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α-H Elimination from Homoleptic Bis(1-aza-1,3-diene)titanium: Formation of a New Metallacyclic Titanium Alkylidene Complex[†]

Joachim Scholz[*,‡] and Helmar Görls[§]

Institute of Sciences, Department of Chemistry, University of Koblenz-Landau,
Universitätsstrasse 1, D-56070 Koblenz, Germany, and
Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-Universität Jena,
August-Bebel-Strasse 2, D-07743 Jena, Germany

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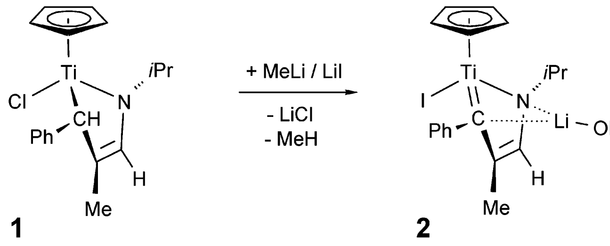
Summary: Reduction of TiCl$_4$(THF)$_2$ *with 2 equiv of Mg in the presence of 2 equiv of a sterically demanding 1-aza-1,3-diene leads to the first homoleptic early-transition-metal 1-aza-1,3-diene complex, Ti(1-aza-1,3-diene)*$_2$*. Subsequent addition of MeLi and elimination of methane results in the formation of a novel metallacyclic titanium alkylidene complex, which affords the opportunity to compare structural data of Ti−C- and Ti═C-bonded ligands within the same molecule.*

Alkylidene complexes of early transition metals have been proposed as intermediates in a variety of important C−C and C−H activation reactions.[1] For example, titanium alkylidene complexes are thought to play a key role both as catalysts in olefin polymerization and olefin metathesis reactions[2] and in stoichiometric transformations: e.g., olefination of carbonyl compounds.[3] However, stable alkylidene complexes of group 4 metals that have been isolated and structurally characterized are still rare. Some of them have been prepared by α-H elimination reactions from corresponding alkyl complexes which commonly can be induced by thermal means or by addition of a strong donor ligand: e.g., trimethylphosphine.[4] Moreover, it has been observed that the elimination reaction proceeds readily when the α-hydrogen is embedded in a sterically crowded coordination environment and when it can be transferred to a carbanionic acceptor ligand. In addition, α-H elimination reactions are even more favored when the C−H bond concerned is already activated by an agostic interaction with the metal center.[5]

Recently, we reported the titanium(1-aza-1,3-diene) complex **1**, which exactly meets the conditions for the preparation of alkylidene complexes. Actually, addition of MeLi to **1** led to the formation of unstable [CpTi-(1-aza-1,3-diene)Me], which decomposes with methane elimination into the novel titanium alkylidene complex **2**, even at room temperature (eq 1).[6]



(1)

Interestingly, most of the titanium alkylidene complexes that have been isolated up to now contain at least one stabilizing cyclopentadienyl ring, and consequently, very few non-cyclopentadienyl titanium alkylidene complexes have been prepared.[7,8] However, the molecular structure of **2** shows that the short Ti═C bond is part of a five-membered metallacycle, which in addition to the cyclopentadienyl ring probably causes the exceptionally high stability of this new type of alkylidene complex. To find arguments for this hypothesis and to prove if 1-aza-1,3-diene complexes are generally suitable precursors for the synthesis of alkylidene complexes, we have tried to transfer the homoleptic 1-aza-1,3-diene complex **4** into a metallacyclic alkylidene complex.

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[*] To whom correspondence should be addressed. E-mail: scholz@uni-koblenz.de.

[†] Monoazadiene Complexes of Early Transition Metals. 6. Part 5: ref 9.

[‡] University of Koblenz-Landau.

[§] Friedrich-Schiller-Universität Jena.

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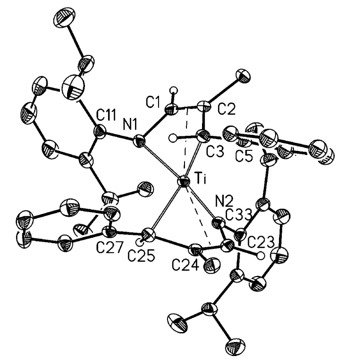
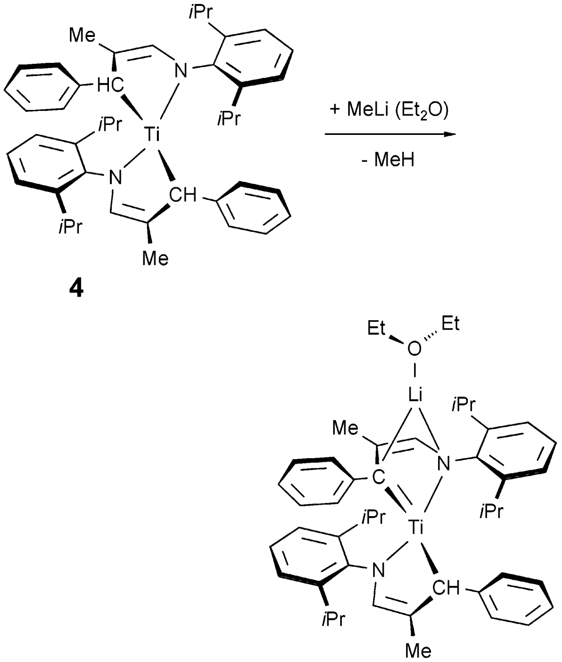


