Monoazadiene Complexes of Early Transition Metals. 2.[1] Syntheses and Structures of Titanium 1-Aza-1,3-diene Complexes and Their Reactions with Ketones†

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The novel dark green or violet and air-sensitive 1-aza-1,3-diene titanocene complexes $Cp_2Ti[N(R^1)CH{=}C(R^2)CH(Ph)]$ [R^1 = *t*-Bu, R^2 = H (**7a**); R^1 = C_6H_4-4-Me, R^2 = H (**7b**); R^1 = c-C_6H_{11}, R^2 = Me (**7c**)] were prepared by the complexation of the 1-aza-1,3-dienes **1a**−**c** to the titanocene "Cp_2Ti" generated in situ by reduction of Cp_2TiCl_2 with magnesium. The solid-state structure of **7c** shows a bent azatitanacyclic ring with a fold angle of 130.9(4)°. A series of electron-deficient 14e 1-aza-1,3-diene titanium complexes $CpTi[N(R^1)CH{=}C(Me)CH(Ph)]Cl$ [R^1 = c-C_6H_{11} (**8a**), *t*-Bu (**8b**), C_6H_4-2-Me (**8c**), C_6H_4-4-Me (**8d**)] has also been prepared by reduction of $CpTiCl_3$ with magnesium in the presence of the 1-aza-1,3-dienes $R^1N{=}CHC(Me){=}CH(Ph)$ **1c**−**f**. These new complexes were isolated as air-sensitive brown (**8a**,**b**) or dark red (**8c**,**d**) crystals in 50−65% yield. The X-ray crystal structure of **8c** revealed that the coordination geometry for the 1-aza-1,3-diene ligands has substantial σ^2,π-η^4-metallacyclopent-4-ene character. The 1-aza-1,3-diene complexes **8a**,**c**,**d** only exhibit *supine* geometry as confirmed by ^{1}H NMR spectroscopy, while **8b** exists in both the conventional *supine* geometry and the *prone* geometry, which is demonstrated by quite different ^{1}H NMR chemical shift values. Addition of **8c** to 1 equiv of acetophenone gives the seven-membered metallacyclic ring system $CpTi[N(C_6H_4\text{-}4\text{-}Me)CH{=}C(Me)CH(Ph)C(Me)PhO]$ (**9**), whose structure has also been characterized by NMR spectral data and by X-ray diffraction analysis. In contrast to **8c**, the 1-aza-1,3-diene titanocene complex $Cp_2Ti[N(c\text{-}C_6H_{11})CH{=}C(Me)CH(Ph)]$ (**7c**) does not react with acetophenone even at high temperatures.

Introduction

The metal-promoted coupling of unsaturated organic substrates constitutes a powerful strategy for carbon−carbon bond formations in organic synthesis.[2] Among the reductants employed for such reactions are several group 4 early transition metal−diene complexes. These complexes have received considerable current attention because of their unique M−C bonding properties and their high reactivity toward a broad range of electrophiles and unsaturated hydrocarbons.[3] Thus, several groups have described many examples where diene complexes react with 1 or 2 equiv of an organic carbonyl reagent to form seven- or nine-membered metallacycles.[4]

In the course of our research directed toward the reactivity of metal-coordinated heterodienes, we recently reported the syntheses and the first structural study of 1-aza-1,3-diene zirconocene complexes $Cp_2Zr[N(R^1)CH{=}C(R^2)CH(Ph)]$ (**2**) (R^1 = C_6H_4-2-Me, C_6H_4-4-Me; R^2 = H, Me).[1] Complexes **2** are available as air- and moisture-

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† MAD is used as an acronym for 1-aza-1,3-dienes (*mono*aza*d*ienes) in general. In this paper we will use MAD when *N*-alkyl-(*E*)-cinnamaldimines $(R^1)N{=}CHC(R^2){=}CH(Ph)$ (R^1 = *t*-Bu, c-C_6H_{11}; R^2 = H, Me) or *N*-aryl-(*E*)-cinnamaldimines (R^1 = C_6H_4-2-Me, C_6H_4-4-Me; R^2 = H, Me) are meant.

(1) (a) Part 1: Scholz, J.; Nolte, M.; Krüger, C. *Chem. Ber.* **1993**, *126*, 803. (b) Part 3: Kahlert, S.; Görls, H.; Scholz, J. *Angew. Chem.*, in press.

(2) (a) Seebach, D. *Angew. Chem.* **1990**, *102*, 1363; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1320. (b) *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987. (c) *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Eds.; Springer-Verlag: Berlin, 1989.

(3) (a) Negishi, E.; Takahashi, T. *Aldrichim. Acta* **1985**, *18*, 31. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (c) Akita, M.; Matsuoka, K.; Asami, K.; Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1987**, *327*, 193. (d) Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (e) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (f) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (g) Dang, Y.; Geise, J. H. *J. Organomet. Chem.* **1991**, *405*, 1. (h) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807. (i) Erker, G. *Pure Appl. Chem.* **1992**, *64*, 393. (j) Erker, G.; Berlekamp, M.; Lopez, L.; Grehl, M.; Schönecker, B.; Krieg, R. *Synthesis* **1994**, 212.

(4) Seven-membered metallacycles: (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Nakamura, A. *Chem. Lett.* **1981**, 671. (b) Kai, Y.; Kanehisa, N.; Miki, K.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3735. (c) Erker, G.; Dorf, U. *Angew. Chem.* **1983**, *95*, 800; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 777; *Angew. Chem. Suppl.* **1983**, 1120. (d) Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 494. Nine-membered metallacycles: (e) Ausema, J. B.; Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas.* **1987**, *106*, 465. (f) Yasuda, H.; Okamoto, T.; Matsuoka, Y.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1989**, *8*, 1139. (g) Noe, R.; Wingbermühle, D.; Erker, G.; Krüger, C.; Bruckmann, J. *Organometallics* **1993**, *12*, 4993.

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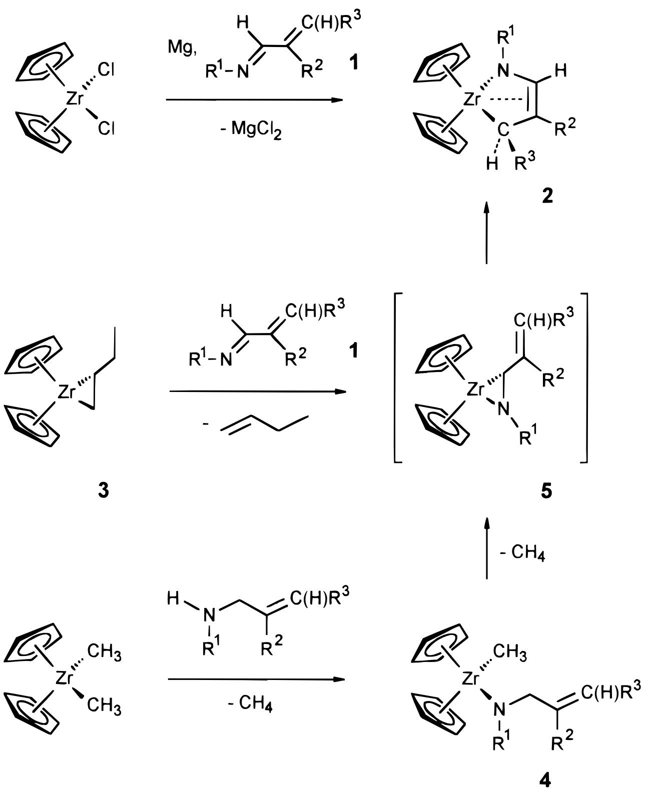
Scheme 1



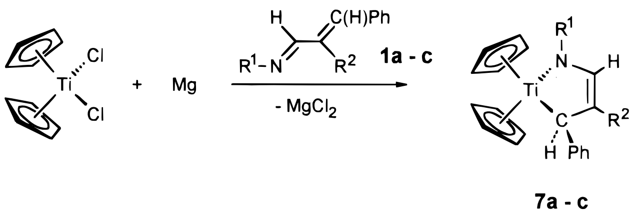
sensitive orange crystals in ca. 60−70% yield, when Cp_2ZrCl_2 is reduced with magnesium in the presence of 1-aza-1,3-dienes **1** (Scheme 1).

Two different synthetic methods have been explored in attempts to find another preparative route to the zirconocene 1-aza-1,3-diene complexes.[5] Thus, the zirconocene equivalent Cp_2Zr(1-butene), **3**, prepared from Cp_2ZrCl_2 and 2 equiv of *n*-butyllithium[6] undergoes a clean ligand exchange with 1-aza-1,3-dienes to form **2** (R^1 = *t*-Bu, CH_2Ph, Ph; R^2 = H, R^3 = Me, Ph). A second route to these 1-aza-1,3-diene complexes is based upon the observation that **2** is formed by rearrangement of an η^2-imine zirconocene complex. The required (η^2-imine)zirconium complex **5** (R^1 = $SiMe_3$, Ph; R^2 = R^3 = H) can be generated by C−H activation and loss of methane from the methylzirconocene amide **4** (Scheme 1).[7]

At higher temperatures, the 1-aza-1,3-diene zirconocene complexes **2** (R^1 = C_6H_4-2-Me, R^2 = Me) react with 1 equiv of acetophenone, forming only a single isomer of the new azoxazirconacyclic metallocene compound $Cp_2Zr[N(R^1)CH{=}C(R^2)CH(Ph)CMe(Ph)O]$ (**6**).[1a]

The potential use of 1-aza-1,3-diene zirconocene complexes in other selective carbometalation reactions, together with the total absence of related 1-aza-1,3-diene titanocene derivatives in the literature, has prompted us to initiate a study of the related 1-aza-1,3-diene titanium chemistry. To obtain further insight into the titanium 1-aza-1,3-diene chemistry, we have also explored a series of novel 1-aza-1,3-diene titanium complexes of the type CpTi(MAD)Cl. In this paper, we report for the first time the syntheses and characterization of some examples of this interesting class of heterodiene compounds, including the molecular structures of a 1-aza-1,3-diene $CpTi^{IV}$ and a 1-aza-1,3-diene Cp_2Ti^{IV} complex.

