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Insertion Reactions into the Metal−Alkyl and Metal−Amido Bonds of 1,3-Di(silyl-η-amido)cyclopentadienyl Titanium and Zirconium Complexes

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The synthesis of the methyl complexes $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}Me]$ (M = Ti, Zr) and the results of the insertion reactions into their metal−methyl bonds have been investigated and compared with the similar reactions previously reported for related metal−amido $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(NMe_2)]$ (M = Ti, Zr) and metal−benzyl $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(CH_2Ph)]$ (M = Ti, Zr) compounds. The structural characterization of the resulting η^2-iminocarbamoyl $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}\{\eta^2\text{-}C(NMe_2){=}N(2,6\text{-}Me_2C_6H_3)\}]$, η^2-iminoacyl $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(\eta^2\text{-}CR'{=}NR)]$ (M = Zr, R = 2,6-$Me_2C_6H_3$, R′ = CH_2Ph, Me; M = Zr, R = *t*Bu, R′ = Me; M = Ti, R = 2,6-$Me_2C_6H_3$, R′ = Me), and alkoxo $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}\{OC(CH_2Ph)Ph_2\}]$ complexes and of the asymmetrical bicyclic enediamido compound $[Ti(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}\{(SiMe_2\text{-}\eta\text{-}NtBu)(SiMe_2\text{-}NtBu\text{-}C(\eta\text{-}NR){=}C(Me)(\eta\text{-}NR)\}]$ (R = 2,6-$Me_2C_6H_3$), formed by coupling iminoacyl and iminocarbamoyl ligands, is also described. The molecular structures of the zirconium complexes $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}Me]$ and $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}\{\eta^2\text{-}C(CH_2Ph){=}N(2,6\text{-}Me_2C_6H_3)\}]$- and the titanium derivative $[Ti(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}\{(SiMe_2\text{-}\eta\text{-}NtBu)(SiMe_2\text{-}NtBu\text{-}C(\eta\text{-}NR){=}C(Me)(\eta\text{-}NR)\}]$ (R = 2,6-$Me_2C_6H_3$) have been determined by X-ray diffraction studies.

Introduction

The migratory insertion of unsaturated molecules into the metal−alkyl bonds of transition metal complexes is one of the most important organometallic reactions employed to form C−C bonds under mild conditions. Many catalytic applications and stoichiometric transformations are based on the reactivity of the products resulting from these basic insertion reactions.[1] Versatile transformations of acyl and particularly iminoacyl systems have been reported for cyclopentadienyl group 4[2,3] and group 5[4] metal complexes, and important carbonylation reactions are known for late transition metal compounds.[5,6] Insertion of isocyanides into metal−amido bonds has been less widely studied,[7] and such insertions are only exceptionally[8] preferred to insertions into metal−alkyl bonds.

We have reported previously[9,10] a new class of group 4 metal complexes with a tridentate cyclopentadienyl ligand tethered by two silyl-η-amido groups. These

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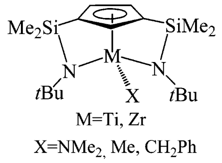
Chart 1



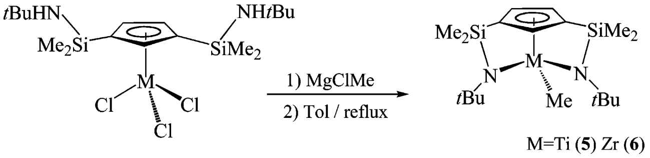
doubly silyl-bridged group 4 metal (CG) amido chelates activated with MAO are efficient catalysts for ethene polymerization despite generating cationic species without the alkyl group required for the insertion reaction. Subsequently, a related singly silyl-η-amido zirconium dicyclopentadienyl compound was reported,[11] which was also found to be an efficient catalyst for olefin polymerization when treated with aluminum activators. Similar observations have been made more recently for $Co^{(I)}$-R alkyl compounds when treated with $B(C_6F_5)_3$[12] or MAO[13] and for $Co^{(I)}$-Cl compounds, without alkyl groups, which show ethene polymerization activity when treated with $LiB(C_6F_5)_4$.[14]

Following the same analogy[15,16] used to relate the silyl-η-amido complexes to bent metallocene systems, the di(silyl-η-amido)cyclopentadienyl compounds might be related to tris(cyclopentadienyl)[17] systems. An analysis of the frontier orbitals based on DFT calculations[10] carried out for this model predicts the high energy of the LUMO orbital of the formally 16-electron $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NR)_2\}R']$ species, which can be used to coordinate the unsaturated insertion reagent (CO, $OCPh_2$, CNR), and only when strongly σ-donor ligands are used does its occupation provide a weak interaction. Moreover, this is the orbital involved in the η^2-coordination of the resulting iminoacyl and iminocarbamoyl ligands.

Generally, a low tendency to undergo insertion reactions should be expected for these types of di(silyl-η-amido)cyclopentadienyl complexes. It was therefore convenient to study the reactivity of the neutral di(silyl-η-amido)cyclopentadienyl complexes represented in Chart 1 and their capacity to undergo insertion reactions of various unsaturated molecules into their unique metal−alkyl and metal−amido bonds.

We report herein the synthesis of the new methyl derivatives $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}Me]$ (M = Ti, Zr) and the use of these and the already reported[9,10] benzyl $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(CH_2Ph)]$ (M = Ti, Zr) and amido $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(NMe_2)]$ (M = Ti, Zr) complexes for a comparative study of the insertion reactions into their metal−methyl, metal−benzyl, and metal-amido bonds. We also report the structural characterization of the resulting η^2-iminocarbamoyl $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}\{\eta^2\text{-}C(NMe_2){=}N(2,6\text{-}Me_2C_6H_3)\}]$, η^2-iminoacyl $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(\eta^2\text{-}CR'{=}NR)]$ (M = Zr, R = 2,6-$Me_2C_6H_3$, R′ = CH_2Ph, Me; M = Zr, R = tBu, R′ = Me; M = Ti, R = 2,6-$Me_2C_6H_3$, R′ = Me), alkoxo $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}\{OC(CH_2Ph)Ph_2\}]$, and enediamido $[Ti\{\eta^5\text{-}C_5H_3\text{-}1\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)\text{-}3\text{-}[SiMe_2\text{-}NtBu\text{-}C(\eta\text{-}NR){=}C(Me)(\eta\text{-}NR)]\}]$ complexes by elemental analysis, NMR spectroscopy, and X-ray diffraction methods.

