Organometallics **1996,** *15,* 5577−5585

Synthesis and Reactivity of [(Amidosilyl)cyclopentadienyl]titanium and -zirconium Complexes. X-ray Molecular Structure of $[Zr\{\eta^5:\eta^1-C_5H_4SiMe_2(\mu-O)\}Cl_2\{H_2N(CHMe)Ph\}]_2$[†]

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New half-sandwich (amidosilyl)cyclopentadienyl complexes of titanium(IV) and zirconium(IV) were synthesized from the chlorosilyl-substituted cyclopentadienyl precursors $[M(\eta^5-C_5H_4SiMe_2Cl)Cl_3]$ (M = Ti (**1a**), Zr (**1b**)). The reaction of $[Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3]$ (**1a**) with LiNHR in the presence of NEt_3 gives the $[Ti(\eta^5:\eta^1-C_5H_4SiMe_2NR)Cl_2]$ (R = ^tBu (**2a**), (±)-CH(Me)Ph (**3a**)) complexes. Similarly, the addition of 2 equiv of $LiN(SiMe_3)_2$ to complex **1a** affords the diamido derivative $[Ti(\eta^5-C_5H_4SiMe_2Cl)Cl\{N(SiMe_3)_2\}_2]$ **(4a)**. The amidotitanium complex $[Ti(\eta^5:\eta^1-C_5H_4SiMe_2NH^tBu)Cl_2(NH^tBu)]$ **(5a)** is prepared, in low yield, by reacting **1a** with $NH_2{}^tBu$ in a 1:3 molar ratio. In this reaction, the presence of **2a** is also detected. The same complexes **2a** and **3a** may also be obtained by reaction of the trichloro compound **1a** with NH_2R and NEt_3 in a 1:1:2 molar ratio. The reaction of **2a** with $Tl(C_5H_5)$ gives the mixed-dicyclopentadienyl derivative $[Ti(\eta^5:\eta^1-C_5H_4SiMe_2N^tBu)(\eta^5-C_5H_5)Cl]$ (**6a**). The dialkyl derivatives $[Ti(\eta^5:\eta^1-C_5H_4SiMe_2NR)R'_2]$ (R = ^tBu, R′ = CH_3 (**7a**), CH_2Ph (**8a**); R = CH(Me)-Ph, R′ = CH_3 (**9a**), CH_2Ph (**10a**)) have been isolated by reaction of 2 equiv of MgClMe or 1 equiv of $Mg(CH_2Ph)_2 \cdot 2THF$ with the dichlorides **2a** and **3a**. The analogous reaction of **2a** with 1 equiv of $MgCl(CH_2Ph)$ affords the chloro alkyl derivative $[Ti(\eta^5:\eta^1-C_5H_4SiMe_2N^tBu)(CH_2Ph)Cl]$ (**11a**). The reaction of complexes **2a** and **3a** with CO_2 leads to their conversion into the reported oxo derivative $[Ti\{\mu-(\eta^5-C_5H_4SiMe_2O)\}Cl_2]_2$ with elimination of alkyl isocyanate O=C=NR (R = ^tBu, (±)-CH(Me)Ph) as the unique organic product. Addition of 1 equiv of $LiN(SiMe_3)_2$ to a diethyl ether solution of $[Zr(\eta^5-C_5H_4SiMe_2Cl)Cl_3]$ **(1b)** gives the monoamido derivative $[Zr(\eta^5-C_5H_4SiMe_2Cl)Cl_2\{N(SiMe_3)_2\}]$ **(2b)**. The related reaction of the zirconium derivative **1b** with $LiNH^tBu$ in the presence of NEt_3 produces a mixture of two compounds, $[Zr(\eta^5:\eta^1-C_5H_4SiMe_2N^tBu)Cl_2]$ **(3b)** and $[Zr(\eta^5-C_5H_4SiMe_2NH^tBu)Cl_3(NEt_3)]$ **(4b)**. Pure **3b** can be isolated by recrystallization of this mixture, but attempts to isolate the pure compound **4b** were unsuccessful. The analogous reaction of **1b** with 1 equiv of LiNHCH(Me)Ph in the presence of NEt_3 gives the related zirconium compound $[Zr\{\eta^5-C_5H_4SiMe_2[NH(CHMe)Ph]\}Cl_3(NEt_3)]$ (**5b**), which cannot be obtained as an analytically pure solid and is identified by ^1H NMR spectroscopy. When water-saturated toluene is used to prepare **5b**, the oxo-zirconium derivative $[Zr\{\eta^5:\eta^1-C_5H_4SiMe_2(\mu-O)\}Cl_2\{H_2N(CHMe)Ph\}]_2$ **(6b)** is obtained by slow precipitation. Compound **6b** has been characterized by X-ray crystallography.

Introduction

Since the report of a new generation of group 4 bent metallocenes containing bridged cyclopentadienyl ligands, suitable as olefin polymerization catalysts to produce high-density polyethylenes and isotactic and syndiotactic polyolefins, there has been increasing interest in the development of the chemistry of such *ansa*-metallocene-based systems.[1] Replacement of cyclopentadienyl ring hydrogens by various substituents has been shown to result in significant changes in both steric and electronic effects on the metal centers.[2] In addition to the *ansa* complexes particular efforts have been made to synthesize cyclopentadienyl rings with a pendant donor group acting as a bidentate ligand bonded to the metal center,[3] where one three-electron amido group occupies the site of one of the cyclopentadienyl rings of the *ansa* complex. The so-called half-sandwich metallocenes of constrained geometry catalysts (CGC), as alternatives to Kaminsky and Brintzinger type catalysts, are highly active systems producing α-olefin polymers and ethylene/α-olefin copolymers with remarkable properties.[4] While mono- and dicyclopentadienyl type derivatives are easily accessible by various standard methods,[5] constrained-geometry complexes of group 4 transition metals have

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[†] Dedicated to Professor Rafael Usón on the ocassion of his 70 birthday.

[‡] X-ray diffraction studies.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

[1] (a) Brintzinger, H. H.; Fisher, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 225.

[2] Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

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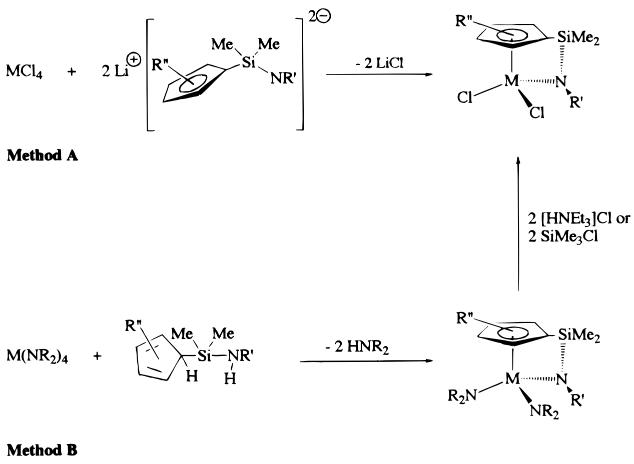
Scheme 1



rarely been described.[4,6] The strategies employed to develop efficient synthetic procedures for such compounds are based on a metathetical reaction using the dilithium salt of the $[(C_5R_4)SiMe_2NR']^{2-}$ dianions (Scheme 1, method **A**) to afford the dichloro derivatives of the type $M[(C_5R_4)SiMe_2NR']Cl_2$ (M = Ti, Zr, Hf)[6c−f] and the reaction of homoleptic metal amides $M(NR_2)_4$ with the bifunctional $[(C_5R_4H)SiMe_2NHR']$ ligand via amine elimination (Scheme 1, method **B**) to produce the diamido $M[(C_5R_4)SiMe_2NR'](NR_2)_2$[6g−k,7] (M = Ti, Zr, Hf) compounds almost quantitatively. Method **A** leads to very poor yields[6k] with unsubstituted cyclopentadienyl rings but seems to be a convenient method for substituted cyclopentadienyl ligands.[6d−f] Method **B** represents an excellent general synthetic method for the diamido half-sandwich derivatives, but subsequent reactions with HCl or $NEt_3{\cdot}HCl$ are required to obtain the corresponding dichlorides[6h,k,7] and may lead to the formation of mixtures or amine adducts where the amine ligand, which makes them undesirable for catalytic purposes, has to be removed by addition of Lewis acids. Recently, Petersen and co-workers have used $SiMe_3Cl$ as an alternative strategy to the protic reagents, providing a suitable quantitative route to the dichloro complexes.[6k]

In this paper, we report efficient synthetic routes to constrained-geometry complexes of titanium from a suitable chlorodimethylsilyl-substituted monocyclopentadienyltitanium complex as starting material.[8] The different behavior observed for the analogous zirconium derivatives is also described. Interestingly, the methods reported here allow the introduction of chiral fragments into the amido group using titanium and zirconium as metal centers and give rise to a potentially useful series of C_1-symmetrical complexes of group IV elements.[9]

Results and Discussion

Titanium Derivatives. Reaction of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**) with LiNHR in the presence of NEt_3 in a 1:1:1 molar ratio, in hexane at −60 °C, led to $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NR)Cl_2]$ (R = ^tBu (**2a**), CH(Me)Ph (**3a**)[9e]) compounds which contain the bidentate η^1-(amidosilyl)-η^5-cyclopentadienyl ligand and which were isolated as orange microcrystalline solids in about 70% yield. In a similar reaction the addition of 1 or 2 equiv of $LiN(SiMe_3)_2$ to $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a)** in hexane at room temperature gives respectively the previously reported[8] monoamido species and the new diamido titanium compound with a (chlorodimethylsilyl)cyclopentadienyl ring, $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl\{N(SiMe_3)_2\}_2]$ **(4a**), obtained as orange crystals in 66% yield (Scheme 2). The isolation of **4a** suggests that both Ti−Cl bonds are more reactive than the Si−Cl bond toward polar $LiNR_2$ reagents.

