Published in final edited form as:

J Am Chem Soc. 2020 April 29; 142(17): 8006–8018. doi:10.1021/jacs.0c02487.

Cp₂Ti(κ^2 -^{*t*}BuNCN^{*t*}Bu): a Complex With an Unusual κ^2 Coordination Mode of a Heterocumulene Featuring a Free Carbene

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Abstract

Although there are myriad binding modes of heterocumulenes to metal centers, the monometallic κ^2 -ECE (E = O, S, NR) coordination mode has not been reported. Herein, the synthesis, isolation, and physical characterization of Cp₂Ti(κ^2 -^{*t*}BuNCN^{*t*}Bu) (**3**) (Cp = cyclopentadienyl, ^{*t*}Bu = *tert*-butyl), a strained 4-membered metallacycle bearing a free carbene, is described. Computational (DFT, CASSCF, QT-AIM, ELF) and solid-state CP-MAS ¹³C spectroscopic analysis indicate that **3** is best described as a free carbene with partial Ti-Cb bonding that results from Ti-N π -bonding mixing with N-C-N s-bonding of the bent N-C-N framework. Reactivity studies of **3** corroborate its carbene-like nature: protonation with [LutH]I results in formation of a Ti-formamidinate (**4**), while oxidation with S₈ yields a Ti-thioureate (**5**). Additionally, a related bridged dititanamidocarbene, (Cp₂Ti)₂(μ - η^1, η^1 -CyNCNCy) (**10**) (Cy = cyclohexyl) is reported. Taken together, this work suggests that the 2-electron reduction of heterocumulene moieties can allow access to unusual free carbene coordination geometries given the proper stabilizing coordination environment from the reducing transition metal fragment.

Graphical Abstract

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ASSOCIATED CONTENT

Complete experimental procedures, computational methods, spectroscopic methods, and associated data(PDF)

Introduction

The isolation of unsaturated, strained metallacycles is challenging as they are often reactive, high-energy species.^{1,2} Nonetheless, group IV metallocenes have been an excellent platform for the isolation of highly strained metallacyclic cores,^{3–5} such as zirconacyclopentatriene,⁶ zirconacyclopentyne,⁷ and hafnacyclopenta-3,4-diene⁸ complexes, among others. With respect to this endeavor, 4-membered metallacycles are particularly important because of their intermediacy in alkene⁹ and alkyne^{10–12} metathesis reactions. Recently, Reiß and Beweries synthesized and described a titanacyclobuta-2,3diene^{13,14} complex *via* salt metathesis of $[\text{rac}(\text{ebthi})\text{TiCl}_2]$ with the deprotonated allene $\text{Li}_2(\text{Me}_3\text{SiC}_3\text{SiMe}_3)$ (Figure 1a) (*rac*-(ebthi) = *rac*-1,2-ethylene-1,1'-bis(tetrahydroindenyl)). This allene-diyl moiety is a model of a decomposition product in alkyne metathesis that arises from deprotonation of the $\beta\text{-C-H}$ in metal-alkylidyne [2+2]-cycloaddition products, though an additional M- $\beta\text{-C}$ interaction is present in similar group VI complexes.^{15–19}

While there are several examples of transition-metal complexes bearing the allene-diyl moiety, there are no structurally characterized monometallic examples of heterocumulene ($\text{E}=\text{C}=\text{E}$, $\text{E} = \text{O}$, NR , S , *etc*) analogues of these 1-metallacyclobuta-2,3-dienes (e.g. complexes of the type $\text{M}(\kappa^2\text{-ECE})$, Figure 1b). Indeed, despite the myriad bonding motifs of CO_2 to transition metals,^{20–23} there are no examples of monometallic $\kappa^2\text{-ECE}$ bonding, although there are several related examples of $\kappa^2\text{-OCO}$ and $\kappa^2\text{-SCS}$ -bound structures in bimetallics (Figure 1d).^{24–32} Similarly, deprotonation of metal-bound formates has resulted in closely related bridging $\mu\text{-}\eta^2, \eta^1\text{-CO}_2$ moieties (Figure 1c).^{33,34} Thus, isolation and characterization of $\kappa^2\text{-ECE}$ complexes could provide new insights and strategies into CO_2 activation and further reactivity.

Group 4 $\kappa^2\text{-(RNCNR)}$ analogues (e.g. $\text{Cp}_2\text{Ti}(\kappa^2\text{-RNCNR})$, **INT2**, Figure 2), have been investigated theoretically.^{35,36} Complexes of this type were thought to be too reactive to isolate;³⁷ however, their intermediacy was proposed by Rosenthal³⁵ in a series of reactions of $\text{Cp}_2\text{Ti}(\eta^2\text{-BTMSA})$ (**1**) (BTMSA = bis(trimethylsilylacetylene)) with various 1,3-disubstituted carbodiimides (Figure 2). These reactions yielded a variety of products stemming from C-N bond cleavage (**2a**, **2b**) or coupling (**2b**), as well as C-C bond coupling

(**2d**), depending on the nature of the carbodiimide substituents.^{35,38,39} We were prompted to revisit the reaction of $\text{Cp}_2\text{Ti}(\eta^2\text{-BTMSA})$ with carbodiimides based on a recent report of Ti-carbodiimide adduct intermediacy in Ticalyzed isocyanide amination.^{40,41} Herein we report the synthesis, experimental characterization, theoretical analysis, and reactivity of $\text{Cp}_2\text{Ti}(\kappa^2\text{-}^t\text{BuNCN}^t\text{Bu})$ (**3**), an isolable example of reactive complex **INT2** with free “titana-N-heterocyclic carbene” character, as well as a related bimetallic free carbene, $(\text{Cp}_2\text{Ti})_2(\mu\text{-}\eta^1, \eta^1\text{-CyNCNCy})$. Complex **3** represents the first example of a structurally characterized monometallic complex with a κ^2 -bound heterocumulene.

Results and Discussion

Reaction of the masked $\text{Cp}_2\text{Ti}^{\text{II}}$ precursor $\text{Cp}_2\text{Ti}(\eta^2\text{-BTMSA})$ (**1**) with $^t\text{BuNCN}^t\text{Bu}$ in pentane at room temperature for 10 minutes led to a color change from brown to deep red. Overnight crystallization of the reaction mixture at $-35\text{ }^\circ\text{C}$ afforded the C_{2v} -symmetrical product $\text{Cp}_2\text{Ti}(\kappa^2\text{-}^t\text{BuNCN}^t\text{Bu})$, **3**, as a dark red crystalline solid in 92% yield in gram-scale quantities (eq 1). The isolation of **3** was surprising given previous reports that reaction of **1** with $^t\text{BuNCN}^t\text{Bu}$ yields $[\text{Cp}_2\text{Ti}(\text{CN})]_4$ (**2a**) (Figure 2), albeit at $60\text{ }^\circ\text{C}$ and extended reaction times.^{35,38,39} In fact, **3** is stable for months under ambient conditions in an N_2 atmosphere.

