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α-Hydrogen Elimination from (1-Aza-1,3-diene)titanium Complexes: Synthesis of Metallacyclic Titanium – Alkylidene Complexes**

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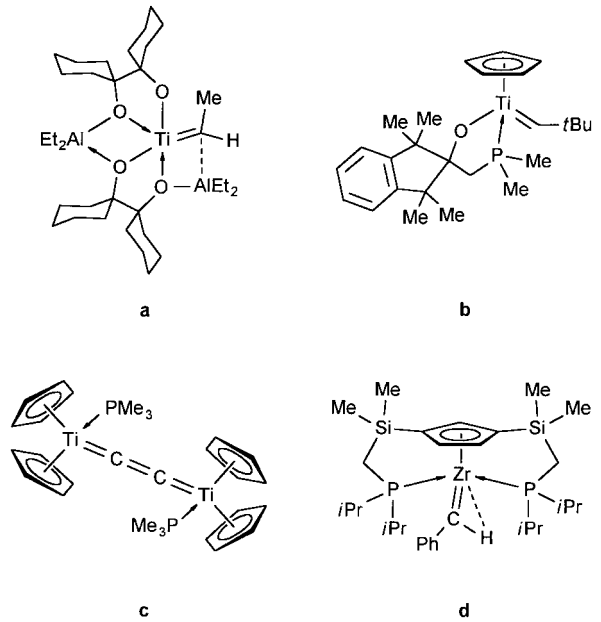
Alkylidene – metal intermediates play a key role in several important reactions such as transition metal catalyzed olefin and alkyne polymerization, olefin metathesis, or olefination of carbonyl compounds. Therefore there is a great deal of interest in model studies with defined and isolable alkylidene complexes, and several methods for the synthesis of such compounds have already been developed.[1] Among the alkylidene – metal complexes of the titanium group, the methylidene titanocene [$Cp_2Ti{=}CH_2$] has gained special significance. Its application in organic synthesis[2] is attributed to the fact that it is relatively readily generated in situ from different compounds such as bis(cyclopentadienyl)titanacyclobutane complexes,[3] dimethyltitanocene,[4] or [$Cp_2TiCH_2 \cdot Me_2AlCl$] (Tebbe reagent).[5] To date, however, very few alkylidene – metal complexes of the titanium group have been isolated and characterized by X-ray structure analysis (Scheme 1).[6–9]



Scheme 1. Selected, structurally characterized alkylidene complexes of titanium and ziroconium complexes. **a**: Ti – C 1.933(6) Å, δ(Ti=*C*) = 202.1 (main components);[6] **b**: Ti – C 1.911(3) Å, δ(Ti=*C*) = 278.1;[7] **c**: Ti – C 2.051(2) Å, δ(Ti=*C*) = 258.1;[8] **d**: Zr – C 2.024(4) Å, δ(Zr=*C*) = 229.4.[9]

