

Substituted 1,4-Diaza-1,3-butadiene Monocyclopentadienyl Titanium Complexes. Crystal Structure of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^i\text{PrNCH=CHN}^i\text{Pr})\text{Me}$

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We report the synthesis of 1,4-diaza-1,3-butadiene (dad) complexes $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-R}'_2\text{-dad})\text{Cl}$ ($\text{R} = \text{H, Me}$; $\text{R}' = ^i\text{Pr, } ^t\text{Bu}$) by reaction of $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3$ ($\text{R} = \text{H, Me}$) with the dilithium salts of diisopropyl- and di-*tert*-butyl-substituted 1,4-diaza-1,3-butadienes ($\text{Li}_2[\text{R}'_2\text{-dad}]$). Alkylation of the pentamethylcyclopentadienyl diisopropyl and di-*tert*-butyl derivatives with methylmagnesium chloride and methyllithium gave complexes $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^i\text{Pr}_2\text{-dad})\text{Me}$ and $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^t\text{Bu}_2\text{-dad})\text{Me}$, respectively. Addition of excess water to di-*tert*-butyl chloro complexes gave the oxo-bridged complexes $[\{\text{Ti}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-}^t\text{Bu}_2\text{-dad})\}_2(\mu\text{-O})]$ ($\text{R} = \text{H, Me}$). The temperature-dependent spectroscopic behavior of $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-}^t\text{Bu}_2\text{-dad})\text{Cl}$ and $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-}^t\text{Bu}_2\text{-dad})\}_2(\mu\text{-O})]$ complexes was studied. The crystal structure of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^i\text{Pr}_2\text{-dad})\text{Me}$ was determined by X-ray crystal diffraction on a single crystal and shows a distorted trigonal bipyramidal structure.

Introduction

Diazabutadienes (dad) have been extensively employed as coordinating ligands for the later transition metals¹ but have only more recently been employed with lanthanoids² and group 4³ and group 5 metals.⁴ As described, ligands of this type can act as either neutral or dianionic ligands in various coordination modes (from $\eta^1\text{-N}$ to $\eta^4\text{-N}_2\text{C}_2$ (σ^2 , π)), and the N-substituents can regulate the steric demand at the metal center. The diazadiene ligand in groups 4 and 5 cyclopentadienylmetal complexes⁵ is bound to the metal center as an enediamide ligand, and their structures can be compared to those adopted by the group 4 metal buta-1,3-diene complexes $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(1,3\text{-diene})$ and $\text{M}(\eta^5\text{-C}_5\text{H}_5)(1,3\text{-diene})\text{Cl}$ ($\text{M} = \text{group 4 metal}$). The σ^2, π -enediamido ligand can adopt two conformations (*supine* or *prone*) relative to the cyclopentadienyl ligand, and it exhibits dynamic behavior amenable to NMR spectroscopy investigation.

Herein we report the synthesis of some isopropyl- and *tert*-butyl-substituted 1,4-diaza-1,3-butadiene ($\text{R}_2\text{-dad}$) complexes of titanium, their reactivity toward alkylating reagents, and their hydrolysis reactions.

Results and Discussion

$\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3$ ($\text{R} = \text{H}$, **1**; $\text{R} = \text{Me}$, **2**) complexes react in a 1:1 molar ratio with the dilithium salts of isopropyl- and *tert*-butyl-substituted 1,4-diaza-1,3-butadienes ($\text{R}'_2\text{-dad}$, $\text{R}' = ^i\text{Pr}$, **3**; $\text{R}' = ^t\text{Bu}$, **4**)⁶ to give the corresponding $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-R}'_2\text{-dad})\text{Cl}$ ($\text{R} = \text{H}$, $\text{R}' = ^i\text{Pr}$, **5**; $\text{R} = \text{Me}$, $\text{R}' = ^i\text{Pr}$, **6**; $\text{R} = \text{H}$, $\text{R}' = ^t\text{Bu}$, **7**; $\text{R} = \text{Me}$, $\text{R}' = ^t\text{Bu}$, **8**) complexes in moderate to good yields. Two of the chloride atoms were replaced by a diazabutadiene ligand (eq 1) with the formation of lithium chloride. The isopropyl complexes **5** and **6** precipitated as red crystals,

