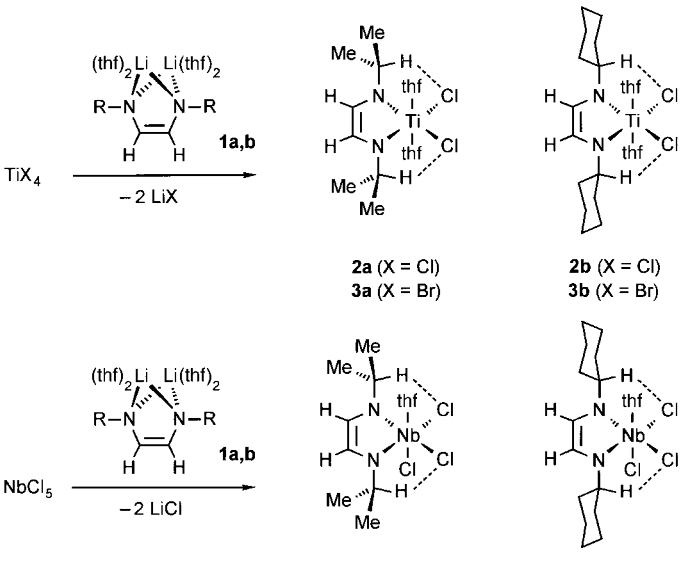
(1,4-Diaza-1,3-diene)titanium and -niobium Halides: Unusual Structures with Intramolecular C–H···Halogen Hydrogen Bonds[**]

Thomas Spaniel, Helmar Görls, and Joachim Scholz*

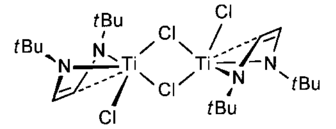
In recent years the number of systematic investigations of hydrogen bonds for the development of syntheses for supramolecules and of crystal engineering has risen dramatically.[1] Hereby, the interest is switching more and more to those hydrogen bonds which do not involve the conventionally strong O–H···O and N–H···O bonds (energies 20–40 kJ mol^{-1}). In many organic and organometallic compounds C–H units frequently function as H-bonding donors and form weak hydrogen bonds (energies <20 kJ mol^{-1}) with suitable H-bonding accpetors, mainly oxygen (C–H···O) or nitrogen (C-H···N).[2] However, it is still under debate whether chlorine or other halogen atoms can also be H-bonding acceptors. Whereas on the one hand the existence of C–H···Cl hydrogen bonds has been questioned,[3] a few individual examples of such interactions have been known since 1982.[2a] However, nearly all these compounds are saltlike and contain Cl$^-$ ions. To date there are hardly any compounds known in which chlorine atoms are covalently bound and nevertheless participate in C–H···Cl hydrogen bonds. Most of the C–H···Cl interactions found so far are concerned with intermolecular interactions,[4] which in addition have only been observed in the crystal.[2a, 5]

In studies on the chemistry of (1,4-diaza-1,3-diene) halide complexes of the early transition metals we have established that these C–H···Cl hydrogen bonds with covalently bound chlorine do indeed exist and that they can occur not only in the solid state but also in solution.[6, 7] We report here on the synthesis of bis(isopropyl)glyoxaldiimine- and bis(cyclohexyl)glyoxaldiiminetitanium and -niobium halides and show that intramolecular C–H···halogen hydrogen bonds can even considerably influence the molecular geometry of these 1,4-diaza-1,3-diene complexes.

The new bis(isopropyl)glyoxaldiimine- and bis(cyclohexyl)glyoxaldiiminetitanium- and -niobium halides can be prepared in moderate to good yields by the reaction of the dilithium (1,4-diaza-1,3-diene) compounds **1a, b** with the respective metal halides in a molar ratio of 1:1 (Scheme 1). The titanium chloride and the titanium bromide complexes **2a**, **b** and **3a**, **b**, respectively, precipitate as bright red crystalline solids,[8] and the niobium compounds **4a**, **b** form amber crystals. They are all air- and moisture-sensitive and are well soluble in THF, less so in diethyl ether, and only sparingly soluble in aliphatic solvents. The ^{1}H NMR spectra of the new 1,4-diaza-1,3-diene complexes contain few signals, which indicate highly symmetrical molecules (Table 1). However, these signals are difficult to assign. For instance, there is no obvious explanation for the surprisingly strong lowfield shift of the methine proton signals of the isopropyl and the cyclohexyl groups of **2a** and **3a** and **2b** and **3b** ($\delta = 6.99$–6.22), respectively.[9] The highfield shift of the signal for the azomethine protons ($\delta = 4.21$–3.75) is also remarkable. In contrast, in the similar bis(*tert*-butyl)glyoxaldiiminetitanium complexes **5** and **6** these signals occur in the olefinic region of the spectra ($\delta = 5.88$ (**5**),[8] 5.78 (**6**)[10a]), where they are expected on the basis of the enediamide structure of these compounds.



