Diazadiene complexes of Group 4 metals
I. Synthesis of mono-, bis- and tris(diazadiene)titanium complexes and the structure of diazadienedichlorotitanium

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Abstract

Exhaustive reduction of diazadienes (dad = R–N=CH–CH=N–R, R = Bu^t, Pr^i) with lithium and subsequent addition of titanium tetrachloride yields the homoleptic diazadiene–titanium complexes [(dad)$_2$Ti] (1, 2) and (dad)$_3$Ti (3) (R = Pr^i). Complexes (dad)TiCl$_2$ (4, 5) are similarly formed from a 1:1 reaction of Li$_2$[dad] with TiCl$_4$. Substitution reaction of 4 (R = Bu^t) afford complexes (dad)TiCl(X) (6–8) (X = N(SiMe$_3$)$_2$, C$_5$H$_5$, CH$_2$CMe$_3$). All compounds are volatile, soluble in unpolar solvents, and intensely coloured. A structure investigation by X-ray diffraction was performed for (Bu^{t}dad)TiCl$_2$ (4): space group $P4_2/n$, $a = 14.774(3)$, $b = 14.792(4)$, $c = 13.322(2)$ Å. It shows a five-coordinate chloro-bridged dimer. The Ti$_2$Cl$_2$ ring is folded along a line through the chlorine atoms, the TiNCCN chelate is folded along a line through the nitrogen atoms, which do not deviate strongly from sp^2 geometry. The bond lengths within the chelate indicate only a partial reduction of the dad. Symmetry arguments and data from the NMR and electronic spectra give indications as to the oxidation state of the metal and dad in the homoleptic complexes as well.

Introduction

Low formal oxidation states of the d-block elements can be stabilized by 1,4-diaza-1,3-diene (dad) ligands of the general type R–N=CH–CH=N–R [1]. The first homoleptic complex with an early transition metal, (dad)$_3$Ti, was prepared with benzildianil as a dad-type ligand [2]. Homoleptic complexes (dad)$_3$Ti and (dad)$_2$Ti with aliphatic dad ligands (R = tert-butyl, isopropyl) were synthesized earlier by co-condensation techniques [3]. Furthermore, there are reports on the synthesis of Cp$_2$Ti(dad) (dad = benzildianil) [2] and of (dad)Ti(OR)$_2$, the latter being prepared by intramolecular coupling of two h^2-iminoacyl functions at group 4 metal centers [4]. Since the dad ligand can be reduced chemically and electrochemically to the radical anion [dad]$^-$ [5] and eventually to the dianion [dad]$^{2-}$ at much more negative potentials [6], the oxidation state of the metal and the dad ligand in such complexes has to be discussed. Because of our interest in applying organometallics and their aza analogues in CVD processes [7], we have set out to develop efficient syntheses of volatile N-alkyl dad complexes.

Here we report a direct chemical synthesis of homoleptic, aliphatic bis- and tris(diazadiene) titanium complexes [(dad)$_n$Ti] ($n = 2$, 3) and the preparation, structure and reactions of (dad)TiCl$_2$.

Experimental

All operations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents (pentane, toluene and THF) as well as the NMR solvents were distilled from Na/K alloy and were saturated with nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-80 SYFT instrument. Chemical shift values δ are given in ppm relative to the TMS standard. IR spectra (as Nujol mull between KBr disks): Perkin-Elmer spectrometer model 325. UV–Vis spectra: Perkin-Elmer spectrometer model 554. Mass spectra: Varian CH 7 spectrometer. Elemental analyses were carried out at the Analytical Service Laboratory of our Institute. The syntheses of the dad ligands were described earlier [1].

Preparation of (dad)Ti complexes

Bis[glyoxalbis(tert-butylimine)]titanium (1)

A 2.7 molar excess of Li wire (0.2 g) was added to a solution of 1.68 g (10 mmol) Bu^t-dad in 20 ml of tetrahydrofuran and stirred overnight. Next a solution of 0.53 ml (0.91 g, 4.9 mmol) of TiCl$_4$ in 10 ml of hexane was added dropwise to the dark red solution at −78 °C. After stirring overnight the solvent was removed *in vacuo*, the solid residue redissolved in 20 ml of hexane, the solution filtered and the solvent removed again. 1 is a red crystalline solid (yield 80%) which sublimes at 85 °C/1 torr.