For this reason we propose that the reaction of **1a** with LiNHR (molar ratio 1:1) proceeds with the formation of the amidotitanium derivative $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_2(NHR)]$ as an intermediate species, which is further transformed by subsequent elimination of HCl from the silicon-bonded chlorine in the presence of NEt_3 with precipitation of $NEt_3{\cdot}HCl$ and formation of compounds **2a** and **3a**. However, reactions with less polar reagents such as water[8] take place at both Si−Cl and Ti−Cl bonds, which are simultaneously hydrolyzed. Similar behavior is also observed in the reaction of **1a** with primary amines (NH_2R), the final product depending on the nature of the amine used to neutralize the HCl evolved in the aminolysis. In the first step the aminolysis of the Si−Cl or Ti−Cl bond can take place and compound **1a** reacts with 1 equiv of NH_2R to give $[Ti(\eta^5\text{-}C_5H_4SiMe_2NHR)Cl_3]$ (**A**) or $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_2NHR]$ (**B**) intermediate species (Scheme 3). In the presence of NEt_3, **A** and **B** are transformed via an intramolecular elimination of HCl involving the second chlorine atom from the Ti−Cl (**A**) or Si−Cl (**B**) bond, with precipitation of $Et_3N{\cdot}HCl$ and formation of the constrained derivatives **2a** and **3a**. When the amine in excess is the primary amine $NH_2{}^tBu$ (1:3 molar ratio), there is a competitive reaction pathway. Species **A** and **B** may react in the same way, with precipitation of $^tBuH_2N{\cdot}HCl$ to give **2a**, or alternatively, the Ti−Cl from **A** or the Si−Cl from **B** may react with a second $NH_2{}^tBu$ molecule, with precipitation of $^tBuH_2N{\cdot}HCl$ and formation of **5a**. In the latter case, the participation of a second Ti−Cl bond cannot be ruled out and the final product obtained is a mixture of **2a**, **5a**, and other unidentified substances, from which only **5a** can be isolated in low yield (16%) after recrystallization from toluene/hexane at −40° C.

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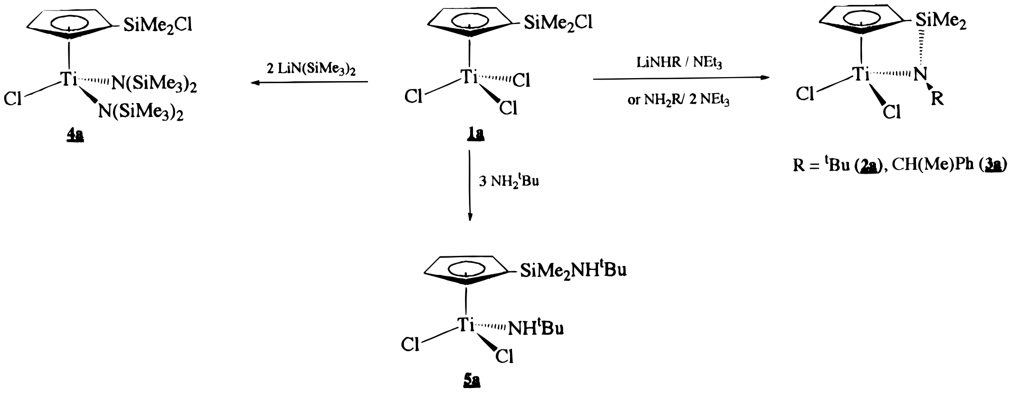
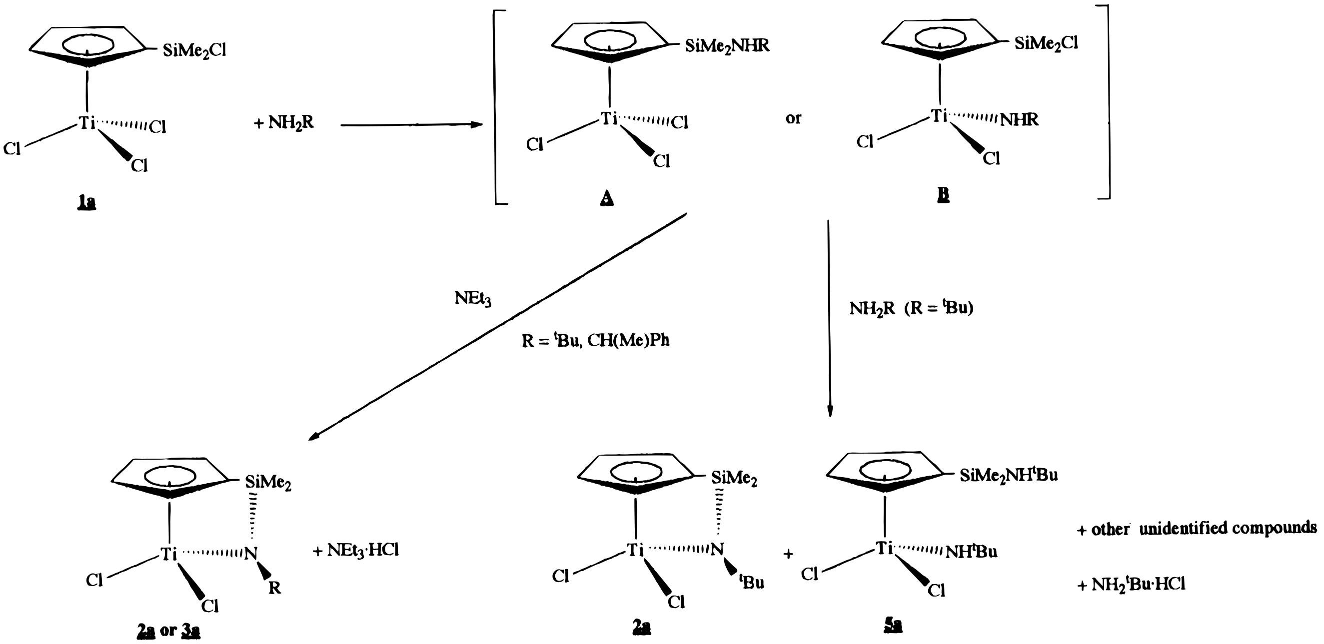
Scheme 2



Scheme 3



The results observed in these reactions allow us to conclude that the Ti–Cl bonds in compound **1a** react selectively with $LiNR_2$ or LiNHR, whereas the reactivity of both Si–Cl and Ti–Cl bonds with NH_2R is very similar. Therefore, the selective aminolysis of either bond is not possible, with similar behavior observed for the reactions with water.[8]

The spectroscopic and analytical data for the new compounds reported in this paper are collected in the Experimental Section and will not be discussed, except where appropriate.

The reactions of **2a** and **3a** with alkylating agents have been studied. Treatment of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N\text{-}{}^tBu)Cl_2]$ (**2a**) with $Tl(C_5H_5)$ in toluene at 100 °C gave the mixed-dicyclopentadienyl derivative $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4\text{-}SiMe_2N^tBu)(\eta^5\text{-}C_5H_5)Cl]$ **(6a)** as red crystals in 71% yield. The addition of 1 equiv of $Mg(CH_2Ph)_2{\cdot}2THF$ or 2 equiv of MgClMe to a cooled (−78 °C) hexane solution of **2a** and **3a** led to the 14-electron dialkyltitanium complexes $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NR)R'_2]$ (R = ^{t}Bu, R′ = CH_3 (**7a**), CH_2Ph (**8a**); R = CHMePh, R′ = CH_3 (**9a**), CH_2Ph (**10a**)), isolated as red or yellow crystals in high yield. The reaction of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2]$ with 1 equiv of $MgCl(CH_2Ph)$ gave the chloro alkyl derivative $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu)(CH_2Ph)Cl]$ (**11a**) as a red solid in 42% yield (Scheme 4).