Scheme 1



Results and Discussion

Synthesis and Characterization of Methyl Complexes. The metal−amido $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(NMe_2)]$ (M = Ti **1**, Zr **2**) and metal−benzyl $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}(CH_2Ph)]$ (M = Ti **3**, Zr **4**) complexes were easily accessible by deprotonation of the di(silylamino)cyclopentadiene $C_5H_4[SiMe_2(NHtBu)]_2$ with strongly basic metal amides $[M(NMe_2)_4]$[18] and metal benzyls $[M(CH_2Ph)_4]$[19] as reported previously.[9,10] However a different synthetic method has to be used to prepare the related methyl derivatives $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)_2\}Me]$ (M = Ti **5**, Zr **6**). They were easily obtained by total alkylation of the mono-cyclopentadienyl complexes $[M\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2NHtBu)_2\}Cl_3]$[20] (M = Ti, Zr) using excess MgClMe, followed by thermal deprotonation with elimination of methane, as shown in Scheme 1. This reaction pathway is consistent with the intermediate formation of the dimethyl compound $[Ti\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}NtBu)(SiMe_2NHtBu)\}Me_2]$, which was detected by its ^1H NMR spectrum (Ti-Me singlets at δ 0.69 and 0.78) after stirring the solution for 12 h at room temperature, although the alternative pathway with initial deprotonation of at least one of the NHtBu groups followed by salt elimination cannot be ruled out.

These methyl compounds were isolated as light yellow **5** and light brown **6** solids in 98% and 85% yield, respectively, and were identified by NMR spectroscopy as C_s symmetric molecules with two equivalent Cp-silyl-η-amido ligands. Crystals of **6** suitable for X-ray diffraction studies were obtained by recrystallization from pentane at −35 °C. The molecular structure of **6** is depicted in Figure 1, and selected bond distances and angles are summarized in Table 1.

The crystal structure of **6** is the first example of a neutral zirconium compound with a tridentate cyclopentadienyl ligand tethered by two silyl-η-amido groups and confirms that the zirconium atom is in a pseudotetrahedral coordination mode largely similar to that found for the related benzyl titanium complex $[Ti\{\eta^5\text{-}$

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6, 9, and 13

	6	9	13
M−Cg[a]	2.1457	2.1932	2.0891
M−N(1)	2.123(2)	2.163(4)	
M−N(2)	2.112(2)	2.167(4)	1.985(3)
M−L	2.318(3) (C10)	2.175(4) (N3) 2.271(5) (C30)	1.936(3) (N4) 2.028(3) (N3)
N(1)−Si(1)	1.738(2)	1.728(4)	1.762(3)
N(2)−Si(2)	1.735(3)	1.739(4)	1.740(3)
C(30)−N(30)		1.286(6)	1.410(4)
C(40)−N(4)			1.397(4)
M−C(30)			2.334(3)
M−C(40)			2.385(3)
C(30)−C(40)			1.411(5)
Cg−M−N(1)	101.23	100.51	
Cg−M−N(2)	100.52	101.21	105.54
Cg−M−L	110.90 (C10)	142.86 (C30) 109.64 (N3)	120.37 (N3) 124.38 (N4)
M−N(1)−Si(1)	104.26(12)		
M−N(2)−Si(2)	104.92(11)		103.80(13)
N(1)−Si(1)−C(1)	95.52(12)		104.47(14)
N(2)−Si(2)−C(4)	94.84(12)		94.49(14)
N(1)−M−N(2)	131.32(10)	128.16(14)	
N(1)−M−L	106.16(10) (C10)	100.02(16) C(30)	
N(2)−M−L	105.77(10) (C10)	95.59(16) C(30) 108.52(15)(N3) 111.44(15) (N3)	106.38(12) (N3) 111.69(11) (N4)
N(3)−C(30)−M(1)		69.1(3)	
C(30)−N(3)−M(1)		77.4(3)	86.97(16)
C(40)−N(4)−M(1)			86.24(18)
N(3)−M(1)-C(1)		33.54(15)	

[a] Cg denotes the centroid of the ring.

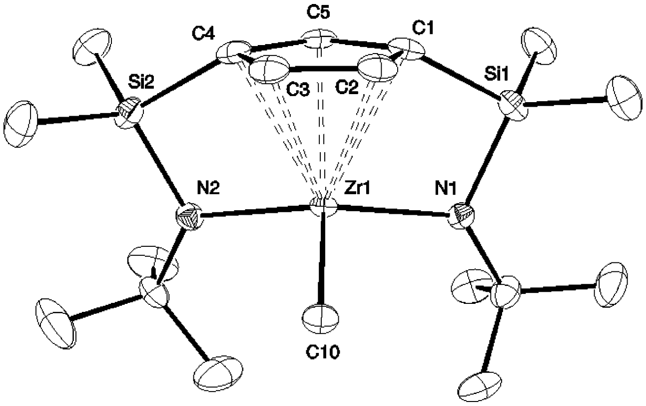

Figure 1. Molecular structure of complex [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}Me], **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for the sake of clarity.

C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}(CH_2Ph)].[10] The N−M−N angle is slightly more open in **6** [131.32(10)°] than in the cationic species [M{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}-{(CH_2Ph)B(C_6F_5)$_3$}]^{9,10} [Ti 126.89(6)°, Zr 126.3(2)°] or in the benzyl titanium compound [Ti{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}(CH_2Ph)] [128.05(6)°].[9]

The Zr−N distances for the silyl-η-amido ligands [2.123(2) and 2.112(2) Å] are slightly longer than those observed in the singly silyl-bridged bis(dimethylamido) derivative [Zr(η^5-$C_5Me_4SiMe_2$-η-N*t*Bu)(NMe_2)$_2$][21] for the Zr−N*t*Bu [2.010(4) Å] and for the Zr−NMe_2 [2.060(5), 2.064(4) Å] bonds. However, the Cg−Zr distance [2.1457 Å] is shorter than that observed [2.233 Å] in the same complex. These differences are in agreement with the higher electron donation of the double silylamido bridge[10] to the metal center.

The Cg−Zr−N [100.52°, 101.23°], Zr−N−Si [104.26(12)°, 104.92(11)°], and C−Si−N [95.52(12)°, 94.84(12)°] angles of the chelated cyclic systems are in the normal range found for related compounds$^{11,21-29}$ or for the cationic doubly bridged complex [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}{(CH_2Ph)B(C_6F_5)$_3$}]:[10] Cg−Zr−N [100.84°, 101.20°], Zr−N−Si [105.56(8)°, 105.68(8)°], and C−Si−N [93.65(8)°, 92.94(9)°].

Insertion Reactions. We have studied the insertion reactions of carbon monoxide (CO), benzophenone ($OCPh_2$), and the isocyanides CNR (R = *t*Bu, 2,6-$Me_2C_6H_3$) into the metal−amido and metal−alkyl bonds of the di(silyl-η-amido)cyclopentadienyl titanium and zirconium [M{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}R] (M = Ti, Zr; R = NMe_2, Me, CH_2Ph) complexes.