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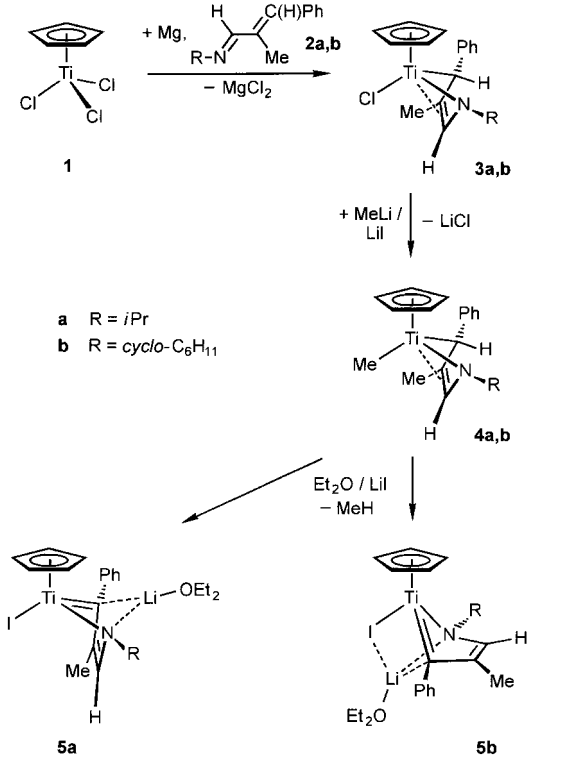
In our studies on 1-aza-1,3-diene complexes of the early transition metals[10] we have established that (1-aza-1,3-diene)titanium complexes exhibit favorable prerequisites for the preparation of titanium–alkylidene complexes: In the 1-aza-1,3-diene complexes the heterodienes are bound to the metal atom as 1-aza-but-2-ene-1,4-diyl dianions and form with these a Ti[CH(R)CH=CHNR] ring.[11] An α-hydrogen elimination at the TiCH group, initiated by the introduction of a neighboring carbanionic methyl group,[12] would lead to a Ti=C alkylidene function, which might be additionally stabilized by conjugation with the C=C bond of the coordinated 1-aza-1,3-diene ligand. We have established that this concept can be applied successfully and report here on the synthesis and structure of novel metallacyclic titanium–alkylidene complexes.

The 1-aza-1,3-diene complexes **3a** and **3b** are formed in the reduction of [CpTiCl$_3$] with magnesium in the presence of the 1-aza-1,3-dienes **2a** and **2b**, respectively (Scheme 2).[11] They



Scheme 2. Synthesis of the titanacyclic alkylidene complexes **5a** and **5b**.

can be isolated as air-sensitive green-brown crystals (**3a**, m.p. 84 °C; **3b**, m.p. 119–122 °C) in yields of up to 67%; the EI mass spectra of the compounds contain intense peaks for the molecular ions.

Their constitution can be deduced unambiguously from the characteristic NMR spectra (Table 1). In each case the 1-aza-1,3-diene is formally reduced to the dianion and bound in the chelate form to the titanium atom, resulting in a 1-aza-2-titanacyclopent-4-ene ring. Furthermore, a crystal structure analysis of **3b**[13] revealed that this Ti(C3-C2=C1-N) ring is folded along the C3–N axis (fold angle $\theta = 67.0(2)^\circ$); the open side of the *cis*-configured heterodiene points in the direction of the Cp ligand (*supine* form, Figure 1).[14] The Ti–C3 and the Ti–N distances of 2.147(3) and 1.902(3) Å, respectively, lie in the range of normal single bonds.[15] The short distances between the titanium atom and the olefinic carbon atoms C1 and C2 (2.323(3) and 2.374(3) Å, respectively) likewise indicate a bonding interaction. Thus, overall the bonding mode of the 1-aza-1,3-diene to the CpTiCl core is best described by the σ^2,π structure type.[16] For the proposed α-

Table 1. NMR spectroscopic data of **3a**, **3b**, **4b**, **5a**, and **5b**.[a]

3a: ^{1}H NMR: $\delta = 7.18$ (t, 2H; *m*-Ph), 7.01 (t, 1H; *p*-Ph), 6.83 (s, 1H; =CH), 6.81 (d, 2H; *o*-Ph), 6.13 (s, 5H; *Cp*), 4.16 (sept., ^3J(H,H) = 6.5 Hz, 1H; *i*-C_3H_7), 2.03 (s, 3H; =CMe), 1.27 (d, ^3J(H,H) = 6.5 Hz, 3H; *i*-C_3H_7), 1.15 (d, ^3J(H,H) = 6.5 Hz, 3H; *i*-C_3H_7), 0.42 (s, 1H; TiCH); ^{13}C NMR: $\delta = 143.11$ (s; *ipso*-Ph), 128.90 (d, ^1J(C,H) = 156 Hz; *o*/*m*-Ph), 128.52 (d, ^1J(C,H) = 156 Hz; *o*/*m*-Ph), 125.39 (d, ^1J(C,H) = 156.5 Hz; *p*-Ph), 118.61 (d, ^1J(C,H) = 172.8 Hz; =CH), 116.12 (s, =*C*Me), 112.97 (d, ^1J(C,H) = 174.4 Hz; Cp), 101.50 (d, ^1J(C,H) = 136.9 Hz; TiCH), 59.66 (d, ^1J(C,H) = 138.5 Hz; *i*-C_3H_7), 25.53 (q, ^1J(C,H) = 125.5 Hz; *i*-C_3H_7), 23.31 (q, ^1J(C,H) = 127.1 Hz; *i*-C_3H_7), 18.55 (q, ^1J(C,H) = 127.1 Hz; =C*Me*)