The ^1H NMR spectra of complexes **2a**, **4a**, **5a**, **7a**, and **8a** show an AA′BB′ spin system (two resonances) for the C_5H_4 ring protons and one singlet for the $SiMe_2$ group, as expected from the symmetry of these compounds.[10] However, compounds **6a** and **11a** display a chiral titanium center and complexes **3a**, **9a**, and **10a** have a chiral carbon atom at the alkylamido pendant group in the molecule. For this reason, their ^1H NMR spectra show an ABCD spin system (four resonances) for the C_5H_4 ring protons and two singlets for the diastereotopic methylsilyl groups.[11] This is also observed in the $^{13}C\{^1H\}$ NMR spectra. Three different resonances corresponding to the distal and proximal C_{ipso} carbon atoms of the cyclopentadienyl ring and one resonance for the $SiMe_2$ group are found for complexes **2a**, **4a**, **5a**, **7a**, and **8a**, whereas the expected five resonances are observed in complexes **3a**, **6a**, and **9a**–**11a**. The chemical shift of the cyclopentadienyl C_{ipso} atom is typically shifted upfield from the other C_5H_4

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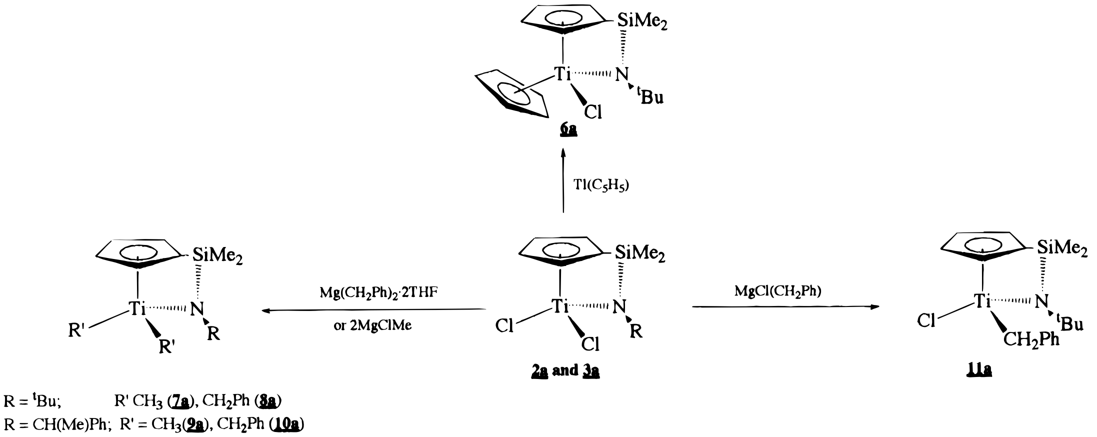
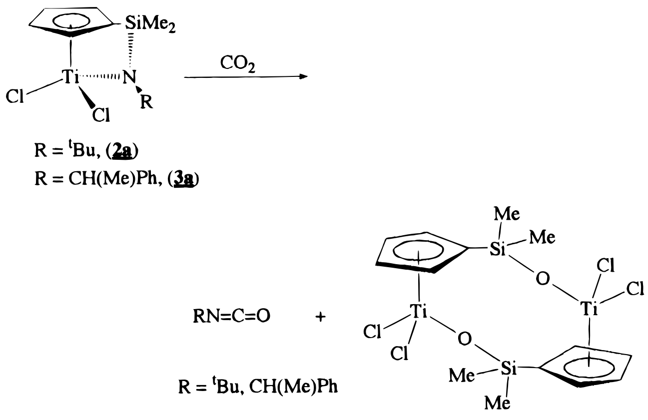
Scheme 4



ring carbon resonances and therefore is diagnostic of the chelation of the appended amido group in these constrained-geometry complexes. The only exception is compound **6a**, which shows the usual behavior observed for most of the mononuclear *ansa*-metallocene dichlorides of the type $[M\{(\eta^5:\eta^5\text{-}C_5H_4)_2SiMe_2\}Cl_2]$.[12] In contrast, the opposite situation is observed in the $^{13}C\{^1H\}$ NMR spectra of complexes without any constrained geometry.[8,13]

Another important feature is that in compounds **7a**-**10a** the titanium atom is a prochiral center and, as we have discussed above, compound **11a** has a chiral ligand arrangement around the titanium atom. These dispositions imply diastereotopic NMR behavior for the CH_2 protons of the benzyl group[14,15] in complexes **8a** and **11a**, whose ^1H NMR spectra show the presence of two sets of doublets, whereas the diastereotopic CH_2 protons of the benzyl group in complex **10a** appear as four doublets, in accordance with the presence of one additional chiral center in the molecule (N−C*H(Me)Ph). The chemical shifts of the methylene carbons in the benzyl complexes **8a**, **10a**, and **11a** (see Experimental Section) are indicative of a normal disposition of the benzyl ligand in solution, although it is well-documented that 12-electron benzyl complexes of titanium are often distorted in order to reduce their electronic unsaturation through interactions of the benzyl ligand with the metal center,[16] whereas 16-electron dibenzylmetallocene complexes adopt a η^1-benzyl bonding mode due to both electronic and steric factors.[17] The NMR data suggest that the constrained-geometry titanium benzyl complexes are more similar to the corresponding dicyclopentadienyl complexes than to the monocyclopentadienyl titanium analogs. The IR spectrum of complex **5a** shows two bands at 3388 and 3306 cm^{-1}, in accordance with the two different N−H bonds present, and the mass spectra of all new compounds agree with their monomeric formulations.

Scheme 5



We have also studied the reactivity of complexes **2a** and **3a** with CO_2. It is well-known that carbonyl organic compounds and various titanium complexes can exchange oxygen and methylene groups. This olefination process involves the exchange reaction between a $[Ti]{=}CH_2$ unit and the C=O group to give [Ti]=O and $C{=}CH_2$.[18] An analogous reaction may occur when the isolobal [Ti]=NR unit reacts with a C=O unit in an imination reaction affording [Ti]=O and the imine derivative C=NR.[19] Stephan and co-workers[20] have recently reported that terminal zirconium phosphinidine complexes $ZrCp_2(PR)(PMe_3)$ react with ketones or aldehydes to produce phosphaalkenes C=PR. Preliminary results show that constrained-geometry derivatives of titanium containing a linked amidocyclopentadienyl ligand can be effective reagents for similar reactions.

An NMR-scale reaction of $[Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NR)Cl_2]$ (R = ^{t}Bu (**2a**), (±)−CH(Me)Ph)**3a**)) with dry CO_2 led to the formation of $[Ti\{\mu\text{-}(OSiMe_2\text{-}\eta^5\text{-}C_5H_4)\}Cl_2]_2$[8] as the major organometallic compound and O=C=NR (R = ^{t}Bu, (±)−CH(Me)Ph) as the unique organic product (Scheme 5). The characterization of the isocyanate products was confirmed by comparison with analytically pure samples purchased from Aldrich. Analogous re-

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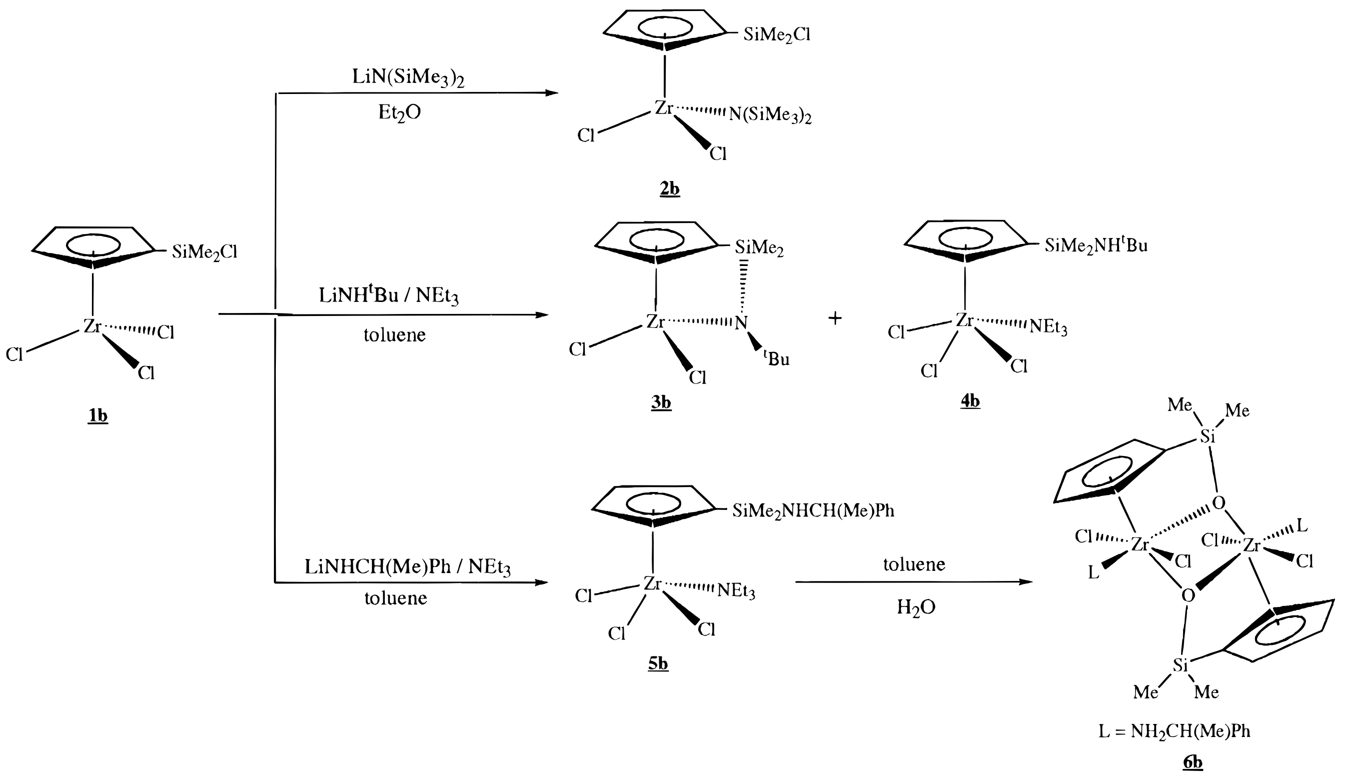
Scheme 6



sults have recently been reported by Petersen et al.,[22a] showing the facile conversion of an appended zirconium silylamido compound into a silyloxy derivative via isocyanate elimination.