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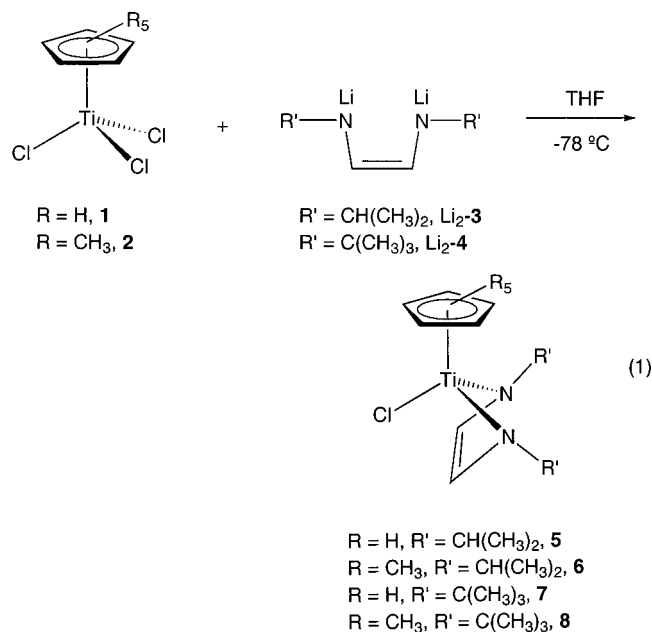
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Table 1. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) Data of Complexes **7** and **11**

^1H NMR	7			11	
	243 K			243 K	318 K
	major	minor	303 K		
$\text{C}(\text{CH}_3)_3$	1.30	1.32	1.31	0.97, 1.40	1.24
C_5H_5	5.83	5.68	5.82	5.59	5.63
NCH	6.58	6.46	6.40	5.56, 5.58	5.60
$^{13}\text{C}\{^1\text{H}\}$ NMR	major	minor			
$\text{C}(\text{CH}_3)_3$	30.7	31.9	30.7	30.8	31.0
$\text{C}(\text{CH}_3)_3$	59.4	63.2	59.4	57.4, 57.6	57.7
NCH	96.5	103.6	96.5	100.8, 101.0	101.7
C_5H_5	108.3	111.7	108.3	104.4	104.6

7 forms violet crystals, and **8** was isolated as a brown solid. Complex **7**, published earlier,^{3c} was prepared by addition of lithiumcyclopentadienide to dichloroglyoxalbis(*tert*-butylimine)titanium. All of the chloro complexes are air and moisture sensitive and all are soluble in aliphatic solvents.

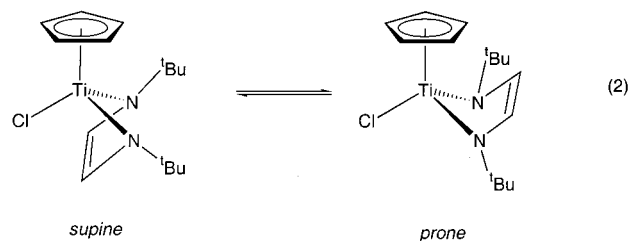


The room-temperature ^1H NMR spectra of complexes **5–8** contain few signals, indicating highly symmetrical molecules (see Experimental Section). The methyl groups of the isopropyl substituents in **5** and **6** appear as two doublets corresponding to two diastereotopic groups. All of the methyl groups of the *tert*-butyl substituents in complexes **7** and **8** appear as singlets in the expected region.

The azomethine protons for all these complexes appear in the olefinic region of the spectra ($\delta = 6.40\text{--}5.78$), consistent with the enediamide structure of these compounds.^{1a,3c,5b}

The ^1H NMR data of complex **7** in C_6D_6 agree with reported values,^{3c} and full NMR characterization was achieved in CDCl_3 (see Table 1). At room temperature, the ^1H NMR spectrum of **7** shows two broad resonance signals for the azomethine and cyclopentadienyl protons. Cooling the NMR sample reveals temperature-dependent dynamic NMR spectra resulting from the typical automerization ("flipping") of the Ti– R_2 -dad framework (eq 2) that is rapid on the NMR time scale

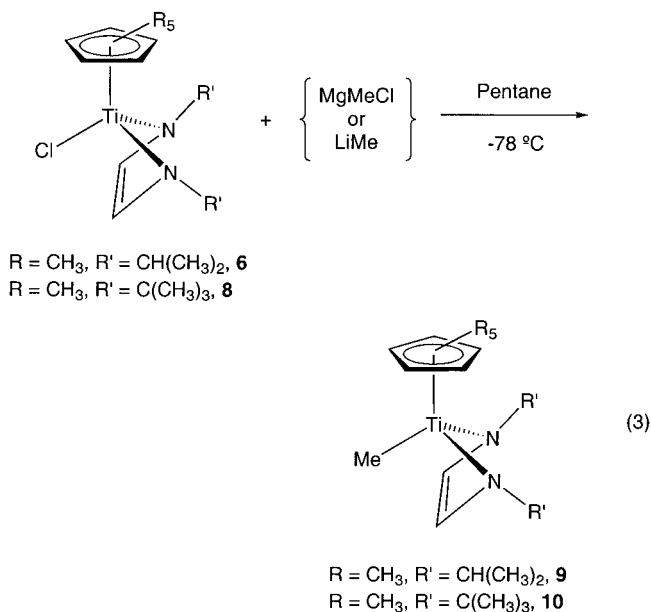
at room temperature. Complexes **5**, **6**, and **8** show no broadening in their proton resonance signals in the range 213–333 K.