^{1}H NMR (C$_6$D$_6$): δ 5.80 (s, 4 H, NCH), 1.24 (s, 36 H, Bu^t). *Anal.* Calc. for C$_{20}$H$_{40}$N$_4$Ti (384.47): C, 62.48; H, 10.49; N, 14.57. Found: C, 62.18; H, 10.42; N, 14.84%. UV–Vis(pentane): λ$_{max}$ (nm(ε cm^2/mmol)): 380 broad (1750), 300 (3400). IR (cm^{-1}): 1220s, 1150m, 870s, 815m, 780s, 600w, 520w.

Bis[glyoxalbis(isopropylimine)]titanium (2)

A procedure analogous to that used for 1 allowed the isolation of 2 as a very air and moisture sensitive red oil (yield 70%, b.p. 105 °C; 1 torr).

^{1}H NMR (C$_6$D$_6$): δ 5.68 (s, 4 H, NCH), 3.58 (sept, 4 H, CHMe$_2$), 1.15 (d, 24 H, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 25.63 (CH$_3$), 57.19 (CH), 105.02 (NCH). *Anal.* Calc. for C$_{16}$H$_{32}$N$_4$Ti (328.36): C, 58.53; H, 9.82; N, 17.06. Found: C, 58.44; H, 10.38; N, 16.90%. The colour of 2 is similar to that of 1. It was not possible to record UV–Vis spectra without some decomposition to 3.

Tris[glyoxalbis(isopropylimine)]titanium (3)

The synthesis was similar to that used for 1 but with a threefold excess of dad with respect to TiCl$_4$ (1.65 g ipr-dad (11.8 mmol); 0.12 g Li (17 mmol); 0.43 ml (0.73 g, 38 mmol) TiCl$_4$). 3 could be isolated as a deep blue crystalline solid (subl. at 110 °C/1 torr). ^{1}H NMR (C$_6$D$_6$: δ 6.34 (s, 6 H, NCH), 4.02 (sept, 6 H, CHMe$_2$), 1.24 (d, 18 H, CH$_3$), 1.14 (d, 18 H, CH$_3$). *Anal.* Calc. for C$_{24}$H$_{48}$N$_6$Ti (468.59): C, 61.52; H, 10.33; N, 17.93. Found: C, 60.46; H, 10.32; N, 18.18%. UV–Vis(pentane): λ$_{max}$ (nm(ε in cm^2/mmol)): 680 (3500), 575 (5500), 480 (3300), 285 (12000), 240 (21000). MS (70 eV): m/z = 328 [(dad$_2$Ti)$^+$], 285 (−C$_3$H$_7$); 181, 169, 142, 125, 97, 83, 70, 56, 43 (100%).

Reaction of 2 with an equimolar amount of ipr-dad reacts immediately to give 3 quantitatively, as monitored by NMR. 2 does not react with further t-Bu-dad or N-aromatic dad.

Dichloro-glyoxalbis(tert-butylimine)titanium (4)

The standard procedure as for 1 was used but with a 1:1 molar ratio of TiCl$_4$ relative to the Bu^t-

dad. After removing the solvent *in vacuo*, the residue was extracted several times in a closed system (two Schlenk tubes connected via a G3 fritte) under reduced pressure with hexane. The solutions showed a red–violet colour. The hexane was removed, and 4 was obtained as a dark green powder (yield 70%) which can be sublimed at 90 °C/1 torr. ^{1}H NMR (C$_6$D$_6$): δ 5.88 (s, 2 H, NCH), 1.14 (s, 18 H, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 30.68 (CH$_3$), 63.01 (C$_q$), 98.21 (C=N). *Anal.* Calc. for TiC$_{10}$H$_{20}$N$_2$Cl$_2$ (287.09): C, 41.84; H, 7.02; N, 9.76. Found: C, 41.87; H, 7.22; N, 10.03%. UV–Vis(toluene): λ$_{max}$ (nm(ε cm^2/mmol)): 520 (250), 340 (2200). Infrared (cm^{-1}): 1370s, 1360s, 1255s, 1060m, 900m, 840s, 785m, 590m, 530w, 390s. MS: m/z = no mol. ion, no Cl-containing fragment ions; 218 ('dadTiH$_2$'), 194 (Ti(H$_2$NBu^t)$_2$), 179(−CH$_3$), 123 (TiH$_2$(H$_2$NBu^t)), 82, 67 ('TiH$_3$NH$_3$'), 58.