Scheme 2



	R^1	R^2
1a / 7a	*t*-Bu	H
1b / 7b	C_6H_4-4-Me	H
1c / 7c	*cyclo*-C_6H_{11}	Me

Results and Discussion

Titanocene 1-Aza-1,3-diene Complexes. The preparative procedure for the novel 1-aza-1,3-diene titanocene complexes $Cp_2Ti[N(R^1)CH{=}C(R^2)CH(Ph)]$ [R^1 = *t*-Bu, R^2 = H (**7a**); R^1 = C_6H_4-4-Me, R^2 = H (**7b**); R^1 = c-C_6H_{11}, R^2 = Me (**7c**)] was analogous to that of the zirconium derivatives **2** (Scheme 2).[1a,8] Thus, addition of magnesium turnings to an equimolar mixture of Cp_2TiCl_2 and the appropriate 1-aza-1,3-diene $(R^1)N{=}CHC(R^2){=}CH(Ph)$ [R^1 = *t*-Bu, R^2 = H (**1a**); R^1 = C_6H_4-4-Me, R^2 = H (**1b**); R^1 = c-C_6H_{11}, R^2 = Me (**1c**)] dissolved in THF resulted in the formation of a dark solution. Removal of the solvent in vacuo and extraction of the product into diethyl ether followed by cooling to −20 °C allowed the isolation of **7a**−**c** as air- and moisture-sensitive violet (**7a**) or dark green crystals (**7b**,**c**) in 60−70% yield. The EI mass spectra of **7a**−**c** clearly confirm their monomeric nature, and the chemical characterization supports the proposed constitution.

The ^1H NMR spectra of **7a**−**c** are similar to those of the 1-aza-1,3-diene zirconocene compounds[1] with two resonances in a 1:1 ratio at δ 5.68 and 5.00 (**7a**) and δ 5.74 and 5.18 (**7b**), as well as at δ 5.55 and 5.04 (**7c**) for the diastereotopic Cp groups. In addition, characteristic resonances due to the 1-aza-1,3-diene ligand are observed. Particularly the signal of the terminal hydrogen atom showing a significant upfield shift [δ 1.18 (**7a**), 1.67

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[5] Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1743.

[6] Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

[7] (a) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776. (b) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Coles, N.; Whitby, R. J.; Blagg, J. *Synlett* **1990**, 271. (d) *Synlett* **1992**, 143.

[8] Stabilization of "Cp_2Ti" generated in situ by reduction of Cp_2TiCl_2 with magnesium has been reported. (a) Review: Pez, G. P.; Amor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1. $Cp_2Ti(CO)_2$: (b) Sikora, D. J.; Moriarty, K. J.; Rausch, M. D. *Inorg. Synth.* **1986**, *24*, 147. $Cp_2Ti(PMe_3)_2$: (c) Stephan, D. W. *Organometallics* **1992**, *11*, 996. (d) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1987**, *320*, 37. (e) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem.* **1985**, *97*, 425; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394. $Cp_2Ti(CNC_6H_3Me_2)_2$: (f) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Engelhardt, H. E.; Herberhold, M. *J. Organomet. Chem.* **1986**, *317*, C38. $Cp_2Ti(PhC{\equiv}CPh)$: (g) Shur, V. B.; Burlakov, V. V.; Volpin, M. E. *J. Organomet. Chem.* **1988**, *347*, 77. (h) Shur, V. B.; Bernadyuk, S. Z.; Bulakov, V. V.; Andrianov, V. G.; Yanovsky, A. I.; Struchkov, Y. T.; Volpin, M. E. *J. Organomet. Chem.* **1983**, *243*, 157.

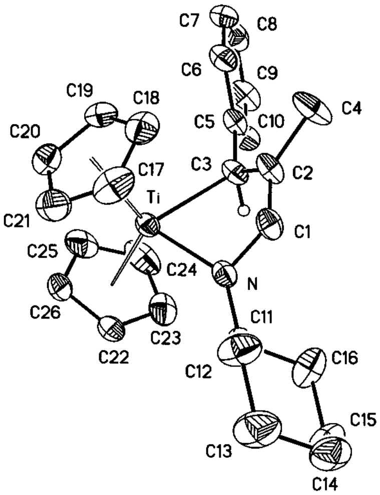

Figure 1. Crystal structure of **7c**, with anisotropic displacement parameters depicting 50% probability (ORTEP plot). All the hydrogen atoms of the molecule (except H3) have been omitted for clarity.

(**7b**), and 0.66 (**7c**)] as compared with the corresponding signal for the late-transition-metal complexes[9] and the signals of the inner 1-aza-1,3-diene hydrogen atoms in the olefinic region [δ 6.87 and 5.44 (**7a**), 6.56 and 5.96 (**7b**), and 6.70 (**7c**)] confirm a distinct metallacyclopentene character. Accordingly the $^1J_{CH}$ coupling constants of the terminal carbon atoms of the 1-aza-1,3-diene ligands are considerably smaller [$^1J_{CH}$ = 140.2 Hz (**7a**), 138.6 Hz (**7b**), and 133.0 Hz (**7c**)] than the usual values for sp^2-hybridized carbon atoms (155−160 Hz)[10] and suggest a considerable amount of rehybridization of the terminal 1-aza-1,3-diene carbon atoms toward sp^3 hybridization.

Crystal Structure of $Cp_2Ti[N(c\text{-}C_6H_{11})CH{=}C(Me)CH(Ph)]$ (7c). To establish the molecular structures of **7a**−**c** in more detail, an X-ray crystal structure analysis of **7c** was carried out. The molecular structure is shown in Figure 1 by an ORTEP drawing with numbering scheme. Selected bond distances and angles are listed in Table 1, and crystallographic data are summarized in the Experimental Section (Table 4).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Cp_2Ti[N(c\text{-}C_6H_{11})CH{=}C(Me)CH(Ph)]$ (7c)

Bond Lengths					
Ti−N	2.016(3)	Ti−C1	2.660(7)	Ti−C2	2.715(9)
Ti−C3	2.278(4)	C1−C2	1.375(6)	C2−C3	1.446(6)
C1−N	1.354(5)	Ti−H3	2.38(3)		

Angles					
Ti−N−C1	102.5(3)	C3−Ti−N	80.3(1)	Ti−C3−C2	90.8(2)
C1−C2−C3	118.6(4)	C2−C1−N	120.3(4)	Ti−C1−H3	85.5(3)
(Ti,N,C3)−(C1,C2,C3,N)	130.9(4)				

The titanium atom may be described as having a pseudotetrahedral geometry if the Cp groups are considered to occupy only two coordination sites and the 1-aza-1,3-diene ligand is assumed to bind via the terminal carbon C3 and the nitrogen atom N. The geometrical parameters associated with the Cp$_2$Ti fragment are unexceptional. Thus the Cp$_c$−Ti−Cp$_c$ angle (Cp$_c$ = center of cyclopentadienyl group) of 128.1(2)° and the average Ti−C$_{Cp}$ distance of 2.424(4) Å are typical of Cp_2TiX_2 complexes.[11] The bent angle between the N−C1−C2−C3 and the N−Ti−C3 planes (130.9°) is remarkably large compared with that (122.4°) for the zirconocene complex $Cp_2Zr[N(C_6H_4\text{-}2\text{-}Me)CH{=}C(Me)CH(Ph)]$.[1a] Nevertheless, the molecular structure of **7c** resembles that of the 1-aza-1,3-diene zirconocene complex **2** and exhibits a structural framework that is quite different from that of the late-transition-metal 1-aza-1,3-diene complexes. It features a pronounced metallacyclopentene character with a short C1−C2 bond [1.375(6) Å] and a longer C2−C3 bond [1.446(6) Å], respectively. This is due to the fact that the 1-aza-1,3-diene ligand is bonded as a dianion to the metal, thus giving the internal C1−C2 bond more π character but the terminal C2−C3 bond more σ character. In late-transition-metal 1-aza-1,3-diene complexes with η^4-π-bonded 1-aza-1,3-diene ligands, these bonds are of approximately equal length.[12] The linkages between the titanium and the 1-aza-1,3-diene termini in **7c** [Ti−C3 2.278(4) Å, Ti−N 2.016(3) Å] are negligibly longer compared with other typical titanium to carbon and titanium to nitrogen σ bonds[13] but still close to the sum of the titanium and nitrogen and the titanium and carbon covalent radii.[14] However, the bond distances between titanium and the internal 1-aza-1,3-diene carbon atoms C1/C2 are substantially longer [Ti−C1 2.660(7) Å, Ti−C2 2.715(9) Å]. Therefore, from covalent radii, it appears that, in contrast to the zirconium counterpart, no π-interaction exists between the titanium and the unsaturated C1−C2 bond in **7c**.

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[9] ^{1}H NMR chemical shifts of MAD ligand protons of selected late-transition-metal MAD complexes are as follows. (a) η^4-{(Ph)CH^3=CH^2-CH^1=N(Ph)}Fe(CO)$_3$ δ (acetone-d_6) = 7.25 (H^1), 6.10 (H^2), 3.45 (H^3): Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem.* **1967**, *6*, 20. Leibfritz, D.; tom Dieck, H. *J. Organomet. Chem.* **1976**, *105*, 255. L'Epplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290. de Chian, A.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 3264. (b) η^4-{(Ph)CH^3=CH^2-CH^1=N(Ph)}Mo(CO)$_2$(PBu$_3$)$_2$ δ (C$_6$D$_6$) = 6.15 (H^1), 4.55 (H^2), 3.20 (H^3): Homann, F.; tom Dieck, H.; Franz, K. D.; Ostoja Starzewski, K. A. *J. Organomet. Chem.* **1973**, *55*, 321. (c) η^4-{(Ph)CH^3=CH^{2}CH^1=N(C$_6$H$_4$-4-Me)}Ru(CO)$_2$(PPh$_3$) δ (CDCl$_3$) = 6.93 (H^1), 5.54 (H^2), 2.12 (H^3): Beers, O. C. P.; Bouman, M. M.; Elsevier: C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1993**, *32*, 3015.