Zirconium Derivatives. The zirconium trichloro complex [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**) reacts with 1 equiv of LiN($SiMe_3$)$_2$, at −78 °C, in a diethyl ether solution to give, after the mixture was warmed to room temperature, the monoamido derivative [Zr(η^5-C_5H_4-$SiMe_2Cl$)Cl_2{N($SiMe_3$)$_2$}] (**2b**), isolated as pale yellow crystals in 83% yield. The use of a more polar solvent such as THF leads to the decomposition of **2b** via $SiMe_3$-Cl elimination. Complex **2b** is easily hydrolyzed and thermally stable, although limited decomposition giving unidentified products can be observed by heating above 80 °C. This selective reactivity of the Zr−Cl bond toward the highly polar lithium amide is similar to that observed for the titanium derivative **1a**, although only one chlorine can be substituted even when using an excess of the amide. However, the reaction of [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**) with 1 equiv of LiNH^{t}Bu in the presence of NEt_3 afforded a mixture of two compounds, the previously reported [Zr(η^5-$C_5H_4SiMe_2N^tBu$)Cl_2] (**3b**) containing the bidentate η^1-(amidosilyl)-η^5-cyclopentadienyl ligand[4a] and the triethylamine adduct [Zr(η^5-$C_5H_4SiMe_2NH^tBu$)Cl_3(NEt_3)] (**4b**). Pure samples of **3b** could be isolated as white crystals in 15% yield by recrystallization of this mixture from toluene at −40 °C, but attempts to isolate pure **4b** were unsuccessful, the latter being characterized by NMR and IR spectroscopy. This behavior indicates that a less polar amide does not react with the Zr−Cl bond but instead preferential aminolysis of the Si−Cl bond takes place and the resulting product is only partially transformed by intramolecular elimination of HCl, as demonstrated by the amount of NEt_3·HCl formed in the course of the reaction, which is always less than expected for a stoichiometric reaction. Similar behavior of half-sandwich zirconium complexes has been observed by other authors.[6g,7] The same behavior was observed when the complex [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**) was treated with 1 equiv of the chiral lithium salt LiNHCH(Me)Ph in the presence of NEt_3, in toluene at −78 °C. After the solution was warmed to room temperature, a yellow solution was obtained, in which the adduct [Zr{η^5-C_5H_4-$SiMe_2$[NH(CHMe)Ph]}Cl_3(NEt_3)] (**5b**) was identified by ^{1}H NMR, although it could not be isolated as a pure solid. The related compound analogous to **3b** could not be detected.

The procedure used to prepare **5b**, but carried out using water-saturated toluene, resulted in the slow precipitation of the oxozirconium derivative [Zr{η^5-C_5H_4-$SiMe_2$(μ-O)}Cl_2{H_2N(CHMe)Ph}]$_2$ **(6b)** as white crystals suitable for X-ray diffraction studies (Scheme 6).

The formation of **6b** results from the hydrolysis of the Si−N bond of **5b**, with elimination of the amine NH_2-CH(Me)Ph coordinated to the metal, and the simultaneous hydrolysis of one Zr−Cl bond to give HCl, eliminated as the corresponding ammonium salt NEt_3·HCl.

Description of the Crystal Structure of {Zr[η^5-$C_5H_4SiMe_2$(μ-O)]Cl_2[H_2NCH(Me)Ph]}$_2$ (6b). Crystals of **6b** suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution. The molecular structure of **6b** obtained by X-ray diffraction is shown in Figure 1. Selected bond distances and bond angles are given in Table 1.

The molecular structure shows a dimer with two Zr[η^5-C_5H_4 $SiMe_2$(O)]Cl_2[NH_2(CHMe)Ph] units bonded by two oxygen atoms which are simultaneously bridging two zirconium atoms and one silicon atom, the two fragments being related by an inversion center. If the centroid of the silyl-substituted ring is considered as a

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(21) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and Hafnium Compounds*; Horwood: London, 1986.

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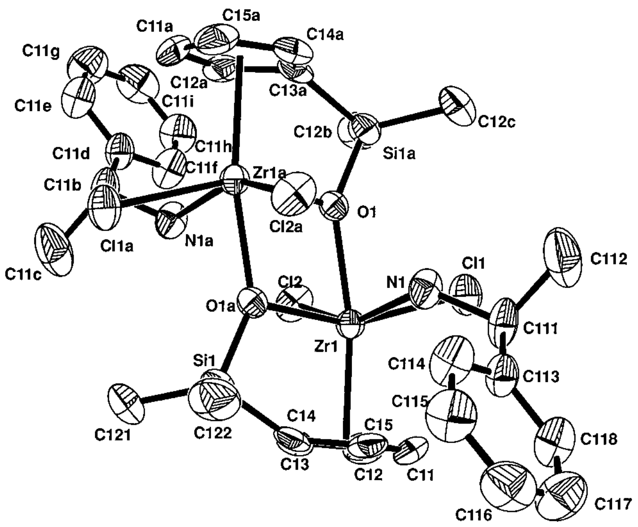

Figure 1. ORTEP drawing of the molecular structure of compound **6b** together with the atomic labeling scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 6b

Zr(1)−O(1a)	2.185(5)	Zr(2)−O(2a)	2.215(5)
Zr(1)−O(1)	2.207(5)	Zr(2)−O(2)	2.188(5)
Zr(1)−N(1)	2.377(6)	Zr(2)−N(2)	2.376(6)
Zr(1)−Cl(1)	2.486(2)	Zr(2)−Cl(3)	2.508(2)
Zr(1)−Cl(2)	2.500(2)	Zr(2)−Cl(4)	2.493(2)
Zr(1)−C(11)	2.565(8)	Zr(2)−C(21)	2.493(7)
Zr(1)−C(12)	2.512(7)	Zr(2)−C(22)	2.564(8)
Zr(1)−C(13)	2.476(7)	Zr(2)−C(23)	2.569(8)
Zr(1)−C(14)	2.493(7)	Zr(2)−C(24)	2.509(7)
Zr(1)−C(15)	2.546(8)	Zr(2)−C(25)	2.480(7)
N(1)−C(111)	1.50(1)	N(2)−C(131)	1.50(1)
Si(1)−C(121)	1.836(1)	Si(2)−C(141)	1.84(1)
Si(1)−C(122)	1.83(1)	Si(2)−C(142)	1.83(1)
Si(1)−O(1a)	1.662(5)	Si(2)−O(2)	1.661(5)
Si(1)−C(13)	1.852(9)	Si(2)−C(25)	1.856(9)
Zr(1)−Cp(1)[a]	2.216	Zr(2)−Cp(2)[b]	2.222
O(1)−Zr(1)−O(1a)	70.0(2)	O(2a)−Zr(2)−O(2)	70.2(2)
O(1a)−Zr(1)−N(1)	86.4(2)	O(2a)−Zr(2)−N(2)	75.3(2)
O(1)−Zr(1)−N(1)	75.3(2)	O(2)−Zr(2)−N(2)	88.1(2)
O(1a)−Zr(1)−Cl(1)	154.9(1)	O(2a)−Zr(2)−Cl(3)	81.8(1)
O(1)−Zr(1)−Cl(1)	86.7(1)	O(2)−Zr(2)−Cl(3)	94.2(1)
N(1)−Zr(1)−Cl(1)	78.4(2)	N(2)−Zr(2)−Cl(3)	154.7(2)
O(1a)−Zr(1)−Cl(2)	96.9(1)	O(2a)−Zr(2)−Cl(4)	86.1(1)
O(1)−Zr(1)−Cl(2)	82.0(1)	O(2)−Zr(2)−Cl(4)	155.3(1)
Cl(1)−Zr(1)−Cl(2)	88.80(8)	Cl(4)−Zr(2)−Cl(3)	88.84(9)
N(1)−Zr(1)−Cl(2)	154.4(2)	N(2)−Zr(2)−Cl(3)	154.7(2)
Cp(1)−Zr(1)−Cl(1)	106.6	Cp(2)−Zr(2)−Cl(3)	102.6
Cp(1)−Zr(1)−Cl(2)	102.1	Cp(2)−Zr(2)−Cl(4)	106.6
Cp(1)−Zr(1)−N(1)	102.7	Cp(2)−Zr(2)−O(2)	96.6
Cp(1)−Zr(1)−O(1a)	96.1	Cp(2)−Zr(2)−O(2)	96.6
Cp(1)−Zr(1)−O(1)	165.9	Cp(2)−Zr(2)−O(2a)	166.4
C(111)−N(1)−Zr(1)	126.6(5)	C(131)−N(2)−Zr(2)	127.2(5)
O(1a)−Si(1)−C(122)	112.8(4)	O(2)−Si(2)−C(142)	112.0(4)
O(1a)−Si(1)−C(121)	111.7(4)	O(2)−Si(2)−C(141)	111.6(4)
C(122)−Si(1)−C(121)	112.1(5)	C(142)−Si(2)−C(141)	113.1(5)
O(1a)−Si(1)−C(13)	93.7(3)	O(2)−Si(2)−C(25)	94.5(3)
C(122)−Si(1)−C(13)	114.1(5)	C(142)−Si(2)−C(25)	113.0(5)
C(121)−Si(1)−C(13)	111.2(5)	C(141)−Si(2)−C(25)	111.3(5)
Si(1)−O(1a)−Zr(1a)	141.6(3)	Si(2)−O(2)−Zr(2)	142.5(3)
Si(1)−O(1a)−Zr(1)	108.2(3)	Si(2)−O(2a)−Zr(2)	107.6(3)
Zr(1)−O(1a)−Zr(1a)	110.0(2)	Zr(2)−O(2a)−Zr(2)	109.8(2)