Scheme 1. Synthesis of the (1,4-diaza-1,3-diene)titanium(IV) and -niobium(V) halides **2a–4a** (R = *i*Pr) and **2b–4b** (R = cyclohexyl).



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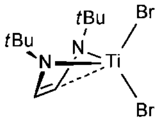

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X-ray crystal structure analyses of **2b** and **4a** were necessary to establish the reasons for these unusual NMR data.[11] The most prominent structural features of **2b** are without doubt the short distances between the chlorine atoms Cl1 and Cl2 and the hydrogen atoms H3 and H7, respectively, of the cyclohexyl rings (each 2.59(4) Å, Figure 1). They are significantly shorter than the sum of the van der Waals radii of chlorine and hydrogen (1.75 and 1.20 Å, respectively)[12] and evidently cause the strong deshielding of H3 and H7, which leads to the unexpected lowfield shift of the ^{1}H NMR signal.

These C–H···Cl hydrogen bonds have significant consequences for the structure of **2b**: The Ti–N distances of 2.034(4) and 2.037(3) Å are large compared to those in other (1,4-diaza-1,3-diene)titanium complexes (Ti–N 1.908(2), 1.910(2) Å (**5**);[8] Ti–N 1.908(2), 1.910(2) Å (**6**)[10]) or in titanium amide compounds (average Ti–N distance

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[*] Priv.-Doz. Dr. J. Scholz, Dipl.-Chem. T. Spaniel
Institut für Anorganische Chemie der Universität Halle-Wittenberg
Kurt-Mothes-Strasse, D-06099 Halle (Germany)
Fax: (+49) 345-55-25621
E-mail: j.scholz@chemie.uni-halle.de

Dr. H. Görls
Institut für Anorganische und Analytische Chemie der Universität Jena (Germany)

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Table 1. NMR spectroscopic data of **2a**, **b**, **3a**, **b**, and **4a**, **b**.[a]

2a: ^{1}H NMR: $\delta = 6.63$ (sept., $^{3}J(\mathrm{H,H}) = 6.6$ Hz, 2H; $\mathrm{NC}H\mathrm{Me_2}$), 4.21 (s, 2H; $\mathrm{HC{=}CH}$), 3.62 (m, 8H; $\mathrm{OCH_2}$, THF), 1.77 (m, 8H; $\mathrm{OCH_2C}H_2$, THF), 1.09 (d, $^{3}J(\mathrm{H,H}) = 6.6$ Hz, 12H; $\mathrm{NCH}Me_2$). ^{13}C NMR: $\delta = 115.87$ (ddd, $^{1}J(\mathrm{C,H}) = 168.4$, $^{2}J(\mathrm{C,H}) = 10.2$, $^{3}J(\mathrm{C,H}) = 6.9$ Hz; $\mathrm{HC{=}CH}$), 68.21 (t; $\mathrm{OCH_2}$, THF), 57.59 (d, $^{1}J(\mathrm{C,H}) = 144.3$ Hz; $\mathrm{N}C\mathrm{HMe_2}$), 26.25 (t; $\mathrm{OCH_2CH_2}$, THF), 24.25 (q, $^{1}J(\mathrm{C,H}) = 125.5$ Hz; $\mathrm{NCH}Me_2$)

2b: ^{1}H NMR: $\delta = 6.22$ (tt, 2H; NCH, *cyclo*-$\mathrm{C_6H_{11}}$), 4.14 (s, 2H; $\mathrm{HC{=}CH}$), 3.62 (m, 8H; $\mathrm{OCH_2}$, THF), 1.97 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.78 (m, 8H; $\mathrm{OCH_2C}H_2$, THF), 1.77 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.65–1.45 (m, 8H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.00 (m, 4H, *cyclo*-$\mathrm{C_6H_{11}}$); ^{13}C NMR: $\delta = 116.20$ (ddd, $^{1}J(\mathrm{C,H}) = 167.9$, $^{2}J(\mathrm{C,H}) = 9.9$, $^{3}J(\mathrm{C,H}) = 6.9$ Hz; $\mathrm{HC{=}CH}$), 68.22 (t, $\mathrm{OCH_2}$; THF), 66.77 (d; *cyclo*-$\mathrm{C_6H_{11}}$), 35.28 (t, $^{1}J(\mathrm{C,H}) = 126.8$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 27.09 (t, $^{1}J(\mathrm{C,H}) = 125.7$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 26.24 (t, $^{1}J(\mathrm{C,H}) = 130.7$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 26.33 (t, $\mathrm{OCH_2}C\mathrm{H_2}$; THF)