We first observed that CO did not react with any of these compounds. This lack of reactivity may be due to the weak electron-donating character of CO, which prevents the coordination of the unsaturated substrate to the metal center in the step before the migratory

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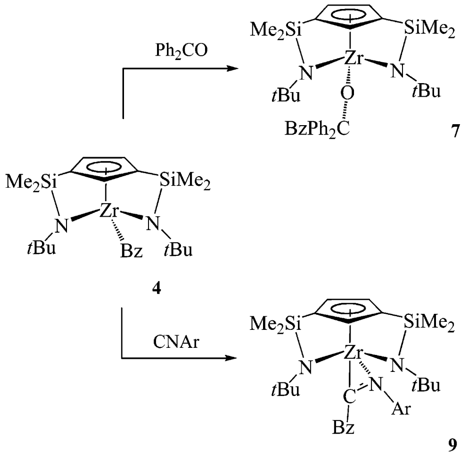
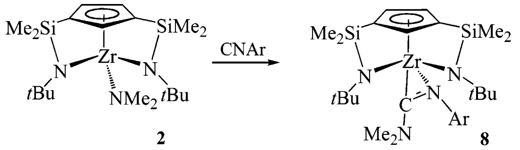
Scheme 2



Scheme 3



insertion.[1] It is also consistent with the absence of a vacant metal orbital in the formally 18-electron metal−amido compounds if the three amido ligands are considered as three-electron donors and the high energy of the vacant metal orbital in the 16-electron metal−alkyl complexes.

Benzophenone did not react with the amido titanium and zirconium complexes despite its more electron-donating character. However, insertion was observed when it was added to a toluene solution of the benzyl zirconium complex **4** (see Scheme 2), where the conversion into the alkoxo derivative [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}{OC(CH_2Ph)Ph_2}] (**7**) was complete after heating for 3 h at 50 °C. Complex **7** was isolated as a yellow microcrystalline solid and characterized by elemental analysis and NMR spectroscopy. However, a similar reaction into the zirconium−methyl bond of complex **6** did not occur, as expected from an electronic perspective due to the lower electron-withdrawing effect of the methyl substituent. Insertion of benzophenone also was not observed in the titanium methyl **5** and benzyl **3** complexes, probably due to the steric crowding associated with the smaller radius of the titanium atom.

The ^{1}H NMR spectrum of complex **7** shows the expected signals for the equivalent silyl-η-amido arms and one singlet at δ 3.61 due to the equivalent methylene protons of the benzyl group which is bound to a Csp^3 atom and observed in the ^{13}C spectrum as a low-field-shifted resonance at δ 88.3, which corresponds to an alkoxo ligand. This behavior confirms that the structure of complex **7** is similar to those described below for complexes **8** and **9**.

The isocyanides CNR (R = *t*Bu, 2,6-$Me_2C_6H_3$) are much more reactive substrates, consistent with their higher electron-donating capacity, although remarkable differences in reactivity are related to their different electrophilic character and steric requirements, the less electronegative and bulkier R substituents providing the less reactive substrates, particularly for the more protected titanium compounds. This is consistent with the lower reactivity observed for the more bulky and less electrophilic CN*t*Bu compared with the more reactive CN(2,6-$Me_2C_6H_3$) for any of the insertion reactions studied. On the other hand, the higher π-bonding contribution makes the metal−amido bond more resistant to insertion reactions, and with very few exceptions[8] the metal−alkyl bonds undergo preferential insertion of organic isocyanides.

As it would be expected, the formally 18-electron dimethylamido derivatives **1** and **2** did not react with CN*t*Bu after being treated for several days at temperatures higher than 100 °C. As shown in Scheme 3, the insertion reaction was only observed for the zirconium complex **2**, despite its stronger Zr−N bond, when its toluene solution treated with CN(2,6-$Me_2C_6H_3$) was heated for 4 h at 100 °C, whereas the titanium complex **1** was recovered unchanged under the same conditions. The different reactivity observed for the titanium and zirconium complexes is consistent with the steric hindrance of the bulkier CN*t*Bu ligand and the larger size of the zirconium atom.

The resulting iminocarbamoyl complex [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}{η^2-C(NMe_2)=N(2,6-$Me_2C_6H_3$)}] (**8**) was isolated as a yellow oily solid and characterized by elemental analysis and NMR spectroscopy.

The ^{1}H and ^{13}C NMR spectra are consistent with the structure proposed in Scheme 3 for compound **8**. The metal, the carbon, and the two nitrogen atoms of the η^2-iminocarbamoyl moiety are located in a plane of symmetry responsible for the equivalency of both N*t*Bu ligands (δ 0.38) and the two aryl-methyl groups of the iminoacyl *Me₂*ArN (δ 2.04) fragment. Nevertheless, the two methyl groups of the migrated dimethylamido ligand are not equivalent and appear as two singlets in the ^{1}H NMR spectrum at δ 2.03 and 2.95. This behavior is consistent with the location of both amido-methyl groups in the plane of symmetry, indicating the high barrier of rotation of the C(sp^2)−NMe_2 bond due to a significant π-bonding contribution. The most relevant features observed in the ^{13}C NMR spectrum of **8** are the low-field signal (δ 213.7) due to the *ipso* carbon of the η^2-iminocarbamoyl ligand and the low value of the difference $\Delta(\delta C_{tert} - \delta CMe)$[30] of 18.4, indicating the small π-bonding contribution of the bridging silylamido ligands, which is lower for the more electron-donating iminocarbamoyl ligands than for the iminoacyl derivatives described below.

The benzyl complexes **3** and **4** did not react when their toluene solutions were heated with CN*t*Bu at temperatures between 20 and 120 °C for several days. However insertion of CN(2,6-$Me_2C_6H_3$) into the zirconium−benzyl bond of complex **4** was observed to give a quantitative conversion into the η^2-iminoacyl complex [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}{η^2-C(CH_2Ph)=N(2,6-$Me_2C_6H_3$)}] (**9**) after heating to 60 °C for 4 h (see Scheme 2). Complex **9** was isolated as a brown solid and identified by elemental analysis and NMR spectroscopy; its molecular structure was determined by X-ray diffraction studies.

The ^{1}H and ^{13}C NMR spectra of **9** show the presence of one *t*Bu (δ 1.21) and two $SiMe_2$ (δ 0.46 and 0.66)

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(30) The difference $\Delta(\delta C_{tert} - \delta CMe)$ in M-NtBu moieties defines the π-bonding contribution in the M−N bond. Wigley, D. E. In *Progress in Inorganic Chemistry*; John Wiley & Sons Inc: New York, 1994; Vol. 42, p 239.