[a] Cp(1) is the centroid of C(11), ..., C(15). [b] Cp(2) is the centroid of C(21), ..., (C25).

single coordination site bonded to Zr, the structure shows a four-membered ring (Cp−Si−O−Zr), instead of the eight-membered ring observed for the related titanium complex.[8]

In the asymmetric unit of the unit cell two moieties are found that make up two different crystallographic but chemically equivalent molecules (data for the second molecule are given in brackets).

The geometry about each Zr atom is a distorted octahedron. The equatorial plane is defined by two chlorine atoms, one oxygen atom, and one nitrogen atom, with the apical positions occupied by the Cp centroid and the other oxygen atom. Angles between ligands in the ecuatorial plane ranged from 78.4(2)° for N(1)−Zr(1)−Cl(1) to 96.9(1)° for O(1a)−Zr(1)−Cl(2). Zr is located 0.476(1) [0.485] Å above the equatorial plane and the apical oxygen atom 1.707(5) [1.709] Å below. The angle between this plane and the Cp ring plane is only 8.5° [8.5°].

The triply bridging oxygen lies in the equatorial plane. The Zr(1)−O(1)−Zr(1a) angle is 110.0(2)° and the Si(1)−O(1a)−Zr(1) and Si(1)−O(1a)−Zr(1a) angles are 108.2 and 141.6°, respectively. The distances from oxygen to the Zr atoms in compound **6b** are very similar: 2.207(5) [2.188(5)] and 2.185(4) [2.215(5)] Å, corresponding to single Zr−O bonds (average single bond distance is 2.2 Å).[21] The Si−O distance of 1.662(5) [1.661(5)] Å seems not to be affected by the loss of π interaction of the Zr−O bonds, with a C(13)−Si(1)−O(1a) angle of 93.7° [94.5°].

It is interesting to remark that this disposition involves an only slightly asymmetric oxygen bridge, in contrast with the observed disposition in $[Zr(\eta^5\text{-}C_5Me_4\text{-}SiMe_2O)(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)]_2$,[22a] where there is a greater difference (2.257(1) and 2.126(1) Å). Several other structures with an oxygen bonded to two zirconium atoms exhibiting both short and long zirconium−oxygen bond distances have been reported.[22b]

The central core of the dimeric structure can be considered as two lateral Zr−Cp−Si−O "oxazirconacycle" rings connected by a central Zr−O−Zr−O ring. When these three rings are viewed together, an eight-membered cycle is observed. A similar ring is present in the titanium compound $[Ti\{\mu\text{-}(OSiMe_2\text{-}\eta^5\text{-}C_5H_4)\}Cl_2]_2$.[8] However, in contrast to the titanium structure, in which this eight-membered cycle shows a "chair conformation", in the zirconium derivative **6b** a planar disposition is observed. The angle between the planes formed by any lateral Zr−Cp−Si−O ring and the central Zr−O−Zr−O ring is 2.5°. The metallic environment has a direct influence in the difference between both structures. Whereas the coordination around the titanium atom is a pseudotetrahedron, the zirconium atom in **6b** is in a pseudooctahedral environment with the Zr−O and Zr−Cp bond axes located in the same Zr_2O_2 core plane.

Conclusions

The work described in this paper represents a new approach to the synthesis of constrained-geometry catalyst precursors by reactions carried out at the Si−Cl bond of chlorodimethylsilyl-substituted cyclopentadienyl compounds. The highly polar $Li[N(SiMe_3)_2]$ selectively attacks the Ti−Cl and Zr−Cl bonds, leading to the formation of metal amides. Less polar Li[NHR] also selectively attacks the Ti−Cl bonds, whereas preferential aminolysis of the Si−Cl bonds takes place for the zirconium derivatives. Reactions with water and amines are preferentially directed to the Si−Cl bonds, particularly in the case of the zirconium complexes,

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(22) (a) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1996**, *15*, 7. (b) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 3087 and references cited therein.

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which can coordinate the amine instead of eliminate HCl. On this basis, reactions of complexes that contain Ti−Cl and Si−Cl bonds with different lithium amides LiNHR, or alternatively with primary amines in the presence of NEt_3, are convenient routes to constrained complexes of the type $[Ti(C_5H_4SiMe_2NR')Cl_2]$.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum-line techniques or a Model HE-63-Pedetrol glovebox. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium−potassium amalgam for hexane, and sodium−benzophenone for diethyl ether). NEt_3 (Fluka) and $NH_2{}^tBu$ and (±)-$NH_2[CH(Me)Ph]$ (Aldrich) were distilled before use and stored over 4 Å molecular sieves. MgClMe and $MgCl(CH_2Ph)$ were purchased from Aldrich as 3 M and 2 M tetrahydrofuran solutions. $LiNH^tBu$ and LiNH(CHMe)Ph were prepared in hexane (in almost quantitative yield) as solvent-free solids from $NH_2{}^tBu$ and (±)-$NH_2[CH(Me)Ph]$ and *n*-butyllithium (Aldrich, 1.6 M in hexane). $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**),[8] $[Zr(\eta^5\text{-}C_5H_4SiMe_2Cl])Cl_3]$ (**1b**),[8] $LiN(SiMe_3)_2$,[23] $Mg(CH_2Ph)_2\cdot 2THF$,[24] and $Tl(C_5H_5)$[25] were prepared by known procedures. CO_2 was purchased from SEO. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. Electron impact (EI) mass spectra were recorded at 70 eV on a Hewlett-Packard 5988 spectrometer, and IR spectra were taken on a Perkin-Elmer 883 spectrophotometer using KBr pellets; only selected MS and IR data are reported. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^1H NMR at 300 MHz, ^{13}C NMR at 75 MHz) spectrometer, and chemical shifts are referenced to residual protons or carbons of the solvents.

Synthesis of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2]$ (2a). A solution of $LiNH^tBu$ (0.34 g, 4.26 mmol) and NEt_3 (0.59 mL, 4.26 mmol) in 30 mL of hexane was quickly added to a cooled (−60 °C) suspension of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**; 1.33 g, 4.26 mmol) in 30 mL of hexane. The reaction mixture was slowly warmed to room temperature and stirred for 10 h, resulting in an orange solution and a white residue. After filtration, the solution was cooled to −30 °C to give orange crystals. Concentration of the mother liquor (10 mL) and subsequent cooling to −30 °C gave a second crop of product, which was characterized as **2a** (1 g, 3.20 mmol, 75% yield). Anal. Calcd for $C_{11}H_{19}NCl_2SiTi$: C, 42.33; H, 6.14; N, 4.49. Found: C, 42.67; H, 6.22; N, 4.78. ^1H NMR (benzene-d_6): δ 0.18 (s, 6H, $SiMe_2$); 1.37 (s, 9H, ^tBu); 6.07 (m, 2H, C_5H_4); 6.60 (m, 2H, C_5H_4). ^1H NMR (chloroform-*d*): δ 0.60 (s, 6H, $SiMe_2$); 1.44 (s, 9H, ^tBu); 6.45 (m, 2H, C_5H_4); 7.06 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ −0.2 ($SiMe_2$); 32.2 (CH_3, ^tBu); 63.7 (C_{ipso}, ^tBu); 110.0 (C_{ipso}, C_5H_4); 125.7, 126.3 (C_{2-5}, C_5H_4).[4,6k] MS: *m/z* [assignment, relative intensity (%)]: 311 [M^+, 1]; 296 [$(M - CH_3)$,$^+$ 100].

By the procedure described above using $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**) (1.59 g, 5.10 mmol), $NH_2{}^tBu$ (0.53 mL, 5.10 mmol), and NEt_3 (1.41 mL, 10.20 mmol), **2a** was again obtained (1 g, 3.20 mmol, 63% yield).