[10] Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*; G. Thieme: Stuttgart, Germany, 1984.

[11] (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

[12] tom Dieck, H.; Stamp, L.; Diercks, R.; Müller, C. *Nouv. J. Chim.* **1985**, *9*, 289.

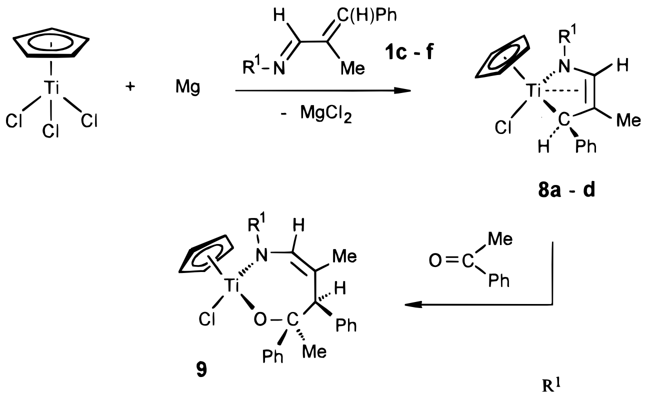
[13] (a) Typical Ti−N bond distances are as follows. Titanium amides Ti−NR$_2$: 1.939 Å (Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1). [(Me$_3$Si)N{CH$_2$CH$_2$N(SiMe$_3$)}$_2$]TiMe$_2$: 1.905(2), 1.910(2), 1.894(5), 1.905(5) Å (Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333). [(C$_5$H$_4$)SiMe$_2$N(*t*-Bu)]Ti(NMe$_2$)$_2$: 1.972(4), 1.924(5), 1.906(4) Å (Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572). [(Me$_3$Si)NCH$_2$CH$_2$N(SiMe$_3$)]$_2$Ti: 1.903(1), 1.906(1) Å (Herrmann, W. A.; Denk, M.; Albach, R. W.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1991**, *124*, 683). (b) Typical Ti−C bond distances are as follows. Cp$_2$Ti[*o*-(CH$_2$)C$_6$H$_4$]: 2.204(4), 2.202(5) Å (Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. F. *J. Chem. Soc., Dalton Trans.* **1984**, 399). Cp$_2$Ti[CH$_2$CH(Ph)CH$_2$]: 2.127(3), 2.113(4) Å (Lee, B. J.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358). Cp$_2$TiMe$_2$: 2.170(2), 2.181(2) Å (Thewalt, U.; Wöhrle, Th. *J. Organomet. Chem.* **1994**, *464*, C17). Cp$_2$Ti(CH$_2$Ph)$_2$: 2.239(6), 2.210(5) Å (Scholz, J.; Rehbaum, F.; Thiele, K.-H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93). [PhC(NSiMe$_3$)$_2$]$_2$TiMe$_2$: 2.122(2) Å (Thiele, K.-H.; Windisch, H.; Windisch, H.; Edelmann, F. T.; Kilimann, U.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1996**, *622*, 713). [(c-C$_6$H$_{11}$)$_2$N]$_2$TiMe$_2$: 2.111(4), 2.118(3) Å (Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978).

[14] Covalent radii of Ti 1.324 Å, of O 0.73 Å, and of C 0.77 Å: (a) Pauling, L. *Die Natur der chemischen Bindung*, 3rd revised ed.; Verlag Chemie: Weinheim, Germany, 1976. (b) Dean, J. A., Ed. *Lange's handbook of chemistry*, 13th ed.; McGraw-Hill: New York, 1985.

One of the most interesting aspects of the molecular structure of **7c** concerns the TiCH group. The hydrogen atom at C3 was located and refined isotropically, revealing a close contact between the titanium and H3 at a distance of 2.38(3) Å. In addition, the acute Ti−C3−H3 angle [85.5(3)°] lends further support to the existence of an interaction of H3 with the metal center in the solid-state structure of **7c**. These Ti−C3−H3 structural parameters compare favorably with the Ti−C−H angle of 93.5(2)° and the Ti···H distance of 2.447(3) Å found in $MeTiCl_3(dmpe)$ or with those of other alkyltitanium complexes[15] where an α agostic interaction has been postulated. Agostic $C-H\rightharpoonup M$ systems normally exhibit characteristic features in their NMR spectra. They may be detected in particular by the value of $^1J_{CH}$, which is lower than that for nonbridged C−H groups. In addition, the ^1H resonances of agostic $C-H\rightharpoonup M$ groups often show high-field shifts.[16] However, both the $^1J_{CH}$ coupling constants of the TiCH α carbon atoms of **7a**−**c**, which are within the range of an sp^3-hybridized carbon atom ($^1J_{CH} = 133.0-138.6$ Hz),[10] and the normal TiC*H* α proton chemical shift values do not give any additional information concerning the agostic behavior of the 1-aza-1,3-diene ligands. Therefore we are reserved to propose a definitive α-agostic interaction, although some structural factors might suggest such a bonding situation.

(Cyclopentadienyl)titanium 1-Aza-1,3-diene Complexes. Teuben et al. have found that the reductive procedure was unsuccessful for the preparation of electron-deficient titanium 1,3-diene complexes of the formula Cp*Ti(1,3-diene)Cl. Reduction of Cp^*TiCl_3 by Na/Hg did take place, but no complexation of the 1,3-diene to the metal could be observed.[17] Therefore, most Cp*Ti(1,3-diene)Cl complexes have successfully been prepared upon treatment of Cp^*TiCl_3 with 1 equiv of (2-buten-1,4-diyl)magnesium.[18] The utility of the 1,3-diene magnesium adduct as a synthon of the 1,3-diene dianion has been widely accepted in the synthesis of 1,3-diene complexes of early transition metals.[19] Surprisingly, no analogous 1-aza-1,3-diene magnesium or dilithium adduct as a synthon of the 1-aza-1,3-diene dianion and starting material for the synthesis of 1-aza-1,3-diene complexes has been developed up to now.

Scheme 3



	R^1
1c / 8a	*cyclo*-C_6H_{11}
1d / 8b	*t*-Bu
1e / 8c	C_6H_4-2-Me
1f / 8d	C_6H_4-4-Me

Fortunately, the simple “one-pot” synthesis described above for the preparation of 1-aza-1,3-diene metallocene complexes is also practicable in synthesizing (cyclopentadienyl)titanium 1-aza-1,3-diene complexes of the type CpTi(MAD)Cl. So the new 1-aza-1,3-diene titanium complexes **8a**−**d** were prepared in THF by reduction of $CpTiCl_3$ with magnesium in the presence of the appropriate 1-aza-1,3-dienes **1c**−**f** (Scheme 3).

Purification of the resulting product by recrystallization from pentane gives the new 1-aza-1,3-diene complexes as brown (**8a**), dark green (**8b**), or dark red (**8c**,**d**) crystals in 50−71% yield. All of these 14e complexes are very air sensitive but thermally quite stable for prolonged periods at 25 °C. They are well soluble in THF, diethyl ether, and all common hydrocarbon solvents but decompose in chloroform.

The ^1H NMR spectra of **8a**,**c**,**d** exhibit resonances for the Cp as well as for the 1-aza-1,3-diene ligand. The ratio of the integrals of the Cp and 1-aza-1,3-diene resonances is consistent with the replacement of two chlorides of $CpTiCl_3$ with one 1-aza-1,3-diene ligand. Furthermore the ^1H NMR spectral data indicate that the 1-aza-1,3-dienes in **8a**,**c**,**d** always adopt the *s-cis* geometry since their NMR spectral patterns compare very closely with those of the 1-aza-1,3-diene zirconocene complexes mentioned above.[1] The chemical shift values of the terminal TiC*H* groups (δ 0.41−0.66) are reminiscent of the terminal anti protons of the 1,3-diene ligands for the structurally well-established 1,3-diene complexes of *supine* conformation.[20,21] Therefore, it is likely that complexes **8a**,**c**,**d** also have the *supine* structure.[22] Moreover, **8a**,**c**,**d** were not found to be fluxional according to ^1H NMR spectroscopy from −80 to +80 °C.

The ^{13}C NMR chemical shifts for the terminal carbon atom of the coordinated 1-aza-1,3-dienes in **8a**,**c**,**d** (δ

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[15] Agostic interactions in titanium alkyl compounds have been reported as follows. (a) $MeTiCl_3(dmpe)$: Ti−H 2.447(3) Å, Ti−C−H 93.5(2)° (Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629). (b) $MeTiCl_3$: Ti−H 2.53 Å, Ti−C−H 101(2)° (Berry, A.; Dawoodi, Z.; Derome, A. E.; Dickinson, J. M.; Downs, A. J.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Payne, M. P.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 520). (c) $Cp^*Ti(CH_2Ph)_3$: Ti−H 2.32, 2.37 Å (Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripiccio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118). (d) $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{Ti(CH_2Ph)_3\}_2]$: Ti−H 2.46, 2.45, 2.48, 2.59 Å (Alvaro, L. M.; Cuenca, T.; Flores, J. C.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1992**, *11*, 3301). (e) $CpCp^*Ti(CH_2PPh_2)_2$: Ti−H 2.46(2) Å, Ti−C−H 93(1)° (Cuenca, T.; Flores, J. C.; Royo, P.; Larsonneur, A.-M.; Choukroun, R.; Dahan, F. *Organometallics* **1992**, *11*, 777). (f) $[Cp^*Ti(CH_2SiMe_3)_2]_2(\mu-O)$: Ti−H 2.422, 2.489 Å (Gómez-Sal, P.; Mena, M.; Palacios, F.; Royo, P.; Carreras, S. M. *J. Organomet. Chem.* **1989**, *375*, 59). (g) $Cp_2Ti(\mu-CH_2)(\mu-Me)PtCl[PPh(Me)_2]$: Ti−H 1.93 Å, Ti−C−H 51.7(3)° (Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319).

