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Synthesis and Structure of the First Homoleptic 1-Aza-1,3-diene Titanium Complex: A Tightrope Walk between Ligand Coordination and Ligand Coupling[†]

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The reaction of $TiCl_4(THF)_2$ or $ZrCl_4(THF)_2$ with Mg in the presence of 1-aza-1,3-dienes (**1**) has been investigated. Reduction of $TiCl_4(THF)_2$ with 2 equiv of Mg in the presence of 2 equiv of $(R^1)N{=}CHC(R^2){=}CH(Ph)$ yields the first homoleptic 1-aza-1,3-diene complex, $[Ti\{N(R^1)CH{=}C(R^2)CH(Ph)\}_2]$ (**7**), but only if the 1-aza-1,3-diene is substituted by a sterically demanding group at the nitrogen atom (**1b**: $R^1 = C_6H_3$-2,6-iPr$_2$, $R^2 = H$). X-ray crystallography indicates a σ^2,π coordination of the heterodienes, which are reduced to 1-azabut-2-ene-1,4-diyl dianions to form folded 1-aza-2-titanacyclopent-4-ene rings. As a byproduct, the bicyclic complex $[\{N(R^1)CH{=}C(R^2)CH(Ph)\}Ti\{N(R^1)CH{=}C(R^2)CH(Ph)CH\{C(R^2){=}CH(Ph)\}N(R^1)\}]$ (**8**) was isolated, which is believed to arise from C═N insertion of **1b** into the Ti−C bond of the intermediate $[\{N(R^1)CH{=}C(R^2)CH(Ph)\}TiCl_2]$, followed by the coordination of a further 1-aza-1,3-diene ligand. The analogous bicyclic zirconium complex $[\{N(R^1)CH{=}C(R^2)CH(Ph)\}Zr\{N(R^1)CH{=}C(R^2)CH(Ph)CH\{C(R^2){=}CH(Ph)\}N(R^1)\}]$ (**6**: $R^1 =$ cyclo-C_6H_{11}, $R^2 = Me$) is the only available product when the reduction of $ZrCl_4(THF)_2$ is performed in the presence of the 1-aza-1,3-diene (cyclo-C_6H_{11})$N{=}CHC(Me){=}CHPh$ (**1a**), which is substituted by a sterically less demanding group at the terminal nitrogen atom. Addition of 2 equiv of benzophenone to **7** affords the titanium complex $[Ti\{OCPh_2CH(Ph)C(R^2){=}CHN(R^1)\}_2]$ (**9**). The solid-state structure of **9** shows the titanium in a distorted-tetrahedral environment, being the center of two folded oxazatitanacycloheptene rings.

Introduction

Increasing development in the chemistry of 1,3-diene complexes of early transition metals over the last several years has been due to their potential applicability both as synthons in various organic reactions and as catalysts in polymerization reactions.[21−2] The M−C bonds in metal s-cis-diene complexes mostly exhibit highly polarized σ-bonding character.[3] Therefore, 1,3-diene complexes of early transition metals undergo a large number of highly selective carbometalations both with unsaturated hydrocarbons and with polar electrophiles containing C−O or C−N multiple bonds.[4] Furthermore, in case of the group 4 metallocene diene complexes the variety of products in these organometallic reactions is even enhanced, as not only the s-cis-diene complexes but also unsaturated η^2-diene complexes often are the actual reacting species.[5] These are intermediates in the isomerization pathway between s-cis-diene and s-trans-diene complexes.

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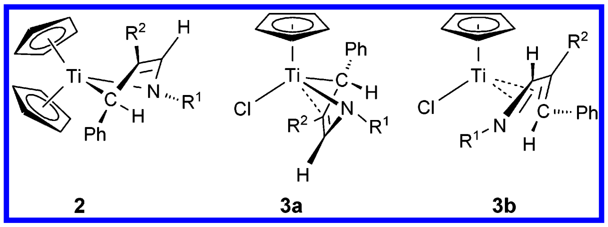
Chart 1. Structures of Cyclopentadienyltitanium 1-Aza-1,3-diene Complexes



Preliminary reports have shown that the substitution of one of the terminal diene carbon atoms by a nitrogen atom may offer a number of interesting options to the organic chemistry of these heterodiene complexes.[6] However, early-transition-metal complexes bearing 1-aza-1,3-diene ligands have attracted less attention. This can probably be ascribed to the fact that, so far, no general method for the preparation of these heterodiene complexes has been developed.

The utility of the magnesium−butadiene adduct $[(C_4H_6)Mg(THF)_2]_n$[7] or its derivatives as a synthon of the diene dianion has been widely accepted in the synthesis of diene complexes of early transition metals. Dilithium but-2-ene-1,4-diyl derivatives such as $[\{C_4H_4(SiMe_3)_2\}\{Li(THF)_2\}_2]$[8] can also be used for transferring dianionic diene ligands to transition metals. However, to our knowledge no efforts have been made so far to explore the preparation of magnesium 1-aza-1,3-diene compounds, and only recently we reported for the first time the reaction of the 1-aza-1,3-diene (*i*Pr)N═CHC(Me)═CH(Ph) with lithium.[1,9] Thus, most of the 1-aza-1,3-diene complexes of early transition metals known up to now have been prepared by simple reduction of transition-metal halides by magnesium or lithium in the presence of 1-aza-1,3-dienes.[10]

The results of NMR and X-ray structural analyses of 1-aza-1,3-diene group 4 metallocenes (**2**) prepared in this way demonstrate that these complexes prefer the σ^2,π-1-metalla-2-azacyclopent-3-ene structure (Chart 1; **3a**).[10a,b] In the case of the monocyclopentadienyltitanium 1-aza-1,3-diene complexes CpTi(1-aza-1,3-diene)Cl (**3**) two orientations of the heterodiene are possible.[10b] The supine structure shows the opening of the heterodiene cup pointing toward the Cp ring (Chart 1; **3a**).[11] The alternative prone isomer (Chart 1; **3b**) is present if the open end of the 1-aza-1,3-diene cup is directed away from the Cp ligand.[11] The preference of the supine geometry of the most CpTi(1-aza-1,3-diene)Cl complexes may primarily be due to the severe steric repulsion between the Cp ligand and substituents on the nitrogen and inner carbon atoms of the coordinated 1-aza-1,3-diene in case of the prone geometry.

So far, no reports on the synthesis and structural analysis of group IV 1-aza-1,3-diene complexes without stabilizing Cp ligands have been published. The potential use of 1-aza-1,3-diene complexes in other selective carbometalation reactions and the catalytic activity toward olefin polymerization processes,[12] together with the fact that early-transition-metal complexes that contain more than one 1-aza-1,3-diene ligand are still unknown, has prompted us to expand our studies with these ligands. Here we describe the synthesis and structural characteristics as well as the results of a typical carbometalation reaction of the first homoleptic titanium 1-aza-1,3-diene complex.

Results and Discussion

Syntheses and Molecular Structures of 1-Aza-1,3-diene Complexes. The metallocene 1-aza-1,3-diene complexes Cp_2M(1-aza-1,3-diene) (**2**) and the monocyclopentadienyl 1-aza-1,3-diene complexes CpTi(1-aza-1,3-diene)Cl (**3**) were prepared by a “one-pot synthesis”.[10a,b] Application of this method to the simple group 4 metal chlorides, i.e., reduction of $TiCl_4(THF)_2$ with 2 equiv of Mg in the presence of 2 equiv of various 1-aza-1,3-dienes (R^1)N═CHC(R^2)═CH(Ph) (**1**: R^1 = cyclo-C_6H_{11}, Ph, C_6H_4-2-Me, C_6H_4-4-Me; R^2 = H, Me) in THF at room temperature as well as at low temperatures, always yielded complex mixtures that were almost insoluble even in THF and were not separable into pure products. Only the attempt to run this reaction with $ZrCl_4(THF)_2$ and (cyclo-C_6H_{11})N═CHC(Me)═CH(Ph) (**1a**) generated a brown solution from which small amounts of dark yellow crystals could be separated (Scheme 1).

