 1313 (m), 1278 (m), 1204 (m), 1167 (m), 1153 (m), 1104 (m), 1042 (m), 1020 (m), 944 (w), 810 (m), 763 (w), 740 (m), 690 (m), 649 (w). EI-MS: m/z 338 $[M - ToINCS - NPh_2]^+$ (20%). Anal. Found (calcd for C₃₈H₄₉N₅STi): C, 69.63 (69.60); H, 7.60 (7.53); N, 10.63 (10.68).

 $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NPh_{2})C(N^{t}Bu)O}$ (30). To a solution of Cp*Ti{MeC(N¹Pr)₂}(NNPh₂) (13; 0.300 g, 0.590 mmol) in benzene (20 mL) was added ^tBuNCO (67.6 µL, 0.590 mmol), all at room temperature. An immediate color change from dark yellow to dark brown was observed. After 16 h, the volatiles were removed under reduced pressure to afford 30 as a dark brown solid. The resultant dark brown solid was washed with cold pentane (3×5 mL), filtered, and dried in vacuo. Yield: 0.184 g (51%). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.62 (2 H, d, ${}^{3}J = 6.5$ Hz, o_{a} -C₆H₅), 7.22 (2 H, t, ${}^{3}J = 6.5$ Hz, m_{a} -C₆H₅), 7.09 (2 H, d, ${}^{3}J = 6.5$ Hz, o_{b} -C₆H₅), 7.01 (2 H, t, ${}^{3}J = 6.5$ Hz, m_{b} -C₆H₅), 6.88 (1 H, t, ${}^{3}J = 6.5$ Hz, p_{a} -C₆H₅), 6.71 (1 H, t, ${}^{3}J = 6.5$ Hz, p_b -C₆H₅), 3.34 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NCH_aMeMe), 2.80 (1 H, app sept, app ${}^{3}J = 6.5$ Hz, NC H_{b} MeMe), 1.96 (15 H, s, C₅Me₅), 1.56 (9 H, s, ^tBu), 1.39 (3 H, s, MeCN₂), 1.17 (3 H, d, ³J = 6.5 Hz, NCH_aMeMe), 1.14 $(3 \text{ H}, d, {}^{3}J = 6.5 \text{ Hz}, \text{NCH}_{a}\text{Me}Me), 1.09 (3 \text{ H}, d, {}^{3}J = 6.5 \text{ Hz},$ NCH_bMeMe), 0.92 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe). 13 C-{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 168.5 (MeCN₂), 152.4 (OC(N)N), 148.1 $(i_a-C_6H_5)$, 147.8 $(i_b-C_6H_5)$, 128.4 (C_5Me_5) , 128.3 $(m_a-C_6H_5)$, 128.1 $(m_b-C_6H_5)$, 121.7 $(p_a-C_6H_5)$, 121.6 $(o_a-C_6H_5)$ C₆H₅), 119.3 (*p*_b-C₆H₅), 117.7 (*o*_b-C₆H₅), 51.90 (NCMe₃), 50.4 (NCH_aMeMe), 49.5 (NCH_bMeMe), 32.9 (NCMe₃), 26.2 (NCH_bMeMe), 25.1 (NCH_bMeMe), 25.0 (NCH_aMeMe), 24.35 (NCH_aMeMe), 13.0 (MeCN₂), 12.9 (C₅Me₅). IR (NaCl plates, Nujol mull, cm⁻¹): v 1653 (m), 1636 (w), 1589 (w), 1559 (w), 1540 (w), 1521 (w), 1506 (w), 1490 (m), 1458 (s), 1335 (w), 1313 (w), 1207 (w), 1175 (w), 1019 (w), 793 (w), 744 (w), 691 (w), 668 (m). Anal. Found (calcd for C₃₅H₅₁N₅OTi): C, 69.52 (69.41); H, 8.42 (8.49); N, 11.48 (11.56).