3b: ^{1}H NMR: $\delta = 7.18$ (t, 2H; *m*-Ph), 7.01 (t, 1H; *p*-Ph), 6.83 (s, 1H; =CH), 6.80 (d, 2H; *o*-Ph), 6.12 (s, 5H; Cp), 3.70 (m, 1H; *cyclo*-C_6H_{11}), 2.02 (s, 3H; =CMe), 1.90 - 1.15 (m, 10H; *cyclo*-C_6H_{11}), 0.43 (s, 1H; TiCH); ^{13}C NMR: $\delta = 143.19$ (s; *ipso*-Ph), 128.90 (d, ^1J(C,H) = 157.7 Hz; *o*/*m*-Ph), 128.49 (d, ^1J(C,H) = 158.2 Hz; *o*/*m*-Ph), 125.36 (d, ^1J(C,H) = 160.9 Hz; *p*-Ph), 119.49 (d, ^1J(C,H) = 173.4 Hz; =CH), 115.77 (s; =*C*Me), 112.97 (d, ^1J(C,H) = 174.1 Hz; Cp), 101.56 (d, ^1J(C,H) = 138.0 Hz; TiCH), 68.32 (d, ^1J(C,H) = 135.4 Hz; *cyclo*-C_6H_{11}), 37.03 (t, ^1J(C,H) = 128.9 Hz; *cyclo*-C_6H_{11}), 34.88 (t, ^1J(C,H) = 125.5 Hz; *cyclo*-C_6H_{11}), 26.68 (t; *cyclo*-C_6H_{11}), 26.59 (t; *cyclo*-C_6H_{11}), 26.36 (t; *cyclo*-C_6H_{11}), 18.46 (q, ^1J(C,H) = 128.0 Hz; =C*Me*)

4b: ^{1}H NMR: $\delta = 7.12$ (t, 2H; *m*-Ph), 9.93 (t, 1H; *p*-Ph), 6.75 (s, 1H; =CH), 6.69 (d, 2H; *o*-Ph), 5.98 (s, 5H; Cp), 3.53 (m, 1H; *cyclo*-C_6H_{11}), 2.02 (s, 3H; =CMe), 1.95 – 1.15 (m, 10H; *cyclo*-C_6H_{11}), – 0.17 (s, 1H; TiCH), – 1.31 (s, 3H; TiMe); ^{13}C NMR: $\delta = 144.27$ (s; *ipso*-Ph), 128.33 (d, ^1J(C,H) = 158.0 Hz; *o*/*m*-Ph), 127.87 (d, ^1J(C,H) = 156.7 Hz; *o*/*m*-Ph), 124.25 (d, ^1J(C,H) = 161.0 Hz; *p*-Ph), 120.74 (d, ^1J(C,H) = 170.6 Hz; =CH), 112.65 (s; =*C*Me), 111.00 (d, ^1J(C,H) = 172.4 Hz; Cp), 97.87 (d, ^1J(C,H) = 135.9 Hz; TiCH), 67.15 (d; *cyclo*-C_6H_{11}), 39.72 (q, ^1J(C,H) = 118.1 Hz; TiMe), 37.17 (t, ^1J(C,H) = 125.0 Hz; *cyclo*-C_6H_{11}), 35.66 (t, ^1J(C,H) = 123.1 Hz; *cyclo*-C_6H_{11}), 26.57 (t; *cyclo*-C_6H_{11}), 26.44 (t; *cyclo*-C_6H_{11}), 26.34 (t; *cyclo*-C_6H_{11}), 18.73 (q, ^1J(C,H) = 123.0 Hz; =C*Me*)