[16] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

[17] Blenkers, J.; Hessen, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459.

[18] (a) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105. (b) Chen, J.; Kai, Y.; Kasai, N.; Yamamoto, H.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1987**, 1545.

[19] (a) Fujita, K.; Ohnuma, Y.; Yasuda, H.; Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201. (b) Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918 and references therein. (c) Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462.

[20] For example: (a) Cp*Ti(2,3-dimethylbuta-1,3-diene)Cl [C_6D_6: $\delta(H_{anti})$ 1.42]; see ref 18. (b) Cp*Zr(2,3-dimethylbuta-1,3-diene)Cl [THF-d_8: $\delta(H_{anti})$ 0.55], Cp*Hf(2,3-dimethylbuta-1,3-diene)Cl [THF-d_8: $\delta(H_{anti})$ 0.37]; see ref 17.

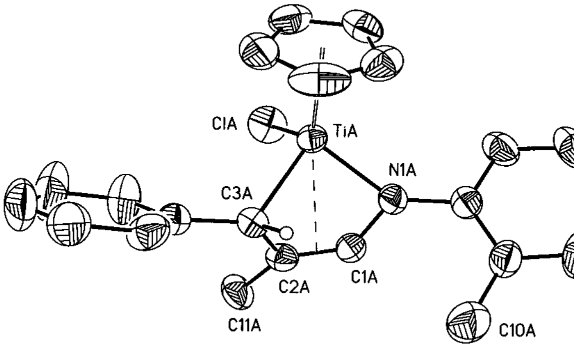

Figure 2. Crystal structure of **8c**, with anisotropic displacement parameters depicting 50% probability (ORTEP plot). Only one of the two independent molecules of **8c** (molecule A) is shown. All the hydrogen atoms of the molecule (except H3) have been omitted for clarity.

101.43−104.27) differ greatly from the corresponding values of the 1-aza-1,3-diene titanocene complexes **7a**−**c** and are significantly shifted to lower field in comparison with other metal σ-bonded carbon atoms of alkyltitanium(IV) compounds.[23] The $^1J_{CH}$ coupling constants of the TiCH methine groups (ca. 137 Hz) are considerably smaller than the usual value for sp^2-hybridized carbon atoms and suggests a considerable amount of rehybridization of these methine carbon toward sp^3 hybridization.[10] On the basis of these NMR data, a strong contribution of a 1-aza-2-titanacyclopent-4-ene structure to the bonding of the 1-aza-1,3-diene ligand is evident.

Crystal Structure of CpTi[N(C_6H_4-2-Me)CH=C(Me)CH(Ph)]Cl (8c). As a typical example of the CpTi(MAD)Cl complexes, CpTi[N(C_6H_4-2-Me)CH=C(Me)CH(Ph)]Cl (**8c**) was subjected to a crystallographic analysis. Purple crystals of **8c** were grown from pentane by slow cooling to −20 °C. The X-ray study clearly confirms the formulation of **8c** based on spectroscopic and analytical data where the 1-aza-1,3-diene ligand lies *supine*. The crystal structure shows the presence of two crystallographically independent molecules per unit cell, which accidentally look like enantiomeric isomers. The molecular structure of one of the crystallographically independent molecules of **8c** (molecule A) is shown in Figure 2. Selected bond distances and angles are listed in Table 2, and crystallographic data are summarized in the Experimental Section (Table 4).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CpTi[N(C_6H_4-2-Me)CH=C(Me)CH(Ph)]Cl (8c)

Bond Lengths

Molecule A

TiA−ClA	2.3083(6)	TiA−N1A	1.923(1)	TiA−C1A	2.332(2)
TiA−C2A	2.382(2)	TiA−C3A	2.141(1)	TiA−H3A	2.47(2)
N1A−C1A	1.383(2)	N1A−C4A	1.404(2)	C1A−C2A	1.387(2)
C2A−C3A	1.438(2)				

Molecule B

TiB−ClB	2.3112(6)	TiB−N1B	1.918(1)	TiB−C1B	2.332(2)
TiB−C2B	2.380(1)	TiB−C3B	2.131(2)	TiB−H3B	2.43(2)
N1B−C1B	1.387(2)	N1B−C4B	1.425(2)	C1B−C2B	1.385(2)
C2B−C3B	1.447(2)				

Bond Angles

Molecule A

N1A−TiA−ClA	114.34(4)	N1A−TiA−C3A	87.60(5)
C3A−TiA−ClA	107.69(4)	C1A−N1A−C4A	123.5(1)
C1A−N1A−TiA	88.13(8)	C4A−N1A−TiA	145.5(1)
N1A−C1A−C2A	121.1(1)	C1A−C2A−C3A	119.3(1)
C2A−C3A−TiA	81.85(8)	TiA−C3−H3A	97.6(4)

sum of angles at N1A: 357.1(1)
(TiA,N1A,C3A)−(N1A,C1A,C2A,C3A) 106.4(4)

Molecule B

N1B−TiB−ClB	112.10(5)	N1B−TiB−C3B	88.42(5)
C3B−TiB−ClB	108.48(4)	C1B−N1B−C4B	121.5(1)
C1B−N1B−TiB	88.26(8)	C4B−N1B−TiB	146.0(1)
N1B−C1B−C2B	121.0(1)	C1B−C2B−C3B	119.9(1)
C2B−C3B−TiB	80.96(8)	TiB−C3−H3B	97.2(4)

sum of angles at N1B: 355.7(1)
(TiB,N1B,C3B)−(N1B,C1B,C2B,C3B) 106.2(4)

The structure of **8c** closely resembles that of the 1,3-diene complexes Cp*Ti(2,3-diphenylbuta-1,3-diene)Cl[18a] and Cp*Hf(2,3-dimethylbuta-1,3-diene)Cl,[17] where the 1,3-diene ligands are bonded to the metal atom in a *supine* fashion too. From covalent radii, it appears that interaction of the titanium atom occurs with all four atoms of the 1-aza-1,3-diene framework. However, the bond lengths indicate considerably stronger bonding to the 1-aza-1,3-diene termini C3 and N than to the internal heterodiene carbon atoms C1 and C2 [Ti−N 1.920(1), Ti−C3 2.136(1), Ti−C2 2.381(1), Ti−C1 2.332(2) Å, average of the two molecules]. The difference $\Delta = [(\text{Ti−C1} + \text{Ti−C2})/2 - (\text{Ti−N} + \text{Ti−C3})/2] = 0.328$ Å is larger than those in predominantly η^4-bonded 1-aza-1,3-diene complexes [e.g., η^4-{(Ph)CH=CHCH=N(C_6H_4-4-Me)}Ru$(CO)_2(PPh_3)$ $\Delta = -0.01$ Å[9c] and η^4-{(Ph)CH=CHCH=N(Ph)}Fe$(CO)_3$ $\Delta = 0.03$ Å[9a]], where all bonded atoms of the 1-aza-1,3-diene framework are approximately equidistant from the metal. On the other hand, Δ of **8c** is considerably smaller than Δ of the corresponding 1-aza-1,3-diene metallocenes **2** ($\Delta = 0.424$ Å)[1] and **7c** ($\Delta = 0.541$ Å). This reflects a larger contribution of the η^4-π bonding of the 1-aza-1,3-diene ligand relative to the σ^2 bonding in **7c**.

Nevertheless, the terminal C2−C3 and N1−C1 bonds [1.442(2) and 1.385(2) Å] as well as the inner C1−C2 distance [1.386(2) Å, average of the two molecules] show nearly the same length as in **7c**, indicating the presence of an 1-aza-2-titanacyclopent-4-ene structure.[24]

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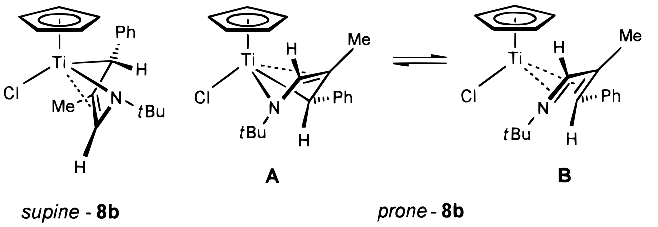
[21] For example: (a) Cp*Nb(2,3-dimethylbuta-1,3-diene)Cl_2 [C_6D_6: $\delta(H_{anti})$ 0.44], CpTa(buta-1,3-diene)Cl_2 [C_6D_6: $\delta(H_{anti})$ 0.40] (Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008). (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410. (c) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1988**, *7*, 2266.

[22] The terms *prone* and *supine* used in this text to describe the mode of 1-aza-1,3-diene orientation in the CpTi(MAD)Cl complexes were introduced originally by Nakamura and Yasuda to express the stereochemistry of early-transition-metal diene complexes. They proposed this nomenclature because the classical *endo* and *exo* nomenclature does not adequately characterize this type of conformation. See ref 3d.

[23] (a) Berger, S.; Bock, W.; Frenking, G.; Jonas, V.; Müller, F. *J. Am. Chem. Soc.* **1995**, *117*, 3820. (b) Elchenbroich, Ch.; Salzer, A. *Organometallics: a concise introduction*; VCH Publishers: Weinheim, Germany, 1989.