3a: ^{1}H NMR: $\delta = 6.99$ (sept., $^{3}J(\mathrm{H,H}) = 6.7$ Hz, 2H; $\mathrm{NC}H\mathrm{Me_2}$), 3.86 (s, 2H; $\mathrm{HC{=}CH}$), 3.62 (m, 8H; $\mathrm{OCH_2}$, THF), 1.77 (m, 8H; $\mathrm{OCH_2C}H_2$, THF), 1.07 (d, $^{3}J(\mathrm{H,H}) = 6.7$ Hz, 12H; $\mathrm{NCH}Me_2$); ^{13}C NMR: $\delta = 113.10$ (ddd, $^{1}J(\mathrm{C,H}) = 169.0$, $^{2}J(\mathrm{C,H}) = 10.5$, $^{3}J(\mathrm{C,H}) = 6.9$ Hz; $\mathrm{HC{=}CH}$), 68.22 (t; $\mathrm{OCH_2}$, THF), 58.60 (d, $^{1}J(\mathrm{C,H}) = 143.3$ Hz; $\mathrm{N}C\mathrm{HMe_2}$), 26.29 (t; $\mathrm{OCH_2C}H_2$, THF), 24.28 (q, $^{1}J(\mathrm{C,H}) = 125.8$ Hz; $\mathrm{NCH}Me_2$)

3b: ^{1}H NMR: $\delta = 6.57$ (tt, 2H; NCH, *cyclo*-$\mathrm{C_6H_{11}}$), 3.75 (s, 2H; $\mathrm{HC{=}CH}$), 3.58 (m, 8H; $\mathrm{OCH_2}$, THF), 1.97 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.77 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.74 (m, 8H; $\mathrm{OCH_2C}H_2$, THF), 1.62–1.43 (m, 6H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.05–0.81 (m, 6H, *cyclo*-$\mathrm{C_6H_{11}}$); ^{13}C NMR: $\delta = 113.37$ (ddd, $^{1}J(\mathrm{C,H}) = 167.5$, $^{2}J(\mathrm{C,H}) = 10.6$, $^{3}J(\mathrm{C,H}) = 6.8$ Hz; $\mathrm{HC{=}CH}$), 68.23 (t, $^{1}J(\mathrm{C,H}) = 144.1$ Hz; $\mathrm{OCH_2}$, THF), 67.64 (d, $^{1}J(\mathrm{C,H}) = 136.9$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 35.33 (t, $^{1}J(\mathrm{C,H}) = 126.4$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 27.04 (t, $^{1}J(\mathrm{C,H}) = 126.4$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 26.67 (t, $^{1}J(\mathrm{C,H}) = 126.0$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 26.29 (t, $^{1}J(\mathrm{C,H}) = 131.6$ Hz; $\mathrm{OCH_2C}H_2$, THF)

4a: ^{1}H NMR (25 °C): $\delta = 5.46$ (br. s, 2H; $\mathrm{HC{=}CH}$), 5.31 (sept., $^{3}J(\mathrm{H,H}) = 6.6$ Hz, 2H; $\mathrm{NC}H\mathrm{Me_2}$), 3.62 (m, 4H; $\mathrm{OCH_2}$, THF), 1.77 (m, 4H; $\mathrm{OCH_2C}H_2$, THF), 1.13 (d, $^{3}J(\mathrm{H,H}) = 6.6$ Hz, 4H; $\mathrm{NCH}Me_2$); ^{1}H NMR (-80 °C): $\delta = 5.50$ (m, 2H; $\mathrm{NC}H\mathrm{Me_2}$), 5.08 (s, 2H; $\mathrm{HC{=}CH}$), 3.62 (m, 4H; $\mathrm{OCH_2}$, THF), 1.77 (m, 4H; $\mathrm{OCH_2C}H_2$, THF), 1.13 (d, $^{3}J(\mathrm{H,H}) = 5.7$ Hz, 6H; $\mathrm{NCH}Me_2$), 1.02 (d, $^{3}J(\mathrm{H,H}) = 5.9$ Hz, 6H; $\mathrm{NCH}Me_2$); ^{13}C NMR: $\delta = 115.83$ (d, $^{1}J(\mathrm{C,H}) = 180.7$ Hz; $\mathrm{HC{=}CH}$), 68.26 (t; $\mathrm{OCH_2}$, THF), 61.05 (d, $^{1}J(\mathrm{C,H}) = 142.7$ Hz; $\mathrm{N}C\mathrm{HMe_2}$), 26.27 (t; $\mathrm{OCH_2C}H_2$, THF), 22.62 (q, $^{1}J(\mathrm{C,H}) = 127.1$ Hz; $\mathrm{NCH}Me_2$)