 $Cp*Ti{MeC(N^{i}Pr)_{2}}{OC(NTol)N(NPh_{2})C(O)O}$ (31). A solution of $Cp*Ti\{MeC(N^{1}Pr)_{2}\}\{N(NPh_{2})C(NTol)O\}$ (24; 0.450 g, 0.700 mmol) in toluene (20 mL) was freeze-pump-thawed three times. The solution was then exposed to CO₂ at a pressure of ca. 1.1 atm at room temperature. After 4 days, the volatiles were removed under reduced pressure to afford 31 as a dark brown solid. The resultant dark brown solid was washed with cold pentane (3×5 mL), filtered, and dried in vacuo. Yield: 0.178 g (37%). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.95 (2 H, d, ${}^{3}J = 6.0$ Hz, o_{a} -C₆H₅), 7.40 (2 H, d, ${}^{3}J = 6.0$ Hz, o_{b} -C₆H₅), 7.29 (2H, t, ${}^{3}J = 6.0$ Hz, m_{a} -C₆H₅), 7.10 (2 H, m, m_{b} -C₆H₅), 7.00 $(4 \text{ H}, \text{m}, \text{overlapping } o \text{- and } m \text{-} C_6 H_4 \text{Me}), 6.98 (1 \text{ H}, \text{m}, p_a \text{-} C_6 \text{H}_5),$ $6.82 (1 \text{ H}, \text{t}, {}^{3}J = 6.0 \text{ Hz}, p_{b}\text{-}C_{6}\text{H}_{5}), 3.47 (1 \text{ H}, \text{app sept, app } {}^{3}J =$ 6.0 Hz, NCH_aMeMe), 3.35 (1 H, app sept, app ${}^{3}J = 6.0$ Hz, $NCH_bMeMe)$, 2.19 (3 H, s, C_6H_4Me), 1.83 (15 H, s, C_5Me_5), 1.44 (3 H, s, MeCN₂), 1.13 (3 H, d, ${}^{3}J = 6.0$ Hz, NCH_aMeMe),

1.09 (3 H, d, ${}^{3}J = 6.0$ Hz, NCH_aMe*Me*), 0.88 (6 H, overlapping 2 × d, ${}^{3}J = 6.0$ Hz, overlapping NCH_b*Me*Me and NCH_bMe*Me*). 1³C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 169.6 (MeCN₂), 152.8 (OC(O)N), 149.9 (OC(N)N), 147.1 (*i*-C₆H₄Me), 146.6 (*i*_b-C₆H₅), 146.2 (*i*_a-C₆H₅), 130.9 (C₅Me₅), 130.4 (*p*-C₆H₄Me), 128.9 (*m*_a-C₆H₅), 128.8 (overlapping *m*-C₆H₄Me and *m*_b-C₆H₅), 123.9 (*o*-C₆H₄Me), 123.1 (*p*_a-C₆H₅), 122.5 (*o*_a-C₆H₅), 121.0 (*p*_b-C₆H₅), 118.2 (*o*_b-C₆H₅), 50.5 (NCH_aMeMe), 50.0 (NCH_bMeMe), 24.3 (NCH_aMe*Me*), 23.9 (NCH_bMe*Me*), 23.5 (overlapping NCH_a. *Me*Me and NCH_b*Me*Me), 21.0 (C₆H₄*Me*), 14.9 (*Me*CN₂), 12.6 (C₅*Me*₅). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1699 (s), 1628 (s), 1592 (s), 1496 (s), 1336 (s), 1207 (m), 1180 (m), 1101 (m), 1017 (w), 862 (w), 794 (m), 746 (m), 690 (w). EI-MS: *m/z* 424 [*M* – NPh₂ – Tol]⁺ (30%). Anal. Found (calcd for C₃₉H₄₉N₅O₃Ti): C, 68.55 (68.51); H, 7.15 (7.22); N, 10.18 (10.24).