The low-temperature (243 K) ^1H NMR spectrum of **7** shows two sets of signals in a ca. 1:3 ratio for the methyl groups of the *tert*-butyl substituents, the protons of the cyclopentadienyl group, and the azomethine protons. From the coalescence temperatures of the azomethine ^1H NMR resonance signals at 293 K, the cyclopentadienyl ^1H NMR signals at 303 K and the methyl of the *tert*-butyl group ^1H NMR signals at 268 K, Gibbs activation energies ΔG^\ddagger between 14.81 and 14.97 kcal mol^{−1} were obtained for the topomerization process of complex **7** (see Table 2).

Reports^{3a,b,e} concerning the low barriers of inversion of the bent chelate rings show that the bonding between the metal and the backbone C atoms is only of minor importance.

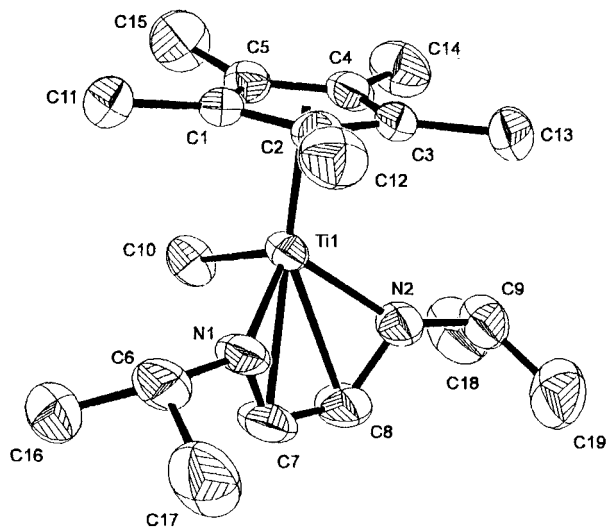
Addition of methylmagnesium chloride to complex **6** proceeds with substitution of the chloride by a methyl group to give complex $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^i\text{Pr}_2\text{-dad})\text{Me}$ (**9**) in good yield (eq 3). Complex **9** precipitated from a pentane solution as red crystals, and its crystal structure was determined from a single-crystal X-ray diffraction study.



Similar attempts to alkylate complex **5** produced an initial reaction but ultimately resulted in a complicated mixture of several compounds, from which no identifiable product could be separated. Although complexes **7** and **8** were recovered unaltered when treated with MgMeCl , treatment of **8** with methyllithium gave complex $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-}^i\text{Bu}_2\text{-dad})\text{Me}$ (**10**) in moderate

Table 2. Dynamic Process Data of Complexes 7 and 11

	T_c (K)	E_a (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	$\Delta G^\ddagger_{298\text{ K}}$ (kcal mol ⁻¹)	$\Delta G^\ddagger_{T_c}$ (Kcal mol ⁻¹)
7						
¹ Bu	268	14.87 ± 2.1	14.34 ± 2.1	-1.73 ± 7.8	14.86 ± 2.1	14.81 ± 2.1
NCH	293	9.65 ± 0.9	9.11 ± 0.9	-20.02 ± 3.5	15.07 ± 0.9	14.97 ± 0.9
C ₅ H ₅	303	14.12 ± 0.6	13.59 ± 0.6	-4.54 ± 2.4	14.94 ± 0.6	14.96 ± 0.6
11						
¹ Bu	308	17.97 ± 0.7	17.41 ± 0.7	9.93 ± 2.5	14.45 ± 0.7	14.35 ± 0.7
NCH	273					

**Figure 1.** ORTEP diagram of the molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity.**Table 3. Selected Bond Lengths [Å] and Angles [deg] for Ti(C₅(CH₃)₅)(ⁱPr₂-dad)CH₃ (**9**)**

bond lengths		angles	
Ti-N(1)	1.926(4)	N(1)-Ti-N(2)	91.6(2)
Ti-N(2)	1.918(4)	N(1)-Ti-C(10)	106.5(2)
Ti-C(10)	2.207(4)	N(2)-Ti-C(10)	105.2(2)
Ti-C(7)	2.359(5)	Ti-N(1)-C(6)	144.5(4)
Ti-C(8)	2.366(5)	Ti-N(1)-C(7)	90.1(3)
Ti-C(1)	2.373(4)	C(6)-N(1)-C(7)	118.9(4)
Ti-C(2)	2.379(4)	Ti-N(2)-C(8)	90.3(3)
Ti-C(3)	2.371(4)	Ti-N(2)-C(9)	145.0(4)
Ti-C(4)	2.377(4)	C(8)-N(2)-C(9)	117.8(4)
Ti-C(5)	2.380(5)	N(1)-C(7)-C(8)	121.4(5)
N(1)-C(6)	1.464(6)	N(2)-C(8)-C(7)	119.9(5)
N(1)-C(7)	1.359(7)	N(1)-Ti-Cp	117.9
N(2)-C(8)	1.376(6)	N(2)-Ti-Cp	119.7
N(2)-C(9)	1.470(6)	C(10)-Ti-Cp	113.2
C(7)-C(8)	1.362(7)	Cp-Ti-Cd	157.9
Ti-Cp	2.053		
Ti-Cd	2.262		