Dichloro-glyoxalbis(isopropylimine)titanium (5)

A procedure analogous to that for 4 gave a red powder (yield > 70%) of a substance, which analyzed approximately as a THF adduct (5a). The ^{1}H NMR (C$_6$D$_6$) showed broad signals. *Anal.* Calc. for C$_8$H$_{16}$N$_2$Cl$_2$Ti·C$_4$H$_8$O (331.14): C, 43.53; H, 7.31; N, 8.46. Found: C, 46.27; H, 7.96; N, 8.32%. Sublimation of the red compound 5a at 100 °C/1 torr leads to green crystals in the form of needles (yield > 50%) of 5b. The ^{1}H NMR spectrum (C$_6$D$_6$) showed again broad signals. *Anal.* Calc. for C$_8$H$_{16}$Cl$_2$N$_2$Ti (259.04): C, 37.09; H, 6.23; N, 10.81. Found: C, 36.50; H, 5.74; N, 10.85%.

Chloro-disilylamido-glyoxalbis(tert-butylimine)-titanium (6)

LiN(SiMe$_3$)$_2$ (0.17 g (1 mmol), prepared from HN(SiMe$_3$)$_2$ and BuLi/hexane) was added at −50 °C to a solution of 0.29 g (1 mmol) of 4 in 10 ml of THF and then stirred overnight at ambient temperature. The working up as for 1 gave 6 as a red–brown solid (yield > 70%, subl. 100 °C/1 torr). ^{1}H NMR (C$_6$D$_6$): δ 5.95 (s, 2 H, NCH), 1.25 (s, 18 H, CCH$_3$), 0.43 (s, 18 H, SiCH$_3$). *Anal.* Calc. for C$_{16}$H$_{38}$ClN$_3$Si$_2$Ti (412.03): C, 46.64; H, 9.30; N, 10.20. Found: C, 46.25; H, 9.13; N, 10.30%.

Chloro-cyclopentadienyl-glyoxalbis(tert-butylimine)-titanium (7)

Lithiumcyclopentadienide (0.07 g, 1 mmol) was added at −50 °C to a solution of 0.29 g (1 mmol) of 4 in 10 ml of THF. The solution was stirred for 6 h at room temperature. The working up as reported for 1 gave 7 as a violet solid (yield 80%, subl. 80 °C/0.7 torr). ^{1}H NMR (C$_6$D$_6$): δ 5.79 (br, 5 H, Cp), 5.42 (br, 2 H, NCH), 1.16 (s, 18 H, CH$_3$). *Anal.*

Calc. for $C_{15}H_{25}ClN_2Ti$ (316.73): C, 56.88; H, 7.96; N, 8.84. Found: C, 56.42; H, 7.75; N, 8.95%.

Chloro-glyoxalbis(tert-butylimine)neopentyl-titanium (8)

A Grignard reagent solution was prepared from 0.22 ml (1.7 mmol) of neopentyl bromide and 45 mg (1.8 mmol) of magnesium in 25 ml of THF. Then 0.5 g (1.7 mmol) of **4** were added and the mixture was stirred for 4 h. Solvent evaporation and subsequent extraction as described above for **1** gave a mixture of red crystals imbedded in a red oil. The product was purified by sublimation at 120 °C/1 torr, when 0.2 g (0.6 mmol) (35%) of **8** could be obtained in the form of red crystals. ^{1}H NMR (C_6D_6): δ 6.16 (s, 2 H, NCH), 1.32 (s, 18 H, Bu^{t}N), 1.18 (s, 9 H, Bu^{t}C), 0.51 (br, s, 2 H, CH$_2$).

X-ray data collection, structure determination, and refinement for 4

A black crystal of **4** obtained by sublimation was mounted in a Lindemann glass capillary under nitrogen. Crystallographic data for **4** were collected on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator and are listed in Table 1. Fractional atomic coordinates are given in Table 2. The position of the titanium atom was determined by a Patterson synthesis using SHELXS-86 [9]. Difference Fourier maps showed the nitrogen and carbon