5a: ^{1}H NMR: $\delta = 6.95$ (t, 2H; *m*-Ph), 6.82 (d, 2H; *o*-Ph), 6.51 (t, 1H; *p*-Ph), 6.17 (s, 1H; =CH), 6.04 (s, 5H; Cp), 4.14 (sept., ^3J(H,H) = 6.5 Hz, 1H; *i*-C_3H_7), 3.37 (q, ^3J(H,H) = 7.0 Hz, 4H; OCH_2CH$_3$), 2.16 (s, 3H; =CMe), 1.20 (d, ^3J(H,H) = 6.5 Hz, 6H; *i*-C_3H_7), 1.10 (t, ^3J(H,H) = 7.0 Hz, 4H; OCH$_2$CH_3); ^{13}C NMR: $\delta = 244.69$ (s; Ti=C), 146.25 (s; *ipso*-Ph), 127.91 (d, ^1J(C,H) = 157.8 Hz; =CH), 127.53 (d, ^1J(C,H) = 154.3 Hz; *o*/*m*-Ph), 126.26 (d, ^1J(C,H) = 156.0 Hz; *o*/*m*-Ph), 119.45 (d, ^1J(C,H) = 152.8 Hz; *p*-Ph), 106.14 (d, ^1J(C,H) = 170.1 Hz; Cp), 101.53 (br. s; =*C*Me), 66.05 (t; O*C*H$_2$CH$_3$), 58.23 (d, ^1J(C,H) = 133.3 Hz; *i*-C_3H_7), 26.55 (q; ^1J(C,H) = 125.9 Hz; *i*-C_3H_7), 18.38 (q, ^1J(C,H) = 125.2 Hz; =C*Me*), 15.54 (q, ^1J(C,H) = 126.3 Hz; OCH_2CH$_3$)

5b: ^{1}H NMR: $\delta = 6.96$ (t, 2H; *m*-Ph), 6.82 (d, 2H; *o*-Ph), 6.52 (t, 1H; *p*-Ph), 6.18 (s, 1H; =CH), 6.06 (s, 5H; Cp), 3.67 (m, 1H; *cyclo*-C_6H_{11}), 3.38 (q, ^3J(H,H) = 6.9 Hz, 4H; OCH_2CH$_3$), 2.15 (s, 3H; =C*Me*), 1.92 – 1.18 (m, 10H; *cyclo*-C_6H_{11}), 1.11 (t, ^3J(H,H) = 6.9 Hz, 4H; OCH$_2$CH_3); ^{13}C NMR: $\delta = 244.62$ (s; Ti=C), 146.42 (s; *ipso*-Ph), 128.02 (d, ^1J(C,H) = 158.4 Hz; =CH), 127.65 (d, ^1J(C,H) = 164.1 Hz; *o*/*m*-Ph), 126.45 (d, ^1J(C,H) = 156.2 Hz; *o*/*m*-Ph), 119.90 (d, ^1J(C,H) = 156.4 Hz; *p*-Ph), 106.40 (d, ^1J(C,H) = 170.9 Hz; Cp), 101.70 (br. s; =*C*Me), 66.17 (t; O*C*H$_2$CH$_3$), 38.05 (t, ^1J(C,H) = 125.6 Hz; *cyclo*-C_6H_{11}), 37.20 (t, ^1J(C,H) = 127.4 Hz; *cyclo*-C_6H_{11}), 27.23, 27.12, 27.02 (t; *cyclo*-C_6H_{11}), 18.35 (q, ^1J(C,H) = 125.9 Hz; =C*Me*), 15.59 (q, ^1J(C,H) = 125.5 Hz; OCH$_2$CH_3)

