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Reactions of Titanocene Bis(trimethylsilyl)acetylene Complexes with Carbodiimides: An Experimental and Theoretical Study of Complexation versus C−N Bond Activation

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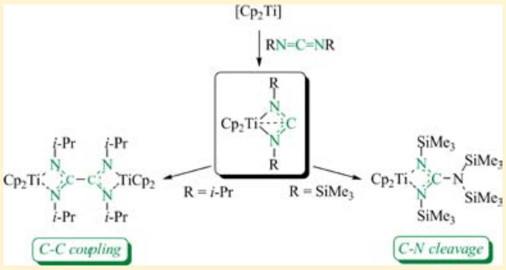
S *Supporting Information*

ABSTRACT: The reaction of the low valent metallocene(II) sources $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp' = η^5-cyclopentadienyl, **1a** or η^5-pentamethylcyclopentadienyl, **1b**) with different carbodiimide substrates RN═C═NR′ **2-R-R′** (R = *t*-Bu; R′ = Et; R = R′ = *i*-Pr; *t*-Bu; SiMe$_3$; 2,4,6-Me-C_6H_2 and 2,6-*i*-Pr-C_6H_3) was investigated to explore the frontiers of ring strained, unusual four-membered heterometallacycles **5-R**. The product complexes show dismantlement, isomerization, or C−C coupling of the applied carbodiimide substrates, respectively, to form unusual mono-, di-, and tetranuclear titanium(III) complexes. A detailed theoretical study revealed that the formation of the unusual complexes can be attributed to the biradicaloid nature of the unusual four-membered heterometallacycles **5-R**, which presents an intriguing situation of M−C bonding. The combined experimental and theoretical study highlights the delicate interplay of electronic and steric effects in the stabilization of strained four-membered heterometallacycles, accounting for the isolation of the obtained complexes.



INTRODUCTION

Metallacycles of the early or late transition metal elements have risen in the last decades from lab curiosities to a significant class of compounds. They often play a key role in versatile catalytic processes,[1] for example, the chromium mediated tetramerization of ethylene to 1-octene.[2] In the past, we had been interested in the synthesis, reaction, and computational studies of three-, four-, and five-membered titana-, zircona-, and hafnacycles.[3] Especially noteworthy in this context were the bis(trimethylsilyl)acetylene containing group 4 metallocene complexes $Cp'_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp' = substituted or unsubstituted η^5-cyclopentadienyl; M = Ti, Zr, Hf; L = THF, pyridine, PMe_3), which can also be formulated as metallacyclopropenes,[3j] and which serve as excellent precursors for metallocene fragments. In this respect, bond cleavages of C−H, C−C, Si−C, P−C, N−H, N−C, N−N, Si−O, N−O, C−O, C−S, C−F, and C−B are observed. This multifaceted reactivity shows the high-potential scope of such metallocene complexes in catalytic or stoichiometric conversions.[3a−j,4]

To explore the frontiers of isolable metallacycles, especially with respect to ring size and ring strain, different approaches were discussed in the past.[3c,5] Most interestingly, the incorporation of heteroatoms into the cyclic structures results in a significant increase of the stability of the ring systems. This methodology was demonstrated by our group on several occasions. Examples include the isolation of a 1-zircona-2,5-disilacyclopent-3-yne,[6] reactions of group 4 metallocene alkyne complexes with diazobenzene,[7] sulfurdiimides[8] and phosphinoamide fragments[9] as well as the formation of unusual nitrogen-containing four- and five-membered metallacycles from the reactions of group 4 metallocenes with carbodiimides.[10] An overview of the product complexes for the latter reaction type is depicted in Scheme 1. Larger aza-metallacycles were described by Xi and co-workers, who reported the unusual synthesis of seven-membered aza-zirconacycloallenes from zirconacyclopropenes and organic nitriles.[11]

In our long-standing effort of exploring unusual structural types, we have shown theoretical evidence for the stabilization of an unusual four-membered metallacycloallene endowed with a unique M−C bond (complex **4**, Scheme 2) in a recent communication.[12] The theoretical analysis has also predicted the four-membered heterometallacycloallene, complex **5-R** to be a candidate for synthetic exploration (Scheme 2).[12] It is very likely that complex **5-R** can result from the reaction of titanocene with carbodiimides. Interestingly, introduction of

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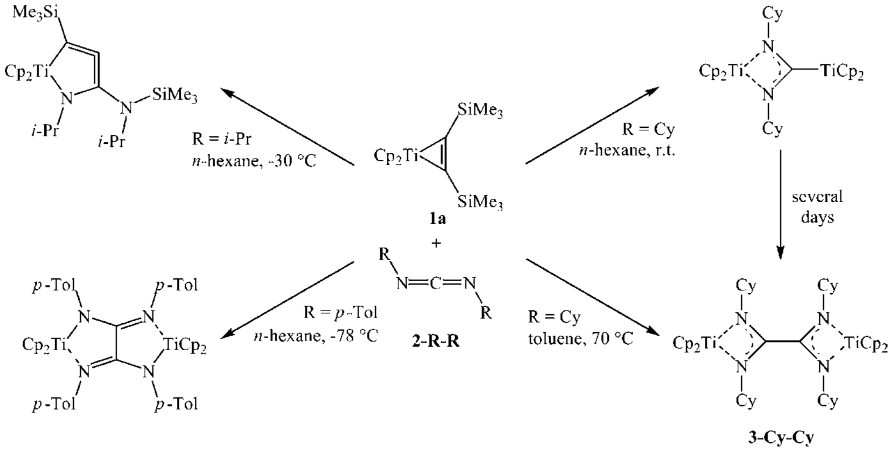
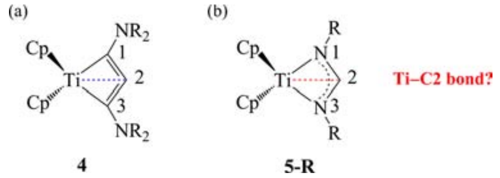
Scheme 1. Products Obtained in the Reaction of the Titanocene Alkyne Complex 1a with Carbodiimides



Scheme 2. Schematic Representations of (a) a Four-Membered Metallacycloallene 4 (NR_2 = Piperidino) and (b) a Hetero-metallacycloallene 5-R



two N atoms into the four-membered metallacycloallene (i.e., complex **5-R**) may act as a perturbation toward the Ti–C2 bonding, which can result in several possible interesting electronic situations for complex **5-R**. This, in turn, can provide important insights toward the realization of novel M–C bonding.

Generally, carbodiimides serve as substrates in different widespread metal complex reactions. Examples for group 4 metallocenes include Floriani's report of the reaction of RN=C=NR′ (R, R′ = *p*-Tolyl) with $[Cp_2Ti(CO)_2]$. In this case, the carbodiimide is coupled reductively to form a twofold chelating ligand. The product obtained can be described as a tetrazadimetallabicycle.[13] The titanaallene intermediate $[Cp^*_2Ti{=}C{=}CH_2]$ was reacted with carbodiimides RN=C=NR′ (R, R′ = *p*-Tol, Cy) to give products, which display a four membered azatitanacyclobutene moiety formed via a formal [2 + 2] cycloaddition reaction.[14]

A similar type of reaction was observed by Bergman et al. for $[Cp_2Zr{=}N(t\text{-Bu})]$ and carbodiimides or other heteroallenes, respectively. In these particular reactions, the carbodiimide and the N(*t*-Bu) fragment form a guanidinate ligand $[(t\text{-Bu})N{-}C({=}NR){-}NR]^{2-}$ which binds to the zirconocene(IV) moiety.[15]

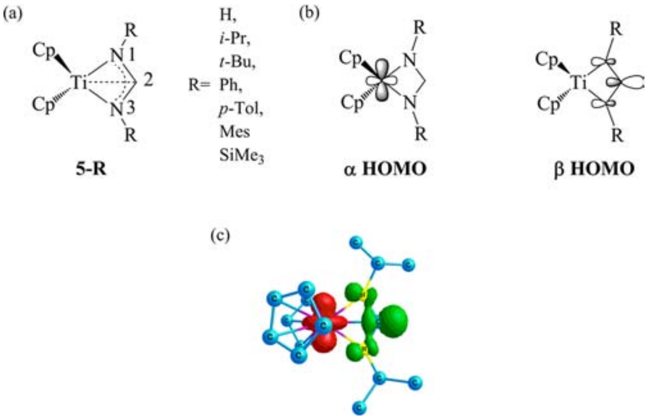
Thus, the vast and multifaceted reaction patterns of carbodiimides including simple complexation, coupling and bond activations as well as results from theoretical investigations[12] motivated us to study the scope of reactivity of this substrate with titanocenes. The formation of various unusual complexes is discussed in an elaborate experimental and theoretical study with respect to stabilization of complex **5-R**, thereby shedding light into the peculiar electronic nature of this type of strained four-membered heterometallacycles. The experimental study involves a range of substituents of varying electronic and steric influences at the carbodiimides following the peculiar revelations from the theoretical analysis on the electronic state of the monometallic complex **5-R**, described at the beginning of the following discussion.

■ RESULTS AND DISCUSSION

Theoretical Analysis. We have carried out electronic structure and bonding analysis of the theoretically predicted four-membered heterometallacycle (complex **5-R**), which is an obvious possibility from the reaction of titanocene with carbodiimides. We did this to get insight about the stabilization factors of the four-membered complex **5-R** in view of its unusual nature. As is already stated, there can be several possible electronic situations for complex **5-R** (Scheme 4). Multi configuration self-consistent field (MCSCF) methods are not a feasible option to study these complexes due to the larger size of the systems. Herein we have analyzed and explained the formation of the titanocene complexes using density functional theory approach (DFT-broken-spin-symmetry) with concomitant experimental observations. Complexes **5-R** with various substituents (Scheme 3a) and all other observed complexes are studied at the B3LYP[16]/def2-SVP[17] level of theory using Gaussian suite of program packages.[18]

Stability checking of the wave function of complexes **5-R** at the B3LYP/def2-SVP level revealed open-shell singlet state (OSSS) character for these complexes. This is in tune with a

Scheme 3. Schematic Representations of (a) a Four-Membered Heterometallacycloallene, 5-R; (b) *α* and *β* HOMO of Complex 5-*i*-Pr; (c) Calculated SCF Spin Density Plot in Complex 5-*i*-Pr (H Atoms Are Removed for Clarity)



delicate and unique Ti−C2 interaction in complex **5-R** (Scheme 2). The stable wave functions for these complexes are obtained using the unrestricted broken-spin-symmetry approach (UBS-B3LYP) followed by optimization of the complex at the same level of theory. The optimized structures of complexes **5-R** are computed to have a planar geometry (Ti−N1−C2−N3 ≈ −0.8° for R = *i*-Pr, Table S3).[12] The angles around N1 and N3, respectively add to 360° in these complexes.