TABLE 1. Crystallographic data of **4**

Chemical formula	$C_{20}H_{40}Cl_4N_4Ti_2$
Molecular mass	574.16
Crystal system	tetragonal
Space group	$P4_2/n$ (No. 86)
a (Å)	14.774(3)
b (Å)	14.792(4)
c (Å)	13.322(2)
V (Å^3)	2911.41
Z	4
D_{calc} (g cm^{-3})	1.310
(Mo K) (cm^{-1})	8.64
Crystal dimensions (mm)	$0.4 \times 0.3 \times 0.5$
Diffractometer	Syntex P2$_1$
λ(Mo Kα) (Å)	0.71069
Scan range (°)	4.5–55.0
h, k, l range	0–20, 0–20, 0–18
Electrons/units cell, $F(000)$	1200
Res. electron density (e/Å^3)	0.6919
Max. shift/e.s.d.	0.043
Reflections measured	3897
Symmetry independent reflections	3170
Significant reflections $F_o > 4\sigma(F_o)$	2665
No. parameters	139
R	0.0363
R_w	0.0369
Weight	0.00005

TABLE 2. Fractional atomic coordinates of **4**

Atom	x/a	y/b	z/c	U_{eq}
Ti1	0.68954(2)	0.13300(2)	0.22167(3)	0.0383(3)
Cl1	0.67239(4)	0.08039(5)	0.37869(4)	0.0643(6)
Cl2	0.84261(4)	0.20190(4)	0.23977(7)	0.0758(8)
C1	0.70706(14)	0.0812(2)	0.0574(2)	0.049(2)
C2	0.62342(14)	0.1240(2)	0.0627(2)	0.049(2)
N1	0.73870(11)	0.03823(11)	0.14120(12)	0.043(2)
C11	0.81250(14)	−0.0300(2)	0.1356(2)	0.051(2)
C12	0.7761(2)	−0.1128(2)	0.0814(2)	0.082(3)
C13	0.8941(2)	0.0078(2)	0.0802(2)	0.078(3)
C14	0.8381(2)	−0.0536(2)	0.2424(2)	0.073(3)
N2	0.57752(11)	0.12099(11)	0.15131(13)	0.042(2)
C21	0.47886(13)	0.1406(2)	0.1572(2)	0.049(2)
C22	0.4292(2)	0.0599(2)	0.1149(3)	0.082(3)
C23	0.4548(2)	0.2260(2)	0.0985(2)	0.080(3)
C24	0.4561(2)	0.1536(2)	0.2668(2)	0.075(3)

atoms. For the structure refinement the program SHELX 76 [8] was used. The hydrogen atoms were calculated in ideal geometrical positions. Refinement of the non-hydrogen atoms with anisotropic temperature factors and of the hydrogen atoms with isotropic thermal parameters led to final values of $R = 0.036$ and $R_w = 0.037$. The graphic representation of the molecule in Fig .1 was performed with the programme ORTEP [10].
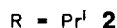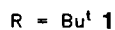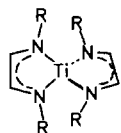
Results and discussion

Syntheses of diazadiene–titanium complexes

Reduction of N-alkyl diazadienes $RN=CH–CH=NR$ (R = tert-butyl, isopropyl) with lithium in tetrahydrofuran rapidly leads to the radical anions Li$^+$[dad]$^-$ [5]. Prolonged stirring with a slight excess of the metal yields the doubly reduced ligand [dad]$^{2-}$ [6]. Occasionally, especially in the presence of an oxidic material such as TiO$_2$, a proton abstraction instead of an electron transfer was observed in the case of ipr-dad [11]. Reactions in different stoichiometries of the solutions of reduced dad with TiCl$_4$ at room temperature lead to intensely coloured solutions from which (dad)Ti complexes **1–5** can be isolated in moderate to good yields (Scheme 1). The purification can occur by sublimation or, for **3**, by distillation *in vacuo* (see Table 3). No Ti complexes with N-aromatic dad have been isolated by this route so far [2, 4].
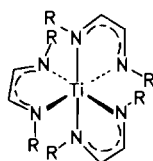
The compounds **1–3** are highly soluble in aprotic solvents and are air and moisture sensitive. The (dad)TiCl$_2$ complexes **4** and **5** are much less soluble in hydrocarbons but are also sensitive to air and water. The ^{1}H NMR data of **1** and **2** in C_6D_6 at ambient temperature agree with reported values [3].

$$n \text{ dad} + m \text{ Li} + \text{TiCl}_4 \longrightarrow (\text{dad})_n\text{TiCl}_{4-m} + m \text{ LiCl}$$

n = 1; m = 2
n = 2, 3; m = 4

R = Bu^t **1**
R = Pr^i **2**

R = Pr^i **3**

Scheme 1.