[a] The NMR spectra were recorded at 25 °C in [D$_8$]THF at 300.075 (^{1}H) and 75.462 MHz (^{13}C) on a Varian-Gemini-300-BB spectrometer. Correct elemental analyses were obtained for all compounds.

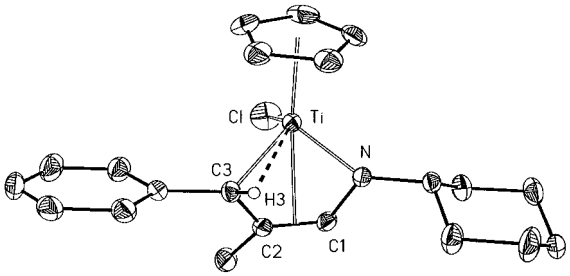


Figure 1. Structure of **3b** in the crystal (ellipsoids are drawn at 40% probability level; all H atoms except H3 were omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti–Cl 2.310(1), Ti–N 1.902(3), Ti–C1 2.323(3), Ti–C2 2.374(3), Ti–C3 2.147(3), C1–C2 1.394(4), C2–C3 1.449(4), C1–N 1.376(4), Ti–H3 2.39(3); N-Ti-C3 87.3(1), N-Ti-Cl 113.76(8), C3-Ti-Cl 109.38(9), Ti-N-C1 88.7(2), Ti-C3-C2 80.1(2), Ti-C3-H3 93(2); sum of angles at N: 356.9(2); fold angle θ: (Ti-N-C3)-(N-C1-C2-C3) = 67.0(2)°.

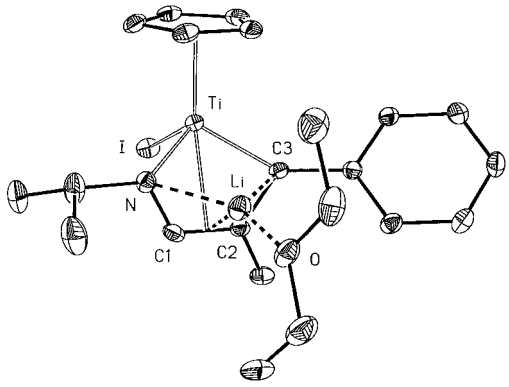


Figure 2. Structure of **5a** in the crystal (ellipsoids are drawn at the 40% probability level; all H atoms were omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti–I 2.7893(6), Ti–N 1.949(3), Ti–C1 2.331(3), Ti–C2 2.358(3), Ti–C3 1.958(3), Li–N 2.074(6), Li–O 1.876(6), Li–C1 2.214(7), Li–C2 2.260(7), Li–C3 2.217(6), C1–C2 1.397(5), C2–C3 1.447(4), C1–N 1.381(4); N-Ti-C3 90.3(1), N-Li-C3 80.3(2), N-Ti-I 106.80(8), C3-Ti-I 110.61(9), Ti-N-C1 87.1(2), Ti-C3-C2 86.3(2); sum of angles at C3: 359.4(2); sum of angles at N: 349.0(2); fold angle θ: (Ti-N-C3)-(N-C1-C2-C3) = 62.3(2)°.

hydrogen transfer it is particularly interesting that the Ti-C3-H3 group shows structural features that are even indicative of an agostic Ti ← H-C interaction (Ti-H3 2.39(3) Å, Ti-C3-H3 93(2)°).[17]

