Vinyltitanium Complexes Containing the [2-(*N*,*N*-Dimethylamino)ethyl]tetramethylcyclopentadienyl Ligand Cp*^{N}. Generation and Reactivity of the Vinylidene Intermediate [(Cp*^{N})(Cp*)Ti=C=CH$_2$] (Cp*^{N} = η^5-C$_5$Me$_4$(CH$_2$)$_2$NMe$_2$, Cp* = η^5-C$_5$Me$_5$)

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The reaction of $[CpTiCl_2]_n$ and Cp*TiCl$_2$(thf) with Cp*^{N}Li (Cp*^{N}, C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$; Cp*, C$_5$Me$_5$) leads to Cp*^{N}CpTiCl (**7**) and Cp*^{N}Cp*TiCl (**8**), respectively. The monochlorides are oxidized by PbCl$_2$ to give Cp*^{N}CpTiCl$_2$ (**9**) and Cp*^{N}Cp*TiCl$_2$ (**10**). The molecular structures of **7** and **10** have been determined by X-ray diffraction analysis, which reveals a chelating bonding mode of the Cp*^{N}−ligand in **7** (Ti−N, 2.437(3) Å) and noncoordination of the NMe$_2$ group in **10**. The fulvene complex Cp*^{N}(C$_5$Me$_4$CH$_2$)TiCH=CH$_2$ (**18**) and the titanacyclobutane Cp*^{N}Cp*TiCH$_2$CH$_2$C=CH$_2$ (**14**), respectively, are formed under mild conditions via the titanocenevinylidene intermediate [Cp*^{N}Cp*Ti=C=CH$_2$] (**17**), generated by α-H transformation from the vinyl complexes Cp*^{N}Cp*Ti(CH=CH$_2$)(CH$_3$) (**15**) and Cp*^{N}Cp*Ti(CH=CH$_2$)$_2$ (**12**). The formation of **14** is suggested to be influenced by the nitrogen-containing side chain in the Cp*^{N}−ligand. A stabilization of **17** by intramolecular Ti−N coordination is not observed under the reaction conditions. Intermolecular trapping of **17** with transition metal carbonyls M(CO)$_6$ leads to the heterobinuclear titanaoxetanes Cp*^{N}Cp*TiOC(=M(CO)$_5$)C=CH$_2$ (**21**, M = Cr (**a**), W (**b**)).

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Introduction

Vinylidene metal complexes have attracted considerable interest in the last decade.[1−4] As part of our work on titanocene vinylidenes we could demonstrate, that [Cp*$_2$Ti=C=CH$_2$] **2**[5] can be favorably generated as an intermediate by thermal methane elimination from Cp*$_2$Ti(CH=CH$_2$)CH$_3$ **1** (Scheme 1).[3j] Species **2** was characterized by various trapping reactions.[6,7] In solution, methane elimination from **1** occurs at temperatures above 10 °C and the fulvene complex **3** is formed by intramolecular CH-activation.[3j]

Whereas titanocene complexes containing a Ti−C double bond can often be isolated as phosphine adducts,[8] attempts to stabilize a mononuclear, terminal titanocenevinylidene **2** by adding trimethylphosphine, pyridine, or tetrahydrofuran (THF) during thermolysis of **1** failed. In this regard, the use of multidentate ligands with accessible donor functions seems to be a more promising way.

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Scheme 1

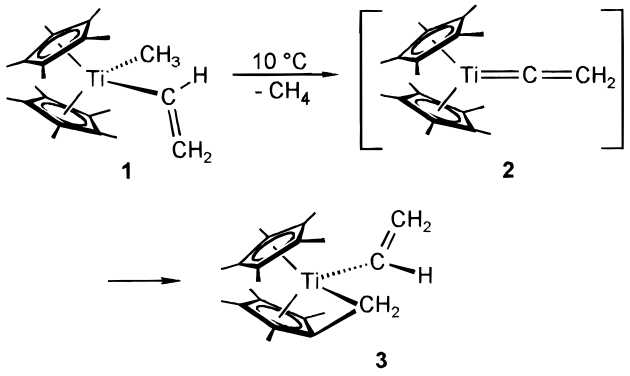
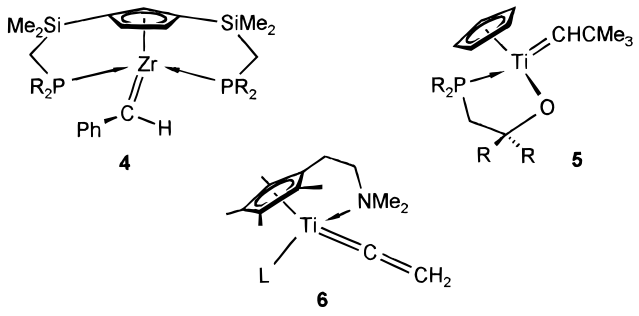


Chart 1

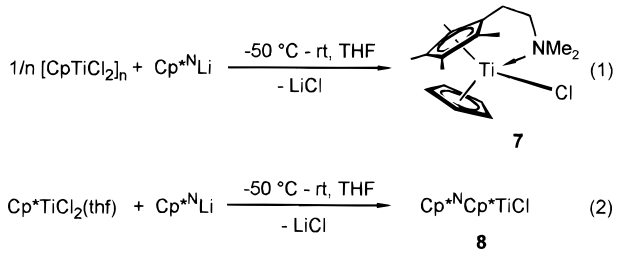


This strategy of stabilizing coordinatively unsaturated metal complexes has been used in preparation of the first isolable alkylidene complex of zirconium **4**[9] and of stable neopentylidene complexes of titanium **5** (Chart 1).[10]

To stabilize a titanocene vinylidene species, we decided to use Cp^{*N}($C_5Me_4CH_2CH_2NMe_2$), a tetramethylcyclopentadienyl ligand with an additional nitrogen donor function in the side chain. The structure of our desired target molecule **6** is shown in Chart 1. The Cp^{*N} ligand system possesses steric requirements similar to Cp*, which turned out to be important for a selective α-H elimination reaction generating a vinylidene group. Steric hindrance of the vinyl rotation around the Ti−C bond in complexes of type **1** seems to be decisive for such H-elimination processes.[6b,c,11] The Cp^{*N} ligand was introduced by Jutzi[12] and has been used for complexation of main group[13] and transition metals.[14] In the field of aminoethyl-substituted cyclopentadienes, a few complexes of group IV metals are known only for non-ring-methylated ligand systems $C_5H_4CH_2CH_2NR_2$ (R = Me,[15] *i*-Pr;[16] R_2 = $(CH_2)_4$, $(CH_2)_5$).[17] We now describe the first examples of Cp^{*N} complexes of titanium and their potential use for generating a vinylidene complex.

Results and Discussion

Chloro Complexes. The syntheses of the required chloro complexes containing the Cp^{*N} ligand were performed by starting from tervalent titanium chloro compounds. While treatment of $TiCl_3(thf)_3$ with 2 equiv of $Cp^{*N}Li$ did not lead to any characterizable products, monocyclopentadienyl complexes of tervalent titanium can be used successfully for preparation of the desired titanocene complexes. Reaction of $[CpTiCl_2]_n$ or $Cp^*TiCl_2(thf)$ with $Cp^{*N}Li$ in THF led to the formation of the new complexes $Cp^{*N}CpTiCl$ **7** and $Cp^{*N}Cp^*TiCl$ **8** (eqs 1 and 2), which were isolated in good yields as



hexane-soluble, turquoise or green crystals, respectively, and characterized by mass spectra or elemental analysis.