(1)

The X-ray crystal structure of **3** is displayed in Figure 3. The structural parameters for **3** are indicative of a system featuring delocalization of π -electron density across the N-C-N atoms of the metallacycle, along with a free singlet carbene, as drawn in eq 1. The C1-N1 (1.3246(13) Å), and C1-N2 (1.3210(13) Å) bond lengths are not far from that of $\text{C}(\text{sp}^2)\text{-N}(\text{sp}^2)$ single bonds (1.355 Å).⁴² The Ti1-N1 and Ti1-N2 bond lengths are close to that of a typical $\text{Ti}^{\text{IV}}\text{-N}(\text{pyrrolide})$ bond,^{43–45} suggestive of an X-type $\text{Ti}^{\text{IV}}\text{-N}$ with little $\text{N}\rightarrow\text{Ti}$ π -donation, consistent with the π -electron density of the nitrogen atoms being delocalized across the N-C-N core in order to stabilize the carbene carbon. The Ti1-C1 distance of 2.2674(10) Å is slightly (but significantly) longer than typical $\text{Ti-C}(\text{sp}^3)$ bonds (for example, the average distance of Ti-CH_3 in $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ is 2.176 Å).⁴⁶ This Ti1-C1 distance is 0.1 Å longer than Beweries’ κ^2 -allene diyl Ti-C distance (2.178 Å, Figure 1A),¹³ but significantly shorter than the analogous Ti-C in Rosenthal’s **2c** (2.599 Å).³⁵

The sum of all internal bond angles of the Ti1-N1-C1-N2 plane add up to 359.97° , and the sum of all bond angles around N1 and N2 add to 359.82° and 359.93° , respectively, all of

which indicate a high degree of planarity in **3**. The N1C1-N2 bond angle of 122.66(9)° is in between the predicted values for singlet (113.1°) and triplet (130.8°) diaminocarbene,^{47,48} and close to the predicted value for a singlet dianionic diamidocarbene (119.5°) (Figure S41). Typically, increasing the steric profile of N-substituents in diamino carbene compounds leads to larger N-C-N bond angles, while other factors such as ring strain may also contribute to the observed value in **3**.^{47,48} The only other structurally characterized 4-membered N-heterocyclic carbenes, $\text{Pr}_2\text{NP}[\text{N}(2,6\text{-}\text{Pr}_2\text{Ph})]_2\text{C}$ and $\text{Pr}_2\text{NB}[\text{N}(2,6\text{-}\text{Pr}_2\text{Ph})]_2\text{C}$, have much smaller N-C-N bond angles of 96.72(13)° and 94.02(16)°, respectively, as well as a significant deviation from planarity in the case of the former (sum of bond angles around nitrogen atoms add to 355.1° and 348.2°).^{49,50}

Given the further reactivity of **INT2**-like structures in previous investigations,^{35,38,39} steric protection around the carbon atom likely aids in isolation of **3**. The percent buried volume (% V_{bur})^{51,52} of **3** is 48.2%, assuming a sphere radius of 3.5 Å and a 2.00 Å distance from the carbene carbon to the center of the sphere.⁵³ In comparison to % V_{bur} values of carbenes determined from complexes of the type $\text{AuCl}(\text{NHC})$, this value far exceeds that of I^tBu (39.6%, $\text{I}^t\text{Bu} = 1,3\text{-}^t\text{Bu}_2\text{-imidazol-2-ylidene}$), and is between the values of IPr (45.4%, $\text{IPr} = 1,3\text{-bis}(2,6\text{-}\text{Pr}_2\text{Ph imidazole-2-ylidene})$ and IPent (49.0%, $\text{IPent} = 1,3\text{-bis}(2,6\text{-dipent-3-yl)imidazole-2-ylidene}$).⁵⁴

Complex **3** is diamagnetic, and thus could potentially be described by three limiting electronic states: (A/B) a “titana-NHC” singlet carbene; (C) a closed-shell structure containing a “stretched” Ti-C bond;³⁵ or (D) a Ti^{III} open-shell singlet antiferromagnetically coupled to a $\text{C}^\bullet$ (Figure 4). Previous DFT calculations (B3LYP/def2-SVP) on various $\text{Cp}_2\text{Ti}(\kappa^2\text{-RNCNR})$ complexes by Jemmis, Schulz, and Rosenthal indicated significant contribution from biradicaloid electronic structures such as D, wherein electron-donating substituents such as ^tBu in **INT2** were proposed to have the strongest Ti-C interaction and the most C character.³⁵

In order to determine the contributions of these three limiting cases, CASSCF calculations were performed on **3**. First, we performed geometry optimizations at the DFT level of theory for several exchange-correlation functionals and found that M06-L/6-311G(d,p)^{55,56} matched the experimentally measured structure very closely (Figure S35). Full computational details and geometries are provided in the Supporting Information. Using that geometry, we performed CAS[14,14] calculations which included all the valence and bonding orbitals for the Ti-N-C-N atoms. The full set of CASSCF orbitals are provided in Figure S36. The HOMO and LUMO CASSCF orbitals are shown in Figure 5a and 5b. The HOMO orbital is primarily the carbon $2p_y$ orbital with smaller contributions from the titanium $3d_z$ orbital, in an apparent σ interaction with a molecular orbital occupation 1.68. The LUMO orbital has a molecular orbital occupation of 0.33 ($\beta = 0.312$),⁵⁷ with contributions from the same orbitals in an apparent σ^* interaction with a nodal plane between the titanium and carbon.

Mayer Bond Order analysis⁵⁸ was performed on the CASSCF natural orbitals, revealing a Ti-C bond order of 0.19. This low bond order suggests that electronic state C is an important, but minor, contributor to the overall electronic structure. Next, Natural Bonding

Orbital (NBO) analysis was performed. Since NBO requires DFT orbitals, we used the orbitals from our DFT calculations using the M06-L functional. The DFT-calculated HOMO is shown in Figure 5c, and shows relatively good consistency with the CASSCF calculations. NBO analysis was performed to obtain the molecular orbital coefficients of the natural atomic orbitals basis (NAOMO),⁵⁹ giving significant contributions from Ti, C1, and N in the HOMO (Figure 5, bottom. Full computational details in Table S5). Additionally, NBO analysis gives a $3d_z^2$ occupation of 0.37; previous analysis of Ti complexes indicate that occupations below ~0.4 correspond to Ti^{IV} ,^{40,60} suggesting that **3** has more Ti^{IV} (A/B/C) character rather than Ti^{III} as in D.