In these compounds the azomethine protons of the Ti-coordinated dad are shifted to higher field (from $\delta \sim 8$ for the free ligand to ~ 6 here). The ^{13}C NMR spectra of 2 and 4 exhibit the signals of the C atoms of the former glyoxalic imine at $\delta = 105.0$ and 98.2, respectively, in contrast to $\delta \sim 160$ in the uncoordinated dad [12]. The strong vibration of the C=N bond in free dad at 1630 cm^{-1} [13] is also absent in the IR spectra of the (dad)Ti complexes. This must not necessarily mean that the dad is reduced to an endiamido ligand, since dad complexes with metals in ordinary oxidation states often do not show any band in the region typical for C=N vibrations [13].

The ^{1}H NMR spectrum of 3 shows the methyl groups of the isopropyl substituents as two doublets. This confirms octahedral coordination around the titanium with D_3 symmetry, leading to the observed inequivalence of the methyl groups. The four-coordinate, presumably tetrahedral complex 2 shows but one doublet for the corresponding group. Reaction of a solution of 2 with traces of oxygen at room temperature gives an immediate colour change from red to a deep blue. Besides signals of the free ligand, the signals of 3 are observed. Extremely sensitive to oxygen, 2 decomposes yielding most probably TiO$_2$ and uncoordinated ipr-dad. Free dad coordinates to residual 2 with the formation of complex 3. Addition of one equivalent of ipr-dad to a solution of 2 also gives complex 3.

The tris-chelate could not be obtained with tert-Bu dad. With the less bulky ipr-dad we have also isolated corresponding complexes (ipr-dad)$_3$M [14, 15] with chromium, vanadium and molybdenum. A t-Bu-dad complex (dad)$_2$Cr is prepared as easily [14] as the well known (dad)$_2$M with M = Ni, Fe, Co or Mn [16].

The preparation of the bis(diazadiene) complexes 1 and 2 from TiCl$_4$ should proceed via (dad)TiCl$_2$. Accordingly, we have synthesized green 4 with just one mole of Li$_2$[dad]. During the preparation of TiCl$_2$(ipr-dad) (**5**) we first obtained a red solid which

is the adduct TiCl$_2$(ipr-dad)·THF (**5a**). The solvent molecule is lost during sublimation. These two compounds show broad NMR signals. There were no indications of temperature dependent conformational changes in any of the NMR experiments [5].

Substitution reactions of complex 4 were successful in which one chloro ligand is substituted by a bis(trimethylsilyl)amino (**6**), a cyclopentadienyl (**7**), or an alkyl (**8**) group. The compounds 6, 7 and 8 were prepared by treatment of 4 with the corresponding lithium or Grignard compounds (Scheme 2, Table 3). They are soluble in hydrocarbons and sensitive to oxygen and water.

The mass spectrum of 3 shows the highest mass at $m/z = 328$ ([dad$_2$Ti]$^+$). The loss of one dad in mass spectra of (dad)$_3$M complexes is typical [14, 16]. Then one isopropyl fragment ($m = 43$) is removed to lead to $m/z = 285$. $m/z = 180/181$ corresponds to the m/z value of 194/195 found for the tert-Bu compound 4. The mass spectrum of 4 exhibits a highest mass peak at $m/z = 218$ (corresponding to a 'Bu^t-dadTiH$_2$'). Intense peaks are observed at $m/z = 194$ (Ti(tBuNH$_2$)$_2$), 179 (–CH$_3$) and at 123 (Ti(tBuNBH$_2$)H$_2$). Typical isotopic patterns for Ti-containing fragment ions are observed as low as $m/z = 67$ (Ti(NH$_3$)H$_2$), indicating that plasma-induced CVD probably should lead to titanium nitrides [7].

The electronic spectra of 1 and 3 are quite different. The tetrahedral 1 shows a very broad band with an absorption maximum around 400 nm. Despite its almost Gaussian shape it is probably a superposition of several absorption bands. The half width calculated from the unperturbed long wavelength part of the curve is 8600 cm^{-1}. On the other hand, 3 shows an absorption minimum at 400 nm, but three bands around 680, 570 (max) and 480 nm with rather high extinction coefficients. These differences are important with respect to the oxidation state of the metal and the dad ligands.