The calculated natural orbital occupation numbers (NOON) of complexes **5-R** are shown in Table 1.[19] We have used this value for describing complex **5-R**. This parameter is reasonable because the complex **5-R** does not represent a perfect biradical (NOON should be close to 100%) but is an appropriate "biradicaloid" species on account of the Ti···C2 interaction. Out of the five resonating structures, **D** and **E** are the major contributors to the resonance hybrid of the molecule (Scheme 4). The NHC-type resonating structures **A**, **B**, and **C** seem to have less contribution to the overall description of the molecule. This electronic assignment of complex **5-R** also draws support from the fact that most of the experimentally observed complexes, described after this section, are found to contain a Ti(III) center, which agrees well with resonating structures **D** and **E**. The smaller singlet (OSSS)-triplet energy gap of the complexes (Table S1, Supporting Information) points toward this type of electronic situation for complex **5-R**. The well-known bond-stretch phenomena of the main-group four-membered rings, where their biradicaloid nature has created a flourishing field in the literature,[19a] are worth recalling in the present context.

Table 1. Calculated NOON (Natural Orbital Occupation Numbers) of Complexes 5-R with Various Substituents at the UB3LYP/def2-SVP Level of Theory

complex	NOON (%)
5-H	34.9
5-*i*-Pr	22.5
5-*t*-Bu	13.6
5-SiMe$_3$	43.1
5-Ph	25.3
5-*p*-Tol	24.3
5-Mes	55.8

We have tried to get an insight into the electronic nature of complex **5-R** also from molecular orbital (MO) analysis using an open-shell singlet calculation. The spin density plot of complex **5-*i*-Pr** shows the distribution of excess spin at the Ti center (0.65) and along the NCN unit with maximum probability at C2 (−0.43). Moreover, the reduced spin density value compared to unity (1.00) at both the centers is indicative of an interaction between the Ti and C2 atoms in the complex. The extent of interaction between the Ti center and the central carbon C2 in complex **5-R** plays a decisive role in determining the stability of this four-membered ring, as was also observed for the four-membered metallacycloallene **4**.[12] Interestingly, the NOONs of complexes **5-R** (corresponding to Ti−C2) decrease with more electron donating substituents (from 34.9% to 13.6% for H and *t*-Bu) and this, in turn, can be correlated well to the shortening of the Ti−C2 distance leading to significant interaction between these two atoms (Table 2). The stronger interaction also gets reflected in the relatively smaller spin density values with more electron donating substituents (Table S2). Furthermore, the Ti−C2 distance in complex **5-*i*-Pr** is 2.316 Å, which is not far from the Ti−C σ bond distance of 2.160 Å in the calculated Cp$_2$TiMe$_2$ complex. Hence, the Ti···C2 interaction in complex **5-R** can be logically termed as a "stretched" chemical bond.

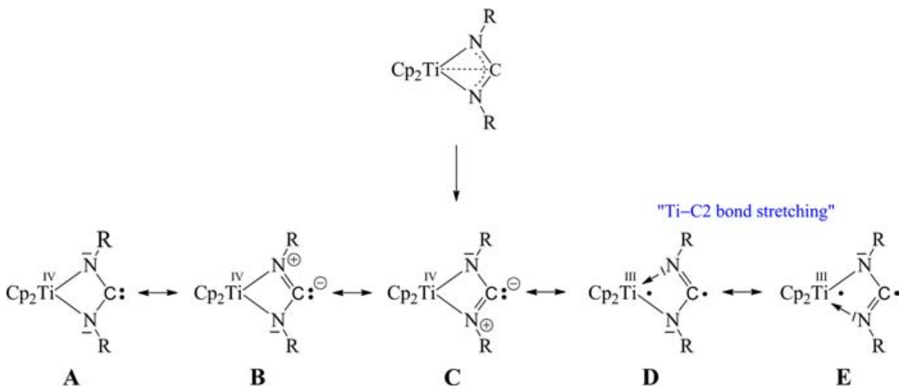
Table 2. Calculated Important Bond Lengths and Interatomic Distance (in Å) of Complexes 5-R with Various Substituents at the UB3LYP/def2-SVP Level of Theory

complex	Ti−N1	Ti−N3	Ti−C2	Ti−C2[a]
5-H	2.077	2.076	2.384	-
5-*i*-Pr	2.050	2.046	2.316	2.632
5-*t*-Bu	2.025	2.024	2.274	-
5-SiMe$_3$	2.124	2.121	2.378	2.623
5-Ph	2.064	2.064	2.370	-
5-*p*-Tol	2.059	2.058	2.364	-
5-Mes[b]	2.189	2.188	2.462	2.684

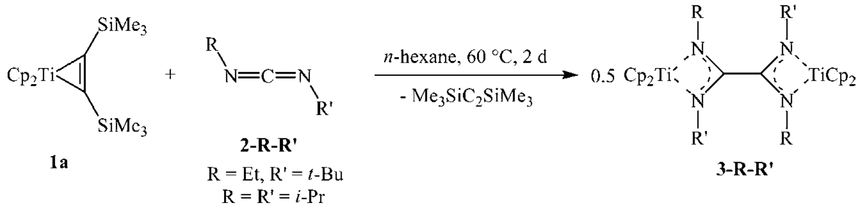
[a] This corresponds to the Ti−C2 distances, as observed in the synthesized coupled or activated complexes with the same substituents. [b] Mes = Mesityl (2,4,6-Me-C$_6$H$_2$).

The Ti−N bond lengths (Table 2) of complexes **5-R** are in good accord with standard Ti−N covalent bond lengths ($\sum r_{\text{cov}} = 2.07$ Å)[20] and importantly, the trend of variation of Ti−N bond lengths reconfirms the better complexation of carbodiimides with more electron donating substituents to the titanocene fragment. The calculated C−N bond lengths (1.310 to 1.321 Å, Table S3) in complexes **5-R** are in the range of elongated C═N double bonds,[20] which is in line with a delocalized NCN unit in the complex (Scheme 4).

Scheme 4. Possible Resonating Structures for Complex 5-R



Scheme 5. Formation of the Dinuclear Complexes 3-R-R′ (R = Et, R′ = *t*-Bu; R = R′ = *i*-Pr)



The higher NOON of complex **5-Mes** can be rationalized by considering both the electronic and steric effects of the Mes groups. Obviously, Mes is more electron donating than a *p*-Tol group, being at the same time very bulky compared to Ph and *p*-Tol groups. The increased steric demand of the Mes group hinders stronger complexation of the respective carbodiimide ligand to the Cp_2Ti moiety, which gets reflected in comparatively higher Ti–N bond lengths (2.189 Å) apart from the Ti–C2 distance (2.462 Å, Table 2). The π acceptability of the $SiMe_3$ groups decreases the electron density at C2, thereby increasing the biradical character (i.e., higher NOON) of complex **5-SiMe$_3$**. So, the crucial outcome is that both electronic as well as steric effects play an important role for the effective complexation of the carbodiimide with the titanocene moiety to result in the four-membered complex **5-R**.

With this background about the influence of substituents on the electronic state of complex **5-R** with the four-membered ring, we set out our goal to explore the reactions of titanocene with some of the carbodiimides having substituents of varying electronic and steric effects (such as *i*-Pr, *t*-Bu, $SiMe_3$, Mes and Dipp (2,6-*i*-Pr-C_6H_3)), as employed theoretically for the monometallic complexes.

Experimental Observations. In accordance with the reaction behavior reported by us in the previous communication,[10a] reaction of the titanocene alkyne complex **1a** and the unsymmetrically substituted carbodiimide *t*-Bu-N=C=N-Et (**2-Et-*t*-Bu**) results in the formation of a dinuclear paramagnetic complex. The reaction takes place in *n*-hexane at 60 °C for two days and yields turquoise, prism-like crystals in 29% yield (Scheme 5). In mass spectrometry, fragments due to the dinuclear complex **3-Et-*t*-Bu** were detected at *m*/*z* 608 $[M]^+$ as well as for the monometallic unit $[Cp_2Ti(\eta^2\text{-Et-N=C=N-}t\text{-Bu})]^+$ at *m*/*z* 304.

Crystals obtained from different solvents and temperatures showed poor quality for X-ray analysis. The connectivity of the molecule could be confirmed, a discussion of bond lengths and angles is however not feasible.

Similarly, the symmetrically substituted carbodiimide *i*-Pr-N=C=N-*i*-Pr (**2-*i*-Pr-*i*-Pr**) was employed under the same reaction conditions to give colorless crystals of complex **3-*i*-Pr-*i*-Pr** (62% yield), which shows the same structural features as **3-Cy-Cy** (Scheme 1). The molecular structure was confirmed by an X-ray analysis, bond lengths and angles resemble those found before for the cyclohexyl substituted complex (Figure 1).[10a] Moreover, mass spectrometry experiments have shown the presence of a molecular ion signal at *m*/*z* 608.

Recently, we reported on the existence of a dinuclear titanocene complex bearing *p*-Tol groups, which was obtained from a similar reaction of the titanocene alkyne complex **1a** with *N*,*N*′-di-*p*-tol-carbodiimide.[10b] This complex, however, displays a different connectivity pattern, which could be attributed to the presence of alkyl vs aryl substituents at the carbodiimide. Hence, we can distinguish between two coordination modes in these dinuclear complexes: diamide (**I**) and diamidinate (**II**) coordination (Scheme 6).