Next, QT-AIM^{61–65} (Figure 6) and ELF⁶⁶ (Figure 7) analyses were carried out on the CASSCF wavefunction to get a more specific picture of the bonding paths and localized electron density. (See SI Figure S39 for similar analysis on the M06-L wavefunction). The QT-AIM bonding paths of **3** (Figure 6) are in agreement with the Ti^{IV} -diamidocarbene (A/B) structure. The lack of a significant β -carbon interaction in **3** is reminiscent of Beweries' stable titanacyclobuta-2,3-diene.¹³ The ELF plot of **3** is bereft of significant electron density between the C and Ti atoms, while localization of electron density is observed behind the C atom outside of the ring, indicative of the carbene lone pair as observed in ELF plots of other free carbenes.¹³

Taken together, the above calculations indicate contributions from all possible contributing electronic states, and that **3** is best described as a free carbene with A/B being the predominant contributor. This is in contrast to previous calculations (B3LYP/def2-SVP, UBS-B3LYP) which indicated that the open shell singlet structure D is the major contributor;^{35,36} however, experimental analysis and reactivity agrees that the NHC-like A/B forms dominate (*vide infra*).

NMR chemical shifts depend on the symmetry and energy of high-lying occupied and low-lying vacant orbitals, and therefore provide additional experimental probes into the identity and accessibility of ground and excited states.^{67–74} Thus, we decided to further investigate the NMR parameters of **3** to better understand its electronic structure.

The room temperature ^{13}C NMR resonance of the Cp rings in **3** is 106.8 ppm, significantly upfield of **1** (117.8 ppm) and indicative of a very electron-rich Ti center. The N-C-N ^{13}C NMR resonance in **3** is 130.0 ppm in C_6D_6 (Figure S2). The room temperature value of 130.0 ppm is 9.2 ppm further upfield of the N-C-N resonance of free $tBuNCN^tBu$, which is somewhat surprising given the typical downfield chemical shift observed for singlet NHC carbene carbon atoms.⁴⁷ Variable temperature solution state ^{13}C NMR spectroscopy demonstrated a change in chemical shift of the N-C-N carbon between 128.5 to 131.6 ppm across a temperature range of 215 to 376 K in C_7D_8 (Figures S4–S6).

The origin of the unusually shielded ^{13}C resonance in **3** was investigated by measuring all three components of the chemical shift tensor using CP-MAS ^{13}C NMR spectroscopy. The measured solid-state ^{13}C NMR spectrum is shown in Figure 8a. Despite some overlapping spinning sidebands in this spectrum, the carbene signal can be fitted by considering only the sidebands that are not covered by other signals. The corresponding fit is shown below the

experimentally measured spectrum in Figure 8a; the corresponding principal components of the shielding tensor are shown in Figure 8b (in parentheses). We further used DFT calculations to calculate the three principal components of the shielding tensor, directly from the crystal structure of **3** (using the hybrid PBE0 functional with a Slater-type triple- ζ basis set in the ADF 2014 code, including relativistic effects through the 2 component zeroth order regular approximation, see SI for details). We compared these results to the calculated shielding tensor of the related *N*-heterocyclic carbene I'Bu. The calculated shielding tensors of **3** and I'Bu are shown in Figure 8b. The isotropic chemical shift of the carbene carbon **3** (calculated at 121 ppm) is more shielded as compared to that of I'Bu (calculated at 230 ppm). This is mainly because the δ_{11} and δ_{33} component of the chemical shift tensor are more shielded in **3**, while the δ_{22} component is fairly similar for both compounds. Importantly, the chemical shift tensor is oriented similarly in both compounds.

Since chemical shift is a property that is directly related to the symmetry and energy of frontier molecular orbitals,⁷⁵ the differing δ_{11} and δ_{33} components indicate different electronic structures between **3** and I'Bu. Thus, we performed a Natural Chemical Shielding (NCS) analysis, that allows for decomposition of the individual components of the shielding tensor into contributions of individual natural localized molecular orbitals (NLMOs), corresponding to bonds and lone-pairs.^{76–78} The large deshielding of the δ_{11} component of I'Bu is due to a high-lying lone-pair on C in combination with a low-lying vacant p-orbital on the same atom; in addition, the bonding s(C–N) orbitals also contribute to deshielding by coupling to the low-lying vacant p-orbital (Figure 8c, right). In **3**, the contributions of the lone-pair on carbon to the deshielding of δ_{11} is similar compared to the NHC; however the bonding s(C–N) orbitals contribute significantly less, because of the wider N–C–N angle. The much more shielded δ_{33} component in **3**, which is oriented perpendicular to the metallacycle-plane, has a more complex origin (*vide infra*). Notably, a similar remarkable shielding along the same direction is observed in metallacyclobutanes that engage in the olefin metathesis reaction.⁷⁹

In addition to the unusually shielded ^{13}C chemical shift of the N–C–N ring, the ^{15}N chemical shift of **3** is quite deshielded, appearing at 246.1 ppm (Figure S3) compared to I'Bu (calculated at 218 ppm). Thus, we further investigated the ^{15}N chemical shift tensors of the nitrogen atoms in **3** and I'Bu. Figure 8d shows the calculated chemical shift tensors of both compounds. In I'Bu, the most deshielded component (δ_{11}) is in the plane of the molecule perpendicular to the N–C(carbene) bond, δ_{22} is oriented along the N–C(carbene) bond, and the most shielded δ_{33} component is oriented perpendicular to the ring, along the direction of the nitrogen lone-pair. The two most deshielded components (δ_{11} and δ_{22}) are directionally perpendicular to the N–C π -bond, indicative of a low-lying vacant $\pi^*(\text{N–C})$ orbital.

In comparison, the orientation of the ^{15}N chemical shift tensor in **3** is significantly different: here, the most shielded δ_{33} component is in the plane of the ring, while δ_{11} and δ_{22} point out of the ring plane (with an angle of roughly 45° with respect to the plane). As a result, upon going from I'Bu to **3** the deshielding in the plane perpendicular to the N–C π -bond (the metallacycle plane) decreases, and the overall deshielding perpendicular to the ring-plane increases. This suggests that upon going from I'Bu to **3**, the N–C π -interaction perpendicular to the ring weakens, while a π -interaction *between* the Ti and N in the plane of the ring