In contrast to **8**, which is extremely air sensitive, **7** is stable in air for a few minutes, probably because of intramolecular coordination of the amino group. A single-crystal X-ray structural analysis revealed that **7** forms monomeric molecules and the side chain is in fact coordinated. The Ti−N bond length of 2.437(3) Å is similar to that found for the dimethylamino-coordinated complex $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ (Ti−N, 2.46 Å).[18] Noteworthy, a rather long distance of 2.461(1) Å for the Ti−Cl bond is observed compared to the monomeric chloro complex Cp^*_2TiCl (Ti−Cl: 2.363(1) Å).[19] Even longer Ti−Cl bonds are known for chloro-bridged titanocene complexes $[Cp_2TiCl]_2$ (∼2.55 Å).[20] Typical values are found for the distances [Cp*N]−Ti (2.0826(2) Å) and [Cp]−Ti (2.0794(1) Å) and for the angle [Cp*N]−Ti−[Cp] (132.73(12)°). ([Cp*N]−Ti and [Cp]−Ti are the perpendicular lines from the best plane through the cyclopentadienyl ring directed to the titanium center).[18,20]

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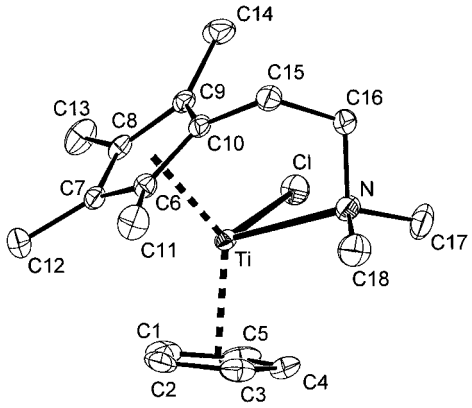
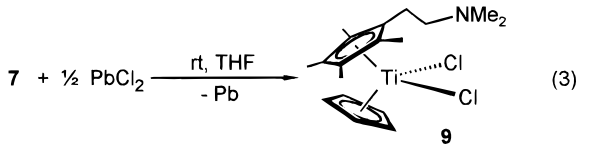
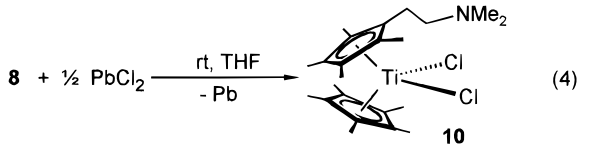


Figure 1. Platon[21] plot of the molecular structure of complex **7** with thermal ellipsoids at the 30% probability level. Selected bond length (Å) and bond angles (deg): Ti−N, 2.437(3); Ti−Cl, 2.4610(7); [Cp*^{N}]−Ti, 2.0826(2); [Cp]−Ti, 2.0794(1); N−Ti−Cl, 84.67(7); [Cp*^{N}]−Ti−[Cp], 132.73-(12).

Oxidation of **7** or **8** with $PbCl_2$ in THF afforded the tetravalent dichlorides $Cp^{*N}CpTiCl_2$ **9** and $Cp^{*N}Cp^*TiCl_2$ **10** as toluene-soluble, red crystalline solids in moderate to good yields (eqs 3 and 4). Formation of **10** is finished





after a few minutes, whereas the reaction to complex **9** is considerably slower. From solutions of **9**, an amorphous solid precipitates, which could only scarcely be redissolved and which prevented the isolation of a pure sample of **9**. In solution, both **9** and **10** are extremely moisture sensitive. Without further purification, complex **10** can be obtained as analytically pure crystals from toluene solution. ^{1}H-NMR and ^{13}C-NMR spectra of the new dichloride complexes are consistent with the structures shown. Typical[14a−c] resonances are observed for the Cp*^{N} ligand in these complexes (Tables 1 and 2). Suitable crystals for an X-ray diffraction study were obtained from toluene solutions of **10**. The structural analysis established the expected bent metallocene type structure (Figure 2). In contrast to **7**, neither an intramolecular nor an intermolecular coordination of the dimethylamino group is observed. The bond distances and angles found for **10** are similar to structural parameters of known titanocene dichlorides.[22]

Attempts to synthesize **9** by reaction of $CpTiCl_3$ with $Cp^{*N}Li$ only led to quantitative formation of $[CpTiCl_2]_n$.

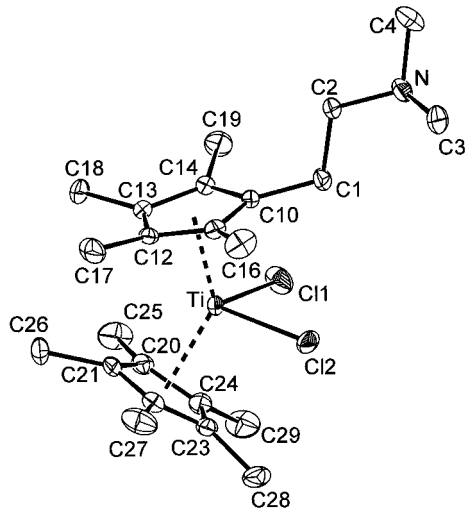
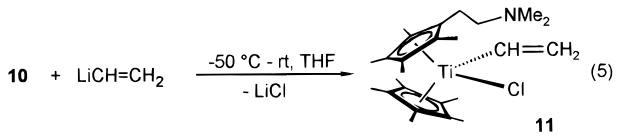


Figure 2. Platon[21] plot of the molecular structure of complex **10** with thermal ellipsoids at the 30% probability level. Selected bond length (Å) and bond angles (deg): Ti−Cl1, 2.348(1); Ti−Cl2, 2.354(1); [Cp*]−Ti, 2.1195(7); [Cp*^{N}]−Ti, 2.1204(7); Cl1−Ti−Cl, 93.33(5); [Cp*]−Ti−[Cp*^{N}], 135.81-(17).

Vinyl Complexes. Treatment of $Cp^{*N}CpTiCl_2$ **9** with an etheral solution of vinyllithium in a molar ratio of 1:1 resulted in isolation of the monochloride **7** as reduction product. This behavior is in contrast to the analogous vinylation reaction of the nonfunctionalized Cp***CpTiCl$_2$,[23] which proceeds without any reduction process. Probably the intramolecular coordination of the amino group in **7** facilitates this reaction.

However, starting from $Cp^{*N}Cp^*TiCl_2$ **10**, syntheses of vinyl complexes can be carried out. **10** reacts with 1 equiv of vinyllithium in THF at −70 °C to give Cp^{*N}-Cp*Ti(CH=CH$_2$)Cl **11** as hexane-soluble, orange crystals in good yield. Recrystallization from hexane afforded analytically pure crystals of **11**. The ^{1}H-NMR



spectrum of **11** shows a typical ABX splitting pattern for the vinyl protons. Chemical shifts of vinyl and Cp* resonances are nearly identical compared to $Cp^*_2Ti(CH{=}CH_2)Cl$[7c] in both ^{1}H-NMR and ^{13}C-NMR spectra.

Reaction of **10** with 2 equiv of vinyllithium at −70 °C primarily led to an orange-yellow solution, which changed its color to deep red by warming above −30 °C. The methylene titanacyclobutane complex **14** (Scheme 2) was obtained from this red solution in good yield. Because of its high solubility, **14** could only be isolated as a red oil, characterized by ^{1}H-NMR, ^{13}C-NMR, and mass spectra. Typical for the titanacyclobutane structure[5b,23] of **14** are the resonances for the *exo*-methylene protons at 5.93 and 5.02 ppm and the high-field-shifted signal for the carbon atom of the β-CH$_2$ group at 4.4 ppm, observed in ^{1}H-NMR and ^{13}C-NMR spectra respectively.