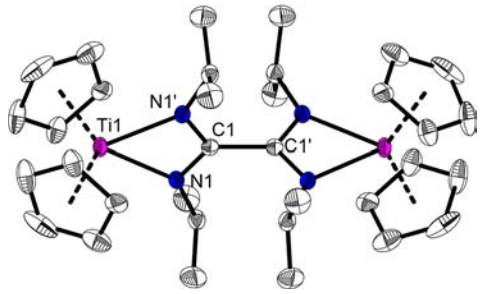
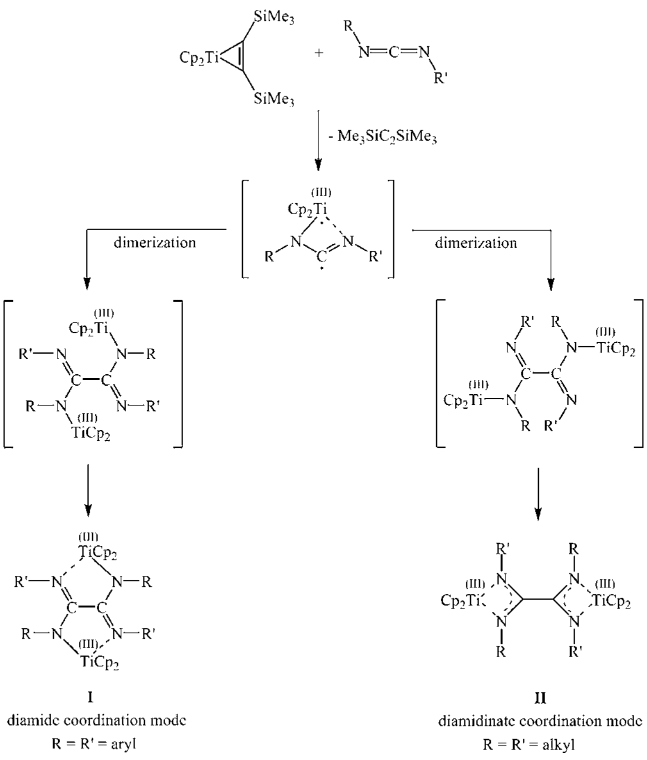


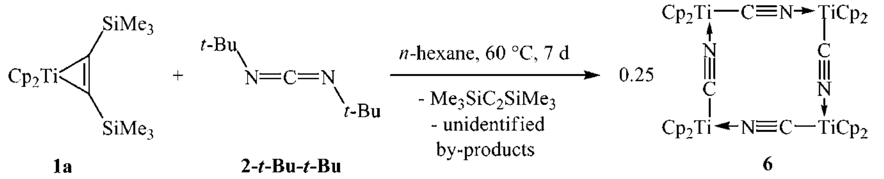
Figure 1. Molecular structure of complex **3-*i*-Pr-*i*-Pr**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.178(3), N1–C1 1.320(3), C1–N1′ 1.320(3), Ti1–N1′ 2.178(3), C1–C1′1.536(8); N1–Ti1–N1′ 60.8(2), Ti1–N1–C1 92.9(2), N1–C1–N1′ 113.4(4), C1–N1′–Ti1 92.9(2), N1–C1–C1′ 123.3(2), N1′–C1–C1′ 123.3(2).

Scheme 6. Different Coordination Modes of Coupled Carbodiimides to Titanocene Fragments[a]

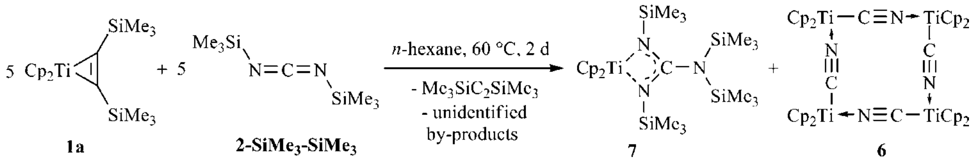


[a] For clarity, possible isomers are not shown; however, formation of these is possible.

Scheme 7. Reaction of **1a** with **2-*t*-Bu-*t*-Bu** To Give the Tetranuclear Complex **6**



Scheme 8. Reaction of **1a** with **2-SiMe$_3$-SiMe$_3$** To Give the Guanidine Complex **7**



In the first step, reduction of the carbodiimide substrate by the highly reducing titanocene(II) fragment[21] takes place to give the titanocene-substrate radical, which then dimerizes to give a dinuclear complex. Fortunately, in case of R = R′ = Cy, we were able to isolate a dinuclear titanocene carbene complex by quenching the intermediate radical with a second equivalent of [Cp$_2$Ti].[10a] Thus, depending on the substituents R and R′, diamide (**I**) (R, R′ = aryl) or diamidinate (**II**) (R, R′ = alkyl) coordination is preferred. This is in accordance with the observation made by us and by Floriani et al.[13]

Additionally, we have used the *t*-Bu substituted carbodiimide *t*-Bu-N=C=N-*t*-Bu (**2-*t*-Bu-*t*-Bu**) to further evaluate the influence of more bulky substituents on the substrate. The reaction was performed in *n*-hexane at 60 °C with stoichiometrically equal amounts of **1a** and the carbodiimide **2-*t*-Bu-*t*-Bu**, resulting in formation of a tetranuclear cyanide bridged titanocene(III) complex **6** (Scheme 7) in 49% yield. Most surprisingly, in this reaction, cleavage of the diimide takes place to yield **6**. The structure of **6** was confirmed by X-ray analysis on red-brown needles obtained by crystallization from a toluene solution at 60 °C. This complex was described before by Thewalt and co-workers, who reacted [Cp$_2$TiCl]$_2$ with sodium cyanide.[22]

Compound **6** is generated at the expense of further unidentified byproduct (Scheme 7). In mass spectrometry, fragments, which correspond to the molecular square **6**, were detected at *m*/*z* 612 [(Cp$_2$TiCN)$_3$]$^+$ and 178 [Cp$_2$Ti]$^+$.

Another attempt to access a four-membered heterotitanacycloallene (complex **5-R**) was made using the alkyne complex **1a** and the trimethylsilyl substituted carbodiimide Me$_3$SiN=C=NSiMe$_3$ (**2-SiMe$_3$-SiMe$_3$**). Reaction in *n*-hexane at 60 °C results in the formation of a deep red solution, from which blue and red brown crystals were obtained after two days. X-ray analysis of these crystals revealed the presence of two different complexes, namely the aforementioned cyanide containing complex **6** (red-brown crystals) and a trimethylsilyl substituted titanium(III) guanidine species (**7**) (blue crystals) (Scheme 8). Attempts to separate both products by means of fractionated recrystallization in different organic solvents failed. Mass spectrometry has shown characteristic fragments due to both complexes, for example, 612 [(Cp$_2$TiCN)$_3$]$^+$ as well as 524 [Cp$_2$Ti{N(SiMe$_3$)CN(SiMe$_3$)$_2$N(SiMe$_3$)}]$^+$ and 365 [Cp$_2$Ti-{N(SiMe$_3$)CN(SiMe$_3$)}]$^+$. It should be noted that metal guanidinate complexes are a common class of organometallic compounds and were described as intermediates in catalytic conversions as well as for synthetic applications.[23]

In complex **7**, the titanium center adopts a strongly distorted tetrahedral coordination geometry (cf. N1−Ti1−N2 61.17(4), Figure 2). The experimentally observed Ti1−N distances (av. 2.194(2) Å) are in the range of a polar titanium nitrogen bond ($\sum r_{\text{cov}}$ = 2.07 Å).[20] Moreover, the four-membered ring is planar with a small deviation from planarity (Ti1−N1−C1−N2 0.75°). The N(SiMe$_3$)$_2$ moiety is orientated perpendicularly to the metallacycle as indicated by the angle between the planes formed by C1,N3,Si3 and N2,C1,N3 (91.4(1)°). The central carbon atom C1 can be described as a slightly distorted sp^2 hybridized carbon atom (N1−C1−N2 114.34(9), N2−C1−N3 122.96(9), N1−C1−N3 122.70(9)°).

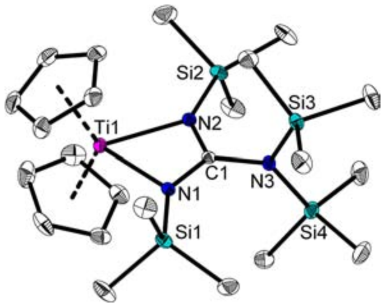
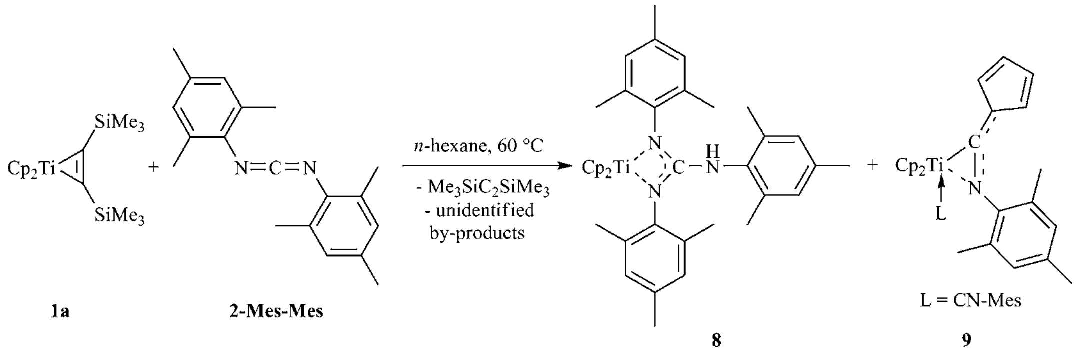


Figure 2. Molecular structure of complex **7**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−N1 2.196(2), Ti1−N2 2.193(1), N1−C1 1.327(1), C1−N2 1.330(1), C1−N3 1.450(2), N1−Si1 1.737(1), N2−Si2 1.736(1), N3−Si3 1.762(1), N3−Si4 1.759(1); N1−Ti1−N2 61.17(4), Ti1−N1−C1 92.22(7), N1−C1−N2 114.34(9), C1−N2−Ti1 92.26(7), N1−C1−N3 122.70(9), N3−C1−N2 122.96(9).