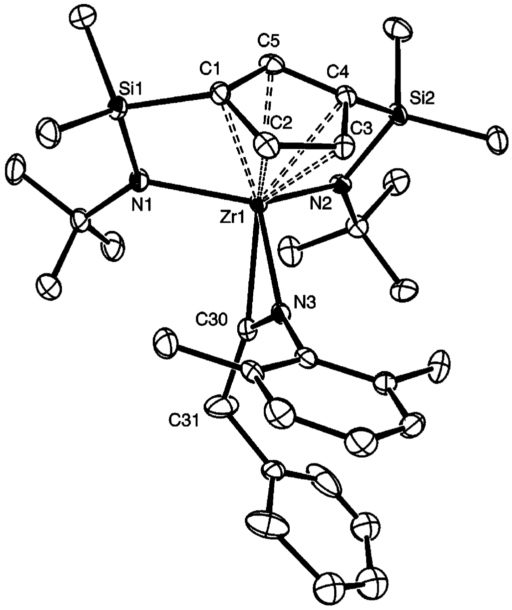


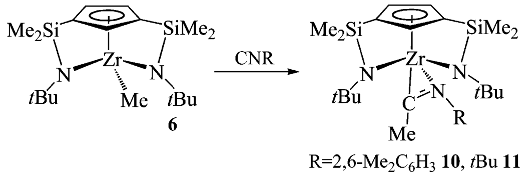
Figure 2. Molecular structure of complex [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}{η^2-C(CH_2Ph)=N(2,6-$Me_2C_6H_3$)}], **9**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for the sake of clarity.

singlets corresponding to two symmetrical $SiMe_2$N*t*Bu units of a C_s symmetric molecule in which the Zr and the N and C atoms of the iminoacyl ligand define the plane of symmetry where the aryl and benzyl-methylidene carbon atoms are also contained. This structural disposition is similar to that proposed above for the related iminocarbamoyl derivative **8** and is consistent with the equivalency of the two aryl-methyl and *t*Bu groups observed as singlets at δ 1.85 and 1.21, respectively, in the ^{1}H NMR spectrum of **8**. In contrast to the behavior discussed above for the iminocarbamoyl complex **8**, the free rotation of the C(sp^2)−CH_2Ph bond also makes the two benzyl methylidene protons observed as one singlet at δ 3.72 equivalent. The most significant signal in the ^{13}C NMR spectrum is that observed at δ 265 for the *ipso* carbon of the η^2-iminoacyl ligand.

The structure proposed for complex **9** was finally confirmed by the X-ray diffraction studies of a single crystal obtained by recrystallization from pentane at −35 °C.

The molecular structure of **9** is represented in Figure 2 along with the labeling system, and bond distances and angles are summarized in Table 1. The zirconium center of complex **9** shows a profoundly distorted trigonal bipyramidal coordination in which the equatorial plane is defined by the iminoacyl-N3 and the two silylamido-N1 and -N2 atoms and the apical positions are occupied by the cyclopentadienyl ring and the iminoacyl-C30 atom. However the constrained Zr1−C30−N3 cycle due to the η^2-coordination of the iminoacyl ligand with a short C30−N3 double bond is responsible for the distortion observed for C30, which is located at a C_g−Zr1−C30 angle of 142.86° (37° away from the linear disposition) rather than occupying the axial position *trans* to the cyclopentadienyl ring. The silylamido Zr1−N1 and Zr1−N2 [2.163(4) and 2.167(4) Å], the ring−centroid Zr−Cg [2.1932 Å], and the Zr−C_{Cp} [between 2.494(5) and 2.518(5) Å] bond distances are slightly longer than those observed for the methyl complex **6**. This is consistent with the less pπ(N)−dπ(Zr) and Cp−dπ(Zr) π-bonding contribution due to the lower electron deficiency of the metal center in a formally 18-electron species containing a three-electron-donor iminoacyl ligand.

Scheme 4



The crystal structure confirms that the Zr1−C30−N3 cycle, the methylene group C31, and the ring *ipso* carbon connected to N3 are coplanar (max. deviation 0.054 Å). The nitrogen (N3) and the carbon (C30) atoms maintain a trigonal-planar environment and are sp^2 hybridized, consistent with the angle sums of 359.3° and 357.9°, respectively.

The orientation of the imino-N facilitates the interaction between the lone pair of its pπ orbital with the LUMO metal orbital to complete the 18-electron configuration. The monoinsertion reaction in singly bridged compounds produces a pseudo-square-pyramidal coordination.[31] However, the diinsertion in the dialkyl derivative [Zr{η^5-C_5Me_4($SiMe_2$-η-N*t*Bu)}Me_2] affords a pseudo-octahedral configuration[27] in which, depending on the R substituent of the isocyanide, one atom of the iminoacyl groups occupies the axial or the equatorial position. When R = *t*Bu, one of the imido-N atoms is in the axial position *trans* to the cyclopentadienyl ring, but when R is a less sterically demanding group (2,6-$Me_2C_6H_3$), one of the imido-N fragments is located in an equatorial position.

The ^{13}C NMR spectrum is also consistent with this proposal and provides additional evidence for the high electron density of the metal resulting from the η^2-coordination of the iminoacyl ligand, as shown by the low value of the difference ($\Delta\delta$ = 19.1),[30] which is an indication of the low π-bonding contribution of the bridging silylamido ligand.

We may conclude that the reactivity of the metal−benzyl bonds is similar to that observed for the related metal−amido bonds, despite being formally 16-electron compounds with one vacant metal orbital. The reactivity found for $OCPh_2$ and CN(2,6-$Me_2C_6H_3$) follows the order of their σ-donor character, whereas the steric hindrance of the bulkier CN*t*Bu ligand may explain its lack of reactivity. Similar electronic effects together with the smaller radius of the titanium and the steric requirements of the ligands used for insertion may be invoked to justify the lack of reactivity of the benzyl-titanium complex **3**.

When similar reactions were studied for the sterically less demanding methyl complexes **5** and **6**, insertion of isocyanide was feasible for both zirconium and titanium complexes when the isocyanides CNR (R = 2,6-$Me_2C_6H_3$, *t*Bu) were used. As shown in Scheme 4, addition of 1 equiv of CNR to toluene solutions of the zirconium complex **6** gave the iminoacyl complexes [Zr{η^5-C_5H_3-1,3-($SiMe_2$-η-N*t*Bu)$_2$}(η^2-CMe=NR)] (R = 2,6-$Me_2C_6H_3$

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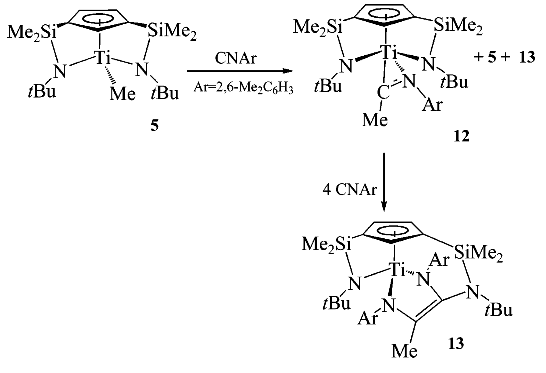
[31] Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

Scheme 5



10, *t*Bu **11**). Formation of **10** proceeded cleanly at room temperature, whereas heating at 50 °C was required to obtain **11** and complete transformation was observed after 12 h. Complexes **10** and **11** were isolated as light brown solids and characterized by elemental analysis and NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra are consistent with the structure found for complex **8**, with two symmetric silyl-η-amido arms and the η^2-iminoacyl ligand located in the plane of symmetry.