The change in color by warming the reaction mixture is consistent with the formation of the divinyl complex

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Scheme 2

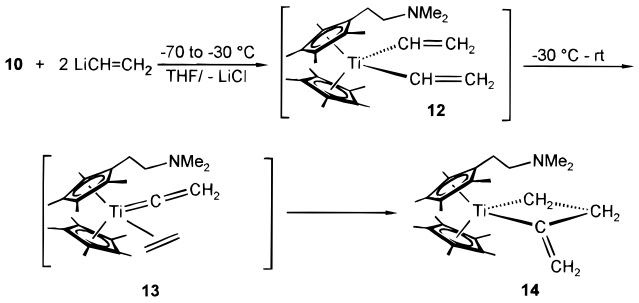


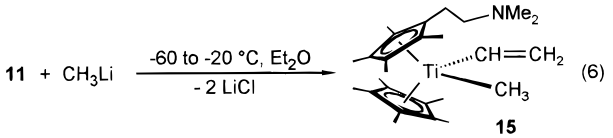
Table 1. Selected ^{1}H-NMR Data for Complexes 9−21[a]

	CH_2N	CH_2CH_2N	$N(CH_3)_2$	$Cp^{*N}CH_3$	Cp^*CH_3
9[b]	2.63	2.11	2.19	2.05 (6), 2.01 (6)	
10[b]	2.64	2.13	2.20	1.99 (6), 1.98 (6)	1.99
11[b]	2.58	2.26	2.15	1.88 (3), 1.86 (3), 1.79 (3), 1.78 (3)	1.78
14[b]	2.40	2.21	2.15	1.75 (3), 1.74 (3), 1.67 (6)	1.66
15[c]	2.40	2.30	2.16	1.77 (6), 1.69 (6)	1.69
16[b]	2.45	2.36	2.17	1.79 (6), 1.73 (6)	1.73
18[d]	2.36	2.38	2.15	1.77 (6), 1.74 (6)	
20	2.32	2.32	2.16	1.82 (3), 1.77 (9)	
21a[c]	2.27	1.96	2.10	1.44 (3), 1.46 (3), 1.48 (3), 1.55 (3)	1.42
21b[e]	2.35	2.06	2.16	1.88 (3), 1.86 (3), 1.81 (3), 1.79 (3)	1.82

[a] Number of protons given in parentheses. [b] C_6D_6, 500 MHz, 25 °C. [c] $C_6D_5CD_3$, 500 MHz, −30 °C. [d] $C_6D_5CD_3$, 500 MHz, 25 °C. [e] THF-d_8, 500 MHz, −30 °C.

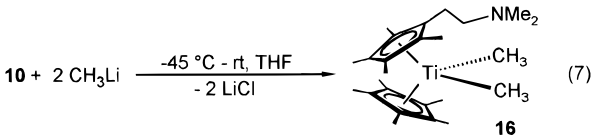
$Cp^{*N}Cp^*Ti(CH{=}CH_2)_2$ **12** at low temperatures and its conversion to **14** proceeding via an α-H elimination step to give **13** as shown in Scheme 2. Analogous to the permethylated system $Cp^*_2Ti(CH{=}CH_2)_2$, attempts to isolate **12** failed.

Methylation of $Cp^{*N}Cp^*Ti(CH{=}CH_2)Cl$ **8** with methyllithium in diethyl ether in a temperature range of −60 to −20 °C afforded $Cp^{*N}Cp^*Ti(CH{=}CH_2)Me$ **15** (eq 6)



(6)

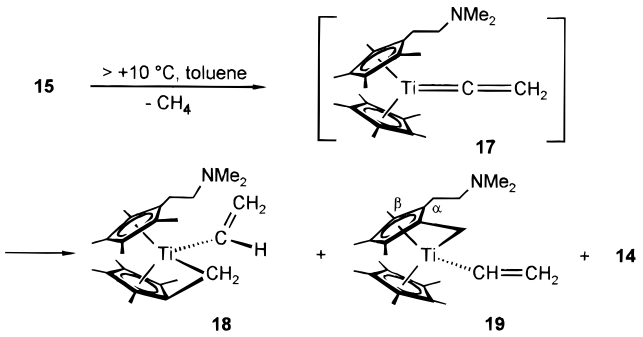
as pale yellow solid in good yield. In this reaction, the dimethyl complex $Cp^{*N}Cp^*TiMe_2$ **16** was formed as byproduct (yield 5% according ^{1}H-NMR). For further characterization, **16** was synthesized independently by reaction of $Cp^{*N}Cp^*TiCl_2$ **10** with two equivalents of methyllithium (eq 7) and was isolated as a yellow solid.



(7)

As noted above, the ^{1}H-NMR and ^{13}C-NMR spectra show nearly identical resonances for the vinyl and methyl group compared to analogous Cp^*_2M complexes. Moreover the resonances for the (dimethylamino)ethyl group of complexes **10**−**16** do not differ significantly (Tables 1 and 2) and are all observed in a typical region.[14a−c] In this regard, a noncoordination of the amino function can be assumed for these complexes.

Scheme 3



Thermal Generation and Reactivity of a Vinylidene Intermediate. Warming a solution of Cp^{*N}-$Cp^*Ti(CH{=}CH_2)Me$ **15** in toluene or hexane to room temperature leads to a significant change in color from yellow to green. As can be seen from ^{1}H-NMR spectra, **15** has already disappeared after stirring for 20 h. A vinylidene complex, stabilized by intramolecular coordination of an amino nitrogen atom according structure **6** could not be detected. Instead, ^{1}H- and ^{13}C-NMR spectra show the formation of different CH activation products from intermediately generated vinylidene species **17** (Scheme 3).

The fulvene complex $Cp^{*N}(C_5Me_4CH_2)Ti(CH{=}CH_2)$ **18** was detected as the main product. **18** could not be separated from the reaction mixture but was clearly identified by the use of {^{1}H, ^{13}C} COSY 2D NMR measurements. The resonances of **18** are (except those for the Cp^{*N} unit) almost identical to those of the known fulvene complex $Cp^*(C_5Me_4CH_2)Ti(CH{=}CH_2)$ **3** (Table 3).[7c]

An interesting feature in the ^{1}H-NMR spectrum is the splitting pattern observed for the vinylic protons. A characteristic broad multiplet at 5.09 pm was assigned to the α-hydrogen atom while the resonances of the β-hydrogen atoms appear as a doublet of doublet as expected. For the fulvene methyl protons, singlets at 1.22, 1.43, 1.59, and 1.92 ppm are found. The methylene group of the fulvene unit is detected in the ^{1}H-NMR spectra at 1.29 and 1.75 ppm and in the ^{13}C-NMR spectra at 76.2 ppm. The Cp^{*N} resonances are observed in a region that is typical (Tables 1 and 2) for noncoordination of the amino nitrogen atom.[14a−c] Remarkably, beside signals for the vinylic carbon atoms of **18** (113.8/208.1 ppm), two other vinyl systems were detected (113.9/208.4 and 113.7/207.7 ppm) in the ^{13}C-NMR spectra in a ratio of 1:2:5.5(**18**), which indicates the presence of two additional fulvene complexes. Altogether the formation of five *tuck-in* isomers was expected, considering that CH activation not only occurs at a Cp* methyl but also at a Cp^{*N} methyl group. For the latter case, H abstraction from a methyl group in α or β position to the (dimethylamino)ethyl substituent leads to the formation of four isomers of $Cp^*(C_5Me_3(CH_2CH_2NMe_2)CH_2)Ti(CH{=}CH_2)$ **19** (Scheme 3). For clarity, only one possible isomer of **19** is shown in Scheme 3.