^a Cp is the centroid of C(1), C(2), C(3), C(4), C(5), and Cd is the midpoint of C(7), C(8).

yield (eq 3) as dark red crystals, while a similar reaction with **7** gave an unresolved mixture of unknown composition.

The Ti-Me group in complexes **9** and **10** shows ¹H and ¹³C NMR chemical shifts at δ 2.05 and 35.7 and at δ 1.90 and 39.5, respectively, indicating relative electronic saturation at the metal center probably due to π coordination of the diazadiene ligand.^{5b,g} An X-ray diffraction study on a single crystal of **9** confirms the σ^2 - π coordination of the diazadiene ligand. An ORTEP diagram of this compound is shown in Figure 1, and selected distances and angles are listed in Table 3.

As Figure 1 shows, the molecule has a monomeric structure, with the pentamethylcyclopentadienyl ring,

the dad ligand, and the methyl group bonded to the titanium center. It can be considered as a distorted trigonal bipyramid with the five-carbon atom ring and the diene group of the dad ligand in apical positions (angle Cp-Ti-Cd of 157.9° where Cp is the centroid of C(1)-C(5) and Cd is the midpoint of C(7)-C(8)). The metal atom is located out of the plane defined by C(10) and the nitrogen atoms (distance Ti-plane N(1)-N(2)-C(10) of 0.908(1) Å), which is parallel to the pentamethylcyclopentadienyl ring (1.4(1)°). Similar coordination geometries have been reported for complexes Ti(η^5 -C₅H₅)(η^4 -1,4-(*p*-C₆H₄OMe)₂-2,3-R₂-dad)Cl (R = H, Me, Ph).^{5d,7}

The structure shows a noncrystallographic plane of symmetry containing the pentamethylcyclopentadienyl ring centroid, the metal center, C(10), and the midpoint of the dad central C-C bond. Therefore the molecule shows the expected two resonances for the methyl groups of the two equivalent ⁱPr substituents as well as one resonance for the azomethine protons.

The ⁱPr₂-dad ligand is coordinated to the metal center by two single Ti-N bonds and additionally through donation of electron density from the diene group to the titanium atom, as evidenced by the Ti-C(7) and Ti-C(8) bond lengths of 2.359(5) and 2.366(5) Å, respectively (Ti-Cd 2.262 Å). This makes the Ti-C(10) bond length of 2.207(4) Å in the region of that found in the Ti(II) complex Ti(1,2-(PMe₂)₂CH₂CH₂)₂Me₂ (2.219(2) Å),⁸ but elongated with respect to the distances found in other methyl-titanium complexes with amino, amido, and amidinate substituents (from 2.110 to 2.1385(17) Å).⁹ The C-C bond length of the diene group (1.362(7) Å) is similar to reported values for related dad complexes showing a π interaction between the double C-C bond and the metal center (1.371(7)-1.390(4) Å).^{5c,d,7,10}

Thus, the five-membered chelate ring is not planar and is folded along the N-N axis by 127.9(2)° with a planar dad ligand (torsion angle N(1)-C(7)-C(8)-N(2) of 0.2(8)°), which locates the central carbon atoms of the ⁱPr substituents toward the pentamethylcyclopentadienyl ligand and the methyl groups forward of this group.

The N-Ti-N angle of 91.6(2)° and the Ti-N bond lengths of 1.926(4) Å (Ti-N(1)) and 1.918(4) Å (Ti-N(2))

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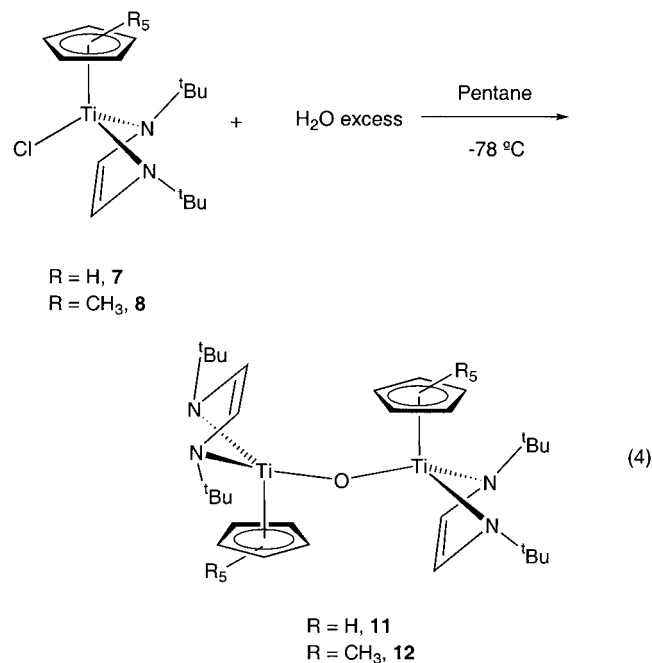
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are in accordance with reported values for related titanium diamide¹¹ and diazadiene complexes.^{3c-f,12} The nitrogen atoms are slightly pyramidalized, as evidenced by the summation of bond angles at N(1) (353.5°) and at N(2) (353.1°).