Treatment of the 1-aza-1,3-diene complexes **3a** and **3b** with methyllithium (one equivalent in each case), which was prepared from methyl iodide and lithium,[18] leads initially to the methyl compounds **4a** and **4b**, respectively. However, these can only be detected, and in the case of **4b** isolated, if the temperature during the reaction is kept below 0 °C. At room temperature the reaction surprisingly leads directly to the new metallacyclic titanium–alkylidene complexes **5a** and **5b**, respectively (Scheme 2). Evidently the methane elimination from methyl compounds **4a** and **4b** proceeds without additional activation under very mild conditions. Compounds **5a** and **5b** are air-sensitive red-brown crystalline solids, which are well soluble, for example, in diethyl ether and *n*-pentane, and decompose first above 200 °C. Already on the basis of ^{13}C NMR spectra it was possible to conclude the presence of alkylidene complexes: for instance, the signals of the metal-bound heterodiene carbon atoms are shifted dramatically to low field (δ = 244.69 (**5a**), 244.62 (**5b**)) compared to those of **3a** and **3b**. They lie in a region that is characteristic for carbene-carbon atoms (see Scheme 1).[19] However, in order to explain how the lithium iodide (initially only detected by elemental analysis) is incorporated in these complexes and with a view to the first characterization of the structure of these metallacyclic titanium–alkylidene complexes, crystal structure determinations of **5a** and **5b** were carried out.[20] The two compounds appear to be similar at least in solution, since their NMR spectra are almost identical (Table 1). Surprisingly, however, the same is not true for the solid-state structures (Figures 2 and 3).

The central building block of **5a** and **5b** is a five-membered titanacycle CpTi(C3-C2=C1-N), which, as for **3b,** is folded along the C3–N axis. However, the orientations of the folds differ: in **5b** the titanacycle displays a *prone*-analogous geometry, it is thus bent towards the Cp ligand (θ = 68.2(2)°); in contrast, in **5a** the five-membered ring is folded away from the Cp ligand (θ = 62.3(2)°), which leads to a *supine* conformation.[14] In both cases the titanium atom is

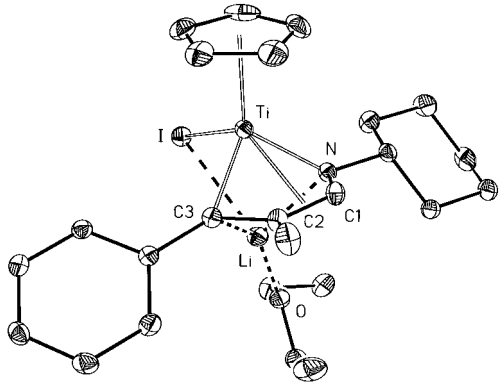


Figure 3. Structure of **5b** in the crystal (ellipsoids are drawn at the 40% probability level; all H atoms were omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti–I 2.8012(7), Ti–N 1.993(2), Ti–C1 2.274(3), Ti–C2 2.324(3), Ti–C3 1.979(3), Li–N 2.127(6), Li–O 1.894(6), Li–I 2.874(6), Li–C1 2.764(7), Li–C2 2.851(6), Li–C3 2.334(6), Ti–Li 2.694(6), C1–C2 1.400(4), C2–C3 1.431(4), C1–N 1.377(4); N-Ti-C3 88.8(1), N-Li-C3 76.9(2), N-Ti-I 96.11(8), C3-Ti-I 95.94(9), Ti-N-C1 82.7(2), Ti-C3-C2 84.3(2); sum of angles at C3: 351.0(2); sum of angles at N: 335.4(2); fold angle θ: (Ti-N-C3)-(N-C1-C2-C3) = 68.2(2)°.

bound to the nitrogen atoms through normal Ti–N σ bonds (Ti–N 1.949(3)(**5a**), 1.993(3) Å (**5b**)).[15] In addition, there are π interactions to the 1-aza-1,3-diene carbon atoms C1 and C2 (2.331(3), 2.358(3) Å (**5a**); 2.274(3), 2.324(3) Å (**5b**)). The most important structural element of **5a** and **5b** is the Ti=C3 bond (1.958(3) (**5a**), 1.973(4) Å (**5b**)). As expected it is shorter than the Ti–C3 single bond of **3b,** and its length approximately corresponds to those of the Ti=C double bonds of the titanium–alkylidene complexes given in Scheme 1.