Although no reaction was observed for the methyl titanium complex **5** with CN*t*Bu, a slow and more complex reaction was observed when 1 equiv of CN(2,6-$Me_2C_6H_3$) was added to a toluene solution of complex **5** heated to 75 °C for 24 h. As shown in Scheme 5, the insertion led initially to the formation of the corresponding iminoacyl complex **12**, unreacted starting material, and a new compound **13**, which was the unique reaction product when 4 equiv of excess CN(2,6-$Me_2C_6H_3$) were added and the reaction mixture heated at 120 °C for 24 h. Pure compound **12** could not be isolated, whereas the new complex **13** was isolated as a red crystalline solid and identified by elemental analysis and NMR spectroscopy. The molecular structure of **13** was also determined by X-ray diffraction methods.

The ^{1}H and ^{13}C NMR spectra of **13** show the presence of two *t*Bu (δ 0.84 and 0.99), four Si*Me* (δ 0.43, 0.53, 0.66, and 0.67), and four aryl-*Me* (δ 1.85, 2.05, 2.41, and 2.69) singlets corresponding to an asymmetric molecule. In addition, two resonances at δ 111.8 and 128.1 were observed in the gHMBC spectrum which were assigned to an asymmetric chelating $-$N-*C*=*C*-N$-$ moiety. These spectral features are consistent with the presence of an asymmetric enediamido ligand formed by coupling of two C(sp^2) atoms, one from the η^2-iminoacyl ligand, resulting from the insertion of CNAr into the Ti$-$Me bond, and the other from the η^2-iminocarbamoyl ligand, resulting from insertion of a second molecule of CNAr into the Ti$-$N*t*Bu bond of one of the silyl-η-amido arms. The formation of the intermediate compound was detected when the reaction was monitored by ^{13}C NMR spectroscopy in a Teflon-valved NMR tube. On heating at 90 °C for 48 h, a mixture of **12**, **13**, and this intermediate complex, with its characteristic η^2-iminoacyl (δ 246) and η^2-iminocarbamoyl (δ 212) signals, was observed. To the best of our knowledge, this is a unique example of coupling reaction between iminoacyl and iminocarbamoyl ligands to give a type of the known diazabutadiene complexes containing a 2-methyl-3-amido-dad ligand in which TiN_2C_2 framework "flipping" is prevented by the bond to the pendant silyl-η-amido bridge.

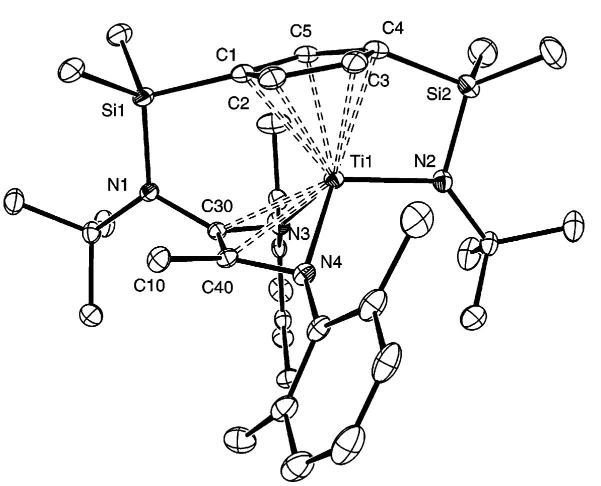


Figure 3. Molecular structure of complex **13**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for the sake of clarity.

This proposal was confirmed by the molecular structure determined by X-ray diffraction studies on a single crystal of **13** isolated from a pentane solution cooled to -20 °C. Figure 3 shows a drawing of the molecular structure of **13**, and selected bond lengths and angles are listed in Table 1.

The titanium atom is at the center of a distorted pseudotetrahedral coordination defined by the centroid of the η^5-cyclopentadienyl ring, the N of the appended silyl-η-amido ligand, and the two N-donors of an asymmetric-chelating enediamido ligand generated by the intramolecular C,C-coupling of the η^2-iminoacyl and η^2-iminocarbamoyl groups. The Ti$-$C$_g$ distance [2.0891 Å], where C$_g$ is the centroid of the cyclopentadienyl ligand, and the Ti$-$N2 bond distance [1.984(3) Å] for the pendant silyl-η-amido ligand are similar to those found for singly bridged dimethylamido derivatives [Ti(η^5-$C_5Me_4SiMe_2$-η-N*t*Bu)($NMe_2)_2$].[21] The Ti$-$N3 and Ti$-$N4 distances [1.936(3) and 2.028(3) Å] for the enediamido ligand are significantly different, the Ti$-$N3 bond distance being similar to the Ti$-$N2 bond, whereas the Ti$-$N4 distance is unexpectedly 0.09 Å longer. The N(4)$-$C(40) and N(3)$-$C(30) bond distances of 1.397(4) and 1.410(4) Å are consistent with the presence of single C$-$N bonds, and the C30$-$C40 distance of 1.411(5) Å is in the range expected for a C=C double bond. The five-membered TiN_2C_2 ring of the dad ligand is folded along the N(3)$-$N(4) axis by 65.8°, providing the less favorable *prone* orientation observed for dad-Ti compounds in solution,[32,33] forced by the bond to the pendant amido group, in contrast with the *supine* conformation reported for group 4 enediamido complexes.[27,32-34] The Ti$-$C30 and Ti$-$C40 bond lengths of 2.334(3) and 2.385(3) Å are in the range expected for the π-coordination to the C=C bond to the titanium center.

Conclusions

We have found that the di(silyl-η-amido)cyclopentadienyl titanium and zirconium complexes are rather

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(32) Amor, F.; Gomez-Sal, P.; Royo, P.; Okuda, J. *Organometallics* **2000**, *19*, 5168.

(33) Scholz, J.; Hadi, G. A.; Thiele, K. H.; Gorls, H.; Weimann, R.; Schumann, H.; Sieler, J. *J. Organomet. Chem.* **2001**, *626*, 243.

(34) Pindado, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1998**, 393.

stable molecules with a very low acidic character that show the metal center sterically protected by two bulky *t*Bu groups. For these reasons their M−NMe$_2$, M−Bz, and M−Me bonds show a limited reactivity where only selected reagents and favorable conditions produce insertion reactions. The absence of reactivity observed for insertion of CO might be associated with the low σ-donor capacity of this ligand, and the reactivity found for OCPh$_2$ and CNR follows the order of their σ-donor character. The lack of reactivity of the benzyl- and the dimethylamido-titanium complexes in comparison with the higher reactivity observed for the zirconium derivatives demonstrates that these insertion reactions are controlled by steric requirements. The M−NMe$_2$ and M−CH$_2$Ph bonds are sterically more protected and less reactive than the M−Me bonds, justifying the idea that only CN(2,6-Me$_2$C$_6$H$_3$) can be inserted into the Zr−NMe$_2$ and Zr−CH$_2$Ph bonds.