Synthesis of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2)\{N(CHMe)Ph\}Cl_2]$ (3a). A suspension of LiNH(CHMe)Ph (0.51 g, 4.02 mmol) and NEt_3 (0.56 mL, 4.02 mmol) in 30 mL of hexane was added to a cooled (−60 °C) suspension of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**) (1.25 g, 4.02 mmol) in 30 mL of hexane. The reaction mixture was stirred at room temperature for 15 h, over which time the color of the solution changed to brown. After filtration, the solution was cooled to −30 °C to give orange-brown crystals. A second crop of product **3a** was obtained after concentration of the mother liquor (1 g, 2.78 mmol, 69% yield). Anal. Calcd for $C_{15}H_{19}NCl_2SiTi$: C, 50.02; H, 5.32; N, 3.89. Found: C, 49.79; H, 5.20; N, 4.08. ^1H NMR (benzene-d_6): δ −0.48 (s, 3H, SiMe); 0.09 (s, 3H, SiMe); 1.50 (d, J = 6.8 Hz, 3H, CMe); 5.99 (m, 1H, C_5H_4); 6.04 (m, 1H, C_5H_4); 6.48 (m, 1H, C_5H_4); 6.49 (m, 1H, C_5H_4); 6.51 (q, J = 6.8 Hz, 1H, CH); 7.01−7.27 (m, 5H, Ph). ^1H NMR (chloroform-*d*): δ −0.29 (s, 3H, SiMe); 0.46 (s, 3H, SiMe); 1.59 (d, J = 6.8 Hz, 3H, CMe); 6.38 (m, 1H, C_5H_4); 6.41 (q, J = 6.8 Hz, 1H, CH); 6.44 (m, 1H, C_5H_4); 7.00 (m, 2H, C_5H_4); 7.23−7.33 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ −2.0 (SiMe); 0.6 (SiMe); 20.0 (C*Me*); 65.4 (*C*Me); 110.6 (C_{ipso}, C_5H_4); 125.1, 125.4, 127.2 (C_{2-5}, C_5H_4); 127.9, 128.9, 129.6 (Ph); 144.6 (C_{ipso}, Ph). MS: *m/z* [assignment, relative intensity (%)] 359 [M^+, 2]; 344 [$(M - CH_3)^+$, 100].

By the procedure described above using $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**) (1.73 g, 5.55 mmol), (±)-$NH_2(CHMe)Ph$ (0.72 mL, 5.55 mmol), and NEt_3 (1.55 mL, 11.12 mmol), **3a** was again obtained (1 g, 2.78 mmol, 50% yield).

Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl\{N(SiMe_3)_2\}_2]$ (4a). A mixture of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**; 0.84 g, 2.69 mmol) and $LiN(SiMe_3)_2$ (0.90 g, 5.40 mmol) in 50 mL of hexane was stirred at room temperature for 10 h and then filtered. The filtrate was concentrated under reduced pressure and cooled to −40 °C to give orange crystals, which were characterized as **4a** (1 g, 1.78 mmol, 66% yield). Anal. Calcd for $C_{19}H_{46}N_2Cl_2Si_5Ti$: C, 40.62; H, 8.25; N, 4.99. Found: C, 40.38; H, 8.57; N, 4.68. ^1H NMR (chloroform-*d*): δ 0.36 (s, 36H, $N(SiMe_3)_2$); 0.81 (s, 6H, $SiMe_2$); 6.63−6.67 (m, 4H, C_5H_4). ^1H NMR (benzene-d_6): δ 0.37 (s, 36H, $N(SiMe_3)_2$); 0.83 (s, 6H, $SiMe_2$); 6.46 (m, 2H, C_5H_4); 6.62 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 2.5 ($SiMe_2$); 7.2 ($SiMe_3$); 117.8, 119.8 (C_{2-5}, C_5H_4); 131.6 (C_{ipso}, C_5H_4).

Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)Cl_2(NH^tBu)]$ (5a). A solution of $NH_2{}^tBu$ (2.73 mL, 26.00 mmol) in 25 mL of toluene was slowly added to a cooled (−60 °C) solution of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ (**1a**; 2.70 g, 8.66 mmol) in 75 mL of toluene. The reaction mixture was warmed to room temperature and then stirred overnight, resulting in an orange solution together with a white residue. Subsequent filtration and removal of the solvent under reduced pressure afforded an orange solid as a mixture of **5a**, **2a**, and other unidentified products. Repeated recrystallization of the mixture from toluene/hexane at −40 °C gave **5a** as an analytically pure sample (0.53 g, 1.38 mmol, 16% yield). Anal. Calcd for $C_{15}H_{30}N_2Cl_2SiTi$: C, 46.76; H, 7.85; N, 7.27. Found: C, 47.21; H, 7.53; N, 7.34. ^1H NMR (benzene-d_6): δ 0.38 (s, 6H, $SiMe_2$); 1.04 (s, 9H, ^tBu); 1.36 (s, 9H, ^tBu); 6.16 (m, 2H, C_5H_4); 6.47 (m, 2H, C_5H_4); 10.5 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 2.3 ($SiMe_2$); 33.3 (CH_3, ^tBu); 34.3 (CH_3, ^tBu); 58.2 (C_{ipso}, ^tBu); 60.1 (C_{ipso}, ^tBu); 116.2, 118.1 (C_{2-5}, C_5H_4); 125.9 (C_{ipso}, C_5H_4). IR (KBr, cm^{-1}): ν(N−H) 3388, 3306. MS: *m/z* [assignment, relative intensity (%)] 369 [$(M - CH_3)^+$, 1]; 334 [$(M{-}CH_3{-}Cl)^+$, 2]; 296 [$(M - CH_3 - NH_2{}^tBu)^+$, 42].

Synthesis of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu)(\eta^5\text{-}C_5H_5)Cl]$ (6a). A mixture of $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2]$ (**2a**; 1.29 g, 4.13 mmol) and $Tl(C_5H_5)$ (1.11 g, 4.13 mmol) in 60 mL of toluene was stirred at 100 °C overnight and then filtered. The filtrate was concentrated under reduced pressure and cooled to −30 °C to give a red solid. Recrystallization from hexane gave a microcrystalline solid that was characterized as **6a** (1 g, 2.93 mmol, 71% yield). Anal. Calcd for $C_{16}H_{24}NClSiTi$: C, 56.22; H, 7.08; N, 4.10. Found: C, 56.01; H, 6.87; N, 4.39. ^1H NMR (benzene-d_6): δ 0.15 (s, 3H, SiMe); 0.54 (s, 3H, SiMe); 1.32 (s, 9H, ^tBu); 5.23 (m, 1H, C_5H_4); 5.87 (m, 1H, C_5H_4); 5.87 (s, 5H, C_5H_5); 6.30 (m, 1H, C_5H_4); 7.07 (m, 1H, C_5H_4). ^1H NMR (chloroform-*d*): δ 0.31 (s, 3H, SiMe); 0.59 (s, 3H, SiMe); 1.37 (s, 9H, ^tBu); 5.73 (m, 1H, C_5H_4); 6.20 (s, 5H, C_5H_5); 6.40 (m, 1H, C_5H_4); 6.66 (m, 1H, C_5H_4); 6.89 (m, 1H, C_5H_4). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 1.2 (SiMe); 4.7 (SiMe); 34.2 (CH_3, ^tBu); 65.7 (C_{ipso}, ^tBu); 113.6 (C_5H_5); 109.8, 121.8, 122.0, 130.1 (C_{2-5}, C_5H_4); 113.2 (C_{ipso} of C_5H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 1.3 (SiMe); 4.8 (SiMe); 34.2 (CH_3, ^tBu); 65.1 (C_{ipso}, ^tBu); 113.8 (C_5H_5); 110.2, 121.4, 122.8, 130.0 (C_{2-5}, C_5H_4) (C_{ipso} of

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C_5H_4 not observed). MS: *m/z* [assignment, relative intensity (%) 341 [M^+, 2]; 326 [$(M - CH_3)^+$, 100].

Synthesis of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Me_2] (7a). A 3 M solution of MgClMe in tetrahydrofuran (3.08 mL, 9.24 mmol) was added to a cooled (−78 °C) suspension of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] (**2a**; 1.44 g, 4.61 mmol) in 50 mL of hexane. After the temperature was raised to 0 °C over 1 h, a yellow solution with a white precipitate was formed. At this temperature the reaction mixture was filtered and the solution was concentrated to 5 mL. Cooling to −40 °C gave yellow crystals of the product, which was characterized as **7a** (1 g, 3.69 mmol, 80% yield). Anal. Calcd for $C_{13}H_{25}NSiTi$: C, 57.55; H, 9.29; N, 5.16. Found: C, 57.05; H, 9.12; N, 4.95. ^1H NMR (benzene-d_6): δ 0.25 (s, 6H, $SiMe_2$); 0.64 (s, 6H, $TiMe_2$); 1.52 (s, 9H, ^tBu); 5.82 (m, 2H, C_5H_4); 6.74 (m, 2H, C_5H_4). ^1H NMR (chloroform-*d*): δ 0.34 (s, 6H, $SiMe_2$); 0.35 (s, 6H, $TiMe_2$); 1.55 (s, 9H, ^tBu); 5.96 (m, 2H, C_5H_4); 7.03 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 1.0 ($SiMe_2$); 34.4 (CH_3, ^tBu); 51.0 ($TiMe_2$); 58.7 (C_{ipso}, ^tBu); 103.9 (C_{ipso}, C_5H_4); 121.2, 122.1 (C_{2-5}, C_5H_4).