The formation of complexes **6** and **7** as depicted in Schemes 7 and 8, respectively, could be explained with a chemical equilibrium of carbodiimide RN=C=NR with cyanamide R$_2$N−CN, which is discussed generally for such compounds.[24] It should be noted that both, bis(trimethylsilyl)cyanamide (Me$_3$Si)$_2$NCN and the corresponding carbodiimide **2-SiMe$_3$-SiMe$_3$** are reported to be stable compounds with respect to tautomerization;[25] however, a metal-assisted migration of SiMe$_3$ groups should be considered for the formation of complexes **6** and **7**.

The cyanamide part of this balance provides the [CN] unit to constitute the tetranuclear complex **6**. The released NR$_2$ fragment in combination with a second molecule of carbodimiide provides the possibility to form a guanidine

Scheme 9. Reaction of Complex 1a with Carbodiimide 2-Mes-Mes



ligand. In case of R = $SiMe_3$, the guanidine complex **7** is formed (Scheme 8), whereas in case of **6**, the released NR_2 moiety remained as unidentified species, possibly due to the known volatility of *t*-Bu groups.

Thus, it can be concluded that an increased steric demand of the carbodiimide substituents favors rupture of the substrate to give C−N activated titanocene complexes. In contrast, as observed for **3-*i*-Pr-*i*-Pr** and **3-Et-*t*-Bu**, smaller substituents induce coordination of the carbodiimide, followed by coupling to give the respective dinuclear complexes. This can be linked to the computed electronic nature of the corresponding monometallic complexes **5-R**, as is delineated in the subsequent section. These results prompted us to further explore the frontiers of steric demand at the heteroallene substrate and use bulky aromatic substituents such as Mes and Dipp.

Reaction of the mesityl substituted carbodiimide **2-Mes-Mes** with the alkyne complex **1a** in *n*-hexane gives a mixture of two unusual and unexpected products. The main product is a titanocene guanidine complex (**8**) (Scheme 9), which is very similar to the above-described complex **7**. Interestingly, in **8** one hydrogen atom is bound to the exocyclic nitrogen atom to give an amine functionality. The origin of the proton is subject to speculations − abstraction from a solvent molecule is one possibility. Another likely explanation could however be found in the structure of the second product **9**, which consists of a coupled cyclopentadiene-[C=N-Mes]-moiety, which is coordinated to a titanocene fragment. Additionally, another [CN-Mes] serves as an additional ligand to stabilize the complex. Thus, abstraction of a proton from a free cyclopentadienyl fragment took place; unfortunately the exact stoichiometry of the reaction as well as the nature of the organometallic byproduct could not be revealed.

Complex **8** is paramagnetic; therefore, similarly as for **7**, no valuable NMR data could be obtained. In mass spectrometry, the molecular ion peak was detected at *m/z* 590.

The molecular structure of complex **8** (Figure 3) shows the bent titanocene fragment coordinated with the guanidinate ligand in a distorted tetrahedral geometry, thus forming a four membered planar metallacycle (deviation from the plane Ti1−N1−C1−N3 of 0.002 Å). The Ti−N distances are in the same range as observed for the structurally similar complex **7**. However, it should be noted that Ti1−N1 (2.1821(16) Å) is slightly shorter than Ti1−N3 (2.2285(15) Å), most likely due to the unsymmetrical guanidine ligand.

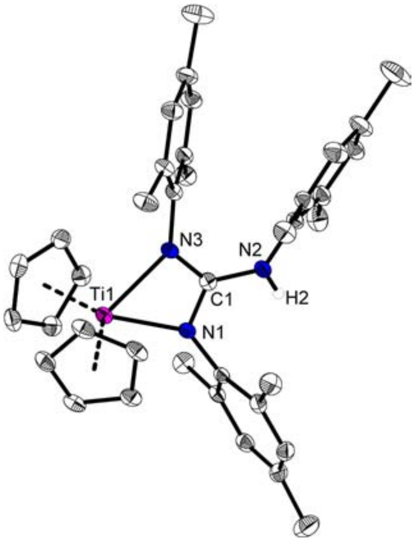


Figure 3. Molecular structure of complex **8**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except H2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−N1 2.1821(16), N1−C1 1.334(2), C1−N3 1.344(2), Ti1−N3 2.2285(15), Ti1−C1 2.660(2), C1−N2 1.373(2); Ti1−N1−C1 95.29(12), N1−C1−N3 111.5(2), C1−N3−Ti1 92.92(11), N3−Ti1−N1 60.25(6), N1−C1−N2 120.0(2), N2−C1−N3 128.5(2).

In complex **9** (Figure 4), the unusual structural motif of a fulvene bound to titanocene and a [CN-Mes] fragment is present. In ^1H NMR experiments, four resonances (ddd) are observed, thus indicating asymmetry due to the restricted rotation of the cyclopentadiene group at C1. Structural data (C1−C2 1.398(3) Å, vide infra) further corroborate the presence of a fulvene unit.

In the molecular structure of complex **9** the titanocene unit is surrounded by two CN groups [CN-Mes], one being an η^1-end-on bound isocyanide group and the second CN unit being coordinated η^2-side-on, thus leading to the formation of a three-membered ring, which is also found in the well-known metallacyclopropenes or other metallacycles. The latter CN fragment is further substituted by the fulvene unit. Bond lengths Ti1−C1 and Ti−N1 are in the range of single bonds ($\sum r_{cov}$ = 2.11 and 2.07 Å, respectively[20]) with the latter being slightly elongated. C1−N1 corresponds to a typical double bond and the fulvene bond C1−C2 is best described as an elongated double bond, thus indicating delocalization of electrons in the side-on coordinated ligand. This is further supported by the almost coplanar arrangement of the cyclopentadiene group with the titanacycle (angle of 1.2(2)°). To the best of our knowledge, transition metal complexes with such fulvene coordination modes find almost no precedent in literature. The only example was published by Poveda and Carmona and co-workers, who prepared unusual palladium-

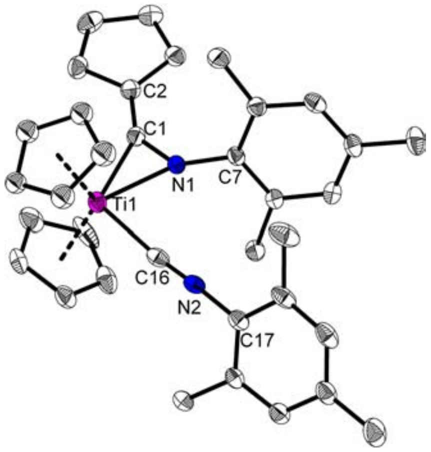


Figure 4. Molecular structure of complex **9**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and the second position of one disordered Cp ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−N1 2.121(2), Ti1−C1 2.110(3), C1−N1 1.277(3), C1−C2 1.398(3), N1−C7 1.425(3), Ti1−C16 2.148(3), C16−N2 1.158(3), N2−C17 1.396(3); Ti1−N1−C1 71.9(1), N1−C1−Ti1 72.93(14), C1−Ti1−N1 35.13(8), C2−C1−N1 137.8(2), C1−N1−C7 135.4(2), C16−N2−C17 172.5(2).

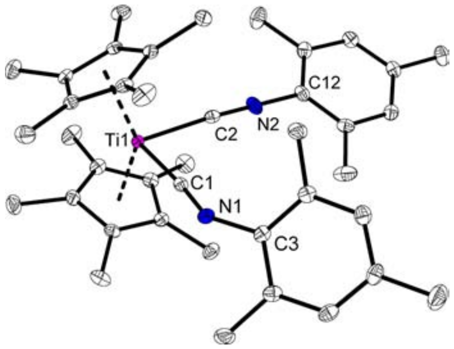


Figure 5. Molecular structure of complex **10**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−C1 2.019(2), C1−N1 1.217(3), Ti1−C2 2.067(2), C2−N2 1.175(3); C1−Ti1−C2 85.04(8), Ti1−C1−N1 174.4(2), C1−N1−C3 142.4(2), Ti1−C2−N2 176.3(2), C2−N2−C12 176.1(2).

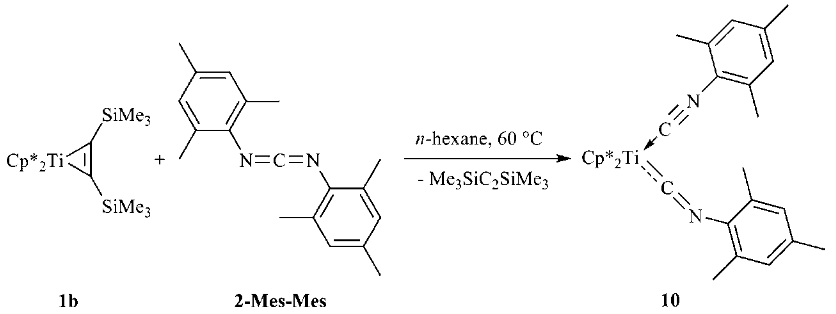
and platinum fulvene-substituted complexes with an uncoordinated NH unit and found a C−C bond distance (fulvene ring carbon to α carbon at fulvene ring) of 1.37(1) Å in Pd[C(NH*t*-Bu)═C(C_4H_3Me)][CH($SiMe_3$)$_2$](CN*t*-Bu)(PMe_3), which is in the same range as found for the titanocene complex **9**.[26] Moreover, Erker et al. reported on formimidoyl-functionalized lithium cyclopentadienides of the type Li[C_5H_4−CH═NAr] (Ar = *p*-Tol, 2,6-Me-C_6H_3, 2,6-*i*-Pr-C_6H_3),[27] displaying a nitrogen-bound metal center and a free CH group.