The ^1H NMR spectrum (THF-d_8) of this zirconium complex **6** reveals three different resonances for olefinic protons (δ 6.34, 6.26, and 5.94), each integrated to one hydrogen, as well as three singlets for three different methyl resonances (δ 1.97, 1.62, and 1.55). These surprising spectroscopic data demonstrate that at least three 1-aza-1,3-diene ligands are bonded to the zirconium atom. However, a singlet at δ 2.42 integrated to one hydrogen which can be assigned to a methine group attached to the zirconium suggests that only one of the 1-aza-1,3-dienes is σ^2,π-coordinated to the zirconium, forming an 1-aza-2-zirconacyclopent-4-ene ring. No other ZrC*H* methine proton resonance was observed. Instead, two doublets at δ 4.95 and 4.82 ($^3J_{H,H}$ = 10 Hz) assigned to two vicinal aliphatic protons indicate that a new ligand system had formed by C−C coupling of two other 1-aza-1,3-dienes. This remarkable structural feature has been confirmed by an X-ray structural analysis.

Molecular Structure of 6. Recrystallization of complex **6** from pentane afforded suitable orange crys-

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(9) The first isolable intermediate produced during the reduction reaction of the 1-aza-1,3-diene (*i*Pr)N═CHC(Me)═CH(Ph) with lithium is the *N,N'*-dilithium hexa-1,5-diene-1,6-diamide $\{[Li(OEt_2)]_2[N(iPr)CH{=}C(Me)CH(Ph)CH(Ph)C(Me){=}CHN(iPr)]\}$. This C−C coupling product is probably formed by dimerization of the initially generated radical anion of the 1-aza-1,3-diene. However, finally the reduction results in the formation of the desired dilithium 1-azabut-2-ene-1,4-diyl compound $\{[Li(OEt_2)]_2[N(iPr)CH{=}C(Me)CH(Ph)]\}$.

(10) (a) Scholz, J.; Nolte, M.; Krüger, C. *Chem. Ber.* **1993**, *126*, 803−809. (b) Scholz, J.; Kahlert, S.; Görls, H. *Organometallics* **1998**, *17*, 2876−2884. (c) Mashima, K.; Matsuo, Y.; Nakahara, S.; Tani, K. *J. Organomet. Chem.* **2000**, *593−594*, 69−76.

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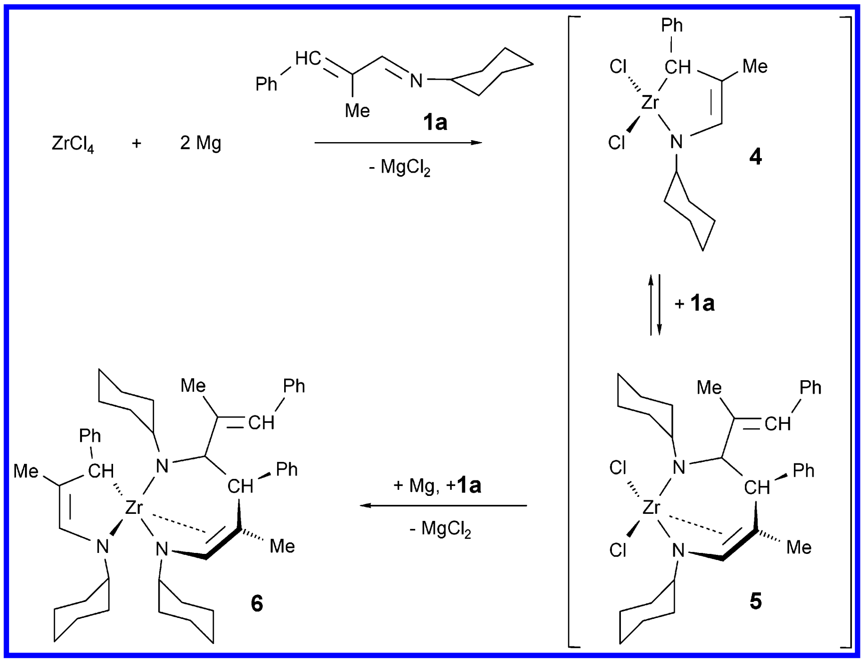
Scheme 1. Proposed Reaction Pathway of the Formation of 6



tals. The molecular structure is provided in Figure 1 with the appropriate atom-labeling scheme for the non-hydrogen atoms. Data collection parameters and selected important bond lengths and bond angles are summarized in Tables 1 and 2.

The new complex contains a metallabicyclic framework which is made up of a five-membered ring comprising the zirconium atom and a s-cis-configured 1-aza-1,3-diene unit and of a seven-membered ring which consists of two 1-aza-1,3-diene molecules that have coupled to form a but-1-ene-1,4-diamide ligand and which is N,N-coordinated to the zirconium. Interestingly, the structure shows that the new single bond between the carbon atoms C19 and C33 (C19−C33 = 1.533(7) Å) has changed these atoms to chiral centers of the molecule. Hence, two diastereoisomers could have been formed; however, only one has been observed in the crystal. It is characterized by a gauche conformation of the phenyl group and the substituted vinyl group at the novel bond (C26−C19−C33−C34 = −54.9(3)°). In solution, too, only a single diastereoisomer of **5** was observed. The large (anti-periplanar) coupling of $^{3}J_{\mathrm{H,H}}$ = 10 Hz of the vicinal protons at C19 and C33 (δ 4.95 and 4.82) places the phenyl group and the substituted vinyl group in a gauche orientation, similar to the solid-state structure.

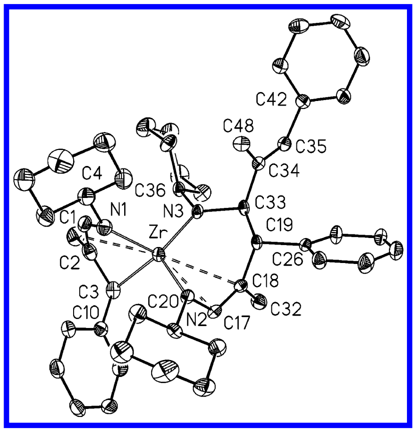


Figure 1. ORTEP drawing of complex **6** (50% probability level) with the atom-labeling scheme (hydrogen atoms have been omitted for clarity).

An interesting feature of the seven-membered metallacyclic ring of **6** is the significant difference in the Zr−N bonding distances. Thus, the Zr−N3 bond length (2.069(4) Å) is comparatively short, indicating a π-donation from the nearly sp^2-hybridized nitrogen atom (summation of bonding angles at N3 359.3(3)°) to the electron-deficient zirconium center. The Zr−N2 distance is noticeably longer (2.120(4) Å), which is certainly a consequence of the formation of a σ,π-distorted η^3-azaallyl unit comprising N2 and the adjacent carbon atoms C17 and C18 (N2−C17 = 1.359(6) Å, C17−C18 = 1.342(7) Å) and its concerted interaction with the zirconium (Zr−C17 = 2.505(5) Å, Zr−C18 = 2.753(5) Å). Unfortunately, to date only few structurally characterized η^3-azaallyl zirconium complexes have been published, but their bonding parameters are largely comparable with those of **6**.[13]

As suggested from NMR data only one of the 1-aza-1,3-dienes is σ^2,π-coordinated to the zirconium, forming a five-membered zirconacycle which is comparable to that of the zirconocene 1-aza-1,3-diene complex $Cp_2Zr[N(C_6H_4\text{-}2\text{-}Me)CH{=}C(Me)CH(Ph)]$.[10a] Thus, the Zr−N1 (2.089(5) Å) and the Zr−C3 distances (2.253(6) Å) as well as the inner C1═C2 bond length (1.380(8) Å) are analogous to those of the zirconocene complex. With respect to the bonding mode of the 1-aza-1,3-diene ligand the characteristic folding of the five-membered chelate ring along the N1−C3 axis by 126.4(2)°, too, is of particular relevance. However, the nitrogen atom N1 is only slightly pyramidalized, as evidenced by the summation of the bond angles about N1 (351.3(3)°).