4b: ^{1}H NMR (25 °C): $\delta = 5.56$ (s, 2H; $\mathrm{HC{=}CH}$), 4.88 (tt, 2H; NCH, *cyclo*-$\mathrm{C_6H_{11}}$), 3.62 (m, 4H; $\mathrm{OCH_2}$, THF), 1.96 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.78 (m, 4H; $\mathrm{OCH_2C}H_2$, THF), 1.77 (m, 4H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.61 (m, 2H; *cyclo*-$\mathrm{C_6H_{11}}$), 1.40–1.05 (m, 10H; *cyclo*-$\mathrm{C_6H_{11}}$); ^{1}H NMR (-80 °C): $\delta = 5.14$ (s, 2H; $\mathrm{HC{=}CH}$), 5.09 (m, 2H; NCH, *cyclo*-$\mathrm{C_6H_{11}}$), 3.62 (m, 4H; $\mathrm{OCH_2}$, THF), 1.80 (m, 4H; $\mathrm{OCH_2C}H_2$, THF), 1.90–0.85 (m, 20H; *cyclo*-$\mathrm{C_6H_{11}}$); ^{13}C-NMR: $\delta = 114.40$ (d, $^{1}J(\mathrm{C,H}) = 180.0$ Hz; $\mathrm{HC{=}CH}$), 69.03 (d, $^{1}J(\mathrm{C,H}) = 141.0$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 68.20 (t; $\mathrm{OCH_2}$, THF), 33.59 (t, $^{1}J(\mathrm{C,H}) = 132.2$ Hz; *cyclo*-$\mathrm{C_6H_{11}}$), 26.46 (t; *cyclo*-$\mathrm{C_6H_{11}}$), 26.31 (t; *cyclo*-$\mathrm{C_6H_{11}}$), 26.25 (t; $\mathrm{OCH_2C}H_2$, THF)

[a] The NMR spectra were recorded at 25 °C, and for **4a**,**b** additionally at -80 °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 analysis were obtained for all compounds.

1.939 Å)[13] and even exceed the sum of the covalent radii (Ti–N 2.024 Å).[14] Thus, a π-bonding contribution can be ruled out for these bonds. It is even more surprising that the two nitrogen atoms are nevertheless trigonal planar surrounded and that the five-membered ring $\mathrm{\overline{Ti(N1\text{-}C1{=}C2\text{-}N2)}}$, in contrast to those in **5** and **6,** is not folded (Ti, N1, N2, C1, and C2 lie in the mirror plane). As in many enamines the sp^2-hybridization of the nitrogen atoms in **2b** evidently results from an interaction of the N electron pairs with the p_π orbitals of the C1=C2 bond.[15] This charge distribution helps to account for why the affected azomethine hydrogen atoms H1 and H2 are so strongly shielded and their ^{1}H NMR signal is shifted to high field. A decrease in the charge density at the titanium atom is associated with the extension of the Ti–N bonds, particularly since the Ti–Cl bonds (2.398(2) and 2.387(2) Å) are also relatively long because of the C–H···Cl bonds.[16] This charge deficit is compensated by two THF ligands, and thus, in contrast to the titanium atoms in **5** and **6**, the titanium atom in **2b** is six-coordinate.

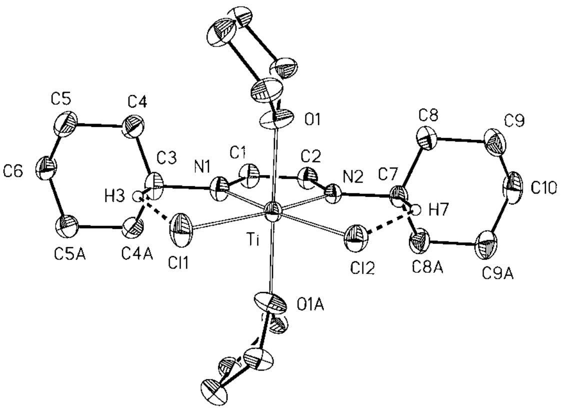
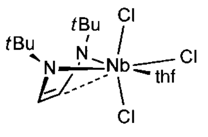


Figure 1. Structure of **2b** in the crystal (ellipsoids are drawn at 40% probability level). Selected bond lengths [Å] and angles [°]: Ti–Cl1 2.399(1), Ti–Cl2 2.386(1), Ti–N1 2.034(4), Ti–N2 2.037(3), Ti–O1 2.102(2), Ti–O1a 2.102(2), N1–C1 1.363(5), N2–C2 1.364(6), C1–C2 1.374(6), H3–Cl1 2.59(4), H7–Cl2 2.59(4); N1-Ti-N2 78.0(1), Cl1-Ti-Cl2 95.56(5), O1-Ti-O2 173.8(1), Ti-Cl1-H3 77(3), Ti-Cl2-H7 78(3), C3-H3-Cl1 137(3), C7-H7-Cl2 131(3); sum of angles at N1 and N2 360° (mirror plane).