Reaction of the permethylated titanocene bis(trimethylsilyl)-acetylene complex **1b** with the same carbodiimide **2-Mes-Mes** unexpectedly yielded the diamagnetic bis(isocyanide) complex **10** as another C−N bond activation product (Scheme 10). ^{1}H NMR analysis in benzene-*d*$_6$ revealed that in solution both isocyanide groups are magnetically equivalent, giving only one set of resonances at 2.08 and 2.46 ppm for the methyl groups at the aromatic rings as well as at 6.68 ppm for the CH protons, respectively. However, single crystal X-ray analysis of complex **10** showed that two different isocyanide ligands are present in the molecule in the solid state (Figure 5). C−N bond lengths are different (C1−N1 1.217(3), C2−N2 1.175(3) Å) and one of the CNAr fragments displays a significant deviation from linearity of the C−N−C_{Ar} unit (C1−N1−C3 142.4(2)°).

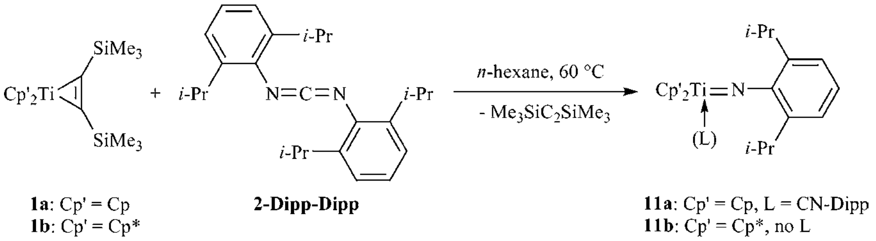
Very recently, a similar complex displaying two inequivalent isocyanide groups was reported by Sita and co-workers. Reaction of dinuclear end-on-bridged dinitrogen complexes {Cp*M[N(*i*-Pr)C(Me)N(*i*-Pr)]}$_2$(μ−η^1:η^1-N_2) (M = Mo, W) with the isocyanide ArNC (Ar = 2,6-Me-C_6H_3) yielded mononuclear species of the type Cp*M[N(*i*-Pr)C(Me)N(*i*-Pr)](C═NAr)(C≡NAr).[28] It should be noted that titanocene bis(isocyanide) complexes are known (e.g., Cp′$_2$Ti(CNAr)$_2$ (Cp′$_2$ = η^5-Me$_2$Si(C_5H_4)$_2$, Ar = 2,6-Me-C_6H_3)[29]); however, to the best of our knowledge, there is no precedent for such strong deviations from linearity in the C−N−C_R unit in titanocene complexes. Previously, such significant bond angle distortions for isocyanide ligands have been assigned to a strong π acceptor character, thus resulting in back-donation of electron density from the metal center into the antibonding π* orbital of the isocyanide triple bond.[30] Because of the presence of an electron donating Cp* ligand, this could also be the case in complex **10**.

On examination of the structures of complexes **9** and **10**, one could assume that the hypothetical Cp analogue of the latter could be an intermediate for the formation of the unusual species **9**. Electron donation from the isocyanide groups may facilitate loss of one Cp ligand, which could then couple with one of the isocyanide groups to yield **9**. Most likely, for the sterically demanding Cp* ligand, this reaction pathway is not possible and thus allows for an isolation of the bis(isocyanide) complex **10**. Similar ligand induced Cp activations were observed before by Takahashi and co-workers, who described that other coordinating substrates such as azobenzene, triphenylphosphine and pyrazine can facilitate coupling reactions by pushing two ligands together at the metal center.[31]

Scheme 10. Reaction of Complex 1b with Carbodiimide 2-Mes-Mes



Scheme 11. Formation of Titanocene Imido Complexes 11a and 11b



This steric effect should also be taken into account when interpreting the formation of complex **9**.

In the reaction of the titanocene bis(trimethylsilyl)acetylene complex **1a** with the carbodiimide **2-Dipp−Dipp**, C−N bond activation takes place to yield a titanocene(IV) imido complex (**11a**) (Scheme 11). The residual [CN-Dipp] moiety serves as an additional ligand to stabilize the metal imido fragment. Performing the same reaction with the permethylated titanocene alkyne complex **1b** results in the formation of a similar imido complex (**11b**); however, due to the higher steric demand of the metallocene unit, in this case, no additional ligand is required to stabilize the metal center.

^{1}H NMR spectra of both titanocene imido complexes are very similar and display sharp signals for the Cp and Cp* protons at 5.99 and 1.86 ppm, respectively, thus indicating C_{2v} symmetry in solution. The IR spectrum of **11a** consists of an intense band at 2160 cm^{-1}, which can be assigned to the C≡N stretch of the isocyanide ligand (cf. 2124 cm^{-1} in $Cp_2Zr(\eta^1\text{-}CNt\text{-}Bu)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[32]).

The molecular structure of complex **11b** was unambiguously determined by X-ray crystallography (Figure 6). It shows the bent titanocene unit coordinated with an imido group to result in a distorted trigonal planar geometry around the Ti center. The Ti1−N1 bond length (1.764(1) Å) is in the range of a double bond ($\sum r_{cov}$ = 1.77 Å[20]) and in good agreement to values found before for other structurally similar titanocene imido complexes (e.g., 1.722(4) Å in $[C_5H_3(SiMe_3)_2]_2Ti{=}NSiMe_3$[33a] and 1.765(3) Å in $Cp^*_2Ti{=}NPh$[33b]). The Ti1−N1−C1 unit is found to be almost linear (178.40(13)°), which is in line with NMR data described above.

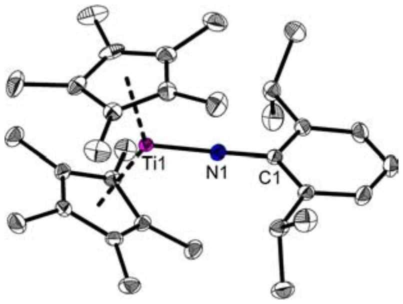
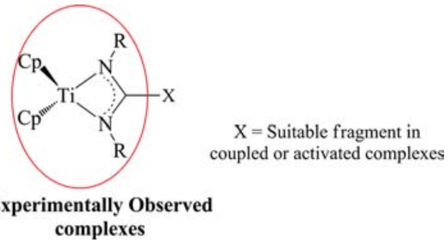


Figure 6. Molecular structure of complex **11b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−N1 1.764(1), N1−C1 1.379(2); Ti1−N1−C1 178.4(1).

Explanations for the Formation of Various Complexes. The intermediacy of the monometallic four-membered heterometallacycle, complex **5-R** in the formation of experimentally observed complexes is evident from Schemes 6 and 12. Now the generation of the above experimental complexes can better be explained considering the respective monometallic complexes **5-R** analyzed theoretically at the beginning. The calculated structural parameters are in good agreement with experimental values for complexes **3-*i*-Pr-*i*-Pr**, **7**, **8**, **9** and **11b** (Table S4−S8).

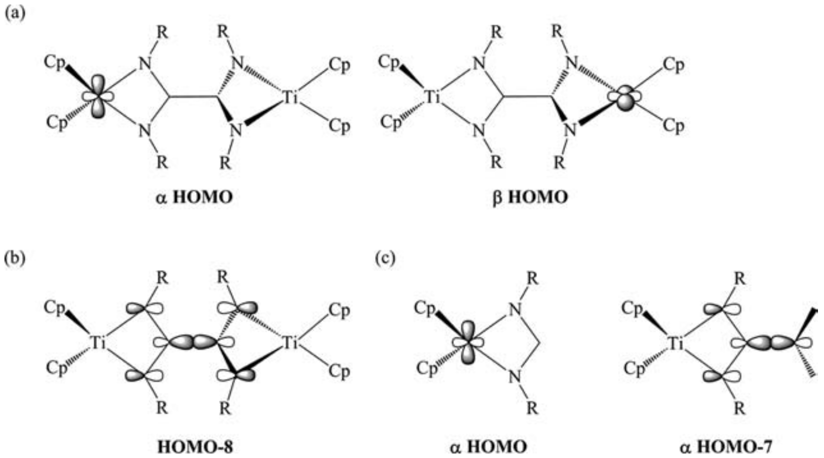
Scheme 12. Schematic Representation of the Experimentally Observed Complexes



Understanding the bonding in complex **5-R** will make it easier to comprehend the bonding in complexes **3-*i*-Pr-*i*-Pr**, **6**−**9**, and **11b**. Depending on the extent of biradical character in complex **5-R**, the β HOMO (or α HOMO) reacts in various ways as is observed above experimentally. Generally, the lesser biradical character of complex **5-*i*-Pr** leads to coordination with another molecule to form complex **3-*i*-Pr-*i*-Pr**, while higher biradical character tends to activate the C−N bond of the carbodiimide to give various activated complexes (**7** and **8**). Despite least biradical character in complex **5-*t*-Bu**, no metallacycle (like also **3-*i*-Pr-*i*-Pr**) is formed in the reaction of *t*-Bu substituted carbodiimide with the titanocene. This can be attributed to the higher steric demand of the *t*-Bu groups as well as to the cyanamide/carbodiimide equilibrium,[24] which rather leads to the formation of complex **6**. It is important to note that the "stretched" Ti−C2 bond of the monometallic complex **5-*i*-Pr** disappears in complex **3-*i*-Pr-*i*-Pr** (Ti···C2 = 2.632 Å, Table 2) which further strengthens the presented interpretation.