develops. The metallacyclic bonding in **3** (Figure 9) is thus characterized by two perpendicular partial p-interactions: the $\pi(\text{N}-\text{C})$ interaction perpendicular to the ring as is seen in the classical NHC bonding picture (not drawn), and one $\pi(\text{Ti}-\text{N})$ interaction in the plane of the ring ($\pi(\text{Ti}-\text{N}) + \sigma(\text{N}-\text{C})$, maroon). This $\pi(\text{Ti}-\text{N})$ interaction constitutes the bonding between an empty d-orbital on Ti pointing into the ring and the N-C-N σ -bond mixed with the C_β lone pair. This bonding and deshielding pattern is analogous to metallacyclobutanes that engage in olefin metathesis (e.g. $\text{Cp}_2\text{Ti}(\text{C}_3\text{H}_6)$).⁴⁸ In these compounds, C_α also shows a large deshielding perpendicular to the metallacycle plane that arises from the magnetic coupling of a high-lying occupied orbital of $\sigma(\text{M}-\text{C}_\alpha)$ symmetry in combination with a low-lying vacant $\text{M}-\text{C}_\alpha$ π^* orbital pointing into the ring in the direction of C_β . Thus, it appears somewhat general that the presence of $\text{M}-\text{E}_\alpha$ π -bonding and the resulting magnetic coupling to the σ framework is responsible for both a large deshielding on the α -atom and a large shielding on the β -atom in the direction perpendicular to the ring. Thus, the NMR tensor analysis agrees with the computational description of the Ti free carbene, and also describes the partial Ti- C_β interaction seen in the CASSCF analysis of **3** (Figure 5). In fact, this interaction can be clearly seen in the HOMO and LUMO of **3** (Figure 5a and 5b), which have both $\pi/\pi^*(\text{Ti}-\text{N})$ symmetry and $\sigma(\text{N}-\text{C})$ symmetry.

Based on the above spectroscopic and computational analysis, the best descriptor of **3** is that of an unusual free Ti^{IV} diamidocarbene, in which the $\sigma(\text{N}-\text{C})$ bonds interact further with the metal via a bond of π -symmetry. This is the first example of an unsupported κ^2 -bound heterocumulene, as well as the first example of a 4-membered metal-containing free N-heterocyclic carbene, although several metal-containing carbene^{80–82} and metal-containing N-heterocyclic carbene coordination complexes have been reported.^{83–89}

Having established a theoretical basis for the carbene-like character of **3**, we next explored sundry reactions with **3** for experimental comparison. First, protonation reactions were carried out, demonstrating that the free carbene is capable of 2-electron Brønsted acid/base chemistry (Figure 10, top). Reaction of **3** with 0.5 equiv or 1.0 equiv of $[\text{LuH}]^+\text{I}^-$ ($[\text{LuH}]^+\text{I}^-$ = lutidinium iodide) in C_6H_6 resulted in the formation of the formamidinate Ti^{III} complex **4** in 47% yield as a crystalline solid with a characteristic color of trivalent Ti. The solution state magnetic moment of **4** was determined to be $1.65(3) \mu_{\text{B}}$ (Evans' method, C_6D_6 , 25 °C), which is near the spin-only value of $1.73 \mu_{\text{B}}$ for an $S = 1/2$ Ti^{III} ground state. The X-ray crystal structure of **4** is presented in Figure 10 (bottom right). The hydrogen atom H1 on the N-C-N carbon atom of **4** was located on the difference map, unambiguously identifying **4** as the Ti^{III} formamidinate. Complex **4** is a rare example of a mononuclear $\text{Ti}(\text{III})$ formamidinate complex,³⁷ though several $\text{Ti}(\text{III})$ amidinate and guanidinate complexes have been isolated.^{90–96} Complex **4** can be oxidized with excess AgOTf , yielding **4-OTf**. The formamidinate C-H can be identified in diamagnetic **4-OTf** by both ^1H NMR spectroscopy and X-ray crystallography (Figure 10, bottom left), providing further evidence for the formamidinate structure of **4**.

Formation of **4**, the product of formal addition of $\text{H}\cdot$ to **3**, is surprising given the expected 2-electron chemistry of a singlet carbene. However, this reaction likely proceeds first through protonation to yield $[\text{Cp}_2\text{Ti}(\kappa^2\text{-}^t\text{BuNCHN}^t\text{Bu})]^+\text{I}^-$ (**4-I**). Protonated **4-I** can then be reduced by another equiv of **3**, leading to a maximum yield of 50% of **4** along with free $^t\text{BuNCN}^t\text{Bu}$

and presumably $[\text{Cp}_2\text{TiI}]_2$, along with several unidentified decomposition products. Supporting this general pathway, maximum yields of 47% of **4** are obtained regardless of whether 0.5 equiv or 1.0 equiv $[\text{LutH}]^+\text{I}^-$ are used. Further, treatment of **4-OTf** with one equiv of **3** results in reduction of **4-OTf** and formation of **4**, consistent with the proposed reactivity of transient **4-I**.

Deprotonation of **4-OTf** by the strong, bulky base NaHMDS results in reformation of the free carbene **3**, demonstrating that the dehydrohalogenation of transition metal formamidinate halide or pseudohalide ligands may be a viable alternative route to free carbene complexes of the type $\text{M}(\kappa^2\text{-RNCNR})$. The regeneration of **3** via deprotonation of **4-OTf** is somewhat reminiscent of some recent examples of formate deprotonation, although a free $\kappa^2\text{-CO}_2$ complex analogous to **3** has not been observed.^{33,34}

2-Electron oxidation of **3** with 0.125 equiv S_8 yields the thioureate complex **5**, in accordance with typical reactions of free N-heterocyclic carbenes with S_8 (Figure 11).^{97,98} Complex **5** is the only example of a crystallographically characterized Ti thioureate. Unfortunately, attempts to synthesize heterobimetallic complexes via coordination of the carbene of **3** have been unsuccessful.⁹⁹

Coordination of $t\text{-BuNCN}^t\text{Bu}$ to Ti is reversible. Reaction of **3** with various other oxidants results in displacement of $t\text{-BuNCN}^t\text{Bu}$ and the formation of Ti^{IV} complexes **6–9** (Figure 12), in analogy to substitution chemistry seen with **1**. Of note is the reaction of **3** with 2 equiv TEMPO, which results in an unusual ring-slipped $\eta^5, \eta^1\text{-Cp}_2\text{Ti}(\text{TEMPO})_2$ (**7**).

Sterics likely plays a primary factor in the stabilization of **3**, so we next revisited the reaction of **1** with the smaller 1,3-dicyclohexylcarbodiimide. Reaction of 2 equiv **1** with 1 equiv 1,3-dicyclohexylcarbodiimide in pentane yielded $(\text{Cp}_2\text{Ti})_2(\mu\text{-}\eta^1, \eta^1\text{-(CyNCNCy)})$ (**10**), which crystallized from the reaction mixture within 10 minutes at room temperature (Figure 13). Complex **10** is paramagnetic ($\mu_{\text{eff}} = 1.98(3) \mu_{\text{B}}$, Evans' method, C_6D_6 , 25 °C).

The reaction of **1** and 1,3-dicyclohexylcarbodiimide had been previously reported to yield dinuclear amidinate-like **2c** in hexanes (Figure 13).³⁶ C_6D_6 solutions of **10** (~0.017 M) stored at room temperature in an inert atmosphere slowly convert to yellow needles of **2c** over a period of approximately 4 days, demonstrating the intermediacy of **10** prior to formation of **2c**.