An important role in the syntheses of these titanium–alkylidene complexes is evidently played by lithium iodide which is generated in the preparation of methyllithium and is present in the reaction mixture.[18] Both in **5a** as well as in **5b** the I^- ion occupies the coordination site at the titanium atom that becomes vacant during the methane elimination so that the piano stool arrangement remains intact in the ligand

sphere of the transition metal atom.[21] In **5b** the titanium atom and the Li^+ ion are additionally bridged by the I^- ion (Li–I 2.874(6) Å). The Li^+ ion is furthermore bound over large distances to the heterodiene termini C3 and N (Li–C3 2.334(6), Li–N 2.127(6) Å) and is coordinatively saturated by a molecule of diethyl ether.[22] In **5a** the *supine* conformation of the CpTi(=C3-C2=C1-N) five-membered ring prevents a bond between the Li^+ and the I^- ion. This missing interaction is compensated by a shorter bond between the Li^+ ion and the nitrogen atom (Li–N 2.074(6) Å) and a π interaction with all three carbon atoms of the heterodiene skeleton (Li–C1 2.217(6), Li–C2 2.260(7), Li–C3 2.214(7) Å). Consequently bonding similar to that in the (1,3-diene)dilithium or (1,4-diaza-1,3-diene)dilithium compounds can be assumed here.[23]

The folding of the CpTi(=C3-C2=C1-N), five-membered ring of **5a** and **5b** prevents the desired conjugation of the Ti=C bond with the C=C bond within the metallacycle, which could additionally stabilize the alkylidene function. Despite this the simple preparation of **5a** and **5b** indicates that stable alkylidene complexes are accessible from (1-aza-1,3-diene)titanium complexes under very mild conditions by α-hydrogen elimination. It still remains unclear why in the formation of **5a** and **5b** lithium iodide is formally added and not lithium chloride which is also present in the same amount. Furthermore, it remains to be proven that a *supine-prone* rearrangement of the 1-aza-1,3-diene ligands in **4a** and **4b** is possible at least for the step involving the α-hydrogen elimination.[24] These questions as well as studies into the reactivity of the new titanium–alkylidene complexes are currently under investigation.

Experimental Section

All work was carried out under argon and in carefully dried, degassed solvents.

3a, **3b**: A solution of [$CpTiCl_3$] **1** (5.00 g, 22.80 mmol) in THF (100 mL) was treated with the appropriate 1-aza-1,3-diene (22.80 mmol: **2a**: 4.27 g; **2b**: 5.18 g) and magnesium (0.554 g, 22.80 mmol) and stirred for 8 h at −20 °C and then for 24 h at room temperature until the metal had completely reacted. Subsequently the solvent was removed under vacuum and the residue was extracted with diethyl ether (100 mL). The extract was concentrated to dryness and the residue was extracted with *n*-pentane (75 mL). After the extract had been left to stand for a long time at −20 °C, **3a** (5.13 g, 67 %; m.p. 84 °C) and **3b** (4.37 g, 51 %; m.p. 119–122 °C) crystallized in the form of green-brown crystals. The crystals of **3b** suitable for the crystal structure analysis were obtained by repeated recrystallization from diethyl ether.

4b: A solution of **3b** (2.10 g, 5.58 mmol) in diethyl ether (100 mL) was treated dropwise at 0 °C with a solution of methyllithium (6.85 mL of a 0.86 M solution), which had been prepared from methyl iodide and lithium in diethyl ether. The reaction mixture was stirred for 2 h at 0 °C. Subsequently the solvent was removed under vacuum and the residue was extracted in cold (ca. 0 °C) *n*-pentane (100 mL) and separated by filtration from the lithium salts. The filtrate was concentrated to dryness under vacuum to leave a brown microcrystalline solid (1.61 g, 81 %; decomposition above 20 °C).