The metal d orbitals in complex **3-*i*-Pr-*i*-Pr** get singly occupied with opposite spin electrons (α and β HOMO, Scheme 13a) to give an almost perfect biradical nature (NOON is 98%) to the complex. This situation can be contrasted with complexes **5-R**, where the Ti···C2 interaction leads to smaller biradical character (i.e., smaller NOON) for the four-membered complexes (Table 1). The allene orbitals of the two RNCNR moieties in complex **3-*i*-Pr-*i*-Pr** interact strongly (HOMO-8, Scheme 13b) to form a C−C single bond (C1−C1′ = 1.542 Å). On the other hand, the allene orbital in complex **5-SiMe$_3$**, because of high biradical character at the central carbon atom, tends to interact with the C−N bond of the corresponding free carbodiimide to form the $N(SiMe_3)_2$-substituted complex **7**. The formation of the exocyclic longer C−N single bond (C1−N3 = 1.448 Å) instead of a shorter multiple bond, corresponding to α HOMO-7 (Scheme 13c)

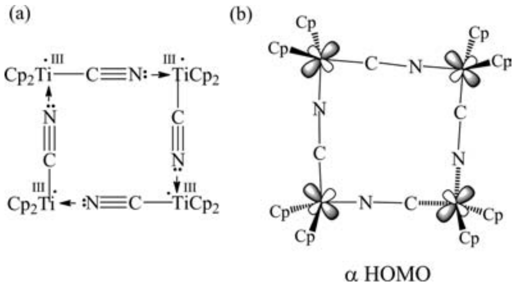
Scheme 13. (a) α and β HOMO of Complex 3-*i*-Pr-*i*-Pr; (b) HOMO-8 of Complex 3-*i*-Pr-*i*-Pr; (c) α HOMO and HOMO-7 of Complex 7



helps in reducing steric crowding around the RNCNR-NR$_2$ (R = SiMe$_3$) unit in complex **7**. The metal d orbital (α HOMO, Scheme 13c) contains the single electron, thus resulting in the paramagnetic nature of this species. A similar bonding situation also exists in complex **8**. The increased Ti−C2 (central carbon of the four-membered ring) distances (Table 2) in complexes **7** and **8** compared to complexes **5-SiMe$_3$** and **5-Mes** are supportive of the disappearance of the "stretched" Ti−C2 bond in these complexes. In the case of permethylated titanocene, no metallacycle is formed from the reaction with **2-Mes-Mes**; instead a bis(isocyanide) complex **10** is generated. The higher steric requirement of the bulky Cp* moieties, which prevents effective complexation between the titanocene and the carbodiimide, is the likely reason for this. Similarly, owing to the increased steric demand of Dipp groups, a titanocene imido complex (**11b**) forms instead of any metallacycle from the reaction of this carbodiimide with titanocene. It reconfirmed the theoretical prediction of the requirement of substituents at the carbodiimide as well as in the Cp moiety with proper steric demand in order to result in a stronger complexation between the titanocene and carbodiimide moiety.

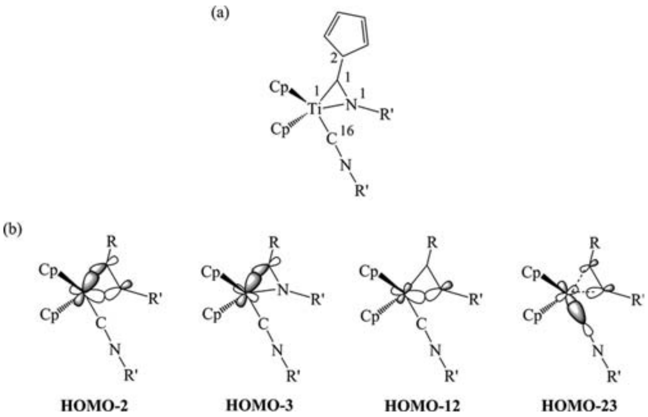
The optimized geometry of complex **6** has a puckered structure, where the four Ti atoms are not coplanar. The α HOMO (Scheme 14b) along with other possible three combinations of these metal d orbitals occupy the four single electrons to account for the paramagnetic nature (i.e., four Ti(III) centers) in complex **6**. Complex **6** can be described as having four pairs of covalent Ti−C bond and dative Ti−N bonds, respectively (Scheme 14a). Higher vacant titanocene orbitals are involved in interactions with the orbitals of the cyano groups to form the tetranuclear structure of the complex.

Scheme 14. (a) Schematic Representation of Complex 6 (b) α HOMO of Complex 6



The singlet state of complex **9** (Cp$_2$Ti(η^2-MesCNC$_5$H$_4$)-(CN-Mes)) is calculated to be more stable than the triplet state by 36.0 kcal/mol. The metal is in the oxidation state of +4 in complex **9**. The important MOs of the complex **9** are shown in Scheme 15. The bond lengths of the Ti1−C1 (2.106 Å) and Ti1−N1 bonds (2.117 Å) suggest stronger complexation of the RCNR′ moiety to the Cp$_2$Ti fragment; HOMO-2, HOMO-3 and HOMO-12 account for this interaction. On the other hand, the Ti1−C16 bonding appears to be a dative contact (2.170 Å), which involves interaction between the orbital of the cyano group with the metal d orbital (HOMO-23, Scheme 15b). Considerable double bond character in the calculated C1−C2 (1.388 Å) as well as in C1−N1 (1.291 Å) bonds of the coordinated RCNR′ moiety is supportive of π conjugation along the N1−C1−C2 unit in complex **9**.

Scheme 15. (a) Schematic Representation of Complex 9 (R′ = Mes); (b) Important Molecular Orbitals of the Complex 9 (R = Cyclopentadiene, R′ = Mes)



So, the study shows a relationship between the biradicaloid nature of the four-membered complex **5-R** as revealed in the initial theoretical analysis and the formation of the Ti(III) complexes from the reaction of titanocenes. The discussion also expands our knowledge about unique M−C bonding,[3k] which are vital in stabilizing unusual molecules such as complex **5-R**. In essence, a judicious choice of substituents (R) with proper balance of electronic and steric influences is necessary for the formation of the crucial Ti−C2 bond and thus to eventually stabilize the four-membered complex (**5-R**) to make it isolable.

■ CONCLUSION

We have described the multifaceted reactivity of titanocenes with carbodiimides as the heterosubstrates. A comprehensive theoretical study reveals that the biradicaloid nature of complex **5-R**, resulting from a "stretched" M−C2 bond, prevents its isolation as a well-defined stable four-membered heterometallacycloallene complex. This peculiar electronic nature of complex **5-R** gets reflected in the various reactions of titanocene with carbodiimides. We found that different ways of stabilization are possible for these types of strained four-membered metallacycles which result in various, more complex structures: (a) Complexation with another titanocene fragment as found by us earlier in the dinuclear complex $Cp_2Ti[(NCy)_2C]TiCp_2$ (Scheme 1).[10] (b) Dimerization as found in complex **3-R-R′**. This is observed in the absence of additional free titanocene and for smaller substituents at the carbodiimide. (c) Substitution at the central carbon atoms as found in complexes **7** and **8**. (d) Activation and dismantlement of the carbodiimide substrate to result in unusual structures such as **6** or **9** as well as in the more commonly known titanocene imido complexes **11**. This pathway is observed for sterically demanding carbodiimides.

It is thus clear that, as described before for four-membered metallacycloallenes,[12] the presence of an interannular M−C2 bond is a crucial factor for the stability of the four-membered heterometallacycloallene. However, the interplay of steric and electronic factors in this context should always be taken into account when addressing this issue synthetically.

■ EXPERIMENTAL DETAILS

General Information. All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. Nonhalogenated solvents were dried over sodium/benzophenone and freshly distilled prior to use. Carbodiimides **2-Et-*t*-Bu**, **2-*i*-Pr-*i*-Pr**, **2-*t*-Bu-*t*-Bu** and **2-SiMe$_3$-SiMe$_3$** are commercially available and were sublimed or distilled prior to use. **2-Dipp−Dipp** and **2-Mes-Mes** were synthesized according to literature procedures.[34] The metallocene alkyne complexes **1a** and **1b** were synthesized as described in literature previously.[35,36] The following instruments were used: NMR spectra: Bruker AV250 and AV300, respectively. ^1H and ^{13}C chemical shifts were referenced to the solvent signals: benzene-d_6 (δ_H 7.16, δ_C 128.0); IR, Nicolet 6700 FT-IR spectrometer with a smart endurance attenuated total reflection (ATR) device and Bruker Alpha FT-IR, respectively; MS, Finnigan MAT 95-XP from Thermo-Electron; Elemental analysis, Leco CHNS-932 elemental analyzer; Melting points, E/Z-Melt, Stanford Research Systems. Melting points are uncorrected and were measured in sealed capillaries.

Computational Details. We have studied all the complexes using the gradient-corrected hybrid density functional theory method B3LYP[16] in combination with the def2-SVP basis set.[17] A restricted approach is used for the closed-shell system, while an unrestricted approach is utilized for the open-shell species. The open-shell singlet complexes **5-R** are treated using unrestricted broken-spin-symmetry approach (UBS-B3LYP). A 50:50 mix (singlet−triplet) initial guess of the HOMO and LUMO orbitals of complexes **5-R** is fed to the SCF calculations to get the broken spin-symmetry solutions for the complexes.[37,38] This formalism works reasonably well for complexes **5-R** since the HOMO and LUMO correspond to the appropriate orbitals that are required for proper mixing. Natural orbital occupation numbers (NOON) are calculated for the optimized geometry of complexes **5-R** to estimate the amount of biradical(oid) character in the species.[19] All the complexes are characterized as minima on the potential energy surface by calculating the vibrational frequency of the complexes at the same level of theory unless otherwise specified. All the computations are carried out using Gaussian03 and Gaussian09 suite of quantum chemical program packages.[18]

Synthesis of $[Cp_2Ti\{\eta^2\text{-}(N\text{-}t\text{-}Bu,N'\text{-}Et)C\}]_2$ (3-Et-*t*-Bu). The alkyne complex **1a** (0.100 g, 0.287 mmol) was dissolved in 5 mL of *n*-hexane. After addition of carbodiimide **2-Et-*t*-Bu** (0.045 mL, 0.287 mmol), a red-brown reaction mixture was obtained and stored at 60 °C for 2 days to complete the reaction. Within this period of time, a microcrystalline solid with a turquoise appearance was formed. After cooling to room temperature, these crystals were separated and dried in vacuum. Yield: 0.050 g (29%). Mp: >300 °C. Anal. Calcd for $C_{34}H_{48}N_4Ti_2$ (608.51 g mol^{-1}): C, 67.11; H, 7.95; N, 9.21. Found: C, 66.78; H, 7.88; N, 9.12. IR (ATR, 16 scans, cm^{-1}): 2961 (m), 2925 (m), 2863 (m), 2723 (w), 2665 (w), 2107 (m), 1621 (w), 1542 (s), 1496 (w), 1472 (w), 1439 (m), 1388 (w), 1367 (m), 1332 (s), 1260 (w), 1230 (w), 1197 (m), 1159 (m), 1060 (w), 1011 (s), 971 (w), 869 (m) 777 (s). MS (CI, *i*-butane): *m*/*z* (%) 608 (100) $[M]^+$, 580 (6) $[M - C_2H_5 - H]^+$, 305 (5) [0.5 M]$^+$, 127 (16) [*t*-BuNCNEt]$^+$.