Figure 1. ORTEP drawing of **4** (50% probability level) with the atom-labeling scheme. All the hydrogen atoms of the molecule (except H1, H3, H23, and H25) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−N1 = 1.949(2), Ti−N2 = 1.939(2), Ti−C1 = 2.132(3), Ti−C2 = 2.374(3), Ti−C3 = 2.317(3), Ti−C23 = 2.357(3), Ti−C24 = 2.399(3), Ti−C25 = 2.132(3), Ti−H3 = 2.35(1), Ti−H25 = 2.28(1), N1−C1 = 1.396(4), C1−C2 = 1.392(4), C2−C3 = 1.469(4), N2−C23 = 1.413(4), C23−C24 = 1.387(4), C24−C25 = 1.470(4); N1−Ti−C3 = 91.24(10), N2−Ti−C25 = 90.30(11), Ti−C3−H3 = 90.8(1), Ti−C25−H25 = 86.2(1); (N1, Ti, C3)(N2, Ti, C25) = 90.7(1), (N1, Ti, C3)(N1, C1, C2, C3) = 116.1(1), (N2, Ti, C25)(N2, C23, C24, C25) = 117.2(1).

Complex **4** was synthesized by reduction of $TiCl_4(THF)_2$ with 2 equiv of Mg in the presence of 2 equiv of the sterically demanding 1-aza-1,3-diene (C_6H_3-2,6-*i*Pr_2)N=CHC(Me)=CH(Ph) (**3**), performed as a "one-pot synthesis".[9] It could be isolated as thermally stable red-brown crystals which are slightly soluble in diethyl ether and toluene but sparingly in pentane. Both the NMR[10] data and the results of the X-ray diffraction analysis clearly indicate that the heterodienes have been doubly reduced upon coordination, and the bonding situation in **4** is best described as that of a 1-titana-2-azacyclopent-3-ene complex (Figure 1).[11]

Evidently, the most interesting structural feature of **4** concerns the bonding parameters of the TiCH groups. Nearly right Ti−C−H angles (Ti−C3−H3 = 90.8(1)°; Ti−C25−H25 = 86.2(1)°) and small Ti···H distances of 2.35(1) and 2.28(1) Å, respectively, which are completely comparable to those of **1** (Ti−C−H = 93.0(2)°, Ti···H = 2.39(3) Å)[6] and in all probability a consequence of an α-agostic interaction, provide a reliable indication of predetermined breaking points within the bond skeleton of the molecule.

Thus, when 1 equiv of MeLi is added to a solution of **4** in diethyl ether, the novel metallacyclic alkylidene complex **5** is formed as a result of the expected facile C−H bond cleavage process in 63% yield (eq 2).[9]



4

5

(2)

Complex **5** is a dark red and extremely air-sensitive crystalline solid, but it can be stored at room temperature under argon for months without decomposition. It seems plausible that the pathway for the formation of **5** involves the generation of the intermediate methyl complex {Li(OEt_2)[(1-aza-1,3-diene)$_2$TiMe]} followed by smooth α-hydrogen abstraction, which is facilitated by the irreversible methane elimination. As judged from NMR spectra, the most convincing indicator to illustrate the dramatic effect on the bonding situation as result of the methane elimination is given by the ^{13}C chemical shift values of the two metal-bonded carbon atoms: Thus, the TiCH resonance concerning the unaffected 1-titana-2-azacyclopent-3-ene ring appears at δ 79.76 ($^1J_{C,H}$ = 131.5 Hz), which is shifted upfield relative to the starting complex **4** but is comparable to signals for