Until now we have had no mechanistic information about the individual events leading to the zirconium

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Table 1. Summary of X-ray Diffraction Data and Overall Refinement Parameters for 1b and 6−9

	1b	6	7	8	9
chem formula	$C_{21}H_{25}N$	$C_{48}H_{63}N_3Zr$	$C_{42}H_{50}N_2Ti$	$C_{63}H_{75}N_3Ti{\cdot}C_4H_{10}O$	$C_{68}H_{70}N_2O_2Ti{\cdot}{}^1/_2C_4H_{10}O$
mol wt	291.42	733.23	630.74	959.22	1032.22
cryst dimens (mm^3)	0.36 × 0.32 × 0.20	0.40 × 0.38 × 0.32	0.38 × 0.34 × 0.30	0.34 × 0.32 × 0.28	0.28 × 0.22 × 0.12
cryst color, shape	yellow prism	orange prism	black-brown prism	brown prism	pale yellow prism
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
temp (°C)		−90	−90	−90	−90
cell params					
a (Å)	17.656(2)	9.098(3)	18.196(2)	12.8723(6)	13.0733(5)
b (Å)	7.7290(1)	12.335(2)	9.3470(9)	16.2430(6)	13.3110(4)
c (Å)	26.880(5)	19.761(4)	22.620(3)	16.4383(4)	19.5635(7)
α (deg)		107.14(1)		62.750(2)	70.838(2)
β (deg)	98.733(9)	92.21(1)	108.454(4)	80.747(2)	81.537(2)
γ (deg)		98.62(1)		75.093(2)	62.963(2)
V ($Å^3$)	3625(1)	2087.2(9)	3649.3(7)	2949.0(2)	2864.34(17)
no. of formula units *Z*	8	2	4	2	2
calcd density ρ_c ($g\ cm^{-3}$)	1.068	1.230	1.148	1.080	1.197
abs coeff μ(Mo Kα) (cm^{-1})	0.61	2.99	2.65	1.85	1.98
scan type	$\phi-\omega$ scan	$\omega-2\theta$ scan	$\phi-\omega$ scan	$\phi-\omega$ scan	$\phi-\omega$ scan
F(000)	1264	824	1352	1034	1102
hkl range	−19 to +18, 0−8, −29 to +29	0−11, −15 to +15, −25 to +25	−20 to +20, 0−10, −25 to +25	0−14, −17 to +18, −17 to +18	−16 to +16, −17 to +17, −25 to +25
θ range (deg)	2.06−23.31	2.27−27.43	2.89−23.36	2.49−23.29	3.44−27.45
no. of unique total data	7138	10 096	8920	10 455	20 628
no. of indep data	4436	9497	5005	8047	12 795
R_{int}	0.080	0.0586	0.053	0.058	0.041
no. of obsd data with $F_o > 4\sigma(F_o)$	2567	5390	3691	5894	9667
no. of params	398	469	431	661	696
restraints	0	0	0	4	0
$R1_{obs}$	0.085	0.069	0.063	0.060	0.063
$wR2_{obs}$	0.214	0.178	0.164	0.179	0.120
$R1_{all}{}^a$	0.143	0.181	0.092	0.084	0.095
$wR2_{all}{}^b$	0.244	0.203	0.180	0.194	0.132
goodness of fit	1.001	0.923	1.019	1.038	1.046
largest diff peak/hole ($e\ Å^{-3}$)	0.234/−0.225	1.057/−0.959	0.333/−0.412	0.847/−0.257	0.792/−0.550

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\{N(R^1)CH{=}C(Me)CH(Ph)\}Zr\text{-}\{N(R^1)CH{=}C(Me)CH(Ph)CH\{C(Me){=}CH(Ph)\}N(R^1)\}]$ (6: R^1 = cyclo-C_6H_{11})

Bond Lengths			
Zr−N1	2.089(5)	Zr−N2	2.120(4)
Zr−N3	2.069(4)	Zr−C1	2.496(6)
Zr−C2	2.543(6)	Zr−C3	2.253(6)
Zr−C17	2.505(5)	Zr−C18	2.753(5)
N1−C1	1.394(8)	C1−C2	1.380(8)
C2−C3	1.448(8)	N2−C17	1.395(6)
C17−C18	1.342(7)	C18−C19	1.532(7)
N3−C33	1.482(6)	C33−C34	1.523(7)
C34−C35	1.329(7)	C19−C33	1.533(7)
Angles			
N1−Zr−N2	102.7(2)	N1−Zr−N3	115.3(2)
N2−Zr−N3	117.9(2)	N1−Zr−C3	88.6(2)
Zr−N1−C1	89.3(3)	Zr−C3−C2	83.8(4)
Zr−N2−C17	88.4(3)	Zr−N3−C33	124.4(3)
C26−C19−C33−C34	−54.9(3)		
(Zr, N1, C3)(C1, C2, C3, N1)	126.4(2)		
(Zr, N1, C3)(Zr, N2, N3)	93.3(2)		
sum of angles at N1	351.3(3)		
sum of angles at N2	343.9(3)		
sum of angles at N3	359.3(3)		

complex **6**, but the net results of this reaction are (i) the formation of a bond between the terminal carbon atom and the imine carbon atom of two 1-aza-1,3-dienes **1a**, yielding a new N,N′-bonded diamide ligand system, and (ii) the anionic coordination of a third 1-aza-1,3-diene **1a**, forming a 1-aza-2-zirconacyclopent-4-ene ring. We assume that the reaction sequence starts with the coordination of one 1-aza-1,3-diene **1a** to the reduced zirconium chloride, forming the intermediate **4** (Scheme 1). The subsequent addition of a second 1-aza-1,3-diene **1a** with C−C coupling corresponds to the common behavior of group 4 metal 1-aza-1,3-diene complexes[6,10] and leads to the seven-membered metallacyclic but-1-ene-1,4-diamide intermediate **5**. In the last step the intermediate **5** is reduced again and coordinated by a third 1-aza-1,3-diene.