The X-ray structure of **10** is presented in Figure 14. Three similar independent molecules were found within the asymmetric unit, one of which is displayed. The C-N bonds of the carbodiimide fragment in **10** are significantly elongated to $> 1.3 \text{ \AA}$, similar to the degree of elongation seen in **3**. The N1C1-N2 bond angle is approximately 137° , and the Ti-N bond lengths of $> 2.0 \text{ \AA}$ are in the range of typical $\text{Ti}^{\text{IV}}\text{-N}$ X-type bonds that lack $\text{N} \rightarrow \text{Ti} \pi$ -donation.^{43–45} The average Ti1-C1 and Ti2-C1 bond distances are $2.310(31) \text{ \AA}$ and $2.307(23) \text{ \AA}$, respectively, both of which exceed the Ti-C distance in **3** ($2.2674(10) \text{ \AA}$). Additionally, the Ti1-N1-C1 bonding plane intersects the Ti2-N2-C1 bonding plane at a dihedral angle of $38.43(10.11)^\circ$, instead of the expected 90° for Ti atoms independently interacting with the orthogonal π bonds of an $\text{RN}=\text{C}=\text{NR}$ heterocumulene. These structural

features indicate that **10** is best described as a free dititanamidocarbene similar to the dimetalloxy carbene proposed by Cummins in Ti-promoted CO₂ coupling.³³

Only two other examples of Ti₂(μ-C(NR)₂) complexes have been structurally characterized, both of which are within structured Ti^{III}/Ti^{III} bimetallic motifs with a μ-η², η²-C(NR)₂ bonding pattern.^{100,101} Both complexes demonstrated similar extents of activation of the carbodiimide moiety in the solid state as observed in **10**, but have shorter Ti-C distances (approx. 2.1 Å); however, due to the rigid bimetallic frameworks, direct structural comparison between these structures is difficult.

DFT calculations were next used to further investigate the structure of **10**. The structure was optimized for both the singlet state (Figure S38) and the triplet state (Figure 15). The free energy of the triplet state was 32.9 kcal/mol lower than the singlet state, and structural parameters of the triplet state matched well with the experimental crystal structure. NBO analysis of **10** and comparative studies of related Ti^{III} complexes further corroborate a Ti^{III}₂ triplet structure on the basis of 3d_z² occupation of values (Table S8). Much like in **3**, the free carbene in **10** can be clearly seen in the HOMO-4 surface.

Conclusions

In conclusion, reaction of Cp₂Ti(BTMSA) (**1**) with sterically encumbered ^tBuNCN^tBu results in the formation of the free carbene complex Cp₂Ti(κ²-^tBuNCN^tBu) (**3**), which contains the first example of a κ²-bound heterocumulene supported by a single metal center. Both experimental solid-state NMR and theoretical analysis of this unusual metallacycle indicate that the free carbene is further stabilized *via* a Ti-NCN π-bonding interaction in the plane of the metallacycle. Similar reaction of CyNCNCy with **1** results in the formation of another free carbene complex, (Cp₂Ti)₂(μ-η², η²-C(NC₆H₁₁)₂) (**10**), which contains another surprising heterocumulene bonding motif: a free dititanamidocarbene. These unique molecules should provide an experimental and theoretical platform for the continued investigation of new modes of metalheterocumulene bonding and reactivity. Further, initial reactivity of the carbene moiety of **3** has been demonstrated, hinting at the rich potential of these types of molecules.

Experimental Section

General Considerations

All chemical manipulations were carried out in a glovebox under a nitrogen atmosphere. Cp₂Ti(BTMSA)¹⁰² was prepared following the literature procedure. CH₃I (Sigma Aldrich) and 1,3-di-*tert*-butylcarbodiimide (TCI) were freeze-pump-thaw degassed three times, brought into the glovebox, and passed through dried basic alumina prior to use. Azobenzene (TCI America) was purified *via* flash chromatography (hexanes), finely ground, and dried *in vacuo* prior to use. 2,2,6,6-Tetramethyl-1-piperidine 1-oxyl (Sigma-Aldrich) was sublimed at 25 °C onto a -78 °C cold finger under dynamic vacuum prior to use. Ph₂S₂ (Sigma-Aldrich), S₈ (Sigma-Aldrich), and 1,3-dicyclohexyl-carbodiimide (Fluka) were dried *in vacuo* overnight prior to use and stored in the glovebox. AgOTf (Sigma-Aldrich) and NaHMDS (Millipore-Sigma) were stored in the glovebox and used as received. 2,6-Lutidinium iodide

was prepared following the literature procedure,¹⁰³ and stored in the glovebox. C₆D₆, C₇D₈, and CDCl₃ were dried *via* vacuum transfer from CaH₂ followed by filtration through dried basic alumina and stored in the glovebox prior to use. Benzene, pentane, tetrahydrofuran, acetonitrile, dichloromethane, and toluene were dried on a Pure Process Technology solvent purification system.

¹H, ¹³C, ¹⁹F, and ¹H¹⁵N HMBC NMR spectra were recorded on Bruker Avance 400 MHz spectrometers. Chemical shifts are reported with respect to residual protio-solvent impurity for ¹H (s, 7.26 ppm for CHCl₃; s, 7.16 ppm for C₆D₅H; p, 2.08 ppm for C₇D₇H), solvent carbons for ¹³C (t, 77.16 ppm for CDCl₃; t 128.08 ppm for C₆D₆; s, 137.48 for *ispo* carbon of C₇D₈), CF₃COOH for ¹⁹F (s, −76.6 ppm in CDCl₃), and N,NMe₂NPh (referenced to NH₃ at 0 ppm) for ¹⁵N (s, 49.5 ppm in C₆D₆).¹⁰⁴ Evans' method measurements were performed following previously outlined procedures.¹⁰⁵ Elemental analyses were performed at Midwest Microlabs. Despite repeated attempts, acceptable elemental analyses for complexes **4-OTf**, **5**, and **6** were not obtained.

X-ray: General Procedure—X-ray data were collected using a Bruker Photon II CMOS diffractometer for data collection at 100(2) or 125(2) K using Mo K α radiation (normal parabolic mirrors). The data intensity was corrected for absorption and decay (SADABS).¹⁰⁶ Final cell constants were obtained from least-squares fits of all measured reflections and the structure was solved and refined using SHELXL-2014/7.39.¹⁰⁷ All nonhydrogen atoms were refined with anisotropic displacement parameters. Details regarding refined data and cell parameters are available in Tables S1–S3. CCDC entries 1923125, 1975943, 1975944, 1975945, 1975961, 1975969, and 1976006 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom, fax: (+44) 1223–336-033, or e-mail: deposit@ccdc.cam.ac.uk. Computational details as well as information related to CP-MAS ¹³C NMR spectroscopy can be found within the Supporting Information of this manuscript.