Surprisingly, in addition to the fulvene complexes **18** and **19**, the titanacyclobutane complex **14** was produced in significant yield during thermolysis of **15**. This is in contrast to the known thermolysis of the permethylated complex $Cp^*_2Ti(CH{=}CH_2)CH_3$ **1**, which leads to the selective formation of $Cp^*(C_5Me_4CH_2)Ti(CH{=}CH_2)$ **3**[7c] as the only product. Obviously, the (dimethylamino)-

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Table 2. Selected ^{13}C-NMR Data for Complexes 9−21

	CH_2N	CH_2CH_2N	$N(CH_3)_2$	$Cp^{*N}CH_3$	Cp^{*N}-ring *C*	Cp^*CH_3	Cp^*-ring *C*
9[a]	59.6	27.6	45.6	13.2, 13.3	130.7, 129.7, 131.7		120.3[e]
10[a]	59.8	26.0	45.7	13.1, 13.2	122.9, 127.9, 129.3, 130.9	13.1	128.9
11[a]	59.8	26.7	45.7	12.59, 12.65, 12.69, 12.74	122.6, 122.9, 123.7, 124.0, 125.7	12.73	123.6
14[a]	60.1	25.7	45.8	11.8, 11.9	114.4, 114.6, 115.3, 115.7, 117.4	11.9	115.3
15[b]	60.1	26.2	45.7	11.9, 12.1	118.7, 119.0, 119.4, 120.0, 121.9	12.3	119.8
16[a]	60.2	26.1	45.6	11.8, 11.9	118.7, 120.0, 121.9	12.1	119.7
18[c]	60.5	26.3	45.7	12.0, 12.1	118.1−129.7[f]		
20	60.6	26.1	45.7	12.1, 12.2, 12.3	118.0−126.0[f]		
21a[b]	59.4	25.7	45.5	11.4, 11.5, 11.6	122.8, 123.1, 123.5, 123.8, 123.8	11.6	123.6
21b[d]	59.8	26.3	45.6	11.6, 11.7, 11.9, 12.0	123.6, 124.3, 124.5, 125.0, 126.3	12.0	124.6

[a] C_6D_6, 125 MHz, 25 °C. [b] $C_6D_5CD_3$, 125 MHz, −30 °C. [c] $C_6D_5CD_3$, 125 MHz, 25 °C. [d] THF-d_8, 125 MHz, −30 °C. [e] C_5H_5. [f] Signals could not be separated from fulvene ring carbon signals.

Table 3. Characteristic ^{1}H- and ^{13}C-NMR Data of Selected Fulvene Complexes LFvTiR (Fv = $(C_5Me_4CH_2)$)

type	comp	L	R	CH_2 (Fv)	CH_3 (Fv)	ring-C (Fv)	R
^{1}H	**18**	Cp^{*N}	CH=CH_2	1.29, 1.75[a]	1.22, 1.43, 1.59, 1.92		4.22,[c] 5.14, 5.60[c]
	3	Cp^*	CH=CH_2	1.24, 1.78[b]	1.22, 1.43, 1.72, 1.91		4.19,[d] 5.11, 5.58[d]
	20	Cp^{*N}	CH_3	1.09, 1.82[b]	1.26, 1.45, 1.68, 1.98		−1.16
		Cp^*	CH_3	1.14, 1.92[b]	1.26, 1.43, 1.67, 2.03		−1.10
^{13}C	**18**	Cp^{*N}	CH=CH_2	76.2	10.6, 10.8, 10.9, 16.7	119.2, 124.1, 126.1, 127.4, 129.7[e]	113.8, 208.1
	3	Cp^*	CH=CH_2	76.2	10.3, 10.6, 10.8, 16.6	119.5, 124.5, 126.0, 126.9, 129.5	113.7, 208.1
	20	Cp^{*N}	CH_3	73.7	10.7, 11.2, 12.1, 14.7	119.6, 124.0, 126.0, 130.4[f]	41.7
		Cp^*	CH_3	73.9	10.6, 11.1, 11.2, 14.7	119.6, 123.9, 125.0, 126.0, 130.1	41.4

[a] Multiplicity not clearly detected. [b] Doublets with J = 4 Hz. [c] Broad doublets with J = 19 Hz. [d] ABX system with J = 3 and 19 Hz. [e] Signals were assigned by comparison to Cp*FvTiR. [f] One signal hidden behind resonances of toluene-d_8.

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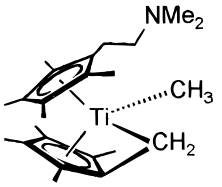
ethyl substitution in **15** supports the formation of **14**. Various experiments show an unchanged ratio of 1:2 (**14**:**18**). In explanation of this behavior, a disproportion reaction of **15** producing the divinyl complex **12** (Scheme 2) and the dimethyl complex **16** can be ruled out, because **16** was not formed during thermolysis. Liberation of ethylene is known to be a typical reaction for vinylfulvene complexes at higher temperatures.[7c] Because **18** is stable even at 70 °C, we suppose that free ethylene is formed from isomers of $Cp^*(C_5Me_3(CH_2CH_2NMe_2)CH_2)Ti(CH{=}CH_2)$ (**19**), probably facilitated by intramolecular NMe_2 coordination. This presumption is supported by the following facts: (a) the ratio **14**:**18** remains unchanged for various thermolysis experiments and (b) only three of five possible fulvene isomers are found after thermolysis. Free ethylene reacts with the vinylidene intermediate **17**, which is generated continuously from **15**, to give the stable titanacyclobutane complex **14** in a [2 + 2]-cycloaddition reaction. The same type of intermolecular reaction with ethylene is known for the permethylated vinylidene complex **2**, which proceeds much faster than the competing intramolecular CH-activation and as a result the titanacyclobutane complex $Cp^*_2TiCH_2CH_2C{=}CH_2$ is formed as the only product.[6c]

For comparison with these results we studied the thermolysis reaction of the dimethyl complex **16**. When heated to 110 °C for 10 h, a solution of **16** in toluene-d_8 turned green. The ^{1}H- and ^{13}C-NMR spectra show the formation of the methylfulvene complex **20** (Chart 2) as main product and additionally four other methylfulvene complexes. Using {^{1}H, ^{13}C} COSY 2D NMR measurements, complex **20** could be unambigiously characterized.

Characteristic signals appear for the fulvene unit and for the Ti−CH_3 group of **20**: $(C_5(CH_3)_4CH_2$, singlets at 1.26, 1.45, 1.68, and 1.98 ppm; $C_5(CH_3)_4CH_2$, doublets at 1.09 and 1.82 ppm with $^2J_{HH}$ = 4.0 Hz; Ti−CH_3, singlet at −1.16 ppm; $C_5(CH_3)_4CH_2$, 73.7 ppm; Ti−CH_3, 41.7 ppm), which are very similar to those found for the complex $(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)TiCH_3$[24] (Table 3). Especially, the existence of five signals for the titanium-bound methyl group with a relative intensity of 1:1:6:6:29 gives evidence for the formation of four additional methylfulvene complexes.

Chart 2



20

In all, CH activation dominates the reactivity of the intermediately generated species $[Cp^{*N}Cp^*Ti{=}C{=}CH_2]$ **17** and $[Cp^{*N}Cp^*Ti{=}CH_2]$. Such a behavior is already known for the intermediates $[Cp^*_2Ti{=}C{=}CH_2]$ **2** (Scheme 1) and $[Cp^*_2Ti{=}CH_2]$.[24]

An intermolecular trapping of the vinylidene intermediate **17**, generated by methane elimination from **15**, may be achieved. In a [2 + 2]-cycloaddition reaction, the Ti−C double bond of **17** reacts with the C≡O bond of a metal carbonyl. Thus, reaction of **15** with $Cr(CO)_6$ or $W(CO)_6$ in hexane at room temperature afforded the titanaoxetane complexes **21a** and **21b** (Scheme 4) as green, microcrystalline solids in moderate yields.