Tuning the 1-Aza-1,3-diene Ligand. The high affinity of 1-aza-1,3-dienes to undergo addition reactions by their imine function should be severely lowered by increasing the steric bulk around the nitrogen atom. Therefore, we hoped to be more successful in preparing homoleptic 1-aza-1,3-diene complexes by using the 1-aza-1,3-diene **1b**. The molecular structure of **1b** (Figure 2, Table 3), which is simply prepared by addition of 1 equiv of 2,6-diisopropylaniline, $H_2NC_6H_3$-2,6-*i*Pr_2, to 1 equiv of cinnamyl aldehyde, PhCH=CHCHO,[14] shows the common feature of 1-aza-1,3-dienes.[9,15]

Thus, the α,β-unsaturated heterodiene chain N1−C1−C2−C3 presents an s-trans conformation with respect to the central single bond C1−C2 (1.438(6) Å),

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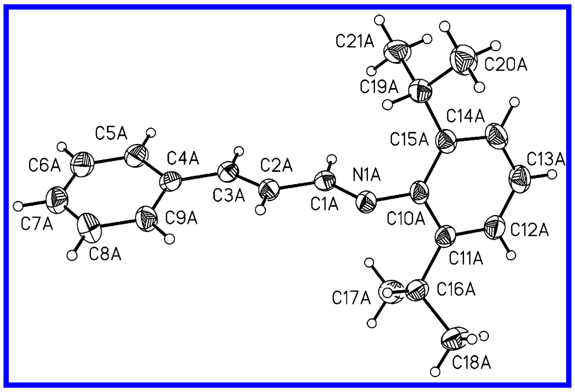


Figure 2. ORTEP drawing of the 1-aza-1,3-diene **1b** (50% probability level) with the atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (C_6H_3-2,6-*i*Pr_2)N=CHCH=CH(Ph) (1b; Molecule A)

Bond Lengths			
N1−C1	1.278(5)	C1−C2	1.438(6)
C2−C3	1.351(5)	N1−C10	1.432(6)
C3−C4	1.454(6)		
Angles			
N1−C1−C2	122.9(4)	C1−C2−C3	122.4(4)
C2−C3−C4	128.4(4)	C1−N1−C10	118.7(4)
N1−C1−C2−C3	173.9(4)	C1−C2−C3−C4	174.6(4)
C2−C1−N1−C10	177.3(4)		

and the N−C1 (1.278(5) Å) and the C2−C3 bond lengths (1.351(5) Å) clearly indicate a double bond. However, the aryl substituent C_6H_3-2,6-*i*Pr_2 at the nitrogen atom is arranged in such a way that the C=N function is largely shielded from the *i*Pr groups. Furthermore, as a consequence of the sterically demanding C_6H_3-2,6-*i*Pr_2 group at the nitrogen the donor properties of the ligand are expected to be weaker, which altogether results in a lower reactivity.

Slow addition of 2 equiv of magnesium turnings to a solution of $TiCl_4$ and 2 equiv of the 1-aza-1,3-diene **1b** in THF at −60 °C and subsequent warming to room temperature leads to a brown-red solution from which the new titanium complex **7** can be isolated as dark brown crystals in 63% yield (Scheme 2).

Complex **7** is thermally stable in the solid state and can be stored under argon at room temperature for several months. It is slightly soluble in diethyl ether, THF, and toluene but only sparingly soluble in aliphatic hydrocarbons. Moreover, solutions of **7** are very sensitive to minute traces of oxygen or water. At room temperature the ^1H NMR spectrum shows only broad resonances in the aromatic as well as in the aliphatic region, which do not supply any helpful information about the structure of **7**. At lower temperatures, the resonances coalesce and split into a large number of signals, as expected. Thus, upon coordination of two molecules of the 1-aza-1,3-diene to the titanium the symmetry of the complex is lowered so that each ligand gives rise to a complete set of resonances which partially overlap. Additionally, as the rotation of the *i*Pr groups at the phenyl rings is obviously frozen at −60 °C, eight separated methyl resonances between δ 1.28 and 0.47 can be observed.

Nevertheless, the resonances of the spin−spin-coupled hydrogen atoms at δ 1.21 (TiC*H*) and 6.06 (C*H*=CHN) as well as at δ 1.14 and 5.49 clearly indicate that the 1-aza-1,3-dienes are reduced upon coordination. Therefore, the bonding situation in **7** is best described as a 1-titana-2-azacyclopent-3-ene complex (**a**) rather than a η^4-1-aza-1,3-diene complex (**b**) (Chart 2).

Scheme 2. Reduction of $TiCl_4$ with Mg in the Presence of 1b

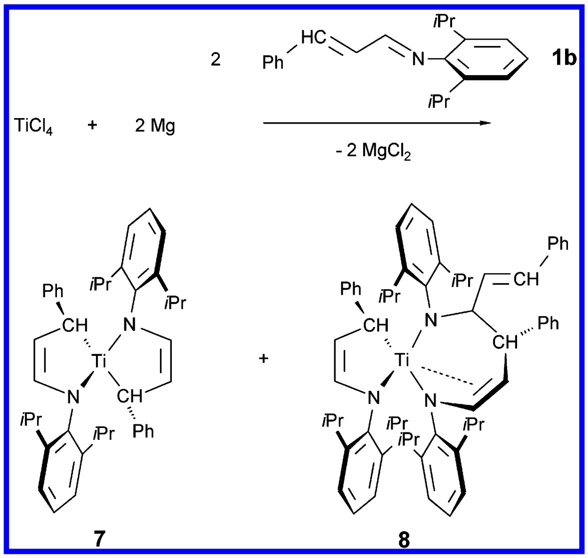
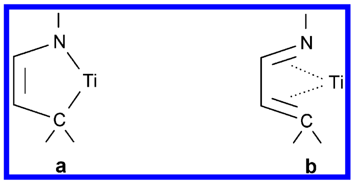


Chart 2. Structural Extremes in the Range of Bonding Modes between Titanium and the 1-Aza-1,3-diene



Admittedly, the available NMR spectral data do not allow a full description of the bonding situation, especially because the poor solubility of **7** at low temperatures precludes observation of ^{13}C resonances. Fortunately, dark brown cubic crystals suitable for an X-ray structure analysis could be grown from diethyl ether.

Molecular Structure of 7. The molecular structure is provided in Figure 3 with the appropriate atom-labeling scheme. Except for H1 and H22 the hydrogen atoms are omitted for clarity. Crystal data are collected

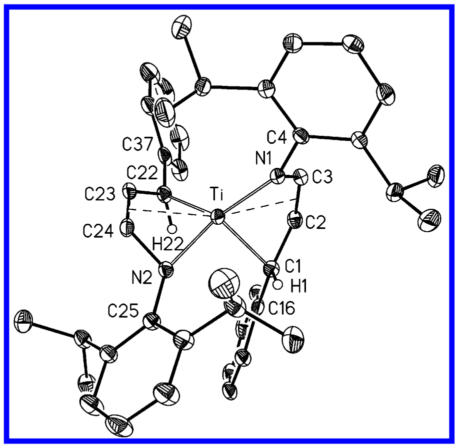


Figure 3. ORTEP drawing of complex **7** (50% probability level) with the atom-labeling scheme. All the hydrogen atoms of the molecule (except H1 and H22) have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Ti[{N(C_6H_3-2,6-*i*Pr_2)CH=CHCH(Ph)]$_2$ (7)

Bond Lengths			
Ti−N1	1.955(3)	Ti−N2	1.943(3)
Ti−C1	2.120(4)	Ti−C2	2.322(4)
Ti−C3	2.431(4)	Ti−C22	2.145(4)
Ti−C23	2.319(4)	Ti−C24	2.317(4)
Ti−H1	2.25(1)	Ti−H22	2.22(1)
C1−C2	1.421(5)	C2−C3	1.375(5)
N1−C3	1.397(5)	C22−C23	1.445(5)
C23−C24	1.382(5)	N2−C24	1.392(4)
Angles			
N1−Ti−N2	129.12(12)	N1−Ti−C1	92.33(13)
N2−Ti−C22	92.32(13)	C1−Ti−C22	105.17(16)
N1−Ti−C22	131.70(14)	N2−Ti−C1	99.77(13)
Ti−N1−C3	85.9(2)	Ti−C1−C2	79.2(2)
Ti−N2−C24	86.4(2)	Ti−C22−C23	77.8(2)
Ti−C1−H1	85.9(5)	Ti−C22−H22	81.6(5)
(Ti, N1, C1)(N1, C3, C2, C1)	118.2(2)		
(Ti, N2, C22)(N2, C24, C23, C22)	117.0(2)		
(Ti, N1, C1)(Ti, N2, C22)	87.0(2)		
sum of angles at N1	355.4(2)		
sum of angles at N2	357.8(2)		