Synthesis of Cp₂Ti(κ ²-^tBuNC^tNBu) (3)—Cp₂Ti(BTMSA) (**1**) (2.03 g, 5.74 mmol, 1 equiv.) was added to a 20 mL vial and dissolved in 15 mL pentane. Then, 1,3-di-*tert*-butylcarbodiimide (888 mg, 5.74 mmol, 1 equiv.) in 1 mL pentane was slowly added. The vial was sealed with a Teflon cap and allowed to stand at room temperature for 10 min while a rapid color change from light brown to red was observed. The reaction mixture was placed at −35 °C overnight to afford the title complex as a dark red crystalline solid (1.75 g, 92%). The title product was isolated via decanting the mother liquor and drying the resulting solid *in vacuo*.

Alternative synthesis of Cp₂Ti(κ ²-^tBuNC^tNBu) (3)—Complex **4-OTf** (59.4 mg, 0.124 mmol, 1 equiv.) was suspended in THF (2 mL) in a 20 mL vial containing a stir bar and cooled to −35 °C. Then, NaHMDS (23.9 mg, 0.124 mmol, 1 equiv.) in THF (4 mL) was slowly added. The reaction was allowed to warm to room temperature and stirred for 90 min. Volatiles were removed *in vacuo*, and the dark residue was suspended in pentane (~6 mL), filtered through a plug of Celite, and dried *in vacuo*. Recrystallization from pentane at −35 °C overnight afforded the title complex as a dark red crystalline solid, which was isolated

via decanting the mother liquor and drying the resulting solid *in vacuo* (15.7 mg, 38%). ^1H NMR (400 MHz, C_6D_6 , 25 °C, δ , ppm): 5.26 (s, 10H, Cp-H), 1.40 (s, 18H, ^tBu -H). ^{13}C NMR (101 MHz, C_6D_6 , 25 °C, δ , ppm): 130.0, 106.8, 58.9, 33.1. ^{15}N NMR (41 MHz, C_6D_6 , 25 °C, δ , ppm): 246.1. Elemental analysis for **3** reproducibly gave values consistent with an additional oxygen atom added to the title complex (calcd, found; for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{Ti}\cdot\text{O}$): C (65.52, 65.27), H (8.10, 8.05), N (8.04, 7.95).

Synthesis of $\text{Cp}_2\text{Ti}^{\text{III}}(\text{tBuNC}(\text{H})\text{N}^t\text{Bu})$ (4**)**—Complex **3** (200 mg, 0.602 mmol, 1 equiv.) and 2,6-lutidinium iodide (142 mg, 0.602 mmol, 1 equiv.) were added to a 20 mL vial containing a Teflon stir bar and suspended in 7 mL C_6H_6 . The reaction was sealed with a Teflon cap and stirred for 2 h at room temperature. Volatiles were removed *in vacuo*, leaving a dark brown residue that was extracted with pentane to give a deep blue extract that was filtered through a plug of Celite (~10 mL pentane, product was extracted until filtrate was colorless). The filtrate was concentrated *in vacuo* to give a deep blue crystalline solid (93.4 mg, 47%). **4** can be recrystallized from minimal pentane at –35 °C over several days to afford crystals suitable for X-ray diffraction.

Synthesis of $\text{Cp}_2\text{Ti}^{\text{III}}(\text{tBuNC}(\text{H})\text{N}^t\text{Bu})$ (4**) with 0.5 equiv lutidinium iodide. **3****—(200 mg, 0.602 mmol, 1 equiv.) and 2,6-lutidinium iodide (71.0 mg, 0.301 mmol, 0.5 equiv.) were added to a 20 mL vial, and the reaction was set up under identical reaction conditions to the above procedure, affording 92.0 mg of the title complex (47%). ^1H NMR (400 MHz, C_6D_6 , 25 °C, δ , ppm): 3.3 (br s). Evans' Method (C_6D_6 , 25 °C): $\mu_{\text{eff}} = 1.65(3) \mu_{\text{B}}$ (triplicate). Elemental analysis (calcd, found; for $\text{C}_{19}\text{H}_{29}\text{N}_2\text{Ti}$): C (68.47, 68.60), H (8.77, 9.26), N (8.40, 8.46).

Alternative synthesis of $\text{Cp}_2\text{Ti}^{\text{III}}(\text{tBuNC}(\text{H})\text{N}^t\text{Bu})$ (4**)**—Complex **4-OTf** (35.1 mg, 0.0726 mmol, 1 equiv.) and **3** (24.8 mg, 0.0726 mmol, 1 equiv.) were added to a 20 mL vial containing a stir bar, and suspended in C_6H_6 (2 mL). The vial was sealed with a Teflon cap and the reaction was stirred for 30 min at room temperature. During the reaction, the color changed from red (heterogeneous) to deep blue-green (homogeneous). Volatiles were removed *in vacuo* and the residue was suspended in pentane (~5 mL), filtered through a plug of Celite, and dried *in vacuo* to afford the title complex, in the presence of some unidentified impurities (25.5 mg). The impurities may be a result of decomposition stemming from a complex containing the constituents of $\text{Cp}_2\text{Ti}(\text{OTf})$ that apparently have similar solubility properties to **5**.

Synthesis of $\text{Cp}_2\text{Ti}(\text{tBuNC}(\text{H})\text{N}^t\text{Bu})(\text{OTf})$ (4-OTf**)**—Complex **4** (70.8 mg, 0.212 mmol, 1 equiv.) and AgOTf (109.5 mg, 0.425 mmol, 2 equiv.) were added to a 20 mL vial containing a Teflon stir bar and suspended in 3 mL CH_3CN . The reaction was sealed with a Teflon cap and stirred for 30 min at room temperature, over which time the color changed from light blue to red along with precipitation of Ag^0 . Volatiles were removed *in vacuo*, leaving a red-brown residue that was suspended in CH_2Cl_2 (~8 mL, extracted until filtrate was colorless) and filtered through a plug of Celite. The extract was concentrated *in vacuo*, redissolved in minimal CH_2Cl_2 , layered with an equal volume pentane, and placed at –35 °C overnight to afford a dark red crystalline solid. The solid was collected on a glass frit, rinsed

with Et₂O (5 × 20 mL), and dried *in vacuo* to afford **4-OTf** (52.1 mg, 51%). ¹H NMR (400 MHz, CDCl₃, 25 °C, δ, ppm): 7.46 (s, 1H, N-CH-N), 6.88 (s, 10H, Cp-H), 1.29 (s, 18H, ^tBu-H). ¹³C NMR (101 MHz, CDCl₃, 25 °C, δ, ppm): 134.7, 122.4, 58.6, 32.4. DEPT-90 NMR (101 MHz, CDCl₃, 25 °C, δ, ppm): 134.7, 122.4. ¹⁹F NMR (376 MHz, CDCl₃, 25 °C, δ, ppm): -76.9 (s, -O₃SCF₃).