Synthesis of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)$(CH_2Ph)_2$] (8a). A solution of $Mg(CH_2Ph)_2 \cdot 2THF$ (1.06 g, 3.03 mmol) in 15 mL of diethyl ether was added to a cooled (−78 °C) suspension of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] (**2a**; 0.94 g, 3.03 mmol) in 30 mL of hexane. The mixture was warmed to room temperature for 2 h, resulting in a deep red solution with a gray precipitate. After filtration the solution was concentrated to 5 mL. Cooling to −40 °C gave dark red crystals of the product, which was characterized as **8a** (1 g, 2.36 mmol, 78% yield). Anal. Calcd for $C_{25}H_{33}NSiTi$: C, 70.90; H, 7.85; N, 3.31. Found: C, 70.57; H, 7.81; N, 2.95. ^1H NMR (benzene-d_6): δ 0.16 (s, 6H, $SiMe_2$); 1.50 (s, 9H, ^tBu); 2.28 (d, $J = 9.5$ Hz, 2H, $TiCH_2$); 2.87 (d, $J = 9.5$ Hz, 2H, $TiCH_2$) 5.44 (m, 2H, C_5H_4); 6.36 (m, 2H, C_5H_4); 6.77−7.15 (m, 10H, Ph). ^1H NMR (chloroform-*d*): δ 0.34 (s, 6H, $SiMe_2$); 1.73 (s, 9H, ^tBu); 2.24 (d, $J = 9.5$ Hz, 2H, $TiCH_2$); 2.85 (d, $J = 9.5$ Hz, 2H, $TiCH_2$); 5.47 (m, 2H, C_5H_4); 6.41 (m, 2H, C_5H_4); 6.75−7.13 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 0.8 ($SiMe_2$); 34.5 (CH_3, ^tBu); 60.3 (C_{ipso}, ^tBu); 81.6 ($TiCH_2$); 106.4 (C_{ipso}, C_5H_4); 125.2, 125.6 (C_{2-5}, C_5H_4); 122.0, 125.8, 128.5 (Ph); 149.8 (C_{ipso}, Ph). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 0.8 ($SiMe_2$); 34.5 (CH_3, ^tBu); 60.5 (C_{ipso}, ^tBu); 80.8 ($TiCH_2$); 105.9 (C_{ipso}, C_5H_4); 121.4, 124.8 (C_{2-5}, C_5H_4); 125.2, 125.3, 128.1 (Ph); 149.5 (C_{ipso}, Ph). MS: *m/z* [assignment, relative intensity (%)] 332 [$(M - C_7H_7)^+$, 90]; 317 [$(M - C_7H_7 - CH_3)^+$, 80]; 91 [$(C_7H_7)^+$, 100].

Synthesis of [Ti{η^5:η^1-$C_5H_4SiMe_2$[N(CHMe)Ph]}Me_2] (9a). The procedure described for the preparation of complex [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Me_2] (**7a**) using [Ti{η^5:η^1-$C_5H_4SiMe_2$[N(CHMe)Ph]}Cl_2] (**3a**; 1.46 g, 4.07 mmol) and a 3 M solution of MgClMe in tetrahydrofuran (2.72 mL, 8.16 mmol) gave **9a** as yellow crystals (1 g, 3.13 mmol, 77%). Anal. Calcd for $C_{17}H_{25}NSiTi$: C, 63.93; H, 7.89; N, 4.39. Found: C, 63.88; H, 8.23; N, 4.73. ^1H NMR (benzene-d_6): δ −0.20 (s, 3H, SiMe); 0.06 (s, 3H, SiMe); 0.67 (s, 3H, TiMe); 0.68 (s, 3H, TiMe); 1.75 (d, $J = 6.6$ Hz, 3H, CMe); 5.80 (m, 1H, C_5H_4); 5.85 (m, 1H, C_5H_4); 5.89 (q, $J = 6.6$ Hz, 1H, CH); 6.70 (m, 2H, C_5H_4); 7.08−7.29 (m, 5H, Ph).$^{13}C\{^1H\}$ NMR (benzene-d_6): δ −1.9 (SiMe); −0.1 (SiMe); 24.5 (C*Me*); 51.0 (TiMe); 51.2 (TiMe); 60.9 (*C*Me); 103.3 (C_{ipso}, C_5H_4); 119.5, 119.6, 122.5, 122.6 (C_{2-5}, C_5H_4); 127.0, 128.4 (Ph, one peak obscured by solvent peak); 146.9 (C_{ipso}, Ph).

Synthesis of [Ti{η^5:η^1-$C_5H_4SiMe_2$[N(CHMe)Ph]}$(CH_2Ph)_2$] (10a). The procedure described to prepare [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)$(CH_2Ph)_2$], **8a** using [Ti{η^5:η^1-$C_5H_4SiMe_2$[N(CHMe)Ph]}Cl_2] (**3a**; 1.08 g, 2.99 mmol) and $Mg(CH_2Ph)_2 \cdot 2THF$ (1.05 g, 2.99 mmol) gave **10a** as dark red crystals (1 g, 2.12 mmol, 71% yield). Anal. Calcd for $C_{29}H_{33}NSiTi$: C, 73.86; H, 7.05; N, 2.97. Found: C, 73.68; H, 7.33; N, 2.92. ^1H NMR (benzene-d_6): δ −0.07 (s, 3H, SiMe); 0.10 (s, 3H, SiMe); 1.61 (d, $J = 6.6$ Hz, 3H, CMe); 2.23 (d, $J = 9.5$ Hz, 1H, $TiCH_2$); 2.33 (d, $J = 9.9$ Hz, 1H, $TiCH_2$); 2.61 (d, $J = 9.9$ Hz, 1H, $TiCH_2$); 2.74 (d, $J = 9.5$ Hz, 1H, $TiCH_2$); 5.44 (m, 1H, C_5H_4); 5.57 (m, 1H, C_5H_4); 5.82 (q, $J = 6.6$ Hz, 1H, CH); 6.37 (m, 1H, C_5H_4); 6.39 (m, 1H, C_5H_4); 6.61−7.29 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ −1.0 (SiMe); 0.2 (SiMe); 25.4 (C*Me*); 62.2 (*C*Me); 81.1 ($TiCH_2$); 82.5 ($TiCH_2$); 105.4 (C_{ipso}, C_5H_4); 122.0, 122.1, 123.8, 123.9 (C_{2-5}, C_5H_4); 125.0, 125.3, 125.7, 126.0, 127.5, 128.5, 128.6, 128.7 (Ph, one peak obscured by solvent peak); 146.5, 148.9, 149.1 (C_{ipso}, Ph). MS: *m/z* [assignment, relative intensity (%)] 380 [$(M - C_7H_7)^+$, 4]; 289 [$(M - 2C_7H_7)^+$, 16]; 91 [$(C_7H_7)^+$, 100].

Synthesis of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)$(CH_2Ph)Cl$] (11a). A 3 M solution of $MgCl(CH_2Ph)$ in tetrahydrofuran (2.16 mL, 6.47 mmol) was added to a cooled (−78 °C) suspension of [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] (**2a**; 2.02 g, 6.47 mmol) in 50 mL of diethyl ether. After warming up to room temperature, the reaction mixture was allowed to stand for 2 h. The $MgCl_2$ formed was removed by filtration, and the volume of the filtrate was reduced in vacuo to 15 mL and cooled to −40 °C to give a dark red solid. Recrystallization from hexane at −40 °C gave a microcrystalline solid that was characterized as **11a** (1 g, 2.72 mmol, 42% yield). Anal. Calcd for $C_{18}H_{26}NClSiTi$: C, 58.78; H, 7.12; N, 3.81. Found: C, 58.95; H, 6.74; N, 3.76. ^1H NMR (benzene-d_6): δ 0.16 (s, 3H, SiMe); 0.22 (s, 3H, SiMe); 1.48 (s, 9H, ^tBu); 2.71 (d, $J = 9.2$ Hz, 1H, $TiCH_2$); 3.22 (d, $J = 9.2$ Hz, 1H, $TiCH_2$); 5.56 (m, 1H, C_5H_4); 5.83 (m, 1H, C_5H_4); 6.11 (m, 1H, C_5H_4); 6.49 (m, 1H, C_5H_4); 6.89−7.15 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 0.7 (SiMe); 1.1 (SiMe); 35.2 (CH_3, ^tBu); 60.0 (C_{ipso}, ^tBu); 83.0 ($TiCH_2$); 107.7 (C_{ipso}, C_5H_4); 121.7, 122.0, 125.2, 125.6 (C_{2-5}, C_5H_4); 122.9, 126.3, 128.5 (Ph); 149.0 (C_{ipso}, Ph).