Reaction of Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (15) with Ar'NCO. To a solution of Cp*Ti{MeC(N'Pr)₂}(NNMe₂) (15; 0.417 g, 1.09) mmol) in benzene (20 mL) was added Ar'NCO (467 µL, 2.18 mmol), all at room temperature. The resulting yellow solution was stirred for 20 h at 60 °C. Volatiles were then removed under reduced pressure to afford $[Cp^*Ti{MeC(N^iPr)_2}(\mu-O)]_2$ (12) and 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O) (34). Sublimation (65-75 °C, 5×10^{-6} mbar) afforded **34** as a white solid. Yield: 76 mg (15%). Diffraction-quality crystals were grown from a concentrated hexane solution at -4 °C. ¹H NMR (C₆D₆, 499.9 MHz, 293 K): δ 7.25 (1 H, t, ³J = 7.5 Hz, p_a -C₆H₃(ⁱPr₂)), 7.14 (2 H, d, ³J = 7.5 Hz, m_a -C₆H₃(ⁱPr₂)), 7.09 (2 H, d, ³J = 7.5 Hz, m_b -C₆H₃(ⁱPr₂)), 7.00 (1 H, t, ${}^{3}J = 7.5$ Hz, p_{b} -C₆ $H_{3}({}^{i}Pr_{2})$), 3.43 (2 H, app sept, app ${}^{3}J$ = 7.0 Hz, NCH_bMeMe), 3.20 (2 H, app sept, app ${}^{3}J$ = 7.0 Hz, NCH_aMeMe), 2.66 (6 H, s, NNMe₂), 1.32 (6 H, d, ${}^{3}J$ = 7.0 Hz, NCH_aMeMe), 1.21 (18 H, m, overlapping NCH_aMeMe, NCH_bMeMe, and NCH_bMeMe). $^{13}C{^{1}H}$ NMR (C₆D₆, 125.7 MHz, 293 K): δ 159.7 (NC(O)N), 152.9 (NC(N)N), 147.2 (o_a- $C_6H_3({}^{1}Pr_2)), 146.4(i_b-C_6H_3({}^{1}Pr_2)), 140.4(o_b-C_6H_3({}^{1}Pr_2)), 130.5(p_a-2))$ $C_6H_3(^{1}Pr_2)), 128.3 \ (i_a-C_6H_3(^{1}Pr_2)), 124.1 \ (m_a-C_6H_3(^{1}Pr_2)), 122.7$ $(m_{\rm b}-C_6{\rm H}_3({}^{\rm i}{\rm Pr}_2)), 122.2 \ (p_{\rm b}-C_6{\rm H}_3({}^{\rm i}{\rm Pr}_2)), 53.5 \ ({\rm NNMe}_2), 29.5$ (CH_aMeMe) 28.3 (CH_bMeMe), 25.0 (CH_aMeMe), 24.3 (overlapping CH_bMeMe and CH_bMeMe), 22.9 (CH_aMeMe). IR (NaCl plates, Nujol mull, cm⁻¹): ν 2289 (w), 2169 (w), 1808 (s), 1646 (s), 1586 (m), 1465 (s), 1393 (s), 1365 (m), 1356 (w), 1290 (w), 1237 (m), 1207 (w), 1172 (w), 1114 (w), 1063 (m), 1041 (w), 965 (m), 936 (w), 908 (w), 862 (w), 810 (w), 801 (m), 777 (m), 754 (w), 725 (s), 706 (m), 690 (m), 640 (m). EI-MS: *m*/*z* 448 [*M*]⁺ (100%), 245 $[M - \text{ArNCO}]^+$ (80%). Anal. Found (calcd for C₆₄H₁₀₄N₈O₃Ti₂): C, 67.99 (68.07); H, 9.20 (9.28); N, 10.02 (9.92).

 $Cp*Ti{MeC(N^{i}Pr)_{2}}{OC(NNMe_{2})N(Tol)C(NTol)O}$ (35). To a solution of Cp*Ti{MeC(N¹Pr)₂}(NNMe₂) (15; 0.300 g, 0.780 mmol) in benzene (20 mL) was added p-TolNCO (0.198 mL, 1.57 mmol), all at room temperature. An immediate color change from dark green to brown was observed, and the solution was left to stand for 16 h. Volatiles were then removed under reduced pressure to afford 35 as a brown solid. The resultant brown solid was washed with cold pentane (3 \times 5 mL), filtered, and dried in vacuo. Yield: 0.308 g (76%). Diffraction-quality crystals were grown by slow cooling of a saturated hexane solution. ¹H NMR (C_6D_6 , 299.9 MHz, 293 K): δ 7.51 (2 H, d, ³J = 8.4 Hz, o_b - C_6H_4 Me), 7.12 (2 H, d, ³J = 8.4 Hz, o_a - C_6H_4 Me), 7.07 (2 H, d, ³J = 8.4 Hz, m_b - C_6H_4 Me), 7.01 (2 H, d, ${}^{3}J = 8.4 \text{ Hz}, m_{a}\text{-}C_{6}H_{4}\text{Me}), 3.71 (1 \text{ H}, \text{app sept, app } {}^{3}J = 6.6 \text{ Hz},$ NCH_aMeMe), 3.42 (1 H, app sept, app ${}^{3}J = 6.6$ Hz, NCH_bMeMe), 2.50 (6H, s, NNMe₂), 2.20 (3 H, s, C₆H₄Me_a), 2.05 (3 H, s, C₆H₄Me_b), 2.02 (15 H, s, C₅Me₅), 1.50 (3 H, s, MeCN₂), 1.26 (3 H, d, ${}^{3}J = 6.6$ Hz, NCH_aMeMe), 1.15 (3 H, d, ${}^{3}J = 6.6$ Hz, NCH_aMeMe), 0.94 (3 H, d, ${}^{3}J = 6.6$ Hz, NCH_bMeMe), 0.85 (3 H, d, ${}^{3}J = 6.6$ Hz, NCH_bMeMe). ${}^{13}C$ -{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 169.7 (MeCN₂), 157.6 (OC(NNMe₂)N), 153.2 (OC(NTol)N), 148.1 (*i*_a-C₆H₄Me), 142.1 (i_b - C_6H_4Me), 134.9 (p_b - C_6H_4Me), 130.1 (o_b - C_6H_4Me), 129.7 (C_5 Me₅), 129.2 (m_a - C_6 H₄Me), 128.6 (overlapping p_a and o_a-C₆H₄Me), 124.3 (m_b-C₆H₄Me), 50.1 (NCH_aMeMe),