Synthesis of Cp₂Ti(κ²-^tBuNC(S)N^tBu) (5)—Complex **3** (50.8 mg, 0.150 mmol, 1 equiv.) and S₈ (4.7 mg, 0.019 mmol, 0.125 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 4 mL C₆H₆, and stirred at 25 °C for 2 h. A slow color change from dark red to brown-yellow was observed over the course of the reaction. After 2 h, the reaction mixture was dried *in vacuo*. The residue was dissolved in a minimum of C₇H₈ (approximately 6 mL), then filtered through Celite and dried *in vacuo* once more. The crude material was recrystallized from C₇H₈/pentane at -35 °C overnight, affording **5** as tan needles (39.6 mg, 72%). ¹H NMR (400 MHz, C₆D₆, 25 °C, δ, ppm): 5.98 (s, 10H, Cp-H), 1.56 (br s, 18H, ^tBu-H). ¹³C NMR (101 MHz, C₆D₆, 25 °C, δ, ppm): 162.9, 117.9, 60.9, 31.6.

Synthesis of Cp₂Ti(Me)I (6)—Complex **3** (50.0 mg, 0.150 mmol, 1 equiv.) and CH₃I (22.3 mg, 0.150 mmol, 1 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 1 mL C₆H₆, and stirred at 40 °C for 16 h. A slow color change from dark red to brown-orange was observed over the course of the reaction. After 16 h, the reaction mixture was dried *in vacuo*. The residue was dissolved in a minimum of C₇H₈ (approximately 4 mL), then filtered through Celite and dried *in vacuo* once more, affording **6** as an orange solid (34.1 mg, 71%). The ¹H NMR was matched to that in the literature.¹⁰⁸ ¹H NMR (400 MHz, C₆D₆, 25 °C, δ, ppm): 5.86 (s, 10H, Cp-H), -0.08 (s, 3H, -CH₃).

Synthesis of Cp₂Ti(TEMPO)₂ (7)—Complex **3** (50.9 mg, 0.150 mmol, 1 equiv.) and 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (47.8 mg, 0.150 mmol, 2 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 2 mL C₆H₆, and stirred at 25 °C for 27 h. A slow color change from dark red to dark red-orange was observed over the course of the reaction. After 27 h, the reaction mixture was dried *in vacuo*. The residue was dissolved in a minimum of pentane (approximately 10 mL), then filtered through Celite and dried *in vacuo* once more, affording a mixture of the title complex and a trace of residual **3**. The resulting solid was rinsed with 3 × 1 mL pentane to remove residual **3**, yielding **7** as an orange solid (25.9 mg, 35%).

Alternative synthesis of Cp₂Ti(TEMPO)₂ (7)—Complex **1** (300 mg, 0.287 mmol, 1 equiv.) and 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (90.2 mg, 0.574 mmol, 2 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 6 mL C₆H₆, and stirred at 25 °C for 1 h. A rapid color change from light brown to orange was observed immediately. After 1 h, the reaction mixture was dried *in vacuo*. The residue was dissolved in a minimum of pentane (approximately 10 mL), then filtered through Celite and dried *in vacuo* once more, affording **7** as a somewhat sticky orange solid (139 mg, 99%). Analytically pure material is more easily obtained via this alternative route than the synthetic route above. Crystalline samples of **7** were afforded by placing a saturated pentane

solution of **7** at $-35\text{ }^{\circ}\text{C}$ for approximately one week. ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 6.33 (s, 10H, Cp-*H*), 1.49–1.43 (m, 8H, $-\text{NC}(\text{Me})_2\text{CH}_2\text{CH}_2$), 1.33–1.27 (m, 4H, $\text{NC}(\text{Me})_2\text{CH}_2\text{CH}_2$), 1.26 (s, 24H, $-\text{CH}_3$). ^{13}C NMR (101 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 117.2, 61.3, 41.3, 27.2 (br), 17.0.

Synthesis of $\text{Cp}_2\text{Ti}(\text{SPh})_2$ (8**)**—Complex **3** (50.5 mg, 0.150 mmol, 1 equiv.) and Ph_2S_2 (31.8 mg, 0.150 mmol, 1 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 2 mL C_6H_6 , and stirred at $40\text{ }^{\circ}\text{C}$ for 17 h. A slow color change from dark red to deep purple was observed over the course of the reaction. After 17 h, the reaction mixture was cooled to room temperature and filtered through a plug of Celite, frozen at $-35\text{ }^{\circ}\text{C}$, and lyophilized *in vacuo*, affording the title complex as a dark powder (47.2 mg, 94% pure with a 6% impurity of unreacted Ph_2S_2 , 74% corrected yield). The ^1H NMR spectrum was matched to that of the literature complex.¹⁰⁹ ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 7.89 (d, $J = 7.6\text{ Hz}$, 4H, Ar-*H*), 7.16 (m, 4H, Ar-*H*, overlapping with residual $\text{C}_6\text{D}_5\text{H}$), 6.98 (t, $J = 7.2\text{ Hz}$, 2H, Ar-*H*), 5.68 (s, 10H, Cp-*H*).

Synthesis of $\text{Cp}_2\text{Ti}(\text{PhNNPh})$ (9**)**—Complex **3** (50.1 mg, 0.150 mmol, 1 equiv.) and PhNNPh (27.6 mg, 0.150 mmol, 1 equiv.) were added to a 20 mL vial containing a Teflon stir bar, dissolved in 3 mL C_6H_6 , and stirred at $40\text{ }^{\circ}\text{C}$ for 17 h. A slow color change from dark red to black was observed over the course of the reaction. After 17 h, the reaction mixture was dried *in vacuo*. The residue was dissolved in a minimum of pentane (approximately 10 mL), then filtered through Celite and cooled to $-35\text{ }^{\circ}\text{C}$ overnight, affording the title complex as a black crystalline solid with some precipitated powder also present. The free crystalline solid was removed from the precipitated residue (16.5 mg, 97% pure with a 3% impurity of pentane, 30% corrected yield). Although the title complex is known,¹¹⁰ ^1H and ^{13}C NMR data have not been presented in the literature previously. ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 7.23 (app br s, 4H, Ar-*H*), 6.89 (t, $J = 7.3\text{ Hz}$, 2H, Ar-*H*), 6.60 (app br s, 4H, Ar-*H*), 5.78 (s, 10H, Cp-*H*). ^{13}C NMR (101 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 158.7, 129.1, 122.0, 112.9. The *ipso* carbon of the azobenzene moiety could not be found, possibly due to broadening from neighboring quadrupolar nitrogen atoms.