The N–C bond lengths of 1.359(7) and 1.376(6) Å for N(1)–C(7) and N(2)–C(8), respectively, are larger than the reported values for analogous free dad ligand (1.269–(2) Å in ^tBu₂-dad¹³ and 1.258(3) Å in (cyclohexyl)₂-dad¹⁴) and are in agreement with reported values for enedi- amide ligands showing slight double-bond character.^{1a} The N–C ⁱPr bond lengths of 1.464(6) Å for N(1)–C(6) and 1.470(6) Å for N(2)–C(9) are consistent with single-bond distances.

Addition of excess water to pentane solutions of complex **5** proceeds with complete decomposition of the starting material to a mixture of unknown composition in which no organometallic components were detected. However the same reaction with complex **6** afforded [Ti-(C₅Me₅)₄(μ-O)]₆,¹⁵ identified from its ¹H and ¹³C NMR spectra.

The addition of excess water to solutions of complexes **7** and **8** proceeds with the formation of brown solutions, from which the oxo-bridged complexes [{Ti(η⁵-C₅R₅)(η⁴-^tBu₂-dad)}₂(μ-O)] (R = H, **11**; Me, **12**) were obtained in good yield (eq 4) as brown-black solids.



The room-temperature ¹H NMR spectra of complexes **11** and **12** again contain few signals, which indicates

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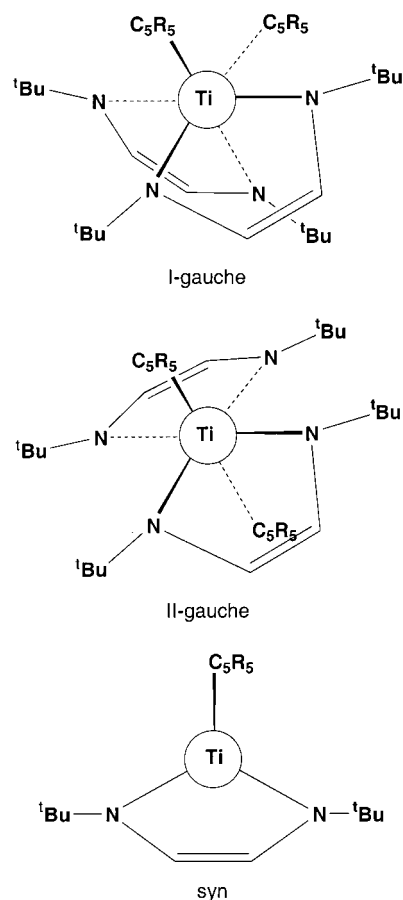
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Chart 1



highly symmetrical molecules (see Table 1 and Experimental Section). All the methyl groups of the *tert*-butyl substituents in complex **12** appear as one singlet in the expected region, while two broad signals in a 1:1 ratio were observed for **11** at room temperature. Variable-temperature NMR spectra of **11** show the *tert*-butyl groups as two resonance signals, the azomethine protons as two doublets of an AB spin system (³J_{HH} = 3.25 Hz), and the protons of the cyclopentadienyl rings as one singlet, indicating the existence, at low temperature, of only one (I-*gauche* in Chart 1) of the possible configurations. We did not take into account any change of the signals of the cyclopentadienyl protons in the temperature range from 243 to 318 K. The dynamic NMR behavior observed for complex **11** (see Table 2) apparently results from the molecule in a frozen configuration rather than from a fluxional process similar to that established for **7**, despite the probability that this process takes place simultaneously.