The steric hindrance of the bulkier CN*t*Bu ligand may explain its lack of reactivity with the benzyl- and dimethylamido-zirconium complexes.

The higher electron-withdrawing effect of Bz in relation to Me groups could explain why benzophenone (a weak σ-donor ligand) reacts with [Zr{η^5-C$_5$H$_3$-1,3-(SiMe$_2$-η-N*t*Bu)$_2$}(CH$_2$Ph)] (**4**) but not with [Zr{η^5-C$_5$H$_3$-1,3-(SiMe$_2$-η-N*t*Bu)$_2$}Me] (**6**). The milder conditions required in all of the insertion reactions with CN(2,6-Me$_2$C$_6$H$_3$), compared with CN*t*Bu, may be due to its lower steric demands and the higher electrophilic character of its carbon atom involved in the nucleophilic migratory insertion.

The reaction of **5** with excess CN(2,6-Me$_2$C$_6$H$_3$) proceeds via a double insertion reaction that leads to the formation of an intermediate species containing η^2-iminoacyl and η^2-iminocarbamoyl ligands, which undergo an unprecedented further C=C coupling reaction to produce an asymmetrical bicyclic enediamido complex.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl; toluene from sodium; hexane from sodium−potassium amalgam. Unless otherwise stated, reagents were obtained from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity VXR-300 or Varian Unity 500 Plus instruments. Chemical shifts, in ppm, are measured relative to residual ^{1}H and ^{13}C resonances for benzene-d_6 used as solvent [7.15 (^{1}H) and 128.0 (^{13}C)], and coupling constants are in Hz. C, H, and N analysis were carried out with a Perkin-Elmer 240 C analyzer.

Preparation of [Ti{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$}Me] (5). MgClMe (0.35 mL, 1.05 mmol), 3 M in THF, was added to a solution of [Ti{η^5-C$_5$H$_3$-1,3-(SiMe$_2$NH*t*Bu)$_2$}Cl$_3$] (0.16 g, 0.3 mmol) in toluene (50 mL) to −78 °C. The reaction mixture was then warmed to room temperature and stirred under reflux for 12 h. The solvent was then removed under vacuum, and the residue was extracted into hexane (2 × 50 mL). After filtration and removal of the solvent, complex **5** was isolated as a light yellow solid (0.12 g, 0.32 mmol, 98%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 0.41 (s, 6H, SiMe), 0.42 (s, 6H, SiMe), 0.59 (s, 3H, TiMe), 1.40 (s, 18H, N*t*Bu), 6.46 (m, 1H, C$_5$H$_3$), 6.61 (m, 2H, C$_5$H$_3$). ^{13}C NMR (300Mz, C$_6$D$_6$, 20 °C, TMS): 1.4 (SiMe), 1.9 (SiMe), 34.7 (N*t*Bu), 39.5 (TiMe), 57.8 (N*t*Bu$_{\rm ipso}$), 115.5 (C$_5$H$_{3-\rm ipso}$), 126.4 (C$_5$H$_3$), 130.1 (C$_5$H$_3$). Anal. Found: C 55.99, H 9.39, N 7.16. Calc: C 56.22, H 9.44, N 7.28.

Preparation of [Zr{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$}Me] (6). MgClMe (0.49 mL, 1.49 mmol), 3 M in THF, was added to a solution of [Zr{η^5-C$_5$H$_3$-1,3-(SiMe$_2$NH*t*Bu)$_2$}Cl$_3$] (0.25 g, 0.49 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was then warmed to room temperature and stirred under reflux for 12 h. The solvent was then removed under vacuum, and the residue was extracted into hexane (2 × 25 mL). After filtration and removal of the solvent, complex **6** was isolated as a light brown solid (0.18 g, 0.42 mmol, 85%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 0.13 (s, 3H, ZrMe), 0.45 (s, 6H, SiMe), 0.46 (s, 6H, SiMe), 1.28 (s, 18H, N*t*Bu), 6.58 (br s, 3H, C$_5$H$_3$). ^{13}C NMR (300Mz, C$_6$D$_6$, 20 °C, TMS): 2.6 (SiMe), 3.0 (SiMe), 26.4 (ZrMe), 35.3 (*t*BuN), 55.3 (N*t*Bu$_{\rm ipso}$), 115.5 (C$_5$H$_{3-\rm ipso}$), 123.8 (C$_5$H$_3$), 131.6 (C$_5$H$_3$). Anal. Found: C 49.93, H 8.41, N 6.55. Calc: C 50.53, H 8.48, N 6.55.

Preparation of [Zr{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$}{η-OC(CH$_2$Ph)(C$_6$H$_5$)$_2$}] (7). A solution of **4** (0.53 g, 1.05 mmol) in toluene (40 mL) was added to a suspension of benzophenone (126 mg, 1.05 mmol) in the same solvent at room temperature. The mixture was stirred for 3 h at 50 °C. After removal of the solvent under vacuum the residue was extracted into hexane (25 mL), and after filtration and removal of the hexane complex **7** (0.62 g, 0.91 mmol, 95%) was isolated as a yellow microcrystalline solid. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 0.52 (s, 6H, SiMe$_2$), 0.55 (s, 6H, SiMe$_2$), 1.34 (s, 18H, N*t*Bu), 3.61 (s, 2H, CH$_2$Ph), 5.59 (m, 1H, C$_5$H$_3$), 6.91 (m, 2H, C$_5$H$_3$), 6.9−7.7 (m, 15H, C$_6$H$_5$). ^{13}C NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 3.4 (SiMe$_2$), 3.4 (SiMe$_2$), 36.1 (N*t*Bu), 50.4 (CH$_2$-Ph), 55.2 (N*t*Bu), 88.3 (OC$_{\rm ipso}$), 118.6 (C$_5$H$_{3-\rm ipso}$), 120.8 (C$_5$H$_3$), 126.3 (C$_5$H$_3$), 127−131 (15C, Ph), 135.5 (C$_6$H$_{3-\rm ipso}$), 137.8 (C$_6$H$_{3-\rm ipso}$), 148.1 (C$_6$H$_{5-\rm ipso}$). Anal. Found: C 64.33, H 7.63, N 3.91. Calc: C 64.76, H 7.34, N 4.08.

