

Aryltitanium(IV) complexes with the η^3 -C,N,N'-pseudofacially coordinating ligand $[\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$. The X-ray crystal structure of $[\text{TiCl}_2(\text{CNN})(\text{O}-i\text{-Pr})]$

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Abstract

Reaction of $[\text{TiCl}_3(\text{O}-i\text{-Pr})]$ with $[\text{Li}(\text{CNN})_2]$ (CNN = monoanionic $\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2$) in 2:1 molar ratio in toluene at -78°C afforded $[\text{TiCl}_2(\text{CNN})(\text{O}-i\text{-Pr})]$ as a 3:2 molar mixture of two stereoisomers. The stereoisomers differ by the mutual position of the chloro and alkoxy ligands. Molecular modelling calculations and an X-ray analysis of one of the stereoisomers indicated that the alkoxy ligand exhibits a strong *trans* preference to the weakest π -donating ligated atom, i.e., the $\text{N}(\text{Me}_2)$ atom of the CNN ligand. The molecular structure of this stereoisomer, as determined by X-ray analysis, involves an octahedral titanium center with an η^3 -*fac*-C,N,N'-bonded CNN ligand. A strong M–O(alkoxy) interaction is illustrated by an almost linear M–O–C bond angle of $172.4(2)^\circ$. As a result of the pseudofacially bonded CNN ligand, the titanium center as well as the central N-donor center are stereogenic resulting in the formation of two enantiomers. A (CNN)titanium(IV) dimethyl complex is accessible via reaction of **1** with two equivalents of MeLi and contains likewise an η^3 -*fac*-C,N,N'-bonded CNN ligand. © 1997 Elsevier Science S.A.

Keywords: Aryltitanium(IV) complexes; Stereoisomers; Monoanionic aryldiamine ligand; Transition metal chemistry

1. Introduction

There is great current interest in ligands that may replace the cyclopentadienyl ligand in early transition metal chemistry. Among the systems that have been developed are aryloxides [1–8] alkoxides [9–13], amides [14–20], benzamidinates [21–24], porphyrines [25,26], carboranes [27], amidodiphosphines [28–30] and β -diketimines [31–35]. In our group we have recently prepared a series of titanium(IV) complexes using the monoanionic aryldiamine ligand $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2]^-$ (abbreviated as NCN, Fig. 1A) [36]. The complexes $[\text{TiR}^1\text{R}^2(\text{NCN})(\text{O}-i\text{-Pr})]$ ($\text{R}^1 = \text{R}^2 = \text{Cl, OTf, Me}$;

$\text{R}^1 = \text{Cl, R}^2 = \text{OTf, Me}$) showed, for example, an interesting catalytic activity in the 1,2-addition reaction of Et_2Zn to benzaldehyde, whereas the (NCN)titanium(IV) bistriflate complex exhibited a unique η^2 -O,O'-bonded triflate ligand to the titanium center [36].

Recently we have shown that substituting the NCN ligand for the CNN ligand (CNN = $[\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$, Fig. 1B) can have a remarkable effect on the reactivity of the resulting CNN–metal complex. This is, for example, clearly illustrated by the difference in reactivity of $[\text{Ta}(\text{=CH}-t\text{-Bu})(\text{NCN})(\text{O}-t\text{-Bu})]$ and $[\text{Ta}(\text{=CH}-t\text{-Bu})(\text{CNN})(\text{O}-t\text{-Bu})]$. Whereas the NCN containing complex only showed a reactivity towards simple alkenes which led to the isolation of an (unstable) tantalacyclobutane [37], the analogous CNN complex showed activity in ring opening metathesis polymerization with the strained cyclic alkenes norbornene and dicyclopentadiene [38].

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described as distorted octahedral with the CNN ligand η^3 -pseudofacially bonded to the metal center. It is worth noting that the ligand arrangement around the metal center in **1a** renders the titanium center stereogenic. The central N donor atom (N(1)) is also stereogenic but the configuration of this stereogenic center is dictated by that of the titanium center. As a result, **1a** exists as a racemic mixture of two enantiomers, i.e., (*OC-6-35-A*)_{Ti}R_N (shown in Fig. 2) and (*OC-6-35-C*)_{Ti}S_N according to the classification described by Leigh [43]. The unit cell of **1a** contains both enantiomers.

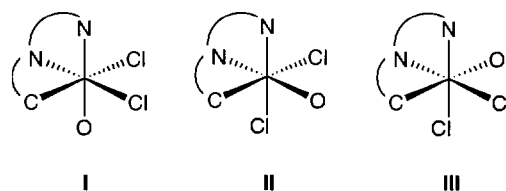
A remarkable feature of the molecular structure of **1a** is the almost linear Ti–O(1)–C(13) bond angle of 172.4(2)° indicating a strong $d\pi$ – $p\pi$ interaction [44–46]. The Ti–N(2) bond distance is significantly longer than the Ti–N(1) bond distance (2.376(3) Å and 2.256(3) Å, respectively) presumably as a result of the strong π -donating O-*i*-Pr ligand *trans* to N(1). Also the Ti–Cl bond distances are markedly different, i.e., the Ti–Cl(1) bond distance is substantially longer (2.3997(13) Å) as compared to Ti–Cl(2) (2.2893(12) Å).

A comparison of the molecular structure of **1a** with that of the closely related NCN–titanium(IV) complex [TiCl₂(NCN)(O-*i*-Pr)] (**2**) [36] shows a similar overall molecular structure, i.e., in both complexes the aryl-diamine ligand is η^3 -pseudofacially coordinated resulting in a stereogenic titanium center with the alkoxy ligand positioned *trans* to a NMe₂ unit. However, some differences associated with the different coordination properties of the CNN and NCN aryl-diamine ligands are observed.

In a terdentate coordinated CNN ligand, the N-donor atoms are positioned mutually *cis* and therefore perfectly set for an η^3 -C,N,N'-pseudofacial coordination. In contrast, a NCN ligand with η^3 -N,C,N-pseudofacial coordination leads to severe steric interactions between both NMe₂ units, because of the small N–Ti–N angle (e.g., for **2** 113.23(10)°). The shorter Ti–N bond distances found in **1a** (mean value 2.316 Å) as compared with these distances found in **2** (mean value 2.400 Å) [36] clearly illustrate this effect. Pseudofacial coordina-

Table 1
Selected bond distances (Å) and angles (deg) found in [TiCl₂(CNN)(O-*i*-Pr)] **1a**

Bond length (Å)			
Ti–Cl(1)	2.3997(13)	Ti–N(1)	2.256(3)
Ti–Cl(2)	2.2893(12)	Ti–N(2)	2.376(3)
Ti–C(1)	2.153(4)	Ti–O(1)	1.733(3)
Bond angles (deg)			
N(2)–Ti–Cl(1)	83.35(8)	