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[9] Synthesis of **4**: to a solution of $TiCl_4(THF)_2$ (3.50 g, 10.48 mmol) and the 1-aza-1,3-diene **3** (6.41 g, 21.00 mmol) in THF (150 mL) were added magnesium turnings (0.51 g, 21.00 mmol) over a period of 8 h at −30 °C. The reaction mixture was warmed to room temperature and stirred until the magnesium was dissolved. Then, the mixture was evaporated to dryness, and the product was extracted with diethyl ether (100 mL) to leave magnesium chloride. The red-brown extract was concentrated to 50 mL and stored at −20 °C. A yield of 5.17 g (7.85 mmol, 75%) of red-brown crystals of **4** was obtained. Mp: 135−138 °C dec. Recrystallization from diethyl ether gave crystals suitable for X-ray diffraction analysis.[11] Anal. Calcd for $C_{44}H_{54}N_2Ti$: C, 80.22; H, 8.26; N, 4.25. Found: C, 79.99; H, 8.20; N, 4.31. See also: Scholz, J.; Kahlert, St.; Görls, H. *Organometallics*, in press. Synthesis of **5**: a solution of **4** (3.55 g, 5.34 mmol) in diethyl ether (100 mL) was treated dropwise at 0 °C with a solution of MeLi (9.0 mL of a 0.6 M solution in diethyl ether). The reaction mixture was stirred for 12 h at room temperature. Subsequently the solvent was removed and the residue was extracted with *n*-pentane. After 1 day at −10 °C, dark red crystals of **5** (2.48 g, 3.36 mmol, 63%) were isolated. Mp: 105 °C dec. Recrystallization from diethyl ether gave crystals suitable for X-ray diffraction analysis.[14] Anal. Calcd for $C_{48}H_{63}LiN_2OTi$: C, 78.03; H, 8.59; N, 3.79. Found: C, 77.87; H, 8.51; N, 3.90.

[10] Selected spectroscopic data are as follows. **4**: ^1H NMR (THF-d_8, 55 °C) δ 6.73 (s, 1H, NC*H*=), 6.50 (s, 1H, NC*H*=), 2.67 (s, 1H, TiC*H*), 2.04 (s, 3H, =C*Me*), 1.52 (s, 3H, =C*Me*), 1.26 (s, 1H, TiC*H*); ^{13}C NMR (THF-d_8, 25 °C) δ 120.65 (d, $^1J_{C,H}$ = 173.9 Hz, N*C*H=), 118.60 (d, $^1J_{C,H}$ = 175.2 Hz, N*C*H=), 111.07 (s, =*C*Me), 109.22 (s, =*C*Me), 105.75 (d, $^1J_{C,H}$ = 125.1 Hz, Ti*C*H), 101.25 (d, $^1J_{C,H}$ = 133.7 Hz, Ti*C*H), 19.83 (q, $^1J_{C,H}$ = 127.1 Hz, =C*Me*), 18.40 (q, $^1J_{C,H}$ = 127.4 Hz, =C*Me*). **5**: ^1H NMR (THF-d_8, 55 °C) δ 6.29 (s, 1H, NC*H*=CMeCH), 4.95 (s, NC*H*=CMeC=), 2.20 (s, 3H, =C*Me*), 2.10 (s, 3H, =C*Me*), 1.41 (s, 1H, TiC*H*); ^{13}C NMR (THF-d_8, 25 °C) δ 236.10 (s, Ti=*C*Ph), 119.30 (d, $^1J_{C,H}$ = 167.7 Hz, N*C*H=CMeCH), 115.91 (s, =*C*Me), 114.46 (s, =*C*Me), 101.22 (d, $^1J_{C,H}$ = 162.0 Hz, N*C*H=CMeC=), 79.76 (d, $^1J_{C,H}$ = 131.5 Hz, Ti*C*H), 21.37 (q, $^1J_{C,H}$ = 125.1 Hz, =C*Me*), 17.23 (q, $^1J_{C,H}$ = 124.5 Hz, =C*Me*) (see the Supporting Information).

[11] Crystal data for **4**: $C_{44}H_{54}N_2Ti$, $M_r = 658.79$, brown prism, size 0.32 × 0.28 × 0.20 mm^3, triclinic, space group $P\bar{1}$, $a = 9.7454(6)$ Å, $b = 10.8348(6)$ Å, $c = 20.2953(6)$ Å, $\alpha = 85.857(3)°$, $\beta = 78.45(3)°$, $\gamma = 66.362(2)°$, $V = 1923.3(1)$ $Å^3$, $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.138$ g cm^{-3}, μ(Mo Kα) = 2.54 cm^{-1}, $F(000) = 708$, 14 283 reflections in h (−12 to +12), k (−14 to +13), l (−26 to +23), measured in the range $3.37° \leq \theta \leq 27.43°$, completeness $\theta_{max} = 98.8\%$, 8679 independent reflections, $R_{int} = 0.0624$, 5582 reflections with $F_o > 4\sigma(F_o)$, 436 parameters, 0 restraints, $R1_{obsd} = 0.072$, $wR2_{obsd} = 0.147$, $R1_{all} = 0.127$, $wR2_{all} = 0.166$, GOF = 1.013, largest difference peak/hole 0.522/−0.483 e $Å^{-3}$.