[24] Remarkably, the 1-aza-1,3-diene ligands in **7c** and **8c** show a profound asymmetry in the bond distances of the N−C1−C2−C3 unit. These intraligand distances compare largely with the corresponding distances in the 1-aza-1,3-diene zirconocene complex **2** mentioned above [C2−C3 1.455(3), C1−C2 1.375(3), C1−N 1.385(2) Å].[1] It is remarkable that a similar asymmetry was also found in Cp*Hf(2,3-dimethylbuta-1,3-diene)Cl, which was attributed to a significant contribution from an η^3,σ-resonance structure.[17] We assume that the asymmetry in the bond distances of the 1-aza-1,3-diene complexes is solely a consequence of the asymmetric bond length sequence which is already found in uncomplexed 1-aza-1,3-dienes, e.g. (C_6H_4-4-Me)N=C^1HC^2(Me)=C^3H(Ph) (**1f**) [C2−C3 1.336(4), C1−C2 1.459(4), C1−N 1.276(3) Å]: Wunderle, J.; Scholz, J.; Hovestreydt, E. *Z. Kristallogr.* **1993**, *208*, 274.

Chart 1



Another remarkable feature of **8c** is seen in the Ti···H3 distance of 2.45(2) Å [Ti−C3−H3 97.4(4)°], which is nearly of the same order as that in **7c**. Obviously this is another example where hydrogen atoms of formally saturated C−H systems closely approach a metal center,[16] by means of which the metallic atom relieves its electronic deficiency.

NMR Evidence of a *Prone* CpTi(MAD)Cl Complex. Of particular interest are the unusual NMR spectra observed for the CpTi(MAD)Cl complex **8b**. Both the ^{1}H and ^{13}C NMR spectra of **8b** show two complete sets of signals which can be attributed to a complex possessing a *supine* 1-aza-1,3-diene ligand and to another exhibiting a *prone* 1-aza-1,3-diene (relative ratio 2:3; Chart 1).

Noteworthy is that there is only a slight chemical shift difference in the ^{13}C resonances of the 1-aza-1,3-diene carbon atoms between the *prone* and *supine* isomer but in contrast there is a marked difference in ^{1}H chemical shift values. Thus, the structurally diagnostic anti proton (TiC*H*) and inner proton (NC*H*=) resonances of *prone*-**8b** occur at δ 4.23 and 5.23, in good agreement with data for the structurally characterized complex Cp*Ti(*prone*-buta-1,3-diene)Cl,[18a] which is predominantly π-diene in character. The terminal anti proton (TiC*H*: δ 0.37) and the inner proton (NC*H*=: δ 6.72) of the 1-aza-1,3-diene ligand of *supine*-**8b** exhibit a far greater dispersion similar to that in complexes such as Cp*Ti(*supine*-isoprene)Cl,[18a] which are predominantly σ-bound in character. These results indicate that the η^4-π (1-aza-1,3-diene)metal character is more pronounced for the *prone* isomer (Chart 1, **B**) as compared with the *supine* isomer. In the range −80 to +100 °C, the isomers *supine*-**8b** and *prone*-**8b** do not interconvert. The presence of both the *supine* and the *prone* coordination geometry in **8b** indicates that the stability of these two 1-aza-1,3-diene orientations seems to be well balanced.[25] Thus, the relative ratio *supine*:*prone* (3:2) must be determined kinetically during the formation of **8b**.[26]

Reaction of CpTi(MAD)Cl with Acetophenone. The 1,3-diene complexes of group 4 metals are known for their reactive metal−carbon bonds. Insertion of compounds with unsaturated carbon−oxygen bonds into these metal−carbon bonds leads to regioselective carbon−carbon bond formation. In recent years, especially the 18e Cp_2M(1,3-diene) complexes have been investigated. They can react with carbonyl compounds via two different pathways:[4c] (a) reaction of the *s-trans*-η^4 isomer through an η^2-coordinated intermediate and C,C-coupling of the η^2-diene with the carbonyl compound and (b) reaction of the *s-cis*-σ^2,π metallacyclopentene isomer through direct nucleophilic attack of the diene terminal carbon atom on the carbonyl functionality.

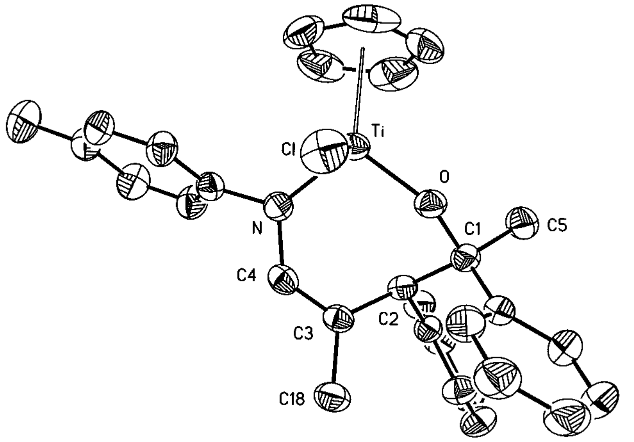


Figure 3. Molecular structure of complex **9**, shown by an ORTEP plot at the 50% probability level.

Unlike the 1,3-diene analogue, the 1-aza-1,3-diene zirconocene complexes **2** only react via the second pathway (b), which proceeds very slowly even at higher temperature.[1] The 1-aza-1,3-diene titanocene complex **7c** proved to be inert toward the insertion of acetophenone, which might be due to the steric hindrance of the metal center. Therefore greater reactivity of the 14e CpTi(MAD)Cl complex **8d** was expected. In fact, **8d** readily reacts with 1 equiv of acetophenone at room temperature in pentane or diethyl ether solution. Chemical analysis shows that the formed complex contains both the 1-aza-1,3-diene and one acetophenone per molecule. Carbon−carbon bond formation between the heterodiene terminus and the carbonyl carbon atom is observed. At the same time, a thermodynamically strong titanium-to-oxygen-linkage is formed (Scheme 3). According to the NMR spectroscopic data, the novel seven-membered azoxametallacyclic titanium complex **9** was obtained in good yield (80%).[27]

The structure and conformation of **9** were confirmed by a single-crystal X-ray diffraction analysis. A view of the molecular structure of **9** is shown in Figure 3 together with the numbering scheme used; selected bond distances and angles are given in Table 3. The metal center may be considered to possess a typical three-legged piano-stool environment, with angles in the range 100.00(8)−102.47(7)° between the legs and with a distance of 2.024(3) Å to the center of the Cp ring.

Complex **9** exhibits a seven-membered metallacyclic framework containing four carbon atoms, an oxygen

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[25] Nakamura et al. found that, on the basis of extended Hückel MO calculations for the model compound CpTi(butadiene)Cl, the *prone* and *supine* isomers were close in energy. The *prone* isomer is a mere 0.7 kcal/mol more stable than the *supine* isomer. Therefore, either a *prone* or a *supine* orientation of the diene is electronically accessible for 14e CpTi(diene)Cl complexes, and the geometrical choice would be determined by small steric and/or electronic perturbation. See ref 18a.

[26] NMR studies of several CpTi(MAD)Cl complexes revealed that, similar to those of the corresponding Cp*Ti(diene)Cl complexes,[18] the steric repulsions between the Cp ligand and substituents on the inner carbon atoms of the 1-aza-1,3-diene ligand may act as the crucial factor in determining the *supine* or *prone* geometry of the coordinated 1-aza-1,3-diene; i.e., the alkyl substitution on the inner carbon atoms brings about the *supine* geometry while nonsubstitution on these carbon atoms always leads to the *prone* geometry: Kahlert, S., Scholz, J. Unpublished results.

[27] Recently Crowe et al. reported the facile participation of a titanocene Cp ligand in a sequence of carbon−carbon bond forming reactions that completely removes the Cp ligand from the titanium center and gives a new titanium complex surprisingly possessing an η^4 1-aza-1,3-diene ligand. This 1-aza-1,3-diene complex cleanly reacts with acetone forming an insertion product similar to **9**: Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 5508.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $CpTi[N(C_6H_4\text{-}4\text{-}Me)CH{=}C(Me)\text{-}CH(Ph)C(Me)PhO]$ (9)

Bond Lengths

Ti−O	1.762(2)	Ti−N	1.935(2)	Ti−Cl	2.3046(9)
O−C1	1.420(3)	N−C4	1.419(3)	N−C19	1.435(3)
C1−C2	1.578(3)	C1−C5	1.525(4)	C1−C6	1.530(4)
C2−C3	1.519(3)	C2−C12	1.523(3)	C3−C4	1.336(3)
C3−C18	1.518(4)				

Bond Angles

O−Ti−N	100.00(8)	O−Ti−Cl	101.45(6)	N−Ti−Cl	102.47(7)
C1−O−Ti	150.1(2)	C4−N−Ti	118.0(2)	C19−N−Ti	127.4(2)
O−C1−C2	103.8(2)	C3−C2−C1	113.4(2)	C4−C3−C2	121.5(2)
C3−C4−N	128.2(2)				

atom, a nitrogen atom, and titanium. Very typically, the azoxatitanacycloheptene ring adopts a folded ring conformation in the solid state similar to that previously observed for the zirconocene complex **6**, which appears (on the basis of the internal angles) to contain very little strain at each of the constituent atoms.[1] To a first approximation the atoms of the *s-cis*-configured 1-aza-1,3-diene unit are arranged coplanar (maximum deviation −0.022 Å); the atoms Ti, N, O, and C1 are also arranged almost in one plane. The angle between these two planes is 127.2(2)°. Much of the rigidity of the cyclic seven-membered framework in **9** is due to the large angle at the ring oxygen atom [Ti−O−C1 150.1(2)°]. This indicates some oxygen to titanium electron π-donation which may serve to decrease the electron deficiency at the Lewis acidic titanium center.[28]

The carbonyl addition product contains three chiral centers as parts of the ring perimeter {[Cp*Ti**(NR−)(O−)Cl], Ti*C**H(Ph)−, and O*C**(Ph)Me−} and thus gives rise to the occurrence of diastereomers. However, the NMR analysis of **9** (for details see Experimental Section) has revealed that only a single isomer is obtained, indicating that this coupling reaction has taken place with high stereoselectivity. Thus, the simple ring expansion of **8d** with acetophenone to produce **9** fits into the general scheme established for the reaction course taken upon addition of carbonyl compounds to early-transition-metal alkyl complexes.