49.7 (NCH_bMeMe), 48.5 (NNMe₂), 24.1 (NCH_aMeMe), 24.1 (NCH_bMeMe), 23.8 (NCH_aMeMe), 23.5 (NCH_bMeMe), 21.1 (C₆H₄Me_b), 21.0 (C₆H₄Me_a), 15.5 (MeCN₂), 12.5 (C₅Me₅). IR (NaCl plates, Nujol mull, cm⁻¹): ν 2805 (m), 2757 (w), 1619 (s), 1599 (s), 1568 (s), 1508 (s), 1458 (s), 1416 (w), 1366 (s), 1340 (m), 1311 (m), 1279 (w), 1255 (m), 1227 (m), 1204 (s), 1171 (w), 1158 (w), 1119 (m), 1105 (m), 1024 (w), 1005 (s), 933 (w), 899 (m), 884 (m), 810 (s), 780 (m), 725 (m), 718 (m), 688 (w), 605 (m). Anal. Found (calcd for C₃₆H₅₂N₆O₂Ti): C, 66.73 (66.65); H, 7.98 (8.08); N, 12.95 (12.96).

Crystal Structure Determinations. Crystal data collection and processing parameters for Cp*Ti{MeC(N¹Pr)₂}(NNPh₂) (13), $Cp*Ti{MeC(N'Pr)_2}(NNMePh)$ (14), $Cp*Ti{MeC(N'Pr)_2}$ - $(NNMe_2)$ (15), $Cp*Ti\{MeC(N^iPr)_2\}\{OC(O)N(NPh_2)C(O)O\}$ (18), $Cp^*Ti\{MeC(N^1Pr)_2\}\{OC(O)-N(NMe_2)C(O)O\}$ (19), Cp^*Ti ${MeC(N^{1}Pr)_{2}}{OC(O)N-(NNMePh)C(O)O}$ (36), Cp*Ti{MeC- $(N^{i}Pr)_{2}$ {N(NPh₂)C(NAr')O} (27), Cp*Ti{MeC(N^{i}Pr)_{2}}{N-(NPh₂)C(NAr')S} (29), 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O) (34), and $Cp*Ti{MeC(N^{1}Pr)_{2}}{OC(NNMe_{2})N(Tol)C(NTol)O}$ (35) are given in the Supporting Information. Crystals were mounted on glass fibers using perfluoro polyether oil and cooled rapidly in a stream of cold N2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.⁷⁴ The structures were solved by direct methods (SIR9275), and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.⁷⁶ Other details of the structure solution and refinements are given in the Supporting Information (CIF data). Full listings of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures have also been deposited at the Cambridge Crystallographic Data Centre. See the Notice to Authors at http://pubs.acs.org/paragonplus/submission/orgnd7/orgnd7 authguide.pdf.

Computational Details. All the calculations have been performed with the Gaussian03 package⁷⁷ at the B3PW91 level.^{78,79} The titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (12 valence electrons) and its associated basis set,⁸⁰ augmented by an f polarization function ($\alpha = 0.869$).⁸¹ The S atom was

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represented by RECP from the Stuttgart group and the associated basis set,⁸² augmented by a d polarization function.⁸³ The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set in all cases, except for the bond energy calculations on Figure 14, where a 6-311++G(d,p) basis set was used.⁸⁴ NBO analyses were performed with NBO 5.0 interfaced with Gaussian.⁸⁵ Full optimization of geometry was performed without any symmetry constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or transition states. Connection between reactant and product through a given transition state was checked by optimization of slightly altered geometries of the transition state along the two directions of the transition state vector associated with the imaginary frequency.

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Supporting Information Available: Text, tables, figures, and CIF files giving X-ray data collection and processing parameters, X-ray crystallographic data for the structure determinations of Cp*Ti{MeC(NⁱPr)₂}(NNPh₂) (13), Cp*Ti{MeC(NⁱPr)₂}(NNMePh) (14), Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (15), Cp*Ti{MeC(NⁱPr)₂}{OC(O)N(NMe₂)C(O)O} (18), Cp*Ti{MeC(NⁱPr)₂}{OC(O)N(NMePh)C(O)O} (19), Cp*Ti{MeC(NⁱPr)₂}{OC(O)N(NMePh)C(O)O} (36), Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(NAr')O} (27), Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(NAr')O} (27), Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(NAr')O} (36), Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(NAr')O} (27), Cp*Ti{MeC(NⁱPr)₂}{N(NPh₂)C(NAr')N(Ar')C(O) (34), and Cp*Ti-{MeC(NⁱPr)₂}{OC(NNMe₂)N(Tol)C(NTol)O} (35), selected distances and angles for 1,2,4-N(Me)₂NC(NAr')N(Ar')C(O) (34), further experimental details, a description of the reactions of 14 with CO₂ and CS₂, and further details of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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