For a thorough discussion of these dad compounds in view of their possible metal oxidation states between zero and four (see below) and their application

R = Bu^t **4**
R = Pr^i **5**

R = Bu^t
R' = N(SiMe$_3$)$_2$ **6**
      C$_5$H$_5$ **7**
      CH$_2$–C$_4$H$_9$ **8**
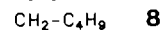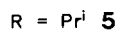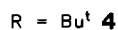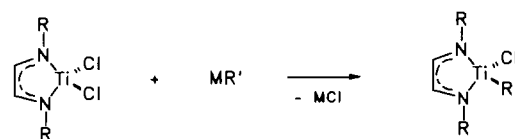
Scheme 2.

TABLE 3. Volatility and colour of compounds 1–8

Ti(Bu^t-dad)$_2$ (1)	90 °C/1 torr (sub.)	red crystals
Ti(Pr^i-dad)$_2$ (2)	105 °C/1 torr (dest.)	red oil
Ti(Pr^i-dad)$_3$ (3)	110 °C/1 torr (sub.)	blue crystals
Bu^t-dadTiCl$_2$ (4)	90 °C/1 torr (sub.)	green crystals
Pr^i-dadTiCl$_2$ (5)	100 °C/1 torr (sub.)	green crystals
Bu^t-dadTiClN(SiMe$_3$)$_2$ (6)	100 °C/1 torr (sub.)	red–brown crystals
Bu^t-dadTiClCp (7)	80 °C/0.7 torr (sub.)	violet crystals
Bu^t-dadTiCl(CH$_2$-Bu^t) (8)	>120 °C/1 torr (sub.)	red crystals

for the deposition of titanium metal, titanium nitrides we studied the structure of **4** by single crystal X-ray diffraction. **4** sublimes as a dark green material, which remains green when finely ground, but which dissolves even in toluene with a red–violet colour. The extinction coefficient in the visible is low. Thus, the colour change when going from the solid state to a molecular solution should be due to a change in the coordination sphere. The phenomenon is paralleled in the solid state colours of complex **5** and its THF adduct **5a**.

Structure of 4

Almost black rectangular crystals of **4** are obtained by sublimation. The structure of the molecule and the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 4.

In the solid state the compound of composition (dad)TiCl$_2$ is a dimer in which the Ti atoms are bridged by two chloro ligands. The two identical halves of the molecule are related by a C_2 axis. The four-membered Ti$_2$Cl$_2$ ring is not planar, the interplane angle is 165.9°. The Ti atoms have the coordination number five if only ligands with lone pair
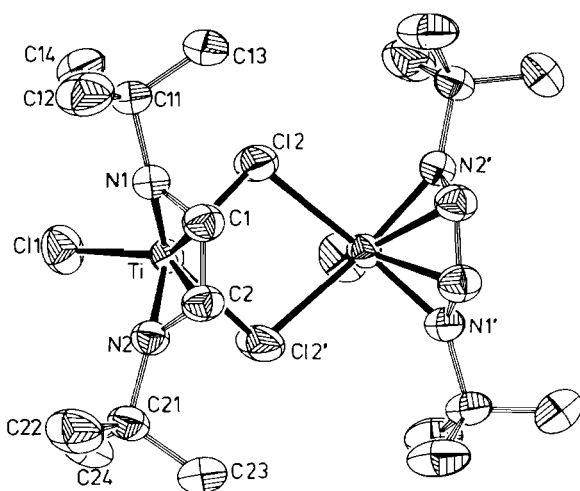
Fig. 1. ORTEP plot of **4** with atomic numbering scheme.

TABLE 4. Selected bond lengths (Å) and angles (°) of **4** with e.s.d.s in parentheses

Bond lengths	
Ti(1)–Cl(1)	2.2463(9)
Ti(1)–Cl(2)	2.4922(9)
Ti(1)–N(1)	1.9084(17)
Ti(1)–N(2)	1.9103(18)
Ti(1)–C(1)	2.3330(20)
Ti(1)–C(2)	2.3360(20)
Ti(1)–Cl(2′)	2.4996(9)
N(1)–C(1)	1.3670(30)
N(1)–C(11)	1.4880(30)
N(2)–C(2)	1.3620(30)
N(2)–C(21)	1.4880(30)
C(1)–C(2)	1.3900(30)