in Table 1, and selected bond lengths and bond angles are presented in Table 4. Both of the 1-aza-1,3-diene ligands of **7** are coordinated to the Ti atom via the terminal carbon and nitrogen atoms, which are disposed in a pseudo-tetrahedral arrangement about the titanium center. Obviously, in this conformation the steric repulsion between the bulky nitrogen substituents is best minimized. The Ti−N (1.955(3) and 1.943(3) Å) as well as the Ti−C_{term} distances (2.120(4) and 2.145(4) Å) are comparable with those found in the monocyclopentadienyltitanium 1-aza-1,3-diene complex **3a** (Ti−N = 1.920(1) Å, Ti−C_{term} = 2.136(1) Å)[10b] and are in the typical range found for Ti−C_{alkyl} and Ti−N_{amide} σ-bonds.[16] Moreover, the relatively close contacts between the titanium atom and the internal heterodiene carbon atoms (Ti−C2 = 2.322(4), Ti−C3 = 2.431(4), Ti−C23 = 2.319(4), and Ti−C24 = 2.317(4) Å) are also comparable with those found for **3a**. Thus, from covalent radii, it appears that interaction of the titanium atom occurs with all four atoms of the 1-aza-1,3-diene framework of both ligands. Nevertheless, the N1−C3 and N2−C24 distances of 1.397(5) and 1.392(4) Å as well as the terminal C1−C2 and C22−C23 distances of 1.421(5) and 1.445(5) Å of the coordinated 1-aza-1,3-dienes are significantly longer than those of the free ligand **1b** (N1−C1 = 1.278(5) Å, C2−C3 = 1.351(5) Å; Table 3). On the other hand, the internal C2−C3 and C23−C24 distances of 1.375(5) and 1.382(5) Å are short compared with that of **1b** (C1−C2 = 1.438(6) Å).

Altogether, the inversion of the bond length sequence from that in the free heterodiene is consistent with a 1-titana-2-azacyclopent-3-ene structure, which demonstrates that the ligands are bound in the 1-azabut-2-ene-1,4-diyl fashion. In accordance with this bonding mode the five-membered rings are folded along the N1−C1 and the N2−C22 axis ("envelope structure") with dihedral angles between the planes defined by (Ti, N1, C1) and (N1, C1, C2, C3) as well as between (Ti, N1, C22) and (N1, C22, C23, C24) measuring 118.2(2) and 117.0(2)°, respectively. Despite the observed folding of the 1-titana-2-azacyclopent-3-ene rings the nitrogen atoms N1 and N2 maintain a planar, sp^2 environment, as the summation of angles at N1 (355.4(2)°) and N2 (357.8(2)°) shows. Apparently, the nitrogen lone pairs are substantially involved in π-bonding to the titanium center.

As in the titanium 1-aza-1,3-diene complexes **2** and **3a** one of the most interesting structural features of **7** concerns the bonding parameters of the TiCH groups. The positions of the hydrogen atoms H1 and H22, which are the anti protons of C1 and C22, were clearly resolved and indicate that these hydrogen atoms are markedly displaced away from titanium and out of the heterodiene planes by 0.57 Å each. Similar displacements of the anti hydrogen atoms out of the ligand plane have been observed for other titanium diene and 1-aza-1,3-diene complexes and are generally thought to be also a consequence of sp^2−sp^3 rehybridization of the terminal carbon atoms upon coordination of the diene ligands to the transition metal.[10b,17] Anyway, nearly rectangular Ti−C−H angles (Ti−C1−H1 = 85.9(5)°; Ti−C22−H22 = 81.6(5)°) and small Ti···H distances of 2.25(1) and 2.22(1) Å, respectively, are observed, which are absolutely comparable with those of MeTiCl_3(dmpe) (Ti−C−H = 93.5(2)°, Ti···H = 2.447(3) Å) or of other alkyltitanium complexes where α-agostic interactions have been postulated.[18] Unfortunately, the NMR spectra of **7** do not give any additional information concerning the α-agostic behavior of the 1-aza-1,3-diene ligands. However, in a forthcoming paper we will describe that this C−H activation in **7** can be used to induce an α-hydrogen abstraction, leading to a novel metallacyclic titanium alkylidene complex.[19]

Compound **7** represents the first homoleptic 1-aza-1,3-diene complex of the early transition metals and shows structural similarities with the known homoleptic titanium 1,3-diene (*t*BuCH=CHCH=CH*t*Bu)$_2$Ti[20] and 1,4-diaza-1,3-diene complexes ($R^1N{=}CR^2CR^2{=}NR^1$)$_2$Ti (R^1 = *i*Pr, *t*Bu, C_6H_4-2-Me; R^2 = H, Me).[21] In all these complexes the diene or heterodiene ligands prefer the metallacyclopentene structure (Chart 2, **a**) which is probably both a consequence of their high π-acceptor capability and significant steric repulsion between the ligands.

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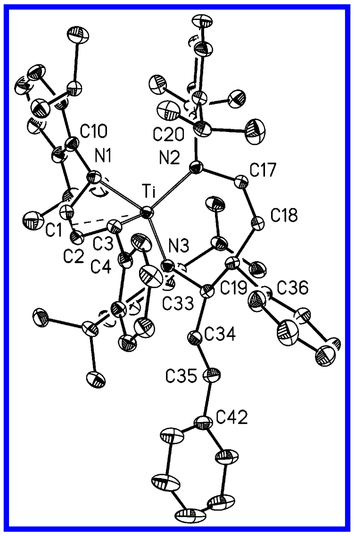

Figure 4. ORTEP drawing of complex **8** (50% probability level) with the atom-labeling scheme (hydrogen atoms have been omitted for clarity).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [{N(R^1)CH=CHCH(Ph)}Ti-{N(R^1)CH=CHCH(Ph)CH{CH=CH(Ph)}N(R^1)] (8: R^1 = C_6H_3-2,6-*i*Pr_2)

Bond Lengths			
Ti−N1	1.960(3)	Ti−N2	1.980(3)
Ti−N3	1.942(3)	Ti−C1	2.373(4)
Ti−C2	2.387(4)	Ti−C3	2.185(3)
N1−C1	1.394(4)	C1−C2	1.367(5)
C2−C3	1.453(5)	N2−C17	1.421(4)
C17−C18	1.339(5)	C18−C19	1.509(5)
N3−C33	1.509(4)	C33−C34	1.508(5)
C34−C35	1.336(5)	C19−C33	1.566(5)
Angles			
N1−Ti−N2	104.59(11)	N1−Ti−N3	125.88(12)
N2−Ti−N3	111.31(11)	N1−Ti−C3	89.41(12)
Ti−N1−C1	88.4(2)	Ti−C3−C2	79.2(2)
Ti−N2−C17	118.3(2)	Ti−N3−C33	118.8(2)
C36−C19−C33−C34	36.3(2)		
(Ti, N1, C3)(C1, C2, C3, N1)	117.6(2)		
(Ti, N1, C3)(Ti, N2, N3)	83.3(2)		
sum of angles at N1	357.5(2)		
sum of angles at N2	359.9(2)		
sum of angles at N3	359.4(2)		

Molecular Structure of the Byproduct 8. When the dark brown mother liquor retained after the separation of **7** subsequently was concentrated and cooled to −10 °C for several days, a very few dark red crystals of a second organometallic product precipitated. The small amount of this product (less than 2%) has precluded its spectroscopic characterization, but fortunately the crystals were suitable for an X-ray structure analysis. A perspective view of the molecular structure of **8** is shown in Figure 4; crystal data are listed in Table 1 and selected bond lengths and angles in Table 5.