Synthesis of $[Cp_2Ti\{\eta^2\text{-}(N\text{-}i\text{-}Pr,N'\text{-}i\text{-}Pr)C\}]_2$ (3-*i*-Pr-*i*-Pr). The titanocene complex **1a** (0.200 g, 0.574 mmol) was dissolved in 5 mL of *n*-hexane. To this solution, carbodiimide **2-*i*-Pr-*i*-Pr** (0.072 g, 0.574 mmol) was added. After 16 h at 60 °C, the color of the solution had changed to greenish-brown and a crystalline green precipitate formed. The reaction mixture was concentrated to a volume of 1 mL and the precipitate was separated from the mother liquor by decantation. The product was washed twice with cold *n*-hexane. Yield: 0.107 g (62%). Mp: 140 °C. Anal. Calcd for $C_{34}H_{48}N_4Ti_2$ (608.51 g mol^{-1}): C, 67.11; H, 7.95; N, 9.21. Found: C, 67.27; H, 7.74; N, 9.09. IR (ATR, 16 scans, cm^{-1}): 2963 (w), 2868 (w), 1644 (m), 1471 (m), 1405 (w),1372 (w), 1341 (m), 1200 (w), 1164 (w), 1144 (m) 1110 (w), 1064 (w), 1004 (m), 783 (s), 761 (w), 580 (w), 451 (m). MS (CI *i*-butane): *m*/*z* (%) 608 (92) $[M]^+$, 543 (5) $[M - Cp - H_2]^+$, 431 (12) $[M - Cp_2Ti]^+$, 304 (2) [0.5 M]$^+$.

Synthesis of $[Cp_2TiCN]_4$ (6). The alkyne complex **1a** (0.100 g, 0.287 mmol) was dissolved in 5 mL of *n*-hexane. After addition of carbodiimide **2-*t*-Bu-*t*-Bu** (0.055 mL, 0.044 g), a deep red reaction mixture was obtained and stored at 60 °C for 12 h to complete the reaction. The solvent was removed under reduced pressure, the formed precipitate was filtered. Finally, the obtained reaction product was dried in vacuum. Red-brown needles of **6** were obtained from a toluene solution at 60 °C after seven days. Yield: 0.029 g (49%). Mp: >400 °C. IR (ATR, 16 scans, cm^{-1}): 2960 (m), 2090 (m), 1692 (m), 1601 (m), 1442 (m), 1362 (m), 1258 (s), 1199 (w), 1086 (w), 1013 (s), 785 (s), 621 (m), 545 (w). MS (CI, *i*-butane): *m*/*z* (%) 612 (100) $[Cp_2Ti(CN)]_3^+$, 586 (5) $[Cp_2Ti(CN)TiCp_2(CN)TiCp_2]^+$, 178 (51) $[Cp_2Ti]^+$.

Synthesis of $[Cp_2Ti\{\eta^2\text{-}(Me_3Si)NCN(SiMe_3)_2N(Me_3Si)\}]$ (7) and $[Cp_2TiCN]_4$ (6). The alkyne complex **1a** (0.100 g, 0.287 mmol) was dissolved in 5 mL of *n*-hexane. After addition of carbodiimide **2-SiMe$_3$-SiMe$_3$** (0.065 mL, 0.053 g), a light brown solution was obtained. After 10 min at room temperature, no obvious reaction was observed. Then the reaction temperature was raised to 60 °C. Within 30 min, a deep red solution was formed and a red-brown solid precipitated. After storing for 2 d at 60 °C blue and red brown crystals were formed. These crystals were separated and finally dried in vacuum. The red-brown crystals were assigned to the tetranuclear cyanide bridged titanocene(III) complex $[Cp_2TiCN]_4$ (**6**). The blue crystals were assigned to the mononuclear guanidine titanocene(III) complex **7**. Attempts to separate both reaction products by fractionated crystallization failed. Therefore, no accurate elemental analysis could be performed. IR (ATR, 16 scans, cm^{-1}): 3099 (w), 2953 (m), 2896 (w), 2208 (w), 2160 (w), 2113 (w), 2025 (m), 1665 (m), 1573 (w), 1504 (w), 1439 (m), 1363 (w), 1300 (w), 1244 (s), 1151 (w), 1098 (m), 1013 (s), 948 (m), 833 (s), 785 (m), 746 (m), 681 (w), 663 (w), 640 (w), 556 (w). MS (CI, *i*-butane): *m*/*z* (%) 834 (8) $[M + H_2O]^+$ (**6**), 612 (37) $[Cp_2Ti(CN)]_3^+$ (**6**), 524 (23) $[M]^+$ (**7**), 381 (27) $[Cp_2Ti(CN)TiCp_2]^+$ (**6**), 365 (11) $[M - N(SiMe_3)_2]^+$ (**7**), 187 $[NCN(SiMe_3)_2]^+$ (**7**).

Table 3. Crystal Data for **3-*i*-Pr-*i*-Pr**, **7**, **8**, **9**, **10**, and **11b**

	3-*i*-Pr-*i*-Pr	**7**	**8**	**9**	**10**	**11b**
Chem. Formula	$C_{34}H_{48}N_4Ti_2$	$C_{23}H_{46}N_3TiSi_4$	$C_{38}H_{44}N_3Ti$	$C_{35}H_{36}N_2Ti$	$C_{47}H_{60}N_2Ti$	$C_{32}H_{47}NTi$
Form. wght. [g mol^{-1}]	608.56	524.89	590.66	532.56	700.87	493.61
Color	colorless	blue	blue	light brown	brown	red
Cryst. System	tetragonal	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$I\bar{4}2m$	Pn	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, [Å]	8.9445(3)	9.176(7)	8.5462(4)	16.2024(6)	13.6940(3)	10.7229(2)
b, [Å]	8.9445(3)	15.95(1)	11.2725(6)	10.7320(4)	30.0123(6)	16.2730(3)
c, [Å]	20.400(1)	10.588(8)	20.5189(10)	16.4713(6)	9.9271(2)	16.3219(3)
α [°]	90.00	90.00	94.375(4)	90.00	90.00	90.00
β [°]	90.00	111.10(2)	90.937(4)	95.448(3)	101.067(1)	90.00
γ [°]	90.00	90.00	94.744(4)	90.00	90.00	90.00
V [Å^3]	1632.1(1)	1446(2)	1963.7(2)	2851.2(2)	4004.05(14)	2848.07(9)
Z	2	2	2	4	4	4
$\delta_{calc.}$, [g cm^{-3}]	1.238	1.205	0.999	1.241	1.163	1.151
μ [mm^{-1}]	0.517	0.477	0.243	0.326	2.049	0.320
λ [Å]	0.71073	0.71073	0.71073	0.71073	1.54178	0.71073
T [K]	173(2)	173(2)	150(2)	150(2)	150(2)	150(2)
no. of rflns collected	4043	24442	28767	39698	31394	48630
no. of indep rflns	1191	11851	7318	5601	6520	6792
no. of rflns with $I > 2\ \sigma(I)$	1036	10820	3787	3034	5480	6360
$R_{int.}$	0.0333	0.0267	0.0662	0.0681	0.0531	0.0298
F(000)	648	566	630	1128	1512	1072
R_1 [$I > 2\sigma(I)$]	0.0462	0.0287	0.0368	0.0412	0.0444	0.0348
wR_2(all data)	0.1242	0.0678	0.0596	0.0872	0.1218	0.0955
Parameters	77	292	392	329	468	321