Bond angles	
Cl(1)–Ti(1)–Cl(2)	98.85(3)
Cl(1)–Ti(1)–N(1)	108.15(5)
Cl(1)–Ti(1)–N(2)	109.09(6)
Cl(1)–Ti(1)–Cl(2′)	103.13(3)
Cl(2)–Ti(1)–Cl(2′)	76.32(2)
N(1)–Ti(1)–N(2)	89.18(7)
N(1)–Ti(1)–C(1)	35.87(7)
N(2)–Ti(1)–C(1)	66.75(7)
N(2)–Ti(1)–C(2)	35.66(7)
C(1)–Ti(1)–C(2)	34.64(7)
Ti(1)–Cl(2)–Ti(1′)	102.58(2)
Ti(1)–N(1)–C(1)	89.24(12)
Ti(1)–N(2)–C(2)	89.48(12)
Ti(1)–C(1)–C(2)	72.82(12)
N(1)–C(1)–C(2)	118.32(19)

Torsion angles (°)	
Cl(1)–Ti(1)–Cl(2A)–Ti(1′)	107.43(3)
Cl(2)–Ti(1)–Cl(2′)–Ti(1′)	11.35(3)
N(1)–C(1)–C(2)–N(2)	0.2(3)
C(2)–C(1)–N(1)–C(11)	162.3(2)

donor sites are taken into account. However, they show a slightly distorted geometry. The angles between the non-bridging and the bridging Cl atoms, Cl1–Ti1–Cl2 (98.85(3)) and Cl1–Ti1–Cl2′ (103.13(3)), are different and, of course, greater than the angle Cl2–Ti–Cl2′ within the ring (76.32(2)°). The two bridging chloro ligands and the two nitrogen atoms can be regarded as the basis of a square pyramid,

while the terminal chlorine atom is on top. This geometrical description, however, does not fully correlate with the bonding. The Ti–N bonds (1.91 Å) are the shortest bonds with the best overlap. The Ti–μ-Cl distances (av. 2.49 Å) are much longer than the terminal Ti–Cl bond (2.246(1) Å). The non-planarity of the Ti(dad) chelate (interplane angle 120.1°) can be discussed in terms of a further bonding interaction between the Ti atom and the two carbon atoms C1, C2 (average distance to Ti: 2.33 Å). These 'bonds' are significantly shorter than in a similar complex reported by Rothwell and co-workers (2.399(6) and 2.408(6) Å [4]). This is surprising since the Rothwell complex is only four-coordinate in the classical sense. The carbon backbones of the chelates in 4 are in an *endo* position, i.e. folded towards the center of the dimer and in the same direction as the folding of the four-membered ring.

The lack of planarity of a large number of early transition metal N–C–C–N chelates has been established by X-ray diffraction methods [4] and has been taken as proof of an endiamido ligand ($=$ dad^{2-}) instead of a diazadiene ligand. The coordination is also reminiscent of the *cisoid* bonding of 1,3-dienes to early transition metals [17]. While the Ti–N and the C1–C2 distances are quite similar in 4 and in the mentioned complex, the C1–N1 and C2–N2 distances are shorter in 4, as are the Ti–C1, Ti–C2 distances.

Oxidation state of the dad ligand

It is difficult to classify the electronic situation of the chelate ligand in 4 as that of either an α-diimine (1,4-diaza-1,3-diene) molecule or an enediamido group. The C1–C2 distance in 4 (1.390(3) Å) is closer to a normal C$=$C bond (~ 1.33 Å) than to a C–C single bond in a conjugated N$=$C–C$=$N system (1.48 Å [18]*) and very similar to an aromatic C–C distance (1.39 Å). The C1–N1 or C2–N2 distances in 4 (1.36 Å) are also slightly closer to the normal CN double bond lengths in dad (1.28 Å [18]*) than to single bond distances C(sp^2)–N (1.49 Å). The intraligand bond lengths are close to those of Ni(dad)$_2$ [16] which was regarded as a Ni(0) complex because of its substitution reactions. But even admitting a very strong delocalization of electrons from the metal to the dad ligand, one would not attribute an oxidation state to nickel higher than $+2$. One could adopt

this view for the Ti compounds. However, the chemical shift values for the azomethine protons and the carbon atoms of the dad backbone in the NMR spectra of the (dad)Ti complexes correspond more to the values of an olefinic system than to an aromatic or even an aldimine system.

Nevertheless it is convenient to describe the dad ligand here as having taken up one electron. There is, of course, strong covalent interaction in all dad metal complexes irrespective of the oxidation state. Hence, paramagnetism will normally not occur. The low barriers of inversion ('flipping') of the bent chelate rings, detected by temperature dependent NMR experiments [4, 19] show that the bonding between the metal and the backbone C atoms is only of minor importance.