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The metal atom is also six-coordinate in the niobium compounds **4a** and **4b**; however, only one THF molecule is required to achieve the octahedral geometry. From the structure of **4a** is clear that this THF molecule, unlike that in the bis(*tert*-butyl)glyoxaldiimine-niobium complex **7**[10b] is coordinated in a *trans* position to a chlorine atom at the niobium atom (Figure 2).[11b, 17] This

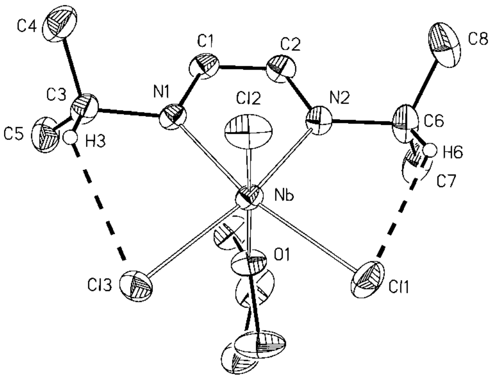

Figure 2. Structure of **4a** in the crystal (ellipsoids are drawn at 40% probability level. Selected bond lengths [Å] and angles [°]: Nb–Cl1 2.3794(8), Nb–Cl2 2.3877(8), Nb–Cl3 2.3955(8), Nb–N1 2.048(2), Nb–N2 2.057(2), Nb–O 2.188(2), N1–C1 1.366(3), N2–C2 1.369(3), C1–C2 1.351(4), Cl3–H3 2.69(4), Cl1–H6 2.68(4); N1-Nb-N2 74.88(8), Cl1-Nb-Cl2 90.90(3), Cl1-Nb-Cl3 101.64(3), Cl2-Nb-Cl3 91.52(3), O-Nb-Cl2 171.90(5), Nb-Cl1-H6 77(3), Nb-Cl3-H3 74(3), C3-H3-Cl3 125(3), C6-H6-Cl1 126(3); sum of angles at N1 359.9(2), at N2 359.6(2)°; fold angle (Nb,N1,N2)-(N1,C1,C2,N2) $\theta = 6.3(2)°$.

arrangement of ligands is therefore preferred because in this way, as in **2b**, two chlorine atoms are found in the plane of the 1,4-diaza-1,3-diene and can form C–H···Cl hydrogen bonds (H–Cl 2.68(4) and 2.69(4) Å; C-H-Cl 125(3) and 126(3)°) with the methine hydrogen atoms of the isopropyl groups. All other characteristic structural features of **4a**, which are attributed to these C–H···Cl bonds, correspond to those of the titanium complex. However, on account of the differing influence of the ligands chlorine and THF at the axial octahedral positions, the $\overline{\mathrm{Nb(N1\text{-}C1{=}C2\text{-}N}}\mathrm{2)}$ five-membered ring is slightly folded along the N1–N2 axis ($\theta = 6.3(2)°$).[18]

The surprising occurrence of intramolecular C–H···halogen hydrogen bonds in the isopropyl- and cyclohexyl-substituted 1,4-diaza-1,3-diene complexes **2**, **3**, and **4** is in agreement with the results obtained by Taylor and Kennard, according to which C–H units frequently occur as H-bond donors, if they are located in the α-position to a nitrogen atom.[2a] Whether other structural prerequisites are generally required for the occurrence of a C–H···halogen hydrogen bond, such as the additional support through a resonance-stabilized ligand system, and to what extent these intramolecular C–H···halogen hydrogen bonds can be varied with respect to the complex geometry and the choice of the halogen atom[19] are currently under investigation.

Experimental Section

All work was carried out under argon with carefully dried, degassed solvents. The ^{1}H and ^{13}C NMR data of the new compounds are given in Table 1.

2a: A solution of **1a** (12.20 mmol), prepared from *i*PrN=CHCH=N*i*Pr (1.71 g, 12.20 mmol) and lithium (0.169 g, 24.40 mmol) in THF (50 mL), was added dropwise at −78°C to a soution of $TiCl_4 \cdot 2THF$ (4.07 g, 12.20 mmol) in THF (150 mL). The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Subsequently the solvent was removed under vacuum and the residue was extracted with diethyl ether (100 mL). Red crystals of **2a** (3.84 g, 78%) precipitated from the extract at −20°C.

2b: Compound **2b** was obtained as described for **2a** by the reaction of **1b** (21.46 mmol), prepared from (*cyclo*-C_6H_{11})N=CHCH=N(*cyclo*-C_6H_{11}) (4.73 g, 21.46 mmol) and lithium (0.298 g, 42.92 mmol), with $TiCl_4 \cdot 2THF$ (7.17 g, 21.47 mmol) in 67% yield (6.95 g). Crystals suitable for the crystal structure analysis were obtained from diethyl ether/THF.