Concluding Remarks

In this paper we have reported the synthesis of a variety of (cyclopentadienyl)titanium complexes bearing 1-aza-1,3-diene ligands. The results of this study show that the $CpTi^{IV}Cl-$ and the $Cp_2Ti^{IV}-$ complex fragments are effective building blocks for the stabilization of a novel series of 1-aza-1,3-diene titanium complexes. The crystal structures of **7c** and **8c** are the first examples of crystallographically characterized 1-aza-1,3-diene titanium complexes.

The CpTi(MAD)Cl complexes **8a**−**d** are more reactive than the previously synthesized 1-aza-1,3-diene zirconocene complexes **2**, which might be due to the steric hindrance of the metal center. From the example presented and discussed in this study, it can be expected that carbon−carbon coupling reactions of carbonyl compounds with the 1-aza-1,3-diene dianion equivalent of $CpTi^{IV}$(MAD) complexes will make a variety of interesting new organic products available in a rather simple and predictable way. Studies aimed at exploring such use of the early-transition-metal 1-aza-1,3-diene complexes which can be treated as equivalents of metalated allylamines and therefore used as homoenolate equivalents are currently being carried out in our laboratory.[29]

Experimental Section

General Considerations. All manipulations and reactions with organometallic compounds were performed in an inert atmosphere (argon) using Schlenk type glassware. Solvents were purified and dried by distillation from sodium/benzophenone or lithium aluminum hydride under argon prior to use. Deuterated THF-d_8 was treated with sodium/potassium alloy, then distilled, and stored under argon. The following spectrometers were used: NMR−JEOL JNM-FX 200 (^{1}H, 199.5 MHz; ^{13}C, 50.1 MHz), Varian Gemini 300 (^{1}H, 300.075 MHz; ^{13}C, 75.462 MHz); MS−Intectra AMD 402 (EI MS, 70 eV). Elemental analyses were carried out at the Mikroanalytisches Laboratorium des Fachbereichs Chemie der Martin-Luther-Universität Halle-Wittenberg, Merseburg, Germany. The starting materials $CpTiCl_3$,[30] Cp_2TiCl_2,[31] and the 1-aza-1,3-dienes **1a**−**f**[32] were prepared according to literature procedures.

X-ray Diffraction of 7c, 8c, and 9. Suitable crystals were grown from saturated pentane (**7c**, **8c**) or diethyl ether solutions (**9**) at −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters were obtained by a least-squares fit of 25 reflections. Three standard reflections were monitored every 2 h. No systematic variations in intensities were found. Data were corrected for Lorentz and polarization effects but not for absorption.[33] The structures were solved by direct methods[34] and refined by full-matrix least-squares procedures against F_o^2.[35] The hydrogen atoms were located from the difference maps and refined isotropically for compounds **7c** and **9**. For compound **8c**, only the hydrogen atoms H1A, H1B, H3A, and H3B were located from the difference map and refined isotropically; all other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. Cell constant and other pertinent data were collected, and are recorded in Table 4.

$Cp_2Ti[N(t\text{-}Bu)CH{=}CHCH(Ph)]$ (7a). A solution of Cp_2TiCl_2 (5.00 g, 20.08 mmol) and **1a** (3.76 g, 20.10 mmol) in 100 mL of THF was stirred with magnesium turnings (0.49 g, 20.16 mmol) for 48 h at room temperature. Subsequently the THF was pumped off and the resultant dark violet solid extracted with 50 mL of diethyl ether. Concentrating and cooling the extract to −20 °C yielded large black violet crystals of **7a** (3.82 g, 10.45 mmol, 52%; mp 103−107 °C). Anal. Calcd for $C_{23}H_{27}NTi$ (M_r = 365.35): C, 75.61; H, 7.45; N, 3.83. Found: C,

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[28] (a) Gau, H.-M.; Lee, C.-S.; Lin, C.-C.; Jiang, M.-K.; Ho, Y.-C.; Kuo, C.-N. *J. Am. Chem. Soc.* **1996**, *118*, 2936. (b) Beckhaus, R.; Strauss, I.; Wagner, T. *J. Organomet. Chem.* **1994**, *464*, 155. (c) Wu, Y.-T.; Ho, Y.-C.; Lin, C.-C.; Gau, H.-M. *Inorg. Chem.* **1996**, *35*, 5948 and literature cited therein.

[29] (a) Ahlbrecht, H. *Chimia* **1977**, *31*, 391. (b) Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205. (c) Ahlbrecht, H.; Farnung, W. *Chem. Ber.* **1984**, *117*, 1. (d) Ahlbrecht, H.; Enders, D.; Santowski, L.; Zimmermann, G. *Chem. Ber.* **1989**, *122*, 1995.

[30] (a) King, R. B. *Organomet. Synth.* **1965**, *1*, 78. (b) Gorsich, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 4211.

[31] Birmingham, J. M. *Adv. Organomet. Chem.* **1964**, *2*, 365.

[32] (a) Doebner, O.; Miller, W. *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 1664. (b) A revised procedure to prepare N-alkylated 1-aza-1,3-dienes will be published in: Kahlert, S. Ph.D. Thesis, Universität Halle, 1998.

[33] *MOLEN: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, **1990**.

[34] Sheldrick, G. M. *SHELXS-86: A Computer Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

[35] Sheldrick, G. M. *SHELXL-93: A Computer Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

Table 4. Crystallographic Data and Details of Data Collection and Refinement for 7c, 8c, and 9

	7c	**8c**	**9**
empirical formula	$C_{26}H_{31}NTi$	$C_{22}H_{22}NClTi$	$C_{30}H_{30}NOClTi$
M_r	405.42	383.76	503.90
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
temp, K	183(2)	293(2)	293(2)
a, Å	7.620(2)	13.804(4)	8.619(3)
b, Å	14.701(3)	14.347(6)	12.784(3)
c, Å	19.106(4)	19.849(2)	23.811(4)
β, deg	94.59(3)		92.49(1)
V, Å^3	2133.4(8)	3931(2)	2621(1)
cryst dimens, mm^3	0.40 × 0.38 × 0.36	0.30 × 0.30 × 0.36	0.42 × 0.38 × 0.20
no. of formula units Z	4	8	4
D_c, g·cm^{-3}	1.262	1.297	1.277
abs coeff μ, mm^{-1}	0.412	0.575	0.451
2θ range, deg	2−55	2−55	2−55
no. of reflns collected	5002	5360	6084
no. of obsd data with $I > 2\sigma(I)$	4851	4887	5942
no. of variables	377	468	416
R1	0.057	0.045	0.043
wR2	0.152	0.120	0.103
rest electron density, e·Å^{-3}	0.48	0.66	0.30

75.43; H, 7.60; N, 3.99. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.15 (t, 2H; *m*-Ph), 7.00 (d, 2H; *o*-Ph), 6.87 (d, $^3J_{HH}$ = 5.4 Hz, 1H; NC*H*═CH), 6.80 (t, 1H; *o*-Ph), 5.68 (s, 5H; Cp), 5.44 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 9.7 Hz, 1H; NCH═C*H*), 5.00 (s, 5H; Cp), 1.28 (s, 9H; C*Me*$_3$), 1.18 (d, $^3J_{HH}$ = 9.7 Hz, 1H; TiC*H*). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 148.04 (s; *i*-Ph), 130.11 (d, $^1J_{CH}$ = 161.3 Hz; N*C*H═CH), 128.66 (d, $^1J_{CH}$ = 158.1 Hz; *o*/*m*-Ph), 124.54 (d, $^1J_{CH}$ = 154.8 Hz; *o*/*m*-Ph), 122.90 (d, $^1J_{CH}$ = 161.3 Hz; *p*-Ph), 108.48 (d, $^1J_{CH}$ = 171.1 Hz; Cp), 102.22 (d, $^1J_{CH}$ = 172.8 Hz; Cp), 100.41 (d, $^1J_{CH}$ = 146.7 Hz; NCH═*C*H), 80.31 (d, $^1J_{CH}$ = 140.2 Hz; Ti*C*H), 60.14 (s; *C*Me$_3$), 32.89 (q, $^1J_{CH}$ = 125.5 Hz; C*Me*$_3$).