The complexes are characterized by comparison of their IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopical data with the recently described analogous decamethyltitanocene complexes.[7d] Typical shifts are found in the ^{1}H-NMR spectrum for the protons of the *exo*-methylene group (δ = 7.37 and 5.55 ppm for **21a**; δ = 7.19 and 6.04 ppm for **21b**). The resonances of the carbene carbon atom appear at δ = 305.3 (**21a**) and δ = 285.6 ppm (**21b**). IR spectroscopically the expected local C_{4v}

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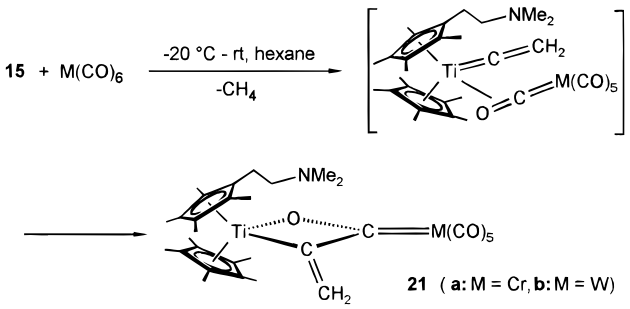
Scheme 4



symmetry for the CO-stretching vibrations of the pentacarbonyl fragment is observed for both complexes.

Conclusion

It has been demonstrated that it is possible to synthesize titanocene type complexes containing one [2-(*N*,*N*-dimethylamino)ethyl]tetramethylcyclopentadienyl ligand (Cp*^{N}). The structure of the monomeric complexes Cp*^{N}CpTiCl **7** and Cp*^{N}Cp*TiCl$_2$ **10** could be determined by X-ray single-crystal structural analyses, which reveal intramolecular coordination of the amino group for the tervalent complex **7** but not for the tetravalent complex **10**.

Vinyl complexes could be obtained starting from Cp*^{N}-Cp*TiCl$_2$ **10**. Thermal methane elimination from the complex Cp*^{N}Cp*Ti(CH=CH$_2$)Me **15** did not lead to the desired stabilization of the intermediately generated [Cp*^{N}Cp*Ti=C=CH$_2$] **17**. Intramolecular CH activation and formation of the fulvene complex Cp*^{N}(C$_5$Me$_4$CH$_2$)-Ti(CH=CH$_2$) **18** is dominating. However, CH activation of the Cp*^{N} ligand in **17** leads to isomeric fulvene complexes Cp*(C$_5$Me$_3$(CH$_2$CH$_2$NMe$_2$)CH$_2$)Ti(CH=CH$_2$) **19**. The unusual formation of the titanacyclobutane complex Cp*^{N}Cp*TiCH$_2$CH$_2$C=CH$_2$ **14** during thermolysis of **15** can be explained by reaction of **17** with ethylene. The ethylene is probably liberated from **19**, supported by intramolecular nitrogen coordination.

In summary, the reactivity of the synthesized [Cp*^{N}-Cp*Ti] complexes, particularly that of the vinylidene intermediate **17**, is very similar compared with the analogous decamethyltitanocene complexes. In this regard, the introduction of an NMe$_2$-functionalized side chain does not seem to be effective enough for stabilization of a short-lived titanocene−vinylidene species. However, the stabilization and even isolation of short-lived species should be possible in principle using ligands like Cp*^{N}. Therefore, it still remains a challenge to find highly reactive species that demonstrate the advantages of Jutzi-type ligands.

Experimental Section

General Considerations. Preparation and handling of the described compounds was performed under rigorous exclusion of air and moisture under a nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried with appropriate drying agents and destilled under a nitrogen atmosphere. ^{1}H- and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d_6, δ = 7.15 ppm; toluene-d_8, δ = 2.32, 6.98, 7.02, and 7.09 ppm; THF-d_8, δ = 1.78 and 3.58 for ^{1}H NMR spectroscopy, benzene-d_6, δ = 127.96 ppm; toluene-d_8, δ = 21.4, 125.7, 128.5, 129.3, and 137.8 ppm; THF-d_8, δ = 25.1 and 67.2 ppm for ^{13}C-NMR spectroscopy). Mass spectroscopic analyses were performed on a Finnigan MAT 95 mass spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1720 X FT-IR spectrometer. Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany, or at the Microchemisches Laboratorium, Institut für Anorganische Chemie der RWTH Aachen, Germany. The following compounds were prepared by literature known procedures: Cp*^{N}H,[12] VinLi,[25] TiCl$_3$-(thf)$_3$,[26] CpTiCl$_3$,[27] [CpTiCl$_2$]$_n$,[28] Cp*TiCl$_3$,[29] and Cp*TiCl$_2$(thf).[30]

Chloro(η^5-cyclopentadienyl)(η^5-1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)titanium (7). At a temperature of −45 °C, 19.9 mL of a freshly prepared solution of Cp*^{N}Li (7.94 mmol) in THF were added dropwise to a light-blue suspension of 1.46 g of [CpTiCl$_2$]$_n$ (7.94 mmol) in 30 mL of THF. The reaction mixture was slowly warmed to room temperature and stirred for 6 h. After the solvent was removed in vacuo, the residue was extracted with 40 mL of toluene and filtered. The resulting turquoise solution was reduced in volume to 10 mL, and 10 mL of hexane was added. A turquoise, crystalline solid is formed (1.8 g, 5.29 mmol, 67%) at −23 °C . Suitable crysals were obtained by recrystallization from hexane. MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 340 (5) (M^+), 305 (1) (M^+ − Cl), 275 (1) (M^+ − C_5H_5), 192 (4) (Cp*^{N} $^+$), 134 (3) (Cp*^{N} − $CH_2NMe_2^+$), 58 (100) ($CH_2NMe_2^+$). Mp: 206−210 °C. Anal. Calcd for $C_{18}H_{27}ClNTi$ (340.54): C, 63.48; H, 7.93; N, 4.11. Found: C, 63.54; H, 7.81;, N, 4.11.

Chloro(η^5-1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)titanium (8). At a temperature of −50 °C, 18.1 mL of a freshly prepared 0.4 M solution of Cp*^{N}Li (7.24 mmol) in THF was added to a blue solution of 1.46 g of Cp*TiCl$_2$(thf) (7.24 mmol) in 30 mL of THF. The formed green solution was warmed to room temperature and the solvent was removed in vacuo. The residue was extracted with 50 mL of toluene. After filtration the solution was reduced in volume to 5 mL and 10 mL of *n*-hexane was added. Green, crystalline needles were formed (1.4 g, 3.41 mmol, 47%) at −23 °C. The product can be recrystallized from hexane. MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 410 (17) (M^+), 375 (2) (M^+ − Cl), 317 (2) (M^+ − Cl − CH_2NMe_2), 275 (16) (M^+ − $C_5(CH_3)_5$), 260 (5) (M^+ − $C_5(CH_3)_5$ − CH_3), 218 (10) (M^+ − $C_5(CH_3)_5$ − CH_2NMe_2), 58 (100) ($CH_2NMe_2^+$). Mp: 55−58 °C.