5a and **5b**: A solution of **3a** (2.64g, 7.86 mmol) and **3b,** respectively, (2.95 g, 7.86 mmol) in diethyl ether (100 mL) was treated dropwise at 0 °C with a solution of methyllithium (5.24 mL of a 1.5 M solution), which had been prepared from methyl iodide and lithium. The reaction mixture was stirred for 24 h at room temperature. Subsequently the solvent was removed under vacuum and the residue was extracted with boiling *n*-pentane.

After the extract had been left to stand for a long time at −5 °C, **5a** (2.23 g, 56 %; m.p. 165 °C) and **5b** (2.67 g, 62 %; m.p. 168 °C) crystallized in the form of red-brown crystals.

Crystals suitable for the crystal structure analyses were obtained by repeated recrystallization from diethyl ether.

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[20] a) Crystal structure analysis of **5a**: $C_{22}H_{31}NOILiTi$, $M_r = 507.22$, crystal dimensions $0.40 \times 0.36 \times 0.35$ mm^3, $a = 10.039(1)$, $b = 14.934(2)$, $c = 15.517(2)$ Å, $\beta = 90.93(1)°$, $V = 2326.0(5)$ Å^3, $T = 183(2)$ K, $\rho_{calcd} = 1.448$ g cm^{-3}, $\mu = 1.705$ mm^{-1}, $F(000) = 1024$, $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71073$ Å, $\omega/2\theta$ scan, 4989 measured reflections ($-h$, $+k$, $\pm l$), $2.44 > \theta > 26.30°$, 4718 independent and 3655 observed reflections [$I > 2\sigma(I)$], 300 refined parameters, direct methods, $R = 0.0328$, $R_w = 0.0529$ [$w = 1/\sigma^2(F_o)$], max. residual electron density 0.677 e Å^{-3}. Crystal structure analysis of **5b**: $C_{25}H_{35}NOILiTi$, $M_r = 547.28$, crystal dimensions $0.40 \times 0.36 \times 0.32$ mm^3, $a = 10.471(2)$, $b = 12.893(2)$, $c = 19.259(3)$ Å, $\beta = 100.13(1)°$, $V = 2559.5(7)$ Å^3, $T = 183(2)$ K, $\rho_{calcd} = 1.420$ g cm^{-3}, $\mu = 1.556$ mm^{-1}, $F(000) = 1112$, $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71073$ Å, $\omega/2\theta$ scan, 5340 measured reflections ($\pm h$, $-k$, $+l$), $2.41 > \theta > 26.32°$, 5186 independent and 3959 observed reflections [$I > 2\sigma(I)$], 276 refined parameters, direct methods, $R = 0.0298$, $R_w = 0.0544$ [$w = 1/\sigma^2(F_o)$], max. residual electron density 0.558 e Å^{-3}. b) Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-407632, CSD-407634, and CSD-407633.

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[22] The Li – I distance in **5b** (2.874(6) Å) is only negligibly longer than that in complexed monomeric lithium iodides: a) [LiI(pmedien)] (pmedien = *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylentriamine): 2.75(3), 2.67(3) Å, C. L. Raston, B. W. Skelton, C. R. Whitaker, A. H. White, *J. Chem. Soc. Dalton Trans.* **1988**, 987 – 990; b) [LiI(NC_5H_3-3,5-$Me_2)_3$]: 2.80(1) Å, C. L. Raston, C. R. Whitaker, A. H. White, *J. Chem. Soc. Dalton Trans.* **1988**, 991 – 995. It is, however, unusual that the Li^+ ion is surrounded by four different bonding partners.

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