Synthesis of $(\text{Cp}_2\text{Ti})_2(\mu\text{-}\eta^2, \eta^2\text{-C}(\text{NC}_6\text{H}_{11})_2)$ (10**)**—Complex **1** (201 mg, 0.577 mmol, 2 equiv.) and 1,3-dicyclohexylcarbodiimide (63.1 mg, 0.305 mmol, 1 equiv.) were charged to a 20 mL scintillation vial and dissolved in 6 mL pentane. The solution changed to dark red and the formation of a dark red-black crystalline solid was observed immediately. Precipitation was allowed to continue at room temperature for 10 min. The reaction was dried *in vacuo*, and the resulting solid was collected on a sintered glass frit, rinsed with pentane ($3 \times 3\text{ mL}$), and dried once more *in vacuo* to afford the title complex as a dark red-black powder (105 mg, 65%). The precipitated crystalline solid was reproducibly suitable for single crystal X-ray diffraction. ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 37.9, 3.4, 2.7, 1.5, 0.9, 0.8, -10.4 . Evans' Method (C_6D_6 , $25\text{ }^{\circ}\text{C}$): $\mu_{\text{eff}} = 1.98(3)\text{ }\mu_{\text{B}}$ (average of 6 runs with 2 batches of material). Elemental analysis for **10** gave values consistent with two additional oxygen atoms added to the title complex (one per Ti atom) (calcd, found; for $\text{C}_{33}\text{H}_{42}\text{N}_2\text{Ti}_2\cdot\text{O}_2$): C (66.68, 67.00), H (7.12, 7.57), N (4.71, 5.06).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

James T. Moore, Brendan J. Graziano, and Dr. Victor G. Young Jr. (UMN) are thanked for crystallographic assistance.

Funding Sources

Financial support was provided by the National Institutes of Health (1R35GM119457), and the Alfred P. Sloan Foundation (I.A.T. is a 2017 Sloan Fellow). C.P.G. acknowledges the Scholarship Fund of the Swiss Chemical Industry for funding. Instrumentation for the University of Minnesota Chemistry NMR facility was supported from a grant through the National Institutes of Health (S10OD011952). X-ray diffraction experiments were performed with a diffractometer purchased through a grant from NSF/MRI (1229400) and the University of Minnesota. We acknowledge the Minnesota Supercomputing Institute (MSI) at the University of Minnesota and the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC0205CH11231, for providing resources that contributed to the results reported within this paper.

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Figure 1.
Examples of unusual binding modes of allenes and heterocumulenes with early transition metals.

Figure 2.

Left: reactions of $\text{Cp}_2\text{Ti}(\text{BTMSA})$ (**1**) with substituted carbodiimides to give **2a-d**, proposed to stem from reactive intermediate **INT2** (Adapted from REF 35). $\text{R} = \text{tBu}, \text{SiMe}_3, \text{Cy}$.

Right: in this work, revisitation of these reactions under ambient conditions reveals several unusual free carbene complexes of Ti.

Figure 3.

Two views of the molecular structure of complex **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: C1-N1 1.3246(13), C1-N2 1.3210(13), Ti1-N1 2.0012(9), Ti1-N2 2.0057(8), Ti1-C1 2.2674(10), N1-C1-N2 122.66(9), Ti1-N1-C1 83.30(6), Ti1-N2-C1 83.21(6), N1-Ti1-N2 70.80(4).

Figure 4.
Possible contributing electronic states for **3**.

Figure 5.

Top: The HOMO and LUMO from the natural orbital CASSCF calculation on **3**. The occupancy is the natural orbital occupancy obtained from the CASSCF density. Bottom: HOMO surface from the DFT (M06-L/6-311G(d,p)) calculation on **3** with NBO-derived molecular orbital coefficients of the natural atomic orbitals.

Figure 6.

Contour plot of the Laplacian of the electron density of 3 in the Ti-N-C-N ring plane. Blue dots represent bond critical points; orange dots represent ring critical points.

Figure 7.
ELF plot of 3 looking at the Ti-N-C-N ring plane.

Figure 8.

a) Solid-state ^{13}C CP-MAS (3.5 kHz) NMR spectrum (top) of **3** and simulated trace (bottom) of the N-C-N carbon atom. The isotropic signal is marked with an arrow, spinning sidebands are marked with * and (partially) covered spinning sidebands are marked with #.

b) Calculated (experimental in parenthesis) chemical shift tensor of the carbene carbon atom **3** (left) and an analogous NHC I'Bu (right). Hydrogen atoms are not shown for clarity. c) Contributions of individual natural localized molecular orbitals (NLMOs) to the deshielding

of the δ_{11} component in **3** (left) and the NHC (right). d) Calculated ^{15}N chemical shift tensor of the nitrogen atoms in **3** (left) and I^tBu (right).

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Figure 9.

Qualitative molecular orbital diagram of the $\text{Cp}_2\text{Ti}^{2+}$ fragment interacting with the dianionic carbodiimide fragment, showing key in-ring orbital interactions, including the in-ring π -interaction between Ti and the a_1 -symmetric N–C bonding orbitals (maroon) that is responsible for the unusual ^{13}C and ^{15}N chemical shifts of the ring.

Figure 10.

Top: Acid/base and oxidation/reduction reactions of **3**. Bottom: Molecular structures of complexes **4** (bottom right) and **4-OTf** (bottom left). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except for H1 in both **4** and **4-OTf**, which was located on the difference map in both structures. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4**: C1-N1 1.356(3), C1-N2 1.265(3), Ti1-N1 2.0626(17), Ti1-N2 2.2148(18), N1-C1N2 116.28(17). **4-OTf**: C1-N1 1.324(2), C1-N2 1.327(2), Ti1-N1 2.0765(15), Ti1-N2 2.0721(16), N1-C1-N2 114.35(17).

Figure 11.

Formation of **5** from **3** and 0.125 equiv S_8 . Right: molecular structure of complex **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Selected bond lengths [Å] and angles [°]: C1-N1 1.364(2), C1-N2 1.3616(19), Ti1-N1 2.0379(13), Ti1-N2 2.0369(13), C1-S1 1.7180(16), N1-C1-N2 108.12(13).

Figure 12.

Reactions of **3** with methyl iodide (top left), 2 equiv TEMPO (top right), diphenyldisulfide (bottom left), and azobenzene (bottom right).

Figure 13.
Reactions of $\text{Cp}_2\text{Ti}(\text{BTMSA})$ (**1**) with 1,3-dicyclohexylcarbodiimide.

Figure 14.

Two views of one of the three molecules of **10** in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are an average of the three molecules in the asymmetric unit: N₁-C₁ 1.313(2), N₂-C₁ 1.317(4), Ti₁-N₁ 2.042(19), Ti₂-N₂ 2.043(15), Ti₁-C₁ 2.310(31), Ti₂-C₁ 2.307(23), N₁-C₁-N₂ 136.6(1.9).

Figure 15.
DFT-Optimized (M06/6-311G(d,p)) unrestricted triplet structure of **10** showing the free carbene HOMO-4 surface.