Dichloro(η^5-cyclopentadienyl)(η^5-1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)titanium (9). A 1.1 g sample of PbCl$_2$ (4.0 mmol) was added at room temperature to a deep blue solution of 2.51 g of Cp*^{N}-CpTiCl **7** (7.38 mmol) in THF. After 4 h at this temperature, the red reaction mixture was evaporated to dryness. The residue was extraced in 50 mL of toluene and filtered. The resulting red solution was reduced in volume to 5 mL. A red solid was obtained (1.45 g, 3.86 mmol, 52%) at −23 °C. ^{1}H-NMR (THF-d_8, 500 MHz, 25 °C): δ 2.01 (s, 6H, Cp*^{N}CH$_3$), 2.05 (s, 6H, Cp*^{N}CH$_3$), 2.11 (m, 2H, CH$_2$CH$_2$N), 2.19 (s, 6H, N(CH$_3$)$_2$), 2.63 (m, 2H, CH$_2$N), 6.25 (s, 5H, C$_5$H$_5$). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C): δ 13.2, 13.3 (Cp*^{N}CH$_3$), 27.6 (CH$_2$CH$_2$N), 45.6 (N(CH$_3$)$_2$), 59.6 (CH$_2$N), 120.3 (s, C$_5$H$_5$), 130.7, 129.7 (Cp*^{N}-ring-C), 131.7 (Cp*^{N}-ipso-C).

Dichloro(η^5-1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)titanium (10). A 0.5 g sample of PbCl$_2$ (1.8 mmol)

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was added at room temperature to a deep blue solution of 1.14 g of $Cp^{*N}Cp^{*}TiCl$ **8** (2.78 mmol) in 30 mL of THF. The color of the suspension rapidly changed to deep red and metallic lead precipitated. After 30 min, the reaction mixture was evaporated to dryness, extracted with 30 mL of toluene, and filtered. The resulting red solution was reduced in volume to 5 mL. Deep red crystals were obtained (0.97 g, 2.17 mmol, 78%) at −23 °C. ^{1}H-NMR (THF-d_8, 250 MHz, 25 °C): δ 1.98 (s, 6H, $Cp^{*N}CH_3$), 1.99 (s, 15H, $C_5(CH_3)_5$ + 6H, $Cp^{*N}CH_3$), 2.13 (m, 2H, CH_2CH_2N), 2.20 (s, 6H, $N(CH_3)_2$), 2.64 (m, 2H, CH_2N). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C, TMS): δ 13.1 + 13.2 ($C_5(CH_3)_5$ + $Cp^{*N}CH_3$), 26.0 (CH_2CH_2N), 45.7 ($N(CH_3)_2$), 59.8 (CH_2N), 122.9 (Cp^{*N}-ring-C), 127.9 (Cp^{*N}-ring-C), 128.9 (s, $C_5(CH_3)_5$), 129.3 (Cp^{*N}-ring-C), 130.9 (Cp^{*N}-ipso-C). MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 410 (4) (M^+ − Cl), 375 (1) (M^+ − 2 Cl), 275 (5) (M^+ − $C_5(CH_3)_5$ − Cl), 218 (5) (M^+ − $C_5(CH_3)_5$ − Cl − CH_2NMe_2), 58 (100) ($CH_2NMe_2^+$). Mp: 137−139 °C. Anal. Calcd for $C_{23}H_{37}Cl_2NTi$ (446.04): C, 61.90; H, 8.30; N, 3.14. Found: C, 61.77; H, 8.26; N, 3.05.

Chloro(η^5-1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)vinyltitanium (11). To a solution of 1.22 g of **10** (2.74 mmol) in 50 mL of THF, 14.8 mL a 0.185 M solution of freshly prepared vinyllithium (2.74 mmol) in Et_2O was added dropwise. The resulting orange-yellow solution was warmed to 0 °C and then evaporated to dryness. The residue was extracted with 60 mL of hexane and filtered. The resulting solution was reduced in volume to 10 mL. Orange crystals were obtained (0.78 g, 1.78 mmol, 65%) at −78 °C. ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ 1.78 (s, 15H, $C_5(CH_3)_5$ + 3H, $Cp^{*N}CH_3$), 1.79 (s, 3H, $Cp^{*N}CH_3$), 1.86 (s, 3H, $Cp^{*N}CH_3$), 1.88 (s, 3H, $Cp^{*N}CH_3$), 2.15 (s, 6H, $N(CH_3)_2$), 2.26 (m, 2H, CH_2CH_2N), 2.58 (m, 2H, CH_2N), 4.96 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HH}$ = 3.3 Hz, 1H, trans =CHH), 5.63 (dd, $^3J_{HH}$ = 13.3 Hz, $^2J_{HH}$ = 3.3 Hz, 1 H, cis =CHH), 5.79 (dd, $^3J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 13.3 Hz, 1 H, TiCH). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C, TMS): δ 12.59 ($Cp^{*N}CH_3$), 12.65 ($Cp^{*N}CH_3$), 12.69 ($Cp^{*N}CH_3$), 12.73 ($C_5(CH_3)_5$), 12.74 (Cp^{*N}-CH_3), 26.7 (CH_2CH_2N), 45.7 [$N(CH_3)_2$], 59.8 (CH_2N), 118.5 (=CH_2), 122.6 (Cp^{*N}-ring-C), 122.9 (Cp^{*N}-ring-C), 123.6 (s, $C_5(CH_3)_5$), 123.7 (Cp^{*N}-ring-C), 124.0 (Cp^{*N}-ring-C), 125.7 (Cp^{*N}-ipso-C), 213.0 (TiCH). MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 437 (4) (M^+), 410 (3) (M^+ − C_2H_3), 275 (9) (M^+ − $C_5(CH_3)_5$ − C_2H_3), 218 (10) (M^+ − $C_5(CH_3)_5$ − C_2H_3 − CH_2NMe_2), 58 (100) ($CH_2NMe_2^+$). Mp: 56−58 °C. Anal. Calcd for $C_{25}H_{40}Cl_2NTi$ (437.61): C, 68.61; H, 9.14; N, 3.20. Found: C: 68.39, H: 9.11, N: 3.25.

(η^5-1-[2-(*N*,*N*-Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)-(2-methylidene)titanacyclobutane (14). To a solution of 0.56 g of **10** (1.26 mmol) in 50 mL of THF at −70 °C, 13.6 mL of a freshly prepared 0.185 M solution of vinyllithium (2.52 mmol) was added dropwise. During addition, an orange-yellow solution was formed. After slowly warming, a change in color occured at temperatures below −30 °C and the resulting red solution was allowed to warm to room temperature. Then the solution was evaporated to dryness, and the residue was extracted with 40 mL of hexane. After filtration, the hexane was evaporated and the product was obtained as a red oil (quantitative yield according ^{1}H-NMR). ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ 0.17 (m, 2H, β-CH_2), 1.65 (2H, $TiCH_2$), 1.66 (s, 15H, $C_5(CH_3)_5$), 1.67 (6H, $Cp^{*N}CH_3$), 1.74 (s, 3H, $Cp^{*N}CH_3$), 1.75 (s, 3H, $Cp^{*N}CH_3$), 2.15 (s, 6H, $N(CH_3)_2$), 2.21 (m, 2H, CH_2-CH_2N), 2.40 (m, 2H, CH_2N), 5.02 (s, =CH_2), 5.93 (s, =CH_2). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C, TMS): δ 4.2 (β-CH_2), 11.8 ($Cp^{*N}CH_3$), 11.8 ($Cp^{*N}CH_3$), 11.9 ($Cp^{*N}CH_3$), 11.9 ($C_5(CH_3)_5$ + $Cp^{*N}CH_3$), 25.7 (CH_2CH_2N), 45.8 ($N(CH_3)_2$), 60.1 (CH_2N), 64.9 ($TiCH_2$), 108.2 (=CH_2), 114.4 (Cp^{*N}-ring-C), 114.6 (Cp^{*N}-ring-C), 115.3 (s, $C_5(CH_3)_5$), 115.5 (Cp^{*N}-ring-C), 115.7 (Cp^{*N}-ring-C), 117.4 (Cp^{*N}-ipso-C), 232.5 (TiC=). MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 429 (1) (M^+), 401 (<1) (M^+ − C_2H_4), 375 (12) (M^+ − C_4H_6), 317 (10) (M^+ − C_4H_6 − CH_2NMe_2), 58 (100) ($CH_2NMe_2^+$).