The structure analysis reveals a molecular geometry which is similar to that of **6**. In fact, the transition metal forms the center of a spirocyclic ring system consisting of a five-membered titana-2-aza-cyclopent-3-ene ring and a seven-membered titana-2,7-diazacyclohept-3-ene ring. Thus, we conclude that the 1-aza-1,3-diene **1b**, despite the bulky N substituent, is still reactive enough to add to the Ti−C bond of an 1-aza-1,3-diene titanium intermediate, as described for the formation of the zirconium complex **6**. However, the very low amount of the C−C coupling product **8** demonstrates that the reaction course depends on the balance between the π-acceptor capability (coordination reaction) and the reactivity of the C=N function (addition reaction) of the 1-aza-1,3-diene, which is mainly influenced by the bulkiness of the nitrogen substituent. Thus, the steric demand of the N-substituent can be used like an adjusting screw to tune the product distribution of this one-pot reaction.

The seven-membered titana-2,7-diazacyclohept-3-ene ring of **8** exhibits a twisted-boat conformation, as is expected for an unsaturated seven-membered ring with bulky substituents. However, due to the smaller radius of the titanium compared with that of zirconium and the stronger steric hindrance in its coordination sphere, no π-interactions between the transition metal and the C17=C18 bond become operative. Moreover, in contrast to **6** there are no substantial differences between the Ti−N2 (1.980(3) Å) and Ti−N3 bond lengths (1.942(3) Å). The nearly perfect trigonal disposition of bonds around N2 (359.9(2)°) and N3 (359.4(2)°) implicates that both nitrogen atoms are sp^2 hybridized and participate as three-electron donors to titanium. The geometry of the titana-2-azacyclopent-3-ene ring is nearly identical with that of the homoleptic titanium complex **7**. The five-membered ring is folded along the N1−C3 vector by 117.6(2)°, which does not differ from the corresponding folding angles of **7** (117.0(2) and 118.2(2)°) and is apparently largely independent of the nature of the coligands. Most interest, however, is again attracted by the structural details of the TiCH group: the hydrogen atom attached to C3 is displaced from the heterodiene plane by 0.75 Å. This unusual structural feature is completed by a distorted Ti−C3−H3 angle of 96.1(5)° together with a short Ti···H3 contact of 2.48(1) Å.

Reaction of 7 with Benzophenone. Recently we reported that monocyclopentadienyltitanium 1-aza-1,3-diene complexes **3**, which can be treated as the equivalent of metalated allylamines and therefore be used as homoenolate equivalents,[6b] readily undergo a carbonyl addition reaction with ketones.[10b] With respect to the first results of these studies it can be expected that carbon−carbon coupling reactions of carbonyl compounds with 1-aza-1,3-diene dianion equivalents other than **3** will make a variety of interesting new organic products available in a rather simple and predictable way. Consequently, we have examined the reaction of the homoleptic 1-aza-1,3-diene complex **7** with benzophenone.

Treatment of the 1-aza-1,3-diene complex **7** with 2 equiv of benzophenone in THF solution at room temperature yielded a brown-yellow solution, which after removal of solvent and extraction of the residue with diethyl ether afforded dark yellow crystals of the titanium complex **9** in high yield (Scheme 3). Chemical analysis confirms that two molecules of benzophenone have been added; thus, two C−C bonds between the heterodiene termini and the carbonyl carbon atoms as well as two strong titanium-to-oxygen linkages have been formed concurrently. According to these findings both in the ^{1}H and in the ^{13}C NMR spectra two sets of typical resonances are depicted, which can be unambiguously assigned to the new chelating ligands [OC-$(Ph)_2$CH(Ph)CH=CHN[C_6H_3-2,6-(*i*$Pr)_2$].

Scheme 3. Addition of Benzophenone to 7

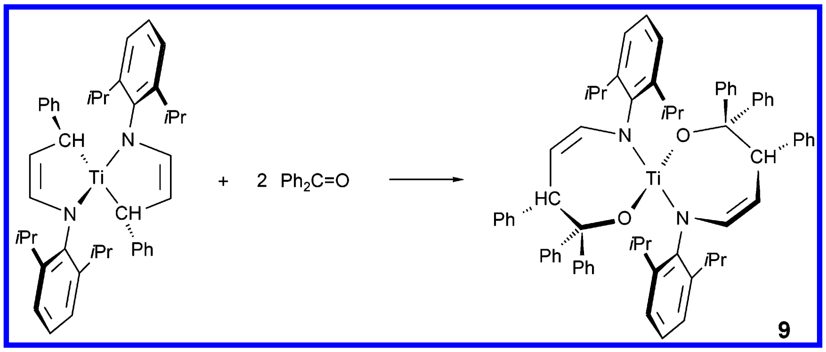

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Ti[OC(Ph)$_2$CH(Ph)CH=CHN(C$_6$H$_3$-2,6-*i*Pr$_2$)]$_2$ (9)

Bond Lengths			
Ti−O1	1.809(1)	Ti−O2	1.823(1)
Ti−N1	1.928(2)	Ti−N2	1.986(2)
O1−C1	1.434(2)	C1−C2	1.601(3)
C2−C3	1.509(3)	C3−C4	1.340(3)
C4−N1	1.418(3)	O2−C35	1.431(2)
C35−C36	1.586(3)	C36−C37	1.516(3)
C37−C38	1.348(3)	C38−N2	1.409(3)

Angles			
O1−Ti−O2	115.16(7)	N1−Ti−N2	113.81(7)
O1−Ti−N1	100.96(7)	O1−Ti−N2	112.77(7)
O2−Ti−N1	102.15(7)	O2−Ti−N2	111.17(7)
Ti−O1−C1	150.1(1)	Ti−O2−C35	139.2(1)
Ti−N1−C4	120.2(1)	Ti−N2−C38	95.0(1)

(Ti, O1, N1)(Ti, N2, O2)	95.7(1)
sum of angles at N1	359.6(2)
sum of angles at N2	355.2(2)

The structure and conformation of **9** in the solid state was confirmed by X-ray diffraction analysis. Single crystals were obtained by recrystallization from diethyl ether. A view of the molecular structure of **9** is shown in Figure 5, together with the numbering scheme used. Selected bond distances and angles are given in Table 6.

The terminal nitrogen and oxygen atoms of the chelating ligands are coordinated in a distorted-tetrahedral geometry around the titanium, the angle between the (Ti, N1, O1) and (Ti, N2, O2) planes measuring 95.7(1)°. Both of the azaoxatitanacycloheptene rings adopt a folded-ring conformation similar to that observed for the reported product of the carbonyl addition reaction of **3a** and acetophenone.[10b] To a first approximation the atoms of the s-cis-configurated 1-aza-1,3-diene building blocks are arranged in a coplanar fashion (maximum deviation ±0.05 Å). Interesting features of the molecular structure of **9** are the different Ti−O−C angles: one of them is remarkably large (Ti−O1−C1 = 150.1(1)°), indicating a pronounced titanium−oxygen π-bonding, which is confirmed by a strikingly short Ti−O1 linkage of 1.809(1) Å.[22] The other Ti−O bond is somewhat longer (Ti−O2 = 1.823(1) Å) but still shorter than the Ti−O σ-bond distance predicted on the basis of covalent radii (ca. 1.98 Å).[23] The amide nitrogen atoms are nearly planar (sum of angles: N1, 359.6(2)°; N2, 355.2(2)°). However, from the Ti−N distances, which are only marginally shorter than expected for a Ti−N σ-bond distance (ca. 2.02 Å),[23] it can be assumed that their available p orbitals do not compete with the oxygen donor orbitals for π-bonding with the metal d acceptor orbitals. The remaining bond lengths and angles of the two seven-membered metallacycles meet expectations.