According to Bottomley,¹⁶ the most common arrangement of the ligands in complexes [M(η⁵-C₅R₅)L₂](μ-O) comprises a linear M–O–M angle and parallel cyclopentadienyl rings analogous to the II-*gauche* configuration in Chart 1 for complex **11**. However, when the ligands are bulky or the M–O–M unit is not linear, there are pronounced steric interactions between L and the cyclopentadienyl ring which are reduced by rotation of one of the M(η-C₅R₅)L₂ units with respect to the other, as we found for complex **11**. The energies of the different configurations are very similar; for complex **11** a Gibbs

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activation energy of $\Delta G^\ddagger_{308\text{ K}} = 14.35 \pm 0.7 \text{ kcal mol}^{-1}$ was found from the coalescence of the *tert*-butyl protons signals at 308 K (see Table 2). The proximity of the C_5H_5 resonance signal to the AB spin system of the azomethine protons does not allow the dynamic behavior of the latter signals to be studied, although its coalescence is reached at 273 K. Complex **12** shows no broadening of the proton resonance signals in the range 213–303 K.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation over sodium/potassium alloy. Li (Panreac), MgMeCl (Aldrich), and LiMe (Aldrich) were used as received. Lithium¹⁷ and Grignard¹⁸ solutions were titrated prior to use. NMR spectra were recorded on a Bruker DRX 400 and a Varian unity 300 spectrometers (^1H , 400.14 MHz, 299.95 MHz; ^{13}C , 75.43 MHz) in CDCl_3 at 298 K. Chemical shifts (in ppm) for ^1H and ^{13}C were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Mass spectra were recorded on a Finigan 8230 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHNO instrument.

Syntheses. Complexes $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ (**1**),¹⁹ $[\text{Ti}(\text{C}_5(\text{CH}_3)_5)\text{Cl}_3]$ (**2**),²⁰ and $\text{R}_2\text{-dad}$ ($\text{R} = \text{iPr}$, **3**; $\text{R} = \text{tBu}$, **4**)^{13,21} were prepared by known procedures.

Preparation of $\text{Li}_2(\text{R}_2\text{-dad})$ ($\text{R} = \text{iPr}$, **Li₂-3; $\text{R} = \text{tBu}$, **Li₂-4**).** Addition of 0.37 g (53.5 mmol) of lithium metal to a THF solution of **3** (3 g, 21.40 mmol) cooled to -78°C (ca. 50 mL) proceeded with darkening of the initially beige solution to dark red. This solution was filtrated and the solvent completely removed to give $\text{Li}_2(\text{iPr}_2\text{-dad})$ (1.50 g, 46%) as a yellow solid. $\text{Li}_2(\text{tBu}_2\text{-dad})$ was prepared in a similar way from metal lithium (0.91 g, 1.31 mmol) and **4** (10 g, 59.40 mmol); yield 9.3 g (86%).

Preparation of $[\text{Ti}(\text{C}_5\text{H}_5)(\text{iPr}_2\text{-dad})\text{Cl}]$ (5**).** Cooled THF (ca. 30 mL) was added to a solid mixture of **1** (1.0 g, 4.56 mmol) and 0.7 g (4.56 mmol) of the dilithium salt of **3**, at -78°C . The mixture was allowed to warm slowly to room temperature. All volatiles were removed, and hexane (ca. 20 mL) was added to give a brown-red solution. The solution was filtrated, concentrated, and cooled to -30°C to give red crystals; yield 0.74 g (57%): ^1H NMR (299.95 MHz, CDCl_3 , 298 K) δ 1.12, 1.17 (d, $^3J_{\text{HH}} = 7 \text{ Hz}$, 6 H, $\text{CH}(\text{CH}_3)_2$), 4.28 (sept., $^3J_{\text{HH}} = 7 \text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.32 (s, 2 H, NCH), 6.39 (s, 5 H, C_5H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.43 MHz, CDCl_3 , 298 K) δ 23.6, 25.2 ($\text{CH}(\text{CH}_3)_2$), 59.6 ($\text{CH}(\text{CH}_3)_2$), 103.2 (NCH), 111.8 (C_5H_5); EI MS m/z 288 (100, M^+), 148 (88, $\text{M}^+ - \text{iPr}_2\text{-dad}$), 113 (39, $\text{M}^+ - \text{iPr}_2\text{-dad} - \text{Cl}$). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{N}_2\text{ClTi}$: C, 54.11; H, 7.28; N, 9.71. Found: C, 53.94; H, 7.27; N, 9.71.

Preparation of $[\text{Ti}(\text{C}_5(\text{CH}_3)_5)(\text{iPr}_2\text{-dad})\text{Cl}]$ (6**).** Compound **6** was prepared in a manner analogous to that used to prepare **5**. Reaction of **2** (0.5 g, 1.74 mmol) with the dilithium salt of **3** (0.27 g, 1.74 mmol) gave **6** as dark red crystals; yield 0.34 g (55%): ^1H NMR (299.95 MHz, CDCl_3 , 298 K) δ 1.08, 1.16 (d, $^3J_{\text{HH}} = 7 \text{ Hz}$, 6 H, $\text{CH}(\text{CH}_3)_2$), 2.04 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 4.49 (sept., $^3J_{\text{HH}} = 7 \text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.19 (s, 2 H, NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.43 MHz, CDCl_3 , 298 K) δ 11.5 ($\text{C}_5(\text{CH}_3)_5$), 21.9, 25.3 ($\text{CH}(\text{CH}_3)_2$), 54.7 ($\text{CH}(\text{CH}_3)_2$), 102.5 (NCH), 121.7 ($\text{C}_5\text{-}$