3a: $TiBr_4$ (4.58 g, 12.46 mmol) was dissolved in THF (150 mL) at −78°C and treated dropwise at this temperature with a solution of **1a** (12.46 mmol), prepared from *i*PrN=CHCH=N*i*Pr (1.75 g, 12.46 mmol) and lithium (0.173 g, 24.92 mmol) in THF (50 mL). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Subsequently the solvent was removed under vacuum and the residue was extracted with diethyl ether (100 mL). Red crystals of **3a** (4.97 g, 81%) precipitated from the extract at −5°C.

3b: Compound **3b** was obtained as described for **3a** by the reaction of **1b** (9.55 mmol), prepared from (*cyclo*-C_6H_{11})N=CHCH=N(*cyclo*-C_6H_{11}) (2.10 g, 9.55 mmol) and lithium (0.133 g, 19.10 mmol), with $TiBr_4$ (3.51 g, 9.55 mmol) in 70% yield (3.83 g).

4a: A solution of **1a** (10.42 mmol), prepared from *i*PrN=CHCH=N*i*Pr (1.46 g, 10.42 mmol) and lithium (0.145 g, 20.84 mmol) in THF (100 mL), was added dropwise to a solution of $NbCl_5$ (2.82 g, 10.42 mmol) in THF (150 mL) at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Subsequently the solvent was removed under vacuum until 50 mL of the solution remained. Diethyl ether (100 mL) was added to this reaction mixture. This led to the precipitation of nearly all the lithium chloride, which was separated from the solution by repeated filtration. The filtrate was kept for several days at −20°C, during this time **4a** precipitated as an ocher, microcrystalline solid. Yellow-brown, analytically pure crystals of **4a** (2.49 g, 58%) were obtained by recrystallization from THF.

4b: Compound **4b** was obtained as described for **4a** by the reaction of **1b** (9.65 mmol), prepared from (*cyclo*-C_6H_{11})N=CHCH=N(*cyclo*-C_6H_{11}) (2.13 g, 9.65 mmol) and lithium (1.34 g, 19.30 mmol), with $NbCl_5$ (2.61 g, 9.65 mmol) in 55% yield (2.61 g). Parallelpiped-shaped amber crystals, which were suitable for an X-ray crystal structure analysis were obtained after recrystallization from THF.

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[4] An interesting example for an intermolecular C–H···Cl hydrogen bond is in the platinum complex $[PtCl\{C_6H_2\text{-}2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(C{\equiv}CH)\}]$: H–Cl 2.60(17) Å, C-H-Cl 157.0(14)°. The intermolecular C–H···Cl bonds in this case lead to the formation of a linear polymer structure: S. L. James, G. Verspui, A. L. Spek, G. van Koten, *Chem. Commun.* **1996**, 1309–1310.

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[6] Publications by Brookhart et al. on the special activity of the catalyst system 1,4-diaza-1,3-diene/$NiBr_2$/methylalumoxane in olefin polymerization provided the stimulation for us to extend our studies on the chemistry of 1,4-diaza-1,3-diene complexes of the early transition metals[7] also to the 1,4-diaza-1,3-diene metal halides: a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6416; b) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005–2007; c) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268.

[7] a) J. Scholz, M. Dlikan, D. Ströhl, A. Dietrich, H. Schumann, K.-H. Thiele, *Chem. Ber.* **1990**, *123*, 2279–2285; b) J. Scholz, A. Dietrich, H. Schumann, K.-H. Thiele, *ibid.* **1991**, *124*, 1035–1039; c) J. Scholz, B. Richter, R. Goddard, C. Krüger, *ibid.* **1993**, *126*, 57–61; d) R. Goddard, C. Krüger, G. A. Hadi, K.-H. Thiele, J. Scholz, *Z. Naturforsch. B* **1994**, *49*, 519–528; e) B. Richter, J. Scholz, B. Neumüller, R. Weimann, H. Schumann, *Z. Anorg. Allg. Chem.* **1995**, *621*, 365–372; f) B. Richter, J. Scholz, J. Sieler, K.-H. Thiele, *Angew. Chem.* **1995**, *107*, 2865–2867; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2649–2651; g) J. Scholz, H. Görls, *Inorg. Chem.* **1996**, *35*, 4378–4382.

[8] tom Dieck et al. have described a red bis(isopropyl)glyoxaldiimine complex of the composition [(*i*PrNCH=CHN*i*Pr)$TiCl_2$(thf)], which can be sublimed at 100°C/1 Torr and thereby loses the THF under the formation of green needles. However, broad signals in the ^{1}H NMR spectrum prevented any comments on the structure. H. tom Dieck, H. J. Rieger, G. Fendesak, *Inorg. Chim. Acta* **1990**, *177*, 191–197.