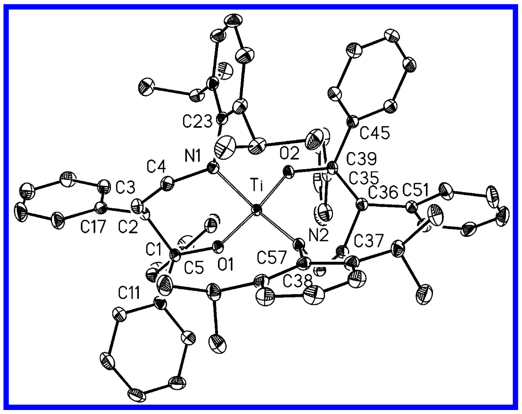

Figure 5. ORTEP drawing of complex **9** (50% probability level) with the atom-labeling scheme (hydrogen atoms have been omitted for clarity).

Concluding Remarks. As a part of an ongoing project, this study reports on our efforts to synthesize homoleptic 1-aza-1,3-diene complexes of the early transition metals. Actually, the first results demonstrate that bis(1-aza-1,3-diene)titanium complexes can be prepared by simply reducing TiCl$_4$(THF)$_2$ in the presence of 1-aza-1,3-dienes. Only if the 1-aza-1,3-dienes are modified by bulky substituents at the nitrogen atom, as in **1b,** are the homoleptic 1-aza-1,3-diene titanium complexes the major products in this one-pot reaction. Otherwise, a second organometallic complex in which three 1-aza-1,3-dienes are coordinated to the metal atom becomes the more prevalent product. However, two of these heterodienes in this byproduct are connected by a new C−C bond, yielding a new stabilizing but-1-ene-1,4-diamide ligand system. The most important structural feature of the novel homoleptic bis(1-aza-1,3-diene)titanium complex concerns the metallacyclopentene structure of the heterodienes combined with an α-agostic TiCH interaction. Due to the distinct alkyl character of the bonds between the titanium and the terminal carbon atoms of the 1-aza-1,3-dienes, the reaction of the new complex with benzophenone fits into the general scheme established for addition reactions of carbonyl compounds to early-transition-metal alkyl complexes.

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[23] Ranges for Ti−O as well as Ti−N σ-bond distances were estimated using covalent radii (Ti, 1.32 Å; O, 0.66 Å; N, 0.70 Å) taken from: Emsley, J. *Die Elemente*; Walter de Gruyter: Berlin, New York, 1994. (b) For typical Ti−O bond distances, see also ref 16.

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (THF, diethyl ether) or $LiAlH_4$ (pentane) under argon and stored over activated 4 Å molecular sieves. Deuterated THF-d_8 was treated with sodium/potassium alloy and then distilled and stored under argon. All glassware was thoroughly oven-dried or flame-dried under vacuum prior to use. Benzophenone was purchased from Aldrich Chemicals and used as received. $TiCl_4(THF)_2$ and $ZrCl_4(THF)_2$ were prepared according to literature procedures.[24] NMR spectra were recorded in THF-d_8 on a Varian 300 BB (^{1}H NMR at 300.075 MHz, ^{13}C NMR at 75.462 MHz) or a Varian UNITY 500 spectrometer (^{1}H NMR at 499.843 MHz, ^{13}C NMR at 125.639 MHz) at 25 °C, unless indicated otherwise. ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances (THF-d_8: δ_H 1.73, δ_C 25.2). $^1J_{C-H}$ values were obtained from gated $^{13}C\{^1H\}$ NMR spectra. Elemental analyses were carried out by the analysis laboratory at the Martin-Luther-University of Halle-Wittenberg. Melting points are uncorrected.

Crystallographic Data Collections and Structure Determination of 1b and 6−9. The crystal structure determination of **6** was carried out on an Enraf-Nonius CAD4 diffractometer; those of **1b** and **7**−**9** were carried out on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. The crystals were mounted under a stream of cold nitrogen, and the data were collected at −90 °C. Crystallographic and experimental details are summarized in Table 1. Data were corrected for Lorentz and polarization but not for absorption effects.[25−27] The structures were solved by direct methods (SHELXS)[28] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[29] Only for the 1-aza-1,3-diene backbone of the compounds **7**−**9** were the hydrogen atoms located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[29] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The files CCDC 205793−205797 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., fax (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).

Preparation and Spectroscopic Data for the 1-Aza-1,3-dienes 1a and 1b. Standard literature procedures were used for the preparation of the 1-aza-1,3-dienes **1a** and **1b**.[14] Thus, equimolar amounts of the cinnamyl aldehyde and the corresponding amine are stirred together at room temperature in ethanol as a solvent for several hours. Subsequently, the reaction mixtures were cooled to 5 °C to precipitate the 1-aza-1,3-dienes. They were purified by recrystallization from diethyl ether (**1a**) or pentane (**1b**).

(cyclo-C_6H_{11})N=CHC(Me)=CH(Ph) (1a). ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 7.97 (s, 1H, C*H*=N), 7.42−7.15 (m, 5H, *Ph*), 6.71 (s, 1H, =C*H*Ph), 3.08 (m, 1H, cyclo-C_6H_{11}), 2.11 (s, 3H, *Me*), 1.85−1.11 (m, 10H, cyclo-C_6H_{11}). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 163.32 (d, $^1J_{C,H}$ = 155.2 Hz, N=*C*H), 138.08 (d, $^1J_{C,H}$ = 151.7 Hz, =*C*HPh), 136.70 (s, =*C*Me−), 136.70 (s, *1*-Ph), 129.24 (d, $^1J_{C,H}$ = 159.0 Hz, *2,6*-Ph), 128.21 (d, $^1J_{C,H}$ = 160.1 Hz, *3,5*-Ph), 127.39 (d, $^1J_{C,H}$ = 161.0 Hz, *4*-Ph), 69.62 (d, $^1J_{C,H}$ = 131.3 Hz, cyclo-C_6H_{11}), 34.45 (t, $^1J_{C,H}$ = 126.4 Hz, cyclo-C_6H_{11}), 25.65 (t, $^1J_{C,H}$ = 127.1 Hz, cyclo-C_6H_{11}), 24.86 (t, $^1J_{C,H}$ = 126.9 Hz, cyclo-C_6H_{11}), 13.37 (q, $^1J_{C,H}$ = 127.9 Hz, =C*Me*-).

(C_6H_3-2,6-*i*Pr_2)N=CHCH=CH(Ph) (1b). ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 7.97 (dd, $^3J_{H,H}$ = 6.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, C*H*=N), 7.61 (m, 2H, *2,6*-Ph), 7.40−7.31 (m, 3H, *4*-Ph, *4*-C_6H_3-2,6-*i*Pr_2, =C*H*−), 7.19 (d, 2H, *3,5*-C_6H_3-2,6-*i*Pr_2), 7.09 (t, 2H, *3,5*-Ph), 6.99 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, =C*H*Ph), 2.98 (sept, $^3J_{H,H}$ = 6.9 Hz, 2H, C*H*Me_2), 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 164.83 (d, $^1J_{C,H}$ = 156.6 Hz, N=*C*H), 150.85 (s, *1*-C_6H_3-2,6-*i*Pr_2), 144.40 (d, $^1J_{C,H}$ = 155.0 Hz, =*C*H−), 137.89 (s, *2,6*-C_6H_3-2,6-*i*Pr_2), 136.84 (s, *1*-Ph), 130.17 (d, $^1J_{C,H}$ = 160.8 Hz, *4*-C_6H_3-2,6-*i*Pr_2), 129.61 (d, $^1J_{C,H}$ = 162.2 Hz, *2,6*-Ph), 129.47 (d, $^1J_{C,H}$ = 159.3 Hz, =*C*HPh), 128.36 (d, $^1J_{C,H}$ = 160.2 Hz, *3,5*-C_6H_3-2,6-*i*Pr_2), 124.63 (d, $^1J_{C,H}$ = 159.2 Hz, *4*-Ph), 123.48 (d, $^1J_{C,H}$ = 155.4 Hz, *3,5*-Ph), 28.67 (d, $^1J_{C,H}$ = 128.3 Hz, *C*HMe_2), 23.82 (q, $^1J_{C,H}$ = 125.6 Hz, CH*Me*$_2$).