Table 4. Crystallographic Data for $\text{Ti}(\text{C}_5(\text{CH}_3)_5)(\text{iPr}_2\text{-dad})\text{CH}_3$ (9**)**

formula	$\text{C}_{19}\text{H}_{34}\text{N}_2\text{Ti}$
M_w	338.38
temp, K	293(2)
wavelength, Å	0.71073
cryst habit	prismatic
color	red
cryst size, mm	$0.25 \times 0.25 \times 0.28$
symmetry	monoclinic, $P2_1/c$
a , Å	15.815(1)
b , Å	8.096(1)
c , Å	16.749(1)
β , deg	107.04(1)
V , Å ³	2050.4(3)
Z	4
D_{calc} , g cm ⁻³	1.096
$F(000)$	736
μ , cm ⁻¹	4.17
scan mode	$\omega/2\theta$, $2.51 < \theta < 25.99$
no. of reflns measd	4158
no. of ind obsd reflns	4010 ($R_{\text{int}} = 0.0295$)
no. reflns obsd	2320 ($I > 2\sigma(I)$)
range of hkl	$0 \leq h \leq 19, 0 \leq k \leq 9, -20 \leq l \leq 19$
standard reflns	3 every 200 reflns
refinement method	full-matrix least-squares on F^2
final R indices ($I > 2\sigma(I)$) ^a	$R1 = 0.0673$, $wR2 = 0.1722$
weighting scheme	calc $\omega = 1/[\sigma^2(F_o^2) + (0.1001P)^2 + 2.1486P]$ where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole, e/Å ³	0.550, -0.402
goodness of fit on F^2	0.985

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

$(\text{CH}_3)_5$; EI MS m/z 358 (100, M^+), 217 (67, $\text{M}^+ - \text{iPr}_2\text{-dad}$). Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{N}_2\text{ClTi}$: C, 60.28; H, 8.65; N, 7.81. Found: C, 59.96; H, 8.69; N, 7.65.

Preparation of $[\text{Ti}(\text{C}_5\text{H}_5)(\text{tBu}_2\text{-dad})\text{Cl}]$ (7**).** Compound **7** was prepared in a manner analogous to that used to prepare **5**. Reaction of **1** (0.30 g, 1.37 mmol) with the dilithium salt of **4** (0.25 g, 1.37 mmol) at -78°C gave violet crystals of **7** (0.25 g, 58%): EI MS m/z 317 (40, M^+), 280 (8, $\text{M}^+ - \text{Cl}$), 147 (40, $\text{M}^+ - \text{tBu}_2\text{-dad}$), 112 (20, $\text{M}^+ - \text{tBu}_2\text{-dad} - \text{Cl}$). Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{N}_2\text{ClTi}$: C, 59.91; H, 7.90; N, 8.85. Found: C, 59.91; H, 8.10; N, 9.03.

Preparation of $[\text{Ti}(\text{C}_5(\text{CH}_3)_5)(\text{tBu}_2\text{-dad})\text{Cl}]$ (8**).** Following a procedure analogous to that described to prepare **5**, **2** (1 g, 3.46 mmol) was reacted with the dilithium salt of **4** (0.63 g, 3.46 mmol) to give **8** as a brown solid; yield 1.20 g (90%): ^1H NMR (299.95 MHz, CDCl_3 , 298 K) δ 1.22 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 1.90 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 5.78 (s, 2 H, NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.43 MHz, CDCl_3 , 298 K) δ 10.2 ($\text{C}_5(\text{CH}_3)_5$), 30.4 ($\text{C}(\text{CH}_3)_3$), 59.8 ($\text{C}(\text{CH}_3)_3$), 99.7 (NCH), 120.2 ($\text{C}_5(\text{CH}_3)_5$); EI MS m/z 387 (42, M^+), 180 (14, $\text{M}^+ - \text{tBu}_2\text{-dad} - \text{Cl}$). Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{N}_2\text{ClTi}$: C, 62.13; H, 9.06; N, 7.25. Found: C, 62.26; H, 9.22; N, 7.48.