$Cp_2Ti[N(C_6H_4\text{-}4\text{-}Me)CH{=}CHCH(Ph)]$ (7b). The reaction was performed by the same method described for the preparation of **7a**, using Cp_2TiCl_2 (5.00 g, 20.08 mmol), **1b** (4.45 g, 20.08 mmol), and magnesium turnings (0.49 g, 20.16 mmol). A yield of 5.29 g (13.25 mmol, 66%) of black-green crystals was obtained (mp ca. 110 °C dec). Anal. Calcd for $C_{26}H_{25}NTi$ (M_r = 399.37): C, 78.19; H, 6.31; N, 3.51. Found: C, 78.10; H, 6.23; N, 3.67. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.18 (t, 2H; *m*-Ph), 7.05 (d, 4H; *o*-Ph, *o*/*m*-C$_6$*H*$_4$-4-Me), 6.83 (t, 1H; *p*-Ph), 6.64 (d, 2H; *o*/*m*-C$_6$*H*$_4$-4-Me), 6.56 (d, $^3J_{HH}$ = 5.4 Hz, 1H; NC*H*═CH), 5.96 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 8.3 Hz, 1H; NCH═C*H*), 5.74 (s, 5H; Cp), 5.18 (s, 5H; Cp), 2.31 (s, 3H; C$_6$H$_4$-4-*Me*), 1.67 (d, $^3J_{HH}$ = 8.1 Hz, 1H; TiC*H*). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 152.58 (s; *i*-C$_6$H$_4$-4-Me), 149.05 (s; *i*-Ph), 133.01 (s; *p*-*C*$_6$H$_4$-4-Me), 131.95 (d, $^1J_{CH}$ = 170.4 Hz; N*C*H═CH), 128.60 (d, $^1J_{CH}$ = 155.5 Hz; *o*/*m*-*C*$_6$H$_4$-4-Me, *o*/*m*-Ph), 128.88 (d, $^1J_{CH}$ = 157.1 Hz; *o*,*m*-*C*$_6$H$_4$-4-Me, *o*/*m*-Ph), 124.74 (d, $^1J_{CH}$ = 155.5 Hz; *o*/*m*-*C*$_6$H$_4$-4-Me, *o*/*m*-Ph), 123.65 (d, $^1J_{CH}$ = 157.6 Hz; *o*/*m*-*C*$_6$H$_4$-4-Me, *o*/*m*-Ph), 122.91 (d, $^1J_{CH}$ = 158.4 Hz; *p*-Ph), 109.71 (d, $^1J_{CH}$ = 155.0 Hz; NCH═*C*H), 109.05 (d, $^1J_{CH}$ = 173.0 Hz; Cp), 104.08 (d, $^1J_{CH}$ = 173.0 Hz; Cp), 79.76 (d, $^1J_{CH}$ = 138.6 Hz; Ti*C*H), 20.69 (q, $^1J_{CH}$ = 126.0 Hz; C$_6$H$_4$-4-*Me*). EIMS, *m*/*z* (relative intensity, assignment): 399 (10, M$^+$), 220 (100, M$^+$ − Cp$_2$Ti), 178 (36, Cp$_2$Ti$^+$), 128 (8, C$_9$H$_6$N$^+$), 91 (10, C$_7$H$_7$$^+$).

$Cp_2Ti[N(c\text{-}C_6H_{11})CH{=}C(Me)CH(Ph)]$ (7c). The reaction was performed by the same method described for the preparation of **7a**, using Cp_2TiCl_2 (5.00 g, 20.08 mmol), **1c** (4.57 g, 20.08 mmol), and magnesium turnings (0.49 g, 20.16 mmol). A yield of 5.31 g (13.10 mmol, 65%) of black-green crystals was obtained (mp 121−124 °C). Subsequent recrystallization from diethyl ether at −5 °C gave crystals suitable for an X-ray analysis. Anal. Calcd for $C_{26}H_{31}NTi$ (M_r = 405.42): C, 77.03; H, 7.71; N, 3.45. Found: C, 76.80; H, 7.60; N, 3.84. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.13 (t, 2H; *m*-Ph), 6.98 (d, 2H; *o*-Ph), 6.81 (t, 1H; *p*-Ph), 6.70 (s, 1H; NC*H*═CMe), 5.55 (s, 5H; Cp), 5.04 (s, 5H; Cp), 3.39 (m, 1H; c-C$_6$H$_{11}$), 2.30 (s, 3H; NCH═C*Me*), 1.91−1.07 (m, 10H; c-C$_6$H$_{11}$), 0.66 (br s, 1H; TiC*H*). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 147.98 (s; *i*-Ph), 132.37 (d, $^1J_{CH}$ = 160.8 Hz; N*C*H═CMe), 128.23 (d, $^1J_{CH}$ = 155.9 Hz; *o*/*m*-Ph), 127.39 (d, $^1J_{CH}$ = 155.3 Hz; *o*/*m*-Ph), 122.76 (d, $^1J_{CH}$ = 157.5 Hz; *p*-Ph), 120.76 (s; NCH═*C*Me), 108.31 (d, $^1J_{CH}$ = 171.4 Hz; Cp), 103.17 (d, $^1J_{CH}$ = 171.1 Hz; Cp), 84.22 (d, $^1J_{CH}$ = 133.0 Hz; Ti*C*H), 66.54, 37.62, 36.10, 27.46, 27.40, 26.90 (C$_6$H$_{11}$), 21.32 (q, $^1J_{CH}$ = 126.0 Hz; NCH═C*Me*). EIMS, *m*/*z* (relative intensity, assignment): 405 (15, M$^+$), 226 (38, M$^+$ − Cp$_2$Ti), 178 (100, Cp$_2$Ti$^+$).

$CpTi[N(c\text{-}C_6H_{11})CH{=}C(Me)CH(Ph)]Cl$ (8a). To a solution of $CpTiCl_3$ (5.00 g, 22.80 mmol) and the 1-aza-1,3-diene **1c** (5.18 g, 22.80 mmol) in THF (150 mL) were added magnesium turnings (0.55 g, 22.80 mmol) over a period of 12 h at −20 °C. The reaction mixture was stirred at ambient temperature 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 for 3 days. A yield of 4.37 g (11.62 mmol, 51%) of large brown crystals of **8a** was obtained (mp 119−122 °C). Anal. Calcd for $C_{21}H_{26}NClTi$ (M_r = 375.78): C, 67.12; H, 6.97; N, 3.73. Found: C, 66.72; H, 6.75; N, 3.81. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 20 °C): δ 7.25 (t, 2H; *m*-Ph), 7.09 (t, 1H; *p*-Ph), 6.83 (s, 1H; NC*H*═CMe), 6.82 (d, 2H; *o*-Ph), 6.17 (s, 5H; Cp), 3.69 (m, 1H; C$_6$*H*$_{11}$), 2.06 (s, 3H; NCH═C*Me*), 1.95−1.17 (m, 10H; C$_6$*H*$_{11}$), 0.41 (s, 1H; TiC*H*). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 142.19 (s; *i*-C$_6$H$_5$), 128.16 (d, $^1J_{CH}$ = 158.6 Hz; *o*/*m*-Ph), 127.87 (d, $^1J_{CH}$ = 158.5 Hz; *o*/*m*-Ph), 124.78 (d, $^1J_{CH}$ = 160.6 Hz; *p*-Ph), 118.58 (d, $^1J_{CH}$ = 173.0 Hz; N*C*H═CMe), 115.17 (s; NCH═*C*Me), 112.41 (d, $^1J_{CH}$ = 173.9 Hz; Cp), 101.43 (d, $^1J_{CH}$ = 137.4 Hz; Ti*C*H), 68.11 (d, $^1J_{CH}$ = 135.4 Hz; *C*$_6$H$_{11}$), 36.16 (t, $^1J_{CH}$ = 129.7 Hz; *C*$_6$H$_{11}$), 34.34 (t, $^1J_{CH}$ = 128.5 Hz; *C*$_6$H$_{11}$), 26.06 (t; *C*$_6$H$_{11}$), 26.05 (t; *C*$_6$H$_{11}$), 25.77 (t; *C*$_6$H$_{11}$), 18.27 (q, $^1J_{CH}$ = 128.0 Hz; NCH═C*Me*). EIMS, *m*/*z* (relative intensity, assignment): 375 (100, M$^+$), 340 (5, M$^+$ − Cl), 309 (4, M$^+$ − Cp), 292 (12, M$^+$ − C$_6$H$_{11}$), 265 (19, M$^+$ − C$_7$H$_{12}$N), 263 (19, M$^+$ − C$_7$H$_{14}$N), 244 (19, M$^+$ − C$_{10}$H$_{10}$), 226 (16, M$^+$ − CpTiCl), 148 (30, CpTiCl$^+$).

$CpTi[N(t\text{-}Bu)CH{=}C(Me)CH(Ph)]Cl$ (8b). The reaction was performed by the same method described for the preparation of **8a**, using $CpTiCl_3$ (5.00 g, 22.80 mmol), **1d** (4.59 g, 22.80 mmol), and magnesium turnings (0.55 g, 22.80 mmol). A yield of 4.62 g (13.22 mmol, 58%) of a dark green crystalline solid composed of a 3:2 mixture (^{1}H NMR) of the *prone* and *supine* isomers was obtained. Anal. Calcd for $C_{19}H_{24}NClTi$ (M_r = 349.74): C, 65.25; H, 6.92; N, 4.00. Found: C, 65.46; H, 7.09; N, 4.14. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): ***supine*-8b** δ 7.18 (m, 3H; *m*/*p*-Ph), 6.87 (s, 1H; NC*H*═CMe), 6.79 (d, $^3J_{HH}$