(η^5-1-[2-(*N*,*N*-Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)-methylvinyltitanium (15). To a solution of 0.57 g of **11** (1.33 mmol) in 50 mL of Et_2O, 7.05 mL of a 0.188 M solution of methyllithium (1.33 mmol) in Et_2O was added dropwise at −60 °C. After the addition was complete, a yellow solution resulted, which was allowed to warm to −20 °C. At this temperature the solvent was evaporated, the residue was extracted with 40 mL of hexane, and filtered and the orange-yellow solution was reduced in volume to 5 mL. A yellow solid was obtained (0.37 g, 0.89 mmol, 67 %) at −78 °C. ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz, 25 °C): δ −0.54 ($TiCH_3$), 1.69 (s, 15H, $C_5(CH_3)_5$ + 6H, $Cp^{*N}CH_3$), 1.77 (s, 6H, $Cp^{*N}CH_3$), 2.16 (s, 6H, $N(CH_3)_2$), 2.30 (br s, 2H, CH_2CH_2N), 2.40 (br s, 2H, CH_2N), 4.14 (d, $^3J_{HH}$ = 17.7 Hz, 1H, *trans* =CHH), 5.46 (m, 2 H, TiCH + *cis* =CHH). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C, TMS): δ 11.9 ($Cp^{*N}CH_3$), 12.1 ($Cp^{*N}CH_3$), 12.3 ($C_5(CH_3)_5$), 26.2 (CH_2-CH_2N), 45.7 ($N(CH_3)_2$), 56.1 ($TiCH_3$), 60.1 (CH_2N), 115.6 (=CH_2), 118.7 (Cp^{*N}-ring-C), 119.0 (Cp^{*N}-ring-C), 119.4 (Cp^{*N}-ring-C), 119.8 (s, $C_5(CH_3)_5$), 120.0 (Cp^{*N}-ring-C), 121.9 (Cp^{*N}-ipso-C), 211.4 (TiCH).

(η^5-1-[2-(*N*,*N*-Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)-dimethyltitanium (16). To a solution of 0.70 g of **10** (1.57 mmol) in 30 mL of THF, 1.96 mL of a 1.6 M solution of methyllithium (13.14 mmol) in Et_2O was added dropwise at −45 °C. After the addition was complete, a yellow solution resulted, which was allowed to warm to room temperature and stirred for 1 h. Then the solvent was evaporated, the residue was extracted with 50 mL of hexane, and filtered and the yellow solution was reduced in volume to 5 mL. A yellow solid was obtained (0.43 g, 1.06 mmol, 68%) at −78 °C. ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ −0.62 (s, 6H, $TiCH_3$), 1.73 (s, 15H, $C_5(CH_3)_5$), 1.73 (s, 6H, $Cp^{*N}CH_3$), 1.79 (s, 6H, $Cp^{*N}CH_3$), 2.17 (s, 6H, $N(CH_3)_2$), 2.36 (m, 2H, CH_2CH_2N), 2.45 (m, 2H, CH_2N). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 25 °C): δ 11.8 ($Cp^{*N}CH_3$), 11.9 ($Cp^{*N}CH_3$), 12.1 ($C_5(CH_3)_5$), 26.1 (CH_2CH_2N), 45.6 ($N(CH_3)_2$), 49.4 ($TiCH_3$), 60.2 (CH_2N), 118.7 (Cp^{*N}-ring-C), 119.7 (s, $C_5(CH_3)_5$), 120.0 (Cp^{*N}-ring-C), 121.9 (Cp^{*N}-ipso-C). MS (EI, 70 eV; *m*/*z* (relative intensity, %): 390 (1) (M^+ − CH_3), 375 (5) (M^+ − 2 CH_3), 317 (3) (M^+ − 2 CH_3 − CH_2NMe_2), 58 (100) ($CH_2NMe_2^+$).

Thermolysis of 15. A cold (−20 °C) solution of 150 mg of **15** (0.36 mmol) in 10 mL of toluene or hexane was allowed to warm to room temperature. The solution turned green and after stirring for 20 h, the solvent was evaporated to give a green oil. NMR spectra showed **18** as main product. ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ 1.22(s, 3H, $C_5(CH_3)_4CH_2$), 1.29 (d, $^2J_{HH}$ could not be detected exactly, $TiCH_2$), 1.43 (s, 3H, $C_5(CH_3)_4CH_2$), 1.59 (s, 3 H, $C_5(CH_3)_4CH_2$), 1.74 (s, 6 H, Cp^{*N}-CH_3), 1.75 (hidden signal, $TiCH_2$), 1.77 (s, 6 H, $Cp^{*N}CH_3$), 1.92 (s, 3 H, $C_5(CH_3)_4CH_2$), 2.15 (s, 6 H, $N(CH_3)_2$), 2.36 (m, 2 H, CH_2N), 2.38 (m, 2 H, CH_2CH_2N), 4.22 (br d, $^3J_{HH}$ = 19.2Hz, 1H, *trans* =CHH), 5.14 (br m, 1 H, TiCH), 5.60 (br d, $^3J_{HH}$ = 14.3 Hz, 1 H, *cis* =CH*H*). ^{13}C{^{1}H}-NMR ($C_6D_5CD_3$, 125 MHz, 25 °C): δ 10.6, 10.8, 10.9 ($C_5(CH_3)_4CH_2$), 12.0, 12.1 (Cp^{*N}-CH_3), 16.7 ($C_5(CH_3)_4CH_2$), 26.3 (CH_2CH_2N), 45.7 ($N(CH_3)_2$), 60.5 (CH_2N), 76.2 ($TiCH_2$), 113.8 (=CH_2), 118.1−121.4 (Cp^{*N}-ring-C), 119.2 ($C_5(CH_3)_4CH_2$), 124.1 ($C_5(CH_3)_4CH_2$), 126.1 ($C_5(CH_3)_4CH_2$), 127.4 ($C_5(CH_3)_4CH_2$), 129.7 ($C_5(CH_3)_4CH_2$), 208.1 (TiCH). MS (EI, 70 eV; *m*/*z* (relative intensity, %)): 401 (4) (M^+), 375 (6) (M^+ − C_2H_2).

Thermolysis of 16. A solution of 60 mg of **16** (0.15 mmol) in 0.8 mL of toluene-d_8 was heated to 110 °C for 10 h. NMR spectra of the resulting green solution showed **20** as the main product. ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz, 25 °C): δ −1.16 (s, 3H, $TiCH_3$), 1.09 (d, $^2J_{HH}$ = 4.0 Hz, 1H, $TiCH_2$), 1.26 (s, 3H, $C_5(CH_3)_4CH_2$), 1.45 (s, 3H, $C_5(CH_3)_4CH_2$), 1.68 (s, 3H, $C_5(CH_3)_4$-CH_2), 1.77 (2s, 9H, $Cp^{*N}CH_3$), 1.82 (s, 3H, $Cp^{*N}CH_3$), 1.82 (hidden, 1H, $TiCH_2$), 1.98 (s, 3H, $C_5(CH_3)_4CH_2$), 2.16 (s, 6H, $N(CH_3)_2$), 2.32 (m, 2H, CH_2CH_2N and 2H, CH_2N). ^{13}C{^{1}H}-NMR ($C_6D_5CD_3$, 125 MHz, 25 °C): δ 10.7 ($C_5(CH_3)_4CH_2$), 11.2

Table 4. Crystal Data, Data Collection Parameters and Convergence Results for 7 and 10

	7	10
formula	$C_{18}H_{27}NClTi$	$C_{23}H_{37}NCl_2Ti$
fw	340.78	446.36
system	orthorhombic	monoclinic
space group (No.)	$Pna2_1$ (33)	$P2_1/n$(14)
a, Å	14.818(3)	9.602(7)
b, Å	8.146(2)	16.80(1)
c, Å	14.138(3)	14.663(9)
β, deg		100.28(6)
U, Å^3	1707(1)	2328(3)
Z	4	4
d_{calc}, g cm^{-3}	1.326	1.274
μ, cm^{-1}	6.47	6.03
θ_{max}, deg	26	26
crystal dimens, mm^3	0.48 × 0.36 × 0.28	0.4 × 0.2 × 0.2
total no. of unique reflns	3727	9493
total no. of unique reflns ($I > \sigma(I)$)	2862	2823
params refined	297	244
R^a	0.034	0.049
$R_w{}^b$	0.036	0.048
GOF^c	1.054	1.059
res el density, e Å^{-3}	0.40	0.35

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$, n_{obs}, number of observations, n_{var}, number of variables refined.