NMR-Scale Reactions of 2a and 3a with CO_2. (A) An NMR tube was charged with [Ti(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] (**2a**; 45 mg, 0.14 mmol) in benzene-d_6 (0.7 mL). After the solution had been cooled to −196 °C, the argon atmosphere was replaced by CO_2, and the NMR tube was immediately sealed. The reaction was followed by ^1H NMR. After 38 h at room temperature, no reaction occurred. After 5 h at 70 °C, the ^1H NMR spectrum showed that all of **2a** had been converted into [Ti{μ-($OSiMe_2$-η^5-C_5H_4)}Cl_2]$_2$ as the major organometallic compound and $^tBuN{=}C{=}O$. ^1H NMR (benzene-d_6): δ 0.91 (s, 9H, ^tBu). The same δ value was obtained from an analytically pure sample (97%) of $^tBuN{=}C{=}O$ obtained commercially from Aldrich. (B) The same procedure was used for [Ti{η^5:η^1-$C_5H_4SiMe_2$[N(CHMe)Ph]}Cl_2 (**3a**; 45 mg, 0.12 mmol). After only 10 h at room temperature, all of **3a** had been converted into [Ti{μ-($OSiMe_2$-η^5-C_5H_4)}Cl_2]$_2$ as the major organometallic compound and (±)-[Ph(Me)HC]N=C=O ^1H NMR (benzene-d_6): δ 1.06 (d, $J = 6.9$ Hz, 3H, CMe); 4.06 (q, $J = 6.9$ Hz, 1H, CH); 6.94−7.05 (m, 5H, Ph). The same δ and *J* values were obtained from analytically pure sample (99%) of (+)-[Ph(Me)HC]N=C=O purchased from Aldrich.

Synthesis of [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_2{$N(SiMe_3)_2$}] (2b). A solution of $LiN(SiMe_3)_2$ (0.23 g, 1.41 mmol) in 20 mL of diethyl ether was added to a solution of [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**; 0.50 g, 1.41 mmol) in 30 mL of diethyl ether at −78 °C. The reaction mixture was warmed to room temperature and then stirred for 12 h, resulting in a pale yellow solution along with a white residue. The mixture was filtered and the solvent was removed under reduced pressure to give **2b** as a pale crystalline solid. Recrystallization of **2b** from diethyl ether at −40 °C gave an analytically pure sample (0.56 g, 1.17 mmol, 83% yield). Anal. Calcd for $C_{13}H_{28}NCl_3Si_3Zr$: C, 32.52; H, 5.83; N, 2.92. Found: C, 32.43; H, 5.60; N, 2.86. ^1H NMR (benzene-d_6): δ 0.19 (s, 18H, $N(SiMe_3)_2$); 0.68 (s, 6H, $SiMe_2$); 6.27 (m, 2H, C_5H_4); 6.53 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 2.5 ($SiMe_2$); 5.0 ($SiMe_3$); 118.1, 123.8 (C_{2-5}, C_5H_4); 125.4 (C_{ipso}, C_5H_4).

Synthesis of the Mixture [Zr(η^5:η^1-$C_5H_4SiMe_2N^tBu$)Cl_2] (3b) and [Zr(η^5-$C_5H_4SiMe_2NH^tBu$)Cl_3(NEt_3)] (4b). A solution of $LiNH^tBu$ (0.22 g, 2.82 mmol) in 20 mL of toluene was slowly added to a solution of [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**; 1.00 g, 2.82 mmol) and NEt_3 (0.39 mL, 2.82 mmol) in 30 mL of toluene at −78 °C. The reaction mixture was warmed to room temperature and then stirred for 12 h, resulting in a pale yellow solution. Subsequent filtration and removal of the solvent under reduced pressure afforded a sticky solid, a

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Table 2. Crystal Data and Structure Refinement Details for Compound 6b

empirical formula	$C_{30}H_{40}Cl_4N_2O_2Si_2Zr_2$
fw	841.06
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cel dimens	$a = 10.301(3)$ Å
	$b = 10.398(2)$ Å
	$c = 19.391(3)$ Å
	$\alpha = 88.69(2)°$
	$\beta = 78.97(2)°$
	$\gamma = 63.18(2)°$
V	1814.5(7) Å^3
Z	2
density (calcd)	1.539 g/cm^3
abs coeff	9.64 cm^{-1}
F(000)	852
cryst size	0.2 × 0.2 × 0.3 mm
θ range for data collection	2−25
index ranges	$0 < h < 12, -12 < k < +12, -12 < l < +22$
no. of rflns collected	6661
no. of indep rflns	6089 ($R_{int} = 0.1396$)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6084/0/379
goodness of fit on F^2	1.127
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0597, wR2 = 0.1557
R indices (all data)	R1 = 0.1100, wR2 = 0.1874
weighting scheme	calcd $w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 10.1458P]$, where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole	+0.851 and −1.109 e/Å^3

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$; $wR2 = \{[\sum w((F_o^2 - F_c^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

mixture of **3b** and **4b**. Recrystallization of the mixture from toluene at −40 °C gave **3b**[4a] (0.15 g, 0.42 mmol, 15% yield) as white crystals, but attempts to isolate pure **4b** were unsuccessful. ^{1}H NMR (benzene-d_6) for **4b**: δ 0.62 (s, 6H, $SiMe_2$); 0.80 (t, 9H, NCH_2CH_3); 1.08 (s, 9H, ^{t}Bu); 2.56 (q, 6H, NCH_2CH_3); 6.05 (br, 1H, NH); 6.85 (m, 2H, C_5H_4); 6.90 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 2.7 ($SiMe_2$); 8.8 (NCH_2CH_3); 33.9 (CH_3, ^{t}Bu); 47.1 (NCH_2CH_3); 49.9 (C_{ipso}, ^{t}Bu); 124.3, 127.3 (C_{2-5}, C_5H_4) (C_{ipso} of C_5H_4 not observed). IR (KBr, cm^{-1}): ν(N−H) 3365.

Synthesis of [Zr{η^5-$C_5H_4SiMe_2$[NH(CHMe)Ph]}Cl_3(NEt_3)] (5b). A suspension of LiNH(CHMe)Ph (0.36 g, 2.82 mmol) in 20 mL of toluene was slowly added to a solution of [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**; 1.00 g, 2.82 mmol) and NEt_3 (0.39 mL, 2.82 mmol) in 30 mL of toluene at −78 °C. The reaction mixture was warmed to room temperature and then stirred for 12 h, resulting in a pale yellow solution. Subsequent filtration and removal of the solvent under reduced pressure afforded **5b** as an impure sticky pale yellow solid. Attempts to isolate **5b** by recrystallization of the mixture were unsuccessful. ^{1}H NMR (benzene-d_6): δ 0.40 (s, 3H, SiMe); 0.52 (s, 3H, SiMe); 0.68 (t, 9H, NCH_2CH_3); 1.31 (d, J = 6.6 Hz, 3H, CMe); 2.36 (q, 6H, NCH_2CH_3); 4.05 (q, J = 6.6 Hz, 1H, CH); 4.70 (m, 1H, N−H); 6.74 (m, 2H, C_5H_4); 6.77 (m, 1H, C_5H_4); 6.84 (m, 1H, C_5H_4); 7.00−7.10 (m, 5H, Ph).

Synthesis of [Zr{η^5:η^1-$C_5H_4SiMe_2$(μ-O)}Cl_2{H_2N(CHMe)Ph}]$_2$ (6b). A solution of **5b** in 20 mL of toluene, prepared from [Zr(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1b**; 0.50 g, 1.41 mmol) as described above, was treated with wet toluene without stirring. This resulted in a slow precipitation of **6b** as white crystals, which were suitable for X-ray analysis (0.17 g, 0.20 mmol, 28% yield based on compound **1b**). Anal. Calcd for $C_{30}H_{42}N_2Cl_4O_2Si_2Zr_2$: C, 42.73; H, 4.98; N, 1.66. Found: C, 42.70; H, 5.03; N, 1.51. ^{1}H NMR (chloroform-d): δ 0.47 (s, 3H, SiMe); 0.72 (s, 3H, SiMe); 1.46 (d, J = 6.6 Hz, 3H, CMe); 4.33 (q, 1H, CH); 5.86 (m, 1H, C_5H_4); 6.69 (m, 1H, C_5H_4); 6.75 (m, 1H, C_5H_4); 7.00 (m, 1H, C_5H_4); 7.20−7.60 (m, 5H, Ph).

Crystal Structure Determination of 6b. A suitably sized white crystal of **6b** was obtained by crystallization from toluene. The crystal was mounted in an Enraf-Nonius Cad-4 automatic four-circle diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.710 73 Å). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXS 90)[26] and refined by least squares against F^2 (SHELXL 93).[27] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the atoms to which they are bonded. Calculations were carried out on an ALPHA AXP (digital) workstation.

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Supporting Information Available: Tables of atomic coordinates, all bond distances and angles, and anisotropic thermal factors for **6b** (5 pages). Ordering information is given on any current masthead page.

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