Preparation of $[\text{Ti}(\text{C}_5(\text{CH}_3)_5)(\text{iPr}_2\text{-dad})\text{CH}_3]$ (9**).** Methylmagnesium chloride (0.32 mL of a 3 M solution in THF) was added to a cooled ethereal solution of **6** (0.34 g, 0.95 mmol) at -78°C (ca. 10 mL), and the reaction mixture was allowed to warm slowly to room temperature overnight. All volatiles were removed in vacuo, and the residue was extracted into pentane (ca. 30 mL), filtrated, concentrated, and cooled to -30°C to obtain **9** as red crystals; yield 0.25 g (78%): ^1H NMR (299.95 MHz, CDCl_3 , 298 K) δ 1.09, 1.14 (d, $^3J_{\text{HH}} = 7 \text{ Hz}$, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.92 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 2.05 (s, 3 H, TiCH_3), 4.19 (sept., $^3J_{\text{HH}} = 7 \text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 5.84 (s, 2 H, NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.43 MHz, CDCl_3 , 298 K) δ 11.0 ($\text{C}_5(\text{CH}_3)_5$), 22.8, 25.4 ($\text{CH}(\text{CH}_3)_2$), 35.7 (TiCH_3), 53.5 ($\text{CH}(\text{CH}_3)_2$), 102.4 (NCH), 117.7 ($\text{C}_5(\text{CH}_3)_5$); EI MS m/z 338 (24, M^+), 323 (87, $\text{M}^+ - \text{CH}_3$), 181 (100, $\text{M}^+ - \text{CH}_3 - \text{iPr}_2\text{-dad}$). Anal. Calcd for $\text{C}_{19}\text{H}_{34}\text{N}_2\text{Ti}$: C, 67.48; H, 10.06; N, 8.29. Found: C, 67.28; H, 9.91; N, 8.18.

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Preparation of [Ti(C₅(CH₃)₅)(^tBu₂-dad)CH₃] (10). Following a procedure analogous to that described to prepare **9**, **8** (0.43 g, 1.11 mmol) was reacted with methyllithium (0.74 mL of a 1.5 M solution in THF) to give **10** as dark red crystals; yield 0.25 g (61%): ¹H NMR (299.95 MHz, CDCl₃, 298 K) δ 1.16 (s, 18 H, C(CH₃)₃), 1.83 (s, 15 H, C₅(CH₃)₅), 1.90 (s, 3 H, TiCH₃), 5.53 (s, 2 H, NCH); ¹³C{¹H} NMR (75.43 MHz, CDCl₃, 298 K) δ 11.5 (C₅(CH₃)₅), 30.5 (C(CH₃)₃), 39.5 (TiCH₃), 58.5 (C(CH₃)₃), 99.4 (NCH), 116.8 (C₅(CH₃)₅); EI MS *m/z* 366 (14, M⁺), 351 (100, M⁺ - CH₃), 183 (69, M⁺ - CH₃ - ^tBu₂-dad). Anal. Calcd for C₂₁H₃₈N₂Ti: C, 68.88; H, 10.38; N, 7.65. Found: C, 68.64; H, 10.06; N, 7.56.

Preparation of [Ti(C₅H₅)(^tBu₂-dad)₂O] (11). Distilled water (12 μL, 0.66 mmol) was added to a cooled solution of **7** (0.30 g, 0.95 mmol) in hexane (ca. 15 mL) at -78 °C, and the mixture was slowly heated to room temperature. The solution was filtrated over anhydrous MgSO₄ and filtrated again, concentrated, and cooled to -30 °C. Complex **11** was obtained as brown-black microcrystals; yield 0.19 g (70%): EI MS *m/z* 576 (100, M⁺), 296 (9, M⁺ - Ti(C₅H₅)(^tBu₂-dad)), 280 (41, M⁺ - Ti(C₅H₅)(^tBu₂-dad)O). Anal. Calcd for C₃₀H₅₀N₄O₂Ti₂: C, 61.31; H, 8.77; N, 9.69. Found: C, 61.47; H, 8.79; N, 9.90.

Preparation of [Ti(C₅(CH₃)₅)(^tBu₂-dad)₂O] (12). Following a procedure analogous to that described to prepare **11**, **8** (0.6 g, 1.55 mmol) was reacted with distilled water (19.5 μL, 1.1 mmol) to give **12** as a brown solid; yield 0.33 g (60%): ¹H NMR (299.95 MHz, CDCl₃, 298 K) δ 1.16 (s, 18 H, C(CH₃)₃), 1.89 (s, 15 H, C₅(CH₃)₅), 5.74 (s, 2 H, NCH); ¹³C{¹H} NMR (75.43 MHz, CDCl₃, 298 K) δ 11.6 (C₅(CH₃)₅), 30.6 (C(CH₃)₃), 57.8 (C(CH₃)₃), 102.0 (NCH), 117.0 (C₅(CH₃)₅). Anal. Calcd for C₄₀H₇₀N₄O₂Ti₂: C, 66.88; H, 9.75; N, 7.80. Found: C, 66.61; H, 9.65; N, 7.55.

Crystal Structure Determination of 9. Red crystals of **9** were obtained by cooling a concentrated pentane solution, and a suitable sized crystal was sealed in a Lindemann tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 4. 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-90,²² SIR97²³) and refined by least-squares against *F*² (SHELXS-97).²⁴ All non hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters.

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Supporting Information Available: Crystallographic data for **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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