Preparation of [Zr{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$}{η^2-C(NMe$_2$)=N(2,6-Me$_2$C$_6$H$_3$)}] (8). CN(2,6-Me$_2$C$_6$H$_3$) (0.12 g, 0.92 mmol) was added to a solution of **2** (0.42 g, 0.92 mmol) in toluene (40 mL). The mixture was heated for 4 h at 100 °C. The solvent was removed under vacuum, and the residue was extracted into pentane (25 mL). After filtration and removal of the solvent complex **8** was isolated as a yellow oil (0.49 g, 0.83 mmol, 91%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 0.57 (s, 6H, SiMe$_2$), 0.72 (s, 6H, SiMe$_2$), 1.38 (s, 18H, N*t*Bu), 2.04 (s, 3H, NMe$_2$), 2.05 (s, 6H, Me$_2$C$_6$H$_3$), 2.95 (s, 3H, NMe$_2$), 6.11 (m, 2H, C$_5$H$_3$), 7.18 (m, 1H, C$_5$H$_3$). ^{13}C NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 3.1 (SiMe$_2$), 5.7 (SiMe$_2$), 19.8 (Me$_2$C$_6$H$_3$), 36.5 (N*t*Bu), 45.0 (NMe$_2$), 54.9 (N*t*Bu), 119.3 (C$_5$H$_{3-\rm ipso}$), 120.2 (C$_5$H$_3$), 124.9 (C$_5$H$_3$), 128.3 (C$_6$H$_3$), 130.6 (C$_6$H$_3$), 131.4 (C$_6$H$_3$), 150.2 (C$_6$H$_{3-\rm ipso}$), 213.7 (CN$_{\rm ipso}$). Anal. Found: C 57.57, H 8.31, N 9.41. Calc: C 57.18, H 8.23, N 9.53.

Preparation of [Zr{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$}{η^2-C(CH$_2$Ph)=N(2,6-Me$_2$C$_6$H$_3$)}] (9). A solution of **4** (0.41 g, 0.81 mmol) in toluene (40 mL) was added to a suspension of CN-(2,6-Me$_2$C$_6$H$_3$) (0.11 g, 0.81 mmol) in the same solvent at room temperature. The mixture was stirred for 4 h at 60 °C. After removal of the solvent under vacuum the residue was extracted into hexane (25 mL), and after filtration and removal of the hexane complex **9** (0.44 g, 0.70 mmol, 86%) was isolated as a light brown solid. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 0.46 (s, 6H, SiMe$_2$), 0.66 (s, 6H, SiMe$_2$), 1.21 (s, 18H, N*t*Bu), 1.85 (s, 6H, Me$_2$C$_6$H$_3$), 3.72 (s, 2H, CH$_2$Ph), 6.21 (m, 1H, C$_5$H$_3$), 7.3 (m, 2H, C$_5$H$_3$), 6.82−7.30 (m, 8H, C$_6$H$_5$). ^{13}C NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): δ 2.9 (SiMe$_2$), 5.2 (SiMe$_2$), 18.9 (Me$_2$C$_6$H$_3$), 36.4 (N*t*Bu), 46.7 (CH$_2$Ph), 55.5 (N*t*Bu), 119.3 (C$_5$H$_3$), 119.6 (C$_5$H$_{3-\rm ipso}$) 126.1 (C$_5$H$_3$), 126.8 (C$_6$H$_5$), 128.3 (C$_6$H$_5$), 128.6 (C$_6$H$_5$), 128.7 (C$_6$H$_5$), 130.8 (C$_6$H$_5$), 131.7 (C$_6$H$_5$), 135.9 (C$_6$H$_{3-\rm ipso}$), 147.5 (C$_6$H$_{5-\rm ipso}$), 265.0 (CN$_{\rm ipso}$). Anal. Found: C, 62.31 H 7.83, N 6.53. Calc: C 62.40, H 7.78, N 6.62.

Preparation of [Zr{η^5-C$_5$H$_3$-1,3-[SiMe$_2$-η-N*t*Bu)]$_2$)}{η^2-CMe=N(2,6-Me$_2$C$_6$H$_3$)}] (10). Toluene (20 mL) was added to a mixture of complex **6**, [Zr{η^5-C$_5$H$_3$-1,3-(SiMe$_2$-η-N*t*Bu)$_2$}Me]

Table 2. Crystallographic Data for the X-ray Structural Analysis of 6, 9, and 13

	6	**9**	**13**
empirical formula	C18 H36 N2 Si2 Zr	C33 H49 N3 Si2 Zr	C36 H54 N4 Si2 Ti
fw	427.89	635.15	646.91
color, shape	colorless/block	yellow/prism	orange/block
cryst size (mm)	0.71 0.479 0.433	0.561 0.443 0.108	0.412 0.396 0.194
cryst syst	monoclinic	monoclinic	triclinic
space group	*P*21/*n* (No.14)	*P*21/*c* (No.14)	$P\bar{1}$ (No.2)
a (Å)	11.3691(15)	11.119(2)	9.7722(10)
b (Å)	13.9028(9)	19.430(4)	11.3369(4)
c (Å)	15.137(2)	15.805(2)	17.0066(16)
α (deg)			98.372(6)
β (deg)	108.131(12)	106.355(11)	102.866(10)
γ (deg)			99.863(7)
V (Å^3)	2273.8(4)	3276.4(10)	1776.2(3)
Z	4	4	2
T (K)	200	200	200
ρ_{calcd} (mg m^{-3})	1.250	1.288	1.210
F_{000}	904	1344	696
radiation	Mo	Mo	Mo
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.591	0.434	0.338
θ range (deg)	3.06−27.50	3.01−27.53	3.04−27.50
data collected (*h*,*k*,*l*)	±14,+18/−17, ±19	±14, ±25, ±20	±12, ±14, ±22
no. of reflns collected	18 641	27 467	36 668
no. of indep reflns/R_{int}	5211/0.0727	7529/0.1751	8058/0.0663
no. of obsd reflns [$I > 2\sigma(I)$]	3843	4388	5192
no. of params refined	208	350	388
R1 (obsd/all)	0.0402/0.0683	0.0636/0.1359	0.0641/0.1097
wR2 (obsd/all)	0.0886/0.1001	0.1210/0.1446	0.1466/0.1654
GOF	1.065	1.020	1.023
max./min. $\Delta\rho$ (e Å^{-3})	0.847/−0.540	0.534/−0.653	0.551/−0.449

(0.55 g, 1.29 mmol), and xylyl isocyanide, CN(2,6-$Me_2C_6H_3$) (0.16 g, 1.29 mmol). The reaction mixture was then stirred for 12 h at room temperature. The solvent was removed under vacuum and the residue extracted into pentane (20 mL). After filtration and removal of the solvent complex **10** was isolated as a light brown solid (0.66 g, 1.19 mmol, 93%). ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): δ 0.47 (s, 6H, SiMe), 0.69 (s, 6H, SiMe), 1.30 (s, 18H, *t*BuN), 1.82 (s, 6H, $Me_2C_6H_3$), 2.05 (s, 3H, CMe), 6.28 (m, 2H, C_5H_3), 6.88−6.98 (m, 3H, C_6H_3) 7.14 (m, 1H, C_5H_3). ^{13}C NMR (300Mz, C_6D_6, 20 °C, TMS): 3.0 (SiMe), 4.9 (SiMe), 18.4 ($Me_2C_6H_3$), 23.4 (CMe), 36.3 (*t*BuN), 55.6 (N*t*Bu$_{ipso}$), 119.2 (C_5H_3), 119.6 (C_5H_{3-ipso}), 126.0 (C_5H_3), 128.6 (C_6H_3), 132.0 (C_6H_3), 147.1 (C_6H_{3-ipso}), 267.1 (CN$_{ipso}$). Anal. Found: C 57.61, H 8.28, N 7.41. Calc: C 58.01, H 8.11, N 7.52.