($C_5(CH_3)_4CH_2$), 12.1 ($C_5(CH_3)_4CH_2$), 12.1 (Cp*^{N}CH_3), 12.2 (Cp*^{N}CH_3), 12.3 (Cp*^{N}CH_3), 14.7 ($C_5(CH_3)_4CH_2$), 26.1 (CH_2-CH_2N), 41.7 (TiCH_3), 45.7 (N(CH_3)$_2$), 60.6 (CH_2N), 73.7 (TiCH_2), 114.6 (Cp*^{N}-ring-C), 115.3 (s, $C_5(CH_3)_5$), 118.0−126.0 (Cp*^{N}-ring-*C*), 119.6, 124.0, 126.0, 130.4 ($C_5(CH_3)_4CH_2$).

Synthesis of 21. To a solution of 150 mg of **15** (0.36 mmol) in 30 mL of hexane was added 0.36 mmol of $Cr(CO)_6$ or $W(CO)_6$ at −20 °C. The reaction mixture was stirred for 1 h and then slowly warmed to room temperature. While stirring for 2 h, a deep green suspension was formed, which was filtered. The resulting green solution was reduced in volume to 20 mL. A green, microcrystalline solid was obtained (**21a**, 0.15g, 0.19 mmol, 51.5%; **21b**, 0.11 g, 40%) at −23 °C. **21a.** IR (KBr): 2815 cm^{-1} w, 2767 w [ν(C−H), N−CH_3], 2040 s, ∼1966 sh m, 1908 vs, 1885 s [ν(CO), 2A1 + E], 1383 m [δ(C−H), N−CH_3], 1277 m [ν(C−N), N−CH_3], 900 m [δ(=CH_2)$_{oop}$], 666 s, 643 m [δ(W−CO)] cm^{-1}. ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz, −30 °C): δ 1.42 (s, 15H, $C_5(CH_3)_5$), 1.44 (s, 3H, Cp*^{N}CH_3), 1.46 (s, 3H, Cp*^{N}CH_3), 1.48 (s, 3H, Cp*^{N}CH_3), 1.55 (s, 3H, Cp*^{N}CH_3), 1.96 (m, 2H, C$H_2$$CH_2$N), 2.10 (s, 6H, N(C$H_3$)$_2$), 2.27 (m, 2H, C$H_2$N), 5.55 (s, 1H, =$CH_2$), 7.37 (s, 1H, =$CH_2$). ^{13}C{^{1}H}-NMR ($C_6D_5$-$CD_3$, 125 MHz, −30 °C): δ 11.4 (Cp*^{N}CH_3), 11.5 (Cp*^{N}CH_3), 11.6 ($C_5(CH_3)_5$ + Cp*^{N}CH_3), 25.7 (CH_2CH_2N), 45.5 (N(CH_3)$_2$), 59.4 (CH_2N), 122.8 (Cp*^{N}-ring-C), 123.1 (Cp*^{N}-ring-C), 123.5 (Cp*^{N}-ring-C), 123.6 ($C_5(CH_3)_5$), 123.8 (Cp*^{N}-ring-C), 126.3 (Cp*^{N}-ipso-C), 133.5 (=CH_2), 209.2 (TiC=), 221.0 (cis CO), 225.4 (trans CO), 305.3 (Cr=C). Mp: 92−94 °C. Anal. Calcd for $C_{31}H_{39}NO_6CrTi$ (621.21): C, 59.93; H, 6.28; N, 2.25. Found: C, 57.61; H, 6.76; N, 2.14. **21b.** IR (KBr): 2816 cm^{-1} w, 2766 w [ν(C−H), N−CH_3], 2053 s, 1968 m, 1913 vs, 1881 s [ν(CO), 2A1 + E], 1384 m [δ(C−H), N−CH_3], 1282 m [ν(C−N), N−CH_3], 910 m [δ(=CH_2)$_{oop}$], 593 m, 572 m [δ(W−CO)] cm^{-1}. ^{1}H-NMR (THF-d_8, 500 MHz, −30 °C): δ 1.79 (s, 3H, Cp*^{N}CH_3), 1.81 (s, 3H, Cp*^{N}CH_3), 1.82 (s, 15H, $C_5(CH_3)_5$), 1.86 (s, 3H, Cp*^{N}CH_3), 1.88 (s, 3H, Cp*^{N}CH_3), 2.06 (m, 2H, CH_2-CH_2N), 2.16 (s, 6H, N(CH_3)$_2$), 2.35 (m, 2H, CH_2N), 6.04 (s, 1H, =CH_2), 7.19 (s, 1H, =CH_2). ^{13}C{^{1}H}-NMR (THF-d_8, 125 MHz, −30 °C, TMS): δ 11.6 (Cp*^{N}CH_3), 11.7 (Cp*^{N}CH_3), 11.9 (Cp*^{N}CH_3), 12.0 ($C_5(CH_3)_5$ + Cp*^{N}CH_3), 26.3 (CH_2CH_2N), 45.6 (N(CH_3)$_2$), 59.8 (CH_2N), 123.6 (Cp*^{N}-ring-*C*), 124.3 (Cp*^{N}-ring-C), 124.5 (Cp*^{N}-ring-*C*), 124.6 ($C_5(CH_3)_5$), 125.0 (Cp*^{N}-ring-C), 127.0 (Cp*^{N}-ipso *C*), 136.7 (=CH_2), 201.5 (cis CO), 204.9 (trans CO), 212.7 (TiC=), 285.6 (W=C). Mp: 129−132 °C. Anal. Calcd for $C_{31}H_{39}NO_6WTi$ (753.04): C, 49.44; H, 5.18; N, 1.86. Found: C, 50.28; H, 5.56; N: 1.76.

X-ray Structure Determination of 7 and 10. Geometry and intensity data were collected with Mo Kα radiation at 203 K on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator (λ = 0.7107 Å). A summary of crystal data, data collection, and convergence results is compiled in Table 4. Due to the modest linear absorption coefficients, no absorption corrections had to be applied to the experimental data. The structures were solved by direct methods[31] and refined on structure factors with the local version of the SDP program suite.[32] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were refined isotropically in the case of **7**, whereas for **10** they were included as riding on the corresponding carbon atoms (C−H = 0.98 Å, U_{iso}(H) = 1.3(U_{eq}(C)). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository numbers CSD-407052 (for **7**) and CSD-407053 (for **10**).

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Supporting Information Available: Tables of positional parameters, displacement parameters, and bond lengths and angles for **7** and **10** and NMR spectra of **9**−**11**, **14**−**16**, **18**, **20**, and **21** (40 pages). Ordering information is given on any current masthead page.

OM970321S

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