Synthesis of [$Cp_2Ti\{\eta^2$-(Mes)NCN(Mes)$_2$NH(Mes)\}] (8) and [$Cp_2Ti(\eta^1$-C═N−Mes)\{η^2-(C_5H_4−C═N−Mes)] (9). The alkyne complex **1a** (0.451 g, 1.29 mmol) was dissolved in 15 mL of *n*-hexane and a solution of the carbodiimide **2-Mes-Mes** (0.381 g, 1.36 mmol) in 15 mL of *n*-hexane was added dropwise at room temperature. The color of the solution changed to dark red and the mixture was stirred at room temperature for 10 h. The volatiles were removed in vacuum and the residue was suspended in 20 mL of *n*-hexane, followed by filtration and storing of the solution at −40 °C. After 3 days, a fine precipitate formed, which was isolated by filtration and recrystallized from a mixture of THF (5 mL) and pentane (3 mL) at room temperature. After two weeks, turquoise crystals of **8** formed, which were isolated, washed with cold pentane and dried in vacuum. Yield (**8**): 0.254 g (33%). Mp: 167 °C (dec.). Anal. Calcd for $C_{38}H_{44}N_3Ti$ (590.64 g·mol^{-1}): C, 77.27; H, 7.51; N, 7,11. Found: C, 77.26; H, 7.56; N, 7.01. IR (ATR, 16 scans, cm^{-1}): 3377 (vw), 2914 (w), 1643 (w), 1602 (w), 1518 (m), 1475 (m), 1440 (m), 1362 (w), 1311 (m), 1254 (w), 1222 (m), 1204 (w), 1145 (w), 1068 (w), 1016 (m), 882 (w), 847 (m), 793 (s), 780 (vs), 699 (s), 568 (s), 545 (s), 510 (m), 467 (s). MS (EI, 70 eV): *m*/*z* (%) 590 (60) [M]$^+$, 525 (100) [M−Cp]$^+$, 413 (29) [M−Cp_2Ti]$^+$, 278 (92) [Mes-NCN-Mes]$^+$, 134 (63) [HNMes]$^+$. Light brown crystalline material of complex **9** was obtained from the concentrated mother liquor of the *n*-hexane extraction at −40 °C (vide supra). Yield (**9**): 0.051 g (7%). ^{1}H NMR (300 MHz, 297 K, benzene-d_6): δ 7.22 (ddd, ^3J = 3.9 Hz, ^4J = 2.0 Hz, ^4J = 1.7 Hz, 1H), 7.20 (ddd, ^3J = 4.3 Hz, ^3J = 2.7 Hz, ^4J = 1.7 Hz, 1H), 6.92 (ddd, ^3J = 4.4 Hz, ^3J = 2.6 Hz, ^4J = 1.8 Hz, 1H), 6.60 (ddd, ^3J = 4.0 Hz, ^4J = 2.0 Hz, ^4J = 1.7 Hz, 1H), 6.58 (m, 2H), 6.33 (m, 2H), 5.51 (s, 10H), 2.09 (s, 3H), 2.04 (s, 6H), 1.83 (s, 3H), 1.70 (s, 6H). ^{13}C NMR (100 MHz, 297 K, benzene-d_6): δ 187.8, 180.7, 153.9, 145.3, 140.0, 134.6, 132.7, 130.0, 128.8, 120.9, 117.9, 117.1, 115.4, 112.4, 105.4, 20.9, 20.6, 20.0, 17.7. IR (ATR, 16 scans, cm^{-1}): 2916 (vw), 2164 (vw), 1638 (w), 1561 (w), 1478 (m), 1438 (w), 1261 (w), 1223 (w), 1095 (m), 1016 (m), 850 (s), 796 (vs), 731 (s), 660 (s), 545 (s), 466 (s), 426 (m). MS (CI, *i*-butane): *m*/*z* (%) 533 (26) [M + H]$^+$, 468 (34) [M−Cp]$^+$, 388 (67) [M-CNMes + H]$^+$, 323 (43) [Cp_2TiCNMes]$^+$. Unfortunately, due to the low yield, no elemental analysis could be performed.

Synthesis of [$Cp^*_2Ti(\eta^1$-CN-Mes)$_2$] (10). The alkyne complex **1b** (0.472 g, 0.97 mmol) was dissolved in 15 mL of *n*-hexane and a solution of the carbodiimide **2-Mes-Mes** (0.282 g, 1.01 mmol) in 15 mL of *n*-hexane was added at room temperature. The mixture was heated at 50 °C for three days, during this time the color of the solution changed to deep red. After cooling to room temperature, all volatiles were removed in vacuum and the black residue was dissolved in 5 mL of *n*-hexane. Upon standing at −78 °C for several weeks, black crystals had formed which were isolated by filtration, washed with 0.2 mL of cold *n*-hexane and dried in vacuum. Yield: 0.235 g (41%). Mp: 150 °C (dec.). Anal. Calcd for $C_{47}H_{60}N_2Ti$ (700.87 g·mol^{-1}): C, 78.92; H, 8.61; N, 4.60. Found: C, 76.42; H, 8.11; N, 4.48. ^{1}H NMR (300 MHz, 297 K, benzene-d_6): δ 6.68 (s, 4H), 2.46 (s, 12H), 2.08 (s, 6H), 1.92 (s, 30H). ^{13}C NMR (100 MHz, 297 K, benzene-d_6): δ 251.7, 134.9, 132.2, 130.6, 129.2, 105.1, 20.9, 20.5, 12.1. IR (ATR, 16 scans, cm^{-1}): 2961 (w), 2908 (m), 2854 (w), 2112 (s), 1801 (w), 1605 (w), 1558 (w), 1541 (w), 1507 (w), 1473 (m), 1437 (s), 1374 (s), 1260 (w), 1199 (w), 1065 (m), 1021 (m), 954 (w), 851 (s), 790 (s), 712 (s), 569 (vs), 465 (vs), 420 (s), 397 (vs), 385 (vs). MS (EI, 70 eV): *m*/*z* (%) 609 (46) [M + H]$^+$, 608 (45) [M]$^+$, 463 (21) [Cp^*_2Ti(CNMes)]$^+$, 318 (56) [Cp^*_2Ti]$^+$, 156 (100) [CNMes + H]$^+$.

Synthesis of [$Cp_2Ti(\eta^1$-C═N−Dipp)\{η^1-N═C−Dipp\}] (11a). The alkyne complex **1a** (0.386 g, 1.06 mmol) was dissolved in 15 mL of *n*-hexane and a solution of the carbodiimide **2-Dipp−Dipp** (0.389 g, 1.07 mmol) in 15 mL of *n*-hexane was added dropwise at room temperature. Immediately upon addition, the color of the solution changed to dark red. The mixture was stirred at room temperature for 6 h, followed by removal of all volatiles in vacuum. The residue was suspended in 20 mL of *n*-hexane and the solution was filtered. The filtrate was concentrated to dryness in vacuum, the product was washed with cold *n*-hexane and dried in vacuum. Yield: 0.425 g (74%). Mp: 105 °C (dec.). Anal. Calcd for $C_{35}H_{44}N_2Ti$ (540.60 g·mol^{-1}): C, 77.76; H, 8.20; N, 5.18. Found: C, 77.57; H, 8.30; N, 5.09. ^{1}H NMR (300 MHz, 297 K, benzene-d_6): δ 7.07 (d, ^3J = 7.5 Hz, 2H), 6.98 (t, ^3J = 6.9 Hz, 1H), 6.66 (d, ^3J = 7.8 Hz, 2H), 6.76 (t, ^3J = 7.5 Hz, 1H), 5.99 (s, 10H), 3.86 (p, ^3J = 6.0 Hz, 1H), 3.53 (p, ^3J = 6.0 Hz, 1H), 1.26 (d, ^3J = 6.0 Hz, 12H); 1.15 (d, ^3J = 6.0 Hz, 12H). ^{13}C NMR (100 MHz, 297 K, benzene-d_6): δ 158.4, 145.5, 133.9, 130.8, 123.9, 122.4, 117.2, 107.8, 30.1, 27.6, 24.6, 22.9. IR (ATR, 16 scans, cm^{-1}): 3062 (vw), 2957 (m), 2925 (w), 2864 (w), 2160 (m), 2028 (vw), 1926 (w), 1619 (vw), 1582 (w), 1458 (w), 1435 (w), 1412 (m), 1384 (w), 1343 (m), 1284 (w), 1258 (w), 1181 (w), 1138 (vw), 1096 (w), 1058 (w), 1016 (w), 935 (w), 780 (vs), 746 (s), 734 (s), 621 (s), 538 (s), 464 (m), 436 (m). MS (CI, *i*-butane): *m*/*z* (%) 540 (53) [M]$^+$.

Synthesis of [Cp*$_2$Ti{η^1-N=C−Dipp}] (11b). The alkyne complex **1b** (0.276 g, 0.57 mmol) was dissolved in 15 mL of toluene and a solution of the carbodiimide **2-Dipp−Dipp** (0.205 g, 1.57 mmol) in 15 mL of toluene was added dropwise at room temperature. The mixture was stirred at room temperature for 2 h, followed by warming to 100 °C for 24 h. During this time, the color changed to bright red. The volatiles were removed in vacuum and the residue was dissolved in 8 mL of hot toluene. Red crystals of complex **11b** were obtained at room temperature. Yield: 0.252 g (66%). Mp: 126 °C (dec.). Anal. Calcd for $C_{32}H_{47}NTi$ (492.59 g·mol^{-1}): C, 77,87; H, 9,60; N, 2,84. Found: C, 74.16; H, 9.39; N, 3.32. Despite repeated analysis and addition of V_2O_5 to ensure full combustion, no better values for C could be obtained; a reason for this could be the presence of residual isocyanide, which could not be removed. ^{1}H NMR (300 MHz, 297 K, benzene-d_6): δ 7.07−7.04 (m, 3H), 3.65 (p, ^3J = 6.0 Hz, 1H), 1.86 (s, 10H), 1.33 (d, ^3J = 6.0 Hz, 12H). ^{13}C NMR (100 MHz, 297 K, benzene-d_6): δ 143.0, 125.5, 124.1, 123.7, 114.1, 29.5, 23.4, 12.2. IR (ATR, 16 scans, cm^{-1}): 2960 (m), 2907 (m), 2867 (w), 2164 (vs), 1629 (vw), 1584 (w), 1435 (s), 1409 (w), 1378 (m), 1362 (w), 1323 (m), 1255 (m), 1181 (m), 1096 (m), 1059 (w), 1021 (w), 934 (m), 791 (s), 745 (vs), 596 (m), 552 (m), 519 (m), 396 (s). MS (EI, 70 eV): *m*/*z* (%) 493 (99) [M]$^+$, 178 (100) [Cp$_2$Ti]$^+$.

Structure Elucidation. Data were collected on the following diffractometers: Bruker Kappa Apex II (**3-*i*-Pr-*i*-Pr** and **7**), STOE-IPDS II (**8** and **9**) and Bruker Kappa APEX II Duo (**10** and **11b**) (Table 3). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods of F^2 (SHELXL-97).[39] For compound **8** contributions of disordered solvent molecules (THF) were removed from the diffraction data with PLATON/SQUEEZE.[40] Diamond was used for graphical representations.[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data of complexes **3-*i*-Pr-*i*-Pr**, **7**, **8**, **9**, **10** and **11b** in cif format and details of the DFT calculations on complexes **3-*i*-Pr-*i*-Pr**, **5-R**, **7**, **8**, **9**, **11b** and full ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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