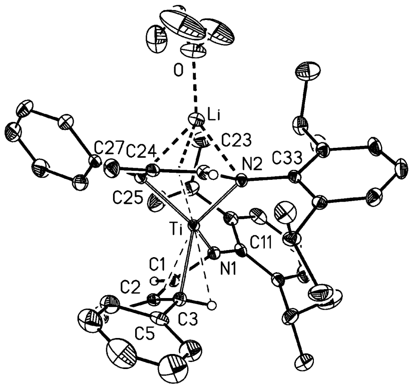

Figure 2. ORTEP drawing of **5** (50% probability level) with the atom-labeling scheme. All the hydrogen atoms of the molecule (except H1, H3, and H23) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−N1 = 1.949(2), Ti−N2 = 1.996(2), Li−N2 = 2.157(6), Li−O = 1.878(6), Ti−C1 = 2.370(3), Ti−C2 = 2.402(3), Ti−C3 = 2.163(3), Ti−C23 = 2.387(3), Ti−C24 = 2.382(3), Ti−C25 = 1.978(3), Li−C23 = 2.208(7), Li−C24 = 2.211(6), Li−C25 = 2.197(6), Ti−H3 = 2.31(1), N1−C1 = 1.409(4), C1−C2 = 1.385(4), C2−C3 = 1.467(4), N2−C23 = 1.421(4), C23−C24 = 1.411(4), C24−C25 = 1.452(4); N1−Ti−C3 = 89.3(1), N2−Ti−C25 = 91.6(1), Ti−C3−H3 = 88.1(1); (N1, Ti, C3)(N2, Ti, C25) = 93.6(1), (N1, Ti, C3)(N1, C1, C2, C3) = 116.4(1), (N2, Ti, C25)(N2, C23, C24, C25) = 120.0(1).

other titanium 1-aza-1,3-diene complexes[12] and is still in the normal range of sp^3-hybridized carbon atoms σ-bonded to titanium.[13] On the other hand, the sp^2-hybridized alkylidene carbon atom gives rise to a singlet at δ 236.10, as expected for alkylidene complexes of early transition metals.[4] Naturally, the very large chemical shift difference of about 150 ppm between these two carbon atoms is reflected by their characteristic structural parameters as well (Figure 2).[14]

The Ti−C3 bond length amounts to 2.163(3) Å, which is not very different from the corresponding Ti−C bonds of **4** (2.132(3) Å) and is typical for a Ti−C σ-bond.[15] In contrast, the Ti−C25 distance inside the metallacyclic alkylidene ring is significantly shorter (1.978(3) Å) and resembles the Ti═C double bond of **2** (1.958(3) Å) or those of other structurally characterized titanium alkylidene complexes.[4] In addition, the X-ray diffraction study reveals that the metallacyclic alkylidene ring is folded along the C25−N2 axis by about 120° and the Li$^+$ ion is located on the "backside" of the heterodiene with nearly equal distances to N2, C23, C24, and C25 (2.157(6)−2.211(6) Å). Altogether, complex **5** affords a unique opportunity to compare NMR spectroscopic and structural data of alkyl (Ti−C) and alkylidene ligands (Ti═C) within the same molecule. Furthermore, the results reported here suggest that stable alkylidene complexes of early transition metals, even without stabilizing Cp ligands, can be readily prepared from suitable 1-aza-1,3-diene complexes. Presently we are investigating whether the reaction of **5** with another 1 equiv of MeLi yields the doubly deprotonated bis(alkylidene)titanium complex, because an α-agostic behavior of the TiCH group of **5** (Ti−H3 = 2.31(1) Å, Ti−C3−H3 = 88.1(1)°) was undoubtedly established.

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Supporting Information Available: Details of the syntheses and characterization of **4** and **5** (NMR and X-ray diffraction data). This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Crystal data for **5**: $C_{48}H_{63}LiN_2OTi$, M_r = 738.84, black-red prism, size 0.32 × 0.30 × 0.28 mm^3, monoclinic, space group $P2_1/c$, a = 12.4292(7) Å, b = 16.7146(9) Å, c = 22.133(1) Å, β = 103.625(3)°, V = 4468.7(4) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.098 g cm^{-3}, μ(Mo Kα) = 2.26 cm^{-1}, F(000) = 1592, 17 242 reflections in h (−16 to +16), k (−19 to +21), l (−28 to +28), measured in the range 3.46° ≤ θ ≤ 27.54°, completeness θ_{max} = 98.7%, 10 162 independent reflections, R_{int} = 0.079, 7219 reflections with $F_o > 4\sigma(F_o)$, 490 parameters, 0 restraints, $R1_{obsd}$ = 0.103, $wR2_{obsd}$ = 0.161, $R1_{all}$ = 0.156, $wR2_{all}$ = 0.1779, GOF = 1.121, largest difference peak/hole 0.513/−0.401 e Å^{-3}.

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