[N(R)CH=C(Me)CH(Ph)]Zr[N(R)CH=C(Me)CH(Ph)CH{C(Me)=CH(Ph)}N(R)] (6: R = cyclo-C_6H_{11}). To a solution of $ZrCl_4(THF)_2$ (5.00 g, 16.38 mmol) and the 1-aza-1,3-diene **1a** (7.50 g, 33.00 mmol) in THF (150 mL) were added magnesium turnings (0.80 g, 32.76 mmol). The reaction mixture was stirred at ambient temperature until the magnesium was dissolved. During this time the color of the solution changed from pale yellow to red-orange. The resulting mixture was evaporated to dryness, and the product was extracted with diethyl ether (100 mL) to leave magnesium chloride. The red-orange extract was concentrated to 50 mL and stored at −20 °C for 3 days to yield 1.2 g (1.55 mmol, 10%) of **6** as an orange solid (mp 152−154 °C dec), which was isolated by filtration. Recrystallization from pentane yielded orange crystals suitable for X-ray structure analysis (Table 1). Anal. Calcd for $C_{48}H_{63}N_3Zr$: C, 75.56; H, 8.21; N, 5.43. Found: C, 75.39; H, 8.30; N, 5.61. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 7.31−6.97 (m, 10H, *Ph*), 6.88 (d, 2H, *2,6-Ph*), 6.74 (t, 1H, *4-Ph*), 6.62 (d, 2H, *2,6-Ph*), 6.34 (s, 1H, =C*H*−), 6.26 (s, 1H, =C*H*−), 5.94 (s, 1H, =C*H*−), 4.95 (d, $^3J_{H,H}$ = 10 Hz, 1H, −C*H*CH−), 4.82 (d, $^3J_{H,H}$ = 10 Hz, 1H, −CHC*H*−), 3.37 (m, 2H, cyclo-C_6H_{11}), 2.95 (m, 1H, cyclo-C_6H_{11}), 2.42 (s, 1H, ZrC*H*), 1.97 (s, 3H, Me), 2.10−1.05 (m, cyclo-C_6H_{11}), 1.62 (s, 3H, Me), 1.55 (s, 3H, Me).

Ti[N(C_6H_3-2,6-*i*Pr_2)CH=CHCH(Ph)]$_2$ (7). To a solution of $TiCl_4(THF)_2$ (3.50 g, 10.50 mmol) and the 1-aza-1,3-diene **1b** (6.12 g, 21.00 mmol) in THF (150 mL) were added magnesium turnings (0.51 g, 21.00 mmol) over a period of 8 h at −60 °C. The reaction mixture was warmed to room temperature and was stirred until the magnesium was dissolved. Then, the mixture was evaporated to dryness, and the product was extracted with diethyl ether (100 mL) to leave magnesium chloride. The dark brown extract was concentrated to 50 mL and stored at −20 °C. A yield of 4.17 g (6.62 mmol, 63%) of dark brown crystals of **7** was obtained. Mp: 150−155 °C dec. Recrystallization from diethyl ether yielded crystals suitable for X-ray structure analysis (Table 1). Anal. Calcd for $C_{42}H_{50}N_2Ti$ (630.73): C, 79.98; H, 7.99; N, 4.44. Found: C, 79.75; H, 7.95; N, 4.51. ^{1}H NMR (500 MHz, THF-d_8, −60 °C): δ 7.17−6.95 (m, 9H, C_6*H*$_3$-2,6-*i*Pr_2, *Ph*, CH=C*H*N), 6.84−6.79 (m, 3H, C_6*H*$_3$-2,6-*i*Pr_2, *Ph*), 6.68 (d, 1H, *Ph*), 6.45 (m, 3H, C_6*H*$_3$-2,6-*i*Pr_2, *Ph*), 6.38 (d, 1H, *Ph*), 6.06 (dd, $^3J_{H,H}$ = 11 Hz, $^3J_{H,H}$ = 5 Hz, 1H, C*H*=CHN), 6.03 (d, 1H, *Ph*), 5.49 (dd, $^3J_{H,H}$ = 10 Hz, $^3J_{H,H}$ = 5 Hz, 1H, C*H*=CHN), 2.99 (m, 2H, C*H*Me_2), 2.80 (m, 1H, C*H*Me_2), 2.72 (m, 1H, C*H*Me_2), 1.28 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 1.21 (m, 4H, TiC*H*, CH*Me*$_2$), 1.14 (d, $^3J_{H,H}$ = 5 Hz, 3H, TiC*H*), 1.05 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.94 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.82 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.72 (d,

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$^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.69 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.47 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$).

[N(R)CH═CHCH(Ph)]Ti[N(R)CH═CHCH(Ph)CH{CH═CH(Ph)}N(R)] (8: R = C_6H_3-2,6-*i*Pr$_2$). The dark brown mother liquor obtained in the procedure mentioned above was subsequently concentrated to a volume of 20 mL and cooled to −10 °C. After standing for several days a very few dark red crystals of the insertion product **8** have been grown, which were studied by X-ray structure analysis (Table 1).

Ti[OC(Ph)$_2$CH(Ph)CH═CHN(C_6H_3-2,6-*i*Pr$_2$)]$_2$ (9). Benzophenone (0.87 g, 4.77 mmol) was added to a solution of the 1-aza-1,3-diene titanium complex **7** (1.50 g, 2.38 mmol) in 100 mL of THF. The reaction mixture was stirred at room temperature for 8 h. Subsequently, the solvent was removed in vacuo and the residual brown-yellow solid was extracted with diethyl ether (100 mL). The extract was concentrated to 50 mL and cooled to −5 °C for 2 days, yielding 1.94 g (82%) of dark yellow crystalline **9**. Crystals of **9** suitable for X-ray structure analysis were obtained by recrystallization from diethyl ether (Table 1). Mp: 165 °C dec. Anal. Calcd for $C_{68}H_{70}N_2O_2Ti$ (995.16): C, 82.07; H, 7.09; N, 2.81. Found: C, 82.00; H, 7.12; N, 2.88. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 7.86−6.25 (m, 40 H; *Ph*, C_6H_3-2,6-*i*Pr$_2$, C*H*═C*H*), 4.82 (d, $^3J_{H,H}$ = 11 Hz, 1H, C*H*Ph), 4.55 (d, $^3J_{H,H}$ = 10 Hz, 1H, C*H*Ph), 3.87, 3.52, 3.18, 2.67 (br m, 4H, C*H*Me$_2$), 1.42 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 1.00 (m, 6H, CH*Me*$_2$), 0.89 (d, $^3J_{H,H}$ = 7 Hz, 3H, CH*Me*$_2$), 0.72 (d, $^3J_{H,H}$ = 6 Hz, 6H, CH*Me*$_2$), 0.48 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$), 0.18 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C; selected signals): δ 148.51, 148.13, 147.48, 146.97, 145.88, 145.07, 140.86, 140.72 (*1*-Ph, *1*,*2*,*6*-*C*$_6$H$_3$-2,6-*i*Pr$_2$), 124.93, 124.42, 123.84, 116.33 (*C*H═*C*H), 114.02, 108.21 (O*C*Ph$_2$), 62.66, 61.95 (*C*HPh), 30.64, 28.85, 28.17, 27.64 (*C*HMe$_2$), 23.79, 23.69, 23.54, 23.33, 23.01 (CH*Me*$_2$).

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1b** and **6**−**9**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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