Preparation of [Zr{η^5-C_5H_3-1,3-[$SiMe_2$-η-N*t*Bu)]$_2$)}{η^2-CMe=N*t*Bu}] (11). CN*t*Bu (0.034 g, 0.40 mmol) was added to a solution of **6** (0.17 g, 0.41 mmol) in toluene (20 mL) at room temperature. The reaction mixture was then heated to 50 °C and stirred for 12 h. The solvent was then removed under vacuum and the residue extracted into pentane (20 mL). After filtration and removal of the solvent complex **11** was isolated as a light brown oily solid (0.18 g, 0.36 mmol, 91%). ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): δ 0.48 (s, 6H, SiMe), 0.70 (s, 6H, SiMe), 1.07 (s, 9H, *t*BuN), 1.20 (s, 18H, *t*BuN), 2.55 (s, 3H, CMe), 6.67 (m, 2H, C_5H_3), 7.23 (m, 1H, C_5H_3). ^{13}C NMR (300Mz, C_6D_6, 20 °C, TMS): 2.8 (SiMe), 5.4 (SiMe), 24.3 (CMe), 29.7 (CN*t*Bu), 36.3 (*t*BuN), 55.3 (N*t*Bu$_{ipso}$), 62.2 (CMe_3), 117.4 (C_5H_{3-ipso}), 120.1 (C_5H_3), 132.9 (C_5H_3), 258.6 (CMe). Anal. Found: C 53.92, H 8.94, N 7.97. Calc: C 54.06, H 8.88, N 8.22.

Formation of [Ti{η^5-C_5H_3-1,3-[$SiMe_2$-η-N*t*Bu)]$_2$)}{η^2-CMe=N(2,6-$Me_2C_6H_3$)}] (12). Transformation of complex **5** into complex **12** is slow, and it is not complete although more than 1 equiv was added to a solution of complex **5** in benzene and the reaction mixture heated to 70 °C. Formation of complex **13** was observed before the transformation of **5** into **12** was complete. Isolation of complex **12** was not possible. ^{1}H NMR of **12** (300 MHz, C_6D_6, 20 °C, TMS): δ 0.45 (s, 6H, SiMe), 0.71 (s, 6H, SiMe), 1.33 (s, 18H, *t*BuN), 1.78 (s, 6H, $Me_2C_6H_3$), 2.14 (s, 3H, CMe), 6.20 (m, 2H, C_5H_3), 6.80−7.1 (m, 3H, $Me_2C_6H_3$), 7.30 (m, 1H, C_5H_3).

Preparation of [Ti(η^5-C_5H_3{($SiMe_2$-η-N*t*Bu)($SiMe_2$-N*t*Bu-C(η-NR)=C(Me)(η-NR)}], R = (2,6-$Me_2C_6H_3$) (13). Four equivalents of CN(2,6-$Me_2C_6H_3$) (0.23 g, 1.80 mmol) were added to a solution of **5** (0.17 g, 0.45 mmol) in toluene (15 mL) at room temperature. The reaction mixture was heated to 75 °C for 24 h and to 120 °C for another 24 h. The solvent was then removed under vacuum and the residue extracted into pentane (20 mL). After filtration and removal of the solvent complex **13** was isolated as a red solid (0.23 g, 0.35 mmol, 80%). ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): 0.43 (s, 3H, SiMe), 0.53 (s, 3H, SiMe), 0.66 (s, 6H, SiMe), 0.84 (s, 9H, *t*Bu), 0.99 (s, 9H, *t*Bu), 1.85 (s, 3H, CMe), 2.05 (s, 3H, $Me_2C_6H_3$), 2.41 (s, 3H, $Me_2C_6H_3$), 2.69 (s, 3H, $Me_2C_6H_3$), 2.71 (s, 3H, $Me_2C_6H_3$), 5.92 (m, 1H, C_5H_3), 6.83 (m, 1H, C_5H_3), 6.84 (m, 1H, C_6H_3), 6.84 (m, 1H, C_6H_3), 6.87 (m, 2H, C_6H_3), 7.01 (m, 1H, C_5H_3), 7.02 (m, 2H, C_6H_3). ^{13}C NMR (300 MHz, C_6D_6, 20 °C, TMS): 1.7 (SiMe), 2.9 (SiMe), 4.0 (SiMe), 7.0 (SiMe), 19.4 (CMe), 20.7 ($Me_2C_6H_3$), 21.8 ($Me_2C_6H_3$), 23.9 ($Me_2C_6H_3$), 24.3 ($Me_2C_6H_3$), 32.0 (N*t*Bu), 33.6 (N*t*Bu), 55.2 (N*t*Bu$_{ipso}$), 59.2 (N*t*Bu$_{ipso}$), 110.9 (C_5H_{3-ipso}), 111.8 (CMe$_{ipso}$), 119.7 (C_5H_3), 121.6 (C_5H_{3-ipso}), 122.2 (C_5H_3), 123.5 (C_5H_3), 124.4 (C_6H_3), 126.8 (C_6H_3), 127.3 (C_6H_3), 128.1 (C=CMe$_{ipso}$), 128.6 (C_6H_3), 129.7 (C_6H_3), 130.9 (C_6H_3), 133.2 (C_6H_3), 133.3 (C_6H_3), 147.6 (C_6H_{3-ipso}), 151.1 (C_6H_{3-ipso}). Anal. Found: C 66.84, H 8.41, N 8.76. Calc: C 66.84, H 8.41, N 8.66.

Crystal Structure Determination. Selected crystals of **6**, **9**, and **13** were mounted on the top of a glass fiber using perfluoropolyether oil and cooled to 200 K. Data collection was performed on a Nonius KappaCCD single-crystal diffractometer. Crystal structure was solved by direct methods and refined using full-matrix least squares on F^2. All non-hydrogen atoms were anisotropically refined except for three carbon atoms in a disordered phenyl ring in compound **9**. All H atoms were placed in calculated positions and refined using a riding model. Crystallographic data and details of refinement of **6**, **9**, and **13** are summarized in Table 2.

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Supporting Information Available: Tables of crystal data, data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for complex **6**, **9**, and **13** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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