[9] NMR data of 1,4-diaza-1,3-dienes for comparison: a) *N*,*N'*-bis(isopropyl)glyoxaldiimine: ^{1}H NMR ([D_8]THF, 20°C): $\delta = 7.83$ (s, 2H; N=CH), 3.44 (sept., ^3J(H,H) = 6.3 Hz, 2H; NC*H*Me$_2$), 1.15 (d, ^3J(H,H) = 6.4 Hz, 12H; NCH*Me*$_2$); ^{13}C NMR ([D_8]THF, 25°C): $\delta =$ 160.28 (ddd, ^1J(C,H) = 160.9, ^2J(C,H) = 9.7, ^3J(C,H) = 9.7 Hz; N=CH), 62.07 (d, ^1J(C,H) = 132.1 Hz; N*C*HMe$_2$), 24.30 (q, ^1J(C,H) = 126.0 Hz;

NCH*Me*$_2$); b) *N,N'*-bis(cyclohexyl)glyoxaldiimine: ^{1}H NMR ([D$_8$]THF, 20°C): $\delta = 7.85$ (s, 2H; N=CH), 3.14 (m, 2H; NC*H*, *cyclo*-C_6H_{11}), 1.83–1.78 (m, 20H; *cyclo*-C_6H_{11}); ^{13}C NMR ([D$_8$]THF, 25°C): $\delta = 160.87$ (ddd, ^1J(C,H) = 161.6, ^2J(C,H) = 11.3, ^3J(C,H) = 8.7 Hz; N=CH), 70.13 (d, ^1J(C,H) = 130.1 Hz; *cyclo*-C_6H_{11}), 34.91 (t, ^1J(C,H) = 127.9 Hz; *cyclo*-C_6H_{11}), 26.52, 25.16 (t; *cyclo*-C_6H_{11}).

[10] a) H. J. Rieger, Dissertation, Universität Hamburg, **1992**; b) J. Scholz, H. Görls, unpublished results.

[11] a) Crystal structure analysis of **2b**: $C_{22}H_{40}N_2O_2Cl_2Ti$, $M_r = 483.36$, red parallelpipeds, crystal dimensions $0.40 \times 0.38 \times 0.36$ mm^3, monoclinic, space group $P2_1/m$ (no. 11), $a = 8.759(2)$, $b = 12.243(2)$, $c = 14.292(3)$ Å, $\beta = 90.49(3)°$, $V = 1532.6(5)$ Å^3, $T = 183(1)$ K, $Z = 2$, $\rho_{calcd} = 1.047$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.470$ mm^{-1}, $F(000) = 516$, Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan, 3877 measured reflections, of which 3648 are symmetry-independent reflections in the range $2.72° \leq \theta \leq 27.41°$, $R_{int} = 0.075$, 3174 reflections with $F_o > 4\sigma(F_o)$, Lorentz and polarization correction, structure solution with direct methods (SHELXS), structure refinement against F_o^2 (SHELX-93), hydrogen atoms localized from difference Fourier syntheses and refined isotropically, 263 parameters, $R_{obs} = 0.056$, w$R2_{obs} = 0.145$, GOOF = 1.057, min./max. residual electron density $-0.89/0.79$ e Å^{-3}; b) crystal structure analysis of **4a**: $C_{12}H_{24}N_2OCl_3Nb$, $M_r = 411.59$, brown parallelpipeds, crystal dimensions $0.40 \times 0.36 \times 0.32$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.451(1)$, $b = 14.461(3)$, $c = 11.764(2)$ Å, $\beta = 99.14(1)°$, $V = 1755.3(5)$ Å^3, $T = 183(1)$ K, $Z = 4$, $\rho_{calcd} = 1.557$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.137$ mm^{-1}, $F(000) = 840$, Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan, 3740 measured reflections, of which 3545 are symmetry-independent reflections in the range $2.42° \leq \theta \leq 26.28°$, $R_{int} = 0.015$, 2930 reflections with $F_o > 4\sigma(F_o)$, Lorentz and polarization correction, absorption correction PSI scan, min./max. transmission 0.213/0.271, structure solution with direct methods (SHELXS), structure refinement against F_o^2 (SHELX-93), hydrogen atoms localized from difference Fourier syntheses and refined isotropically, 237 parameters, $R_{obs} = 0.029$, w$R2_{obs} = 0.073$, GOOF = 1.036, min./max. residual electron density $-0.55/0.34$ e Å^{-3}. c) 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-408006 and CSD-408007.

[12] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, London, **1973**.

[13] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1–S83.

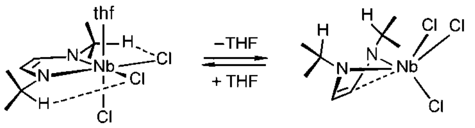
[14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[15] Based on crystal structure investigations of selected enamines a relationship was determined between nitrogen hybridization, C–N bond lengths, and p_π–p_π interactions. A measure for the p_π–p_π interaction is the sum of angles at the N atom. If the sum of angles is 360°, as for **2b** or **4a**, then the nitrogen atom is sp^2-hybridized, which indicates a maximal p_π–p_π interaction. In contrast, if the p_π–p_π interaction decreases then the sp^3 hybridization share of the nitrogen and thus the degree of the pyramidalization increases. a) A. G. Cook, *Enamines*, Marcel Dekker, 2nd ed., New York, **1988**; b) K. L. Brown, L. Damm, J. D. Dunitz, A. Eschenmoser, R. Hobi, C. Kratky, *Helv. Chim. Acta* **1978**, *61*, 3108–135.

[16] a) Ti–Cl bond lengths for comparison: $[TiCl_6]^{2-}$: 2.341(9) Å (average), I. A. Guzei, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 4415–4420; b) $TiCl_4 \cdot (Me_2NCH_2CH_2NMe_2)$: 2.280(3)–2.256(3) Å, P. Sobota, J. Utko, S. Szafert, K. Szczegot, *J. Chem. Soc. Dalton Trans.* **1997**, 679–683; c) $TiCl_4 \cdot 2THF$: 2.293(2) (*trans*), 2.265(23) (*cis*) Å, T. Lis, J. Ejfler, J. Utko, P. Sobota, *Pol. J. Chem.* **1992**, *66*, 93–99; d) G. J. Palenik, *Inorg. Chem.* **1997**, *36*, 3394–3397.

[17] It is also possible to describe the arrangement of the three chlorine atoms in **4a** as *facial* and in **7** as *meridional*. J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd edition Harper & Row, New York, **1978**, p. 448.

[18] In the ^{1}H NMR spectra of **4a** and **4b** recorded at room temperature the signals of the methine protons of the isopropyl and the cyclohexyl groups and those of the azomethine protons are not shifted as far to lowfield and to highfield, respectively, as for the titanium halide complexes. This indicates a rapid exchange process in which the THF is reversibly cleaved from the complex. We assume that an increase in the C–H ⋯ Cl distances is associated with this change in the complex geometry, which leads to the breakage of the hydrogen bonds. At the same time the Nb(N1-C1=C2-N2) ring is also more strongly folded [Eq. (1)]. This molecular dynamic is supported by the low-temperature ^{1}H NMR spectra: At −80°C the equilibrium of this exchange process evidently shifts to the side of the THF complex with a six-coordinate niobium and intact C–H ⋯ Cl bonds, since the signals of the methine protons of the isopropyl or cyclohexyl groups move to lower field and the signals of the azomethine protons move to higher field.



(1)

[19] A great deal of effort has been invested in trying to understand the nature of the hydrogen bonds but a fully satisfactory theory for the explanation of all the properties of the hydrogen bonds still remains to be established. Nevertheless it is indisputable that the C–H ⋯ X interaction (X = O, N, Cl) is not a van der Waals, but mainly an electrostatic interaction. It decreases far more slowly with distance and is therefore still effective at distances that correspond to the van der Waals limits or are larger than these.[1c–e]

Formation of a Novel Amidinium-Bridged Polyhedral Borane Ion by Incorporation of an Acetonitrile Solvent Molecule**

Fangbiao Li, Kenneth Shelly, Carolyn B. Knobler, and M. Frederick Hawthorne*

The derivative chemistry of the polyhedral borane ion $[B_{20}H_{18}]^{2-}$[1] has been of considerable interest for a number of years. Recently, we showed that oxidation of the oxygen-substituted derivatives *ae*-$[B_{20}H_{17}OR]^{4-}$ produced polyhedral borane anions $[\mu\text{-}B_{20}H_{18}OR]^{2-}$,[2] which contained both hydrogen and oxygen bridges. This observation, together with the availability of amine-substituted species suitable as candidate target species for boron neutron capture therapy (BNCT) of cancer,[3] prompted us to extend these studies to the oxidation of *ae*-$[B_{20}H_{17}NH_3]^{3-}$ (**1**, Scheme 1).[3, 4] The ion **1** and related amine derivatives exhibit excellent tumor uptake and selectivity when delivered by liposomes in vivo.[3, 4] This has been attributed to the facile intracellular oxidation of the

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[*] Prof. M. F. Hawthorne, F. Li, Dr. K. Shelly, Dr. C. B. Knobler
Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, CA 90095–1569 (USA)
Fax: (+1)310-825-5490
E-mail: mfh@chem.ucla.edu

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