If one negative charge were on the dad, the Ti atom in 4 would be in the oxidation state $+3$, which might be reasonable in view of the redox potentials of dad [20], coordinated dad [1, 5, 20] and Ti($+4$) compounds. The second reduction step of N-alkyl dad is outside the low potential scan range of typical non-aqueous solvents used for cyclovoltammetry measurements. For the homoleptic complexes 1–3 the redox description may be based on symmetry arguments and the electronic spectra. For the pseudo-tetrahedral case Ti(dad)$_2$ (maximum symmetry D_{2d}), there is no interaction between the two low-lying d-orbitals (symmetry a$_1$, b$_1$) and the π^* orbitals of the two dad (e), but there is symmetry matching with the high energy e-pair d$_{xz,yz}$. Thus much electron density (up to two electrons per dad) can reside on the dad with only partial backbonding (bonding combination [e(π^*)$+$e(d$_{xz,yz}$)]). Low energy electronic transitions from this frontier orbital will have mixed LF and CT character but will be overlap-forbidden and thus not very intense. The e $\rightarrow$ e transition probably has LMCT character.

In the pseudo-octahedral case Ti(dad)$_3$ (symmetry D_3) there is another interesting symmetry condition. Of the three π^* orbital of the three dad ligands (a$_2$, e), only the e pair will have a bonding interaction with a pair of low-lying d-orbitals (d$_{xz,yz}$; the z axis is the C_3 axis). Thus a total of four electrons can be located in this bonding combination [e(π^*)$+$e(d$_{xz,yz}$)]. Depending on the relative energies of the dad and the metal e orbital pair the low-energy electronic absorptions resulting from an e $\rightarrow$ e transition may have MLCT, LMCT or $\pi\pi^*$ character. This absorption band should have components corresponding to the irreducible representations of the direct product. In fact, the electronic spectrum of Ti(dad)$_3$ is quite similar to the intense CT spectrum of the [Fe(dad)$_3$]$^{2+}$ ion [21]. If only four electrons can be delocalized into the dad part of a (dad)$_3$M

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*Biacetylbis(*p*-tolylimine): d(C$=$N) 1.288(7), d(C–C) 1.499(12); chelated to Ru(II): d(C$=$N) 1.278(7), d(C–C) 1.502(10) Å [18a]. Glyoxalbis(2,6-diisopropylphenylimine): d(C$=$N) 1.288(13), d(C–C) 1.518(15); mono-N-coord. to Cu(I): d(C$=$N) 1.288(11) and 1.263(12), d(C–C) 1.460(14) Å [18b]. t-Bu-dad: d(C$=$N) 1.283(6), d(C–C) 1.496(20) Å [18c].

complex—just as in a $(dad)_2M$ complex—the co-existence of both stoichiometries with the same metal can be understood. Volatile homoleptic dad complexes can in principle be the source of metal nitrides, metal rich nitride phases, or metals themselves under appropriate CVD conditions [7].

If two dad ligands in $Ti(dad)_2$ have to take over n electrons to account for the true oxidation state of the metal, the three dad ligands in $Ti(dad)_3$ cannot take over more than n electrons because of symmetry and energy reasons, as outlined above. The partial reduction of the dad is reflected in an upfield chemical shift of the NCH protons of 2.3 ppm (from $\delta(dad) = 8.0$ to $\delta(Ti(dad)_2) = 5.7$). The additional shielding should be less (about 2/3) for the $Ti(dad)_3$ complex, which is indeed the case ($\delta = 6.34$). It is, however, surprising that the (NCH) values suggest an increasing reduction in the series $(dad)TiCl(R) < (dad)TiCl(NSi_2) < (dad)TiCl_2 < (dad)Ti-(dad)$.

The folding of the N1C1C2N2 plane relative to the N1TiN2 plane (120°) is not accompanied by a complete rehybridization of the nitrogen atoms. The sum of the angles at N1 is 354.5(3)°, at N2 354.9(3)°; the N atoms are only about 0.2 Å above the plane of the surrounding three atom. The conformation probably reflects the compromise for σ- and π-donation from reduced dad.

Supplementary material

Further details of the crystal structure investigation are available on request from the Fachinformation-szentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54938, the names of the authors, and the journal citation.

Acknowledgements

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