= 7.3 Hz, 2H; *o*-Ph), 6.21 (s, 5H; Cp), 2.00 (s, 3H; NCH═C*Me*), 1.34 (s, 9H; C*Me*$_3$), 0.41 (s, 1H; TiC*H*); ***prone*-8b** δ 7.18 (m, 5H; Ph), 5.84 (s, 5H; Cp), 5.77 (s, 1H; NC*H*═CMe), 3.93 (s, 1H; TiC*H*), 1.97 (s, 3H; NCH═C*Me*), 1.31 (s, 9H; C*Me*$_3$). ^{1}H NMR (C_6D_6): ***supine*-8b** δ 7.14 (m, 3H; *m*/*p*-Ph), 6.83 (d, $^3J_{HH}$ = 7.3 Hz, 2H; *o*-Ph), 6.72 (s, 1H; NC*H*═CMe), 6.09 (s, 5H; Cp), 2.10 (s, 3H; NCH═C*Me*), 1.05 (s, 9H; C*Me*$_3$), 0.37 (s, 1H; TiC*H*); ***prone*-8b** δ 7.18 (m, 5H; Ph), 5.56 (s, 5H; Cp), 5.23 (s, 1H; NC*H*═CMe), 4.23 (s, 1H; TiC*H*), 1.52 (s, 3H; NCH═C*Me*), 1.16 (s, 9H; C*Me*$_3$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): ***supine*-8b** δ 143.15 (s; *i*-Ph), 128.94 (d, $^1J_{CH}$ = 157.8 Hz; *o*/*m*-Ph), 128.0 (d, $^1J_{CH}$ = 158.0 Hz; *o*/*m*-Ph), 125.66 (d, $^1J_{CH}$ = 161.0 Hz; *p*-Ph), 119.79 (d, $^1J_{CH}$ = 173.6 Hz; N*C*H═CMe), 116.01 (s; NCH═*C*Me), 113.23 (d, $^1J_{CH}$ = 174.1 Hz; Cp), 103.75 (d, $^1J_{CH}$ = 141.4 Hz; Ti*C*H), 62.98 (s; *C*Me$_3$), 31.77 (q, $^1J_{CH}$ = 126.4 Hz; C*Me*$_3$), 20.21 (q, $^1J_{CH}$ = 128.2 Hz; NCH═C*Me*); ***prone*-8b** δ 142.97 (s; *i*-Ph), 126.78 (d, $^1J_{CH}$ = 157.0 Hz; *o*/*m*-Ph), 126.64 (d, $^1J_{CH}$ = 158.0 Hz; *o*/*m*-Ph), 125.41 (d, $^1J_{CH}$ = 161.4 Hz; *p*-Ph), 112.22 (d, $^1J_{CH}$ = 174.3 Hz; Cp), 108.11 (d, $^1J_{CH}$ = 171.3 Hz; N*C*H═CMe), 104.72 (s; NCH═*C*Me), 100.91 (d, $^1J_{CH}$ = 132.4 Hz; Ti*C*H), 59.51 (s; *C*Me$_3$), 30.88 (q, $^1J_{CH}$ = 126.2 Hz; C*Me*$_3$), 18.66 (q, $^1J_{CH}$ = 128.2 Hz; NCH═C*Me*). EIMS, *m*/*z* (relative intensity, assignment): 349 (100, M^+), 314 (14, $M^+ - Cl$), 292 (25, $M^+ - C_4H_9$), 265 (38, $M^+ - C_5H_{12}N$), 263 (38, $M^+ - C_5H_{14}N$), 226 (14, M^+ − CpTiCl), 148 (36, CpTiCl$^+$).

CpTi[N(C_6H_4-2-Me)CH═C(Me)CH(Ph)]Cl (8c). The reaction was performed by the same method described for the preparation of **8a**, using $CpTiCl_3$ (5.00 g, 22.80 mmol), **1e** (5.37 g, 22.80 mmol), and magnesium turnings (0.55 g, 22.80 mmol). A yield of 5.69 g (14.82 mmol, 65%) of dark red crystals was obtained (mp 135−137 °C). Subsequent recrystallization from *n*-pentane or diethyl ether at −5 °C gave crystals suitable for an X-ray analysis. Anal. Calcd for $C_{22}H_{22}NClTi$ (M_r = 383.76): C, 68.86; H, 5.78; N, 3.65. Found: C, 68.59; H, 5.92; N, 3.51. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.26−7.04 (m, 6H; *m*/*p*-C$_6$*H*$_4$-2-Me, *m*/*p*-Ph), 6.90 (d, $^1J_{HH}$ = 7.4 Hz, 3H; *o*-C$_6$*H*$_4$-2-Me, *o*-Ph), 6.73 (s, 1H; NC*H*═CMe), 6.12 (s, 5H; Cp), 2.09 (s, 3H; C$_6$H$_4$-2-*Me*), 2.06 (s, 3H; NCH═C*Me*), 0.66 (s, 1H; TiC*H*). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 152.16 (s; *i*-*C*$_6$H$_4$-2-Me), 142.60 (s; *i*-Ph), 131.83 (s; *o*-*C*$_6$H$_4$-2-Me), 131.04 (d, $^1J_{CH}$ = 155.3 Hz; *C*$_6$H$_4$-2-Me), 128.92 (d, $^1J_{CH}$ = 163.1 Hz; *o*/*m*-Ph), 128.46 (d, $^1J_{CH}$ = 158.0 Hz; *o*/*m*-Ph), 127.08 (d, $^1J_{CH}$ = 161.7 Hz; *C*$_6$H$_4$-2-Me), 126.61 (d, $^1J_{CH}$ = 160.5 Hz; *C*$_6$H$_4$-2-Me), 126.40 (d, $^1J_{CH}$ = 155.9 Hz; *C*$_6$H$_4$-2-Me), 125.57 (d, $^1J_{CH}$ = 160.8 Hz; *C*$_6$H$_4$-2-Me), 122.36 (d, $^1J_{CH}$ = 177.6 Hz; N*C*H═CMe), 116.26 (s; NCH═*C*Me), 113.72 (d, $^1J_{CH}$ = 174.3 Hz; Cp), 103.40 (d, $^1J_{CH}$ = 137.2 Hz; Ti*C*H), 18.22 (q, $^1J_{CH}$ = 128.2 Hz; NCH═C*Me*), 17.88 (q, $^1J_{CH}$ = 127.1 Hz; C$_6$H$_4$-2-*Me*). EIMS, *m*/*z* (relative intensity, assignment): 383 (10, M^+), 234 (27, M^+ − CpTiCl), 148 (48, CpTiCl$^+$), 77 (100, $C_6H_5^+$).

CpTi[N(C_6H_4-4-Me)CH═C(Me)CH(Ph)]Cl (8d). The reaction was performed by the same method described for the preparation of **8a**, using $CpTiCl_3$ (5.00 g, 22.80 mmol), **1f** (5.37 g, 22.80 mmol), and magnesium turnings (0.55 g, 22.80 mmol). A yield of 6.21 g (16.19 mmol, 71%) of dark red crystals was obtained (mp 98−100 °C). Anal. Calcd for $C_{22}H_{22}NClTi$ (383.76): C, 68.86; H, 5.78; N, 3.65. Found: C, 68.34; H, 5.92; N, 3.51. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.26−7.04 (m, 6H; *m*/*p*-C$_6$*H*$_4$-4-Me, *m*/*p*-Ph), 6.73 (s, 1H; NC*H*═CMe), 6.30 (s, 5H; Cp), 2.32 (s, 3H; NCH═C*Me*), 2.14 (s, 3H; C$_6$H$_4$-4-*Me*), 0.54 (s, 1H; TiC*H*). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 150.12 (s; *i*-*C*$_6$H$_4$-4-Me), 142.46 (s; *i*-Ph), 134.80 (s; *p*-*C*$_6$H$_4$-4-Me), 130.09 (d, $^1J_{CH}$ = 157.2 Hz; *o*/*m*-Ph), 128.91 (d, $^1J_{CH}$ = 157.5 Hz; *o*/*m*-Ph), 128.48 (d, $^1J_{CH}$ = 158.5 Hz; *o*/*m*-*C*$_6$H$_4$-4-Me), 125.63 (d, $^1J_{CH}$ = 160.7 Hz; *p*-Ph), 122.34 (d, $^1J_{CH}$ = 159.0 Hz; *o*/*m*-*C*$_6$H$_4$-4-Me), 119.51 (s; NCH═*C*Me), 119.32 (d, $^1J_{CH}$ = 177.0 Hz; N*C*H═CMe), 114.00 (d, $^1J_{CH}$ = 174.4 Hz; Cp), 104.27 (d, $^1J_{CH}$ = 136.6 Hz; Ti*C*H), 18.22 (q, $^1J_{CH}$ = 128.2 Hz; NCH═C*Me*), 17.88 (q, $^1J_{CH}$ = 127.1 Hz; C$_6$H$_4$-4-*Me*). EIMS, *m*/*z* (relative intensity, assignment): 384 (100, M^+), 234 (95, M^+ − CpTiCl), 148 (25, CpTiCl$^+$), 105 (20, $C_8H_7N^+$).

CpTi[N(C_6H_4-2-Me)CH═C(Me)CH(Ph)C(Me)PhO] (9). To a diethyl ether solution (50 mL) of **8d** (1.15 g, 3.0 mmol) was added acetophenone (362 μL, 3.1 mmol) at room temperature via syringe. The mixture was stirred at ambient temperature for 12 h and then concentrated. Cooling of the solution to −20 °C gave **9** as red crystals. The carbonyl addition product was purified by recrystallization from diethyl ether at −5 °C. A yield of 1.20 g (2.4 mmol, 80%) of bright red crystals was obtained (mp 120 °C). Anal. Calcd for $C_{30}H_{30}NOClTi$ (M_r = 503.89): C, 71.50; H, 6.00; N, 2.78. Found: C, 70.94; H, 5.87; N, 2.69. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.56−7.02 (m, 10H; 2Ph), 7.16 (d, $^3J_{HH}$ = 8.1 Hz, 2H; C$_6$*H*$_4$-4-Me), 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 2H; C$_6$*H*$_4$-4-Me), 6.42 (s, 5H; Cp), 6.16 (s, 1H; NC*H*═CMe), 3.53 (s, 1H; C*H*Ph), 2.34 (s, 3H; C$_6$H$_4$-4-*Me*), 1.59 (s, 3H; NCH═C*Me*), 1.33 (s, 3H; OC(*Me*)Ph). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 144.79 (*i*-*C*$_6$H$_4$-4-Me), 139.79 (*i*-Ph), 139.04 (*i*-Ph), 135.67 (*p*-*C*$_6$H$_4$-4-Me), 131.83, 131.61, 130.23, 130.05, 128.82, 128.44, 128.15, 127.97, 127.60, 124.58 (*C*H═*C*(Me), *C*$_6$H$_4$-4-Me, Ph), 117.08 (Cp), 104.93 (O*C*(Me)Ph), 65.67 (*C*HPh), 28.44 (OC(*Me*)Ph), 21.93 (NCH═C*Me*), 20.97 (C$_6$H$_4$-4-*Me*).

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Supporting Information Available: For compounds **7c**, **8c**, and **9**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and all bond distances and angles (21 pages). Ordering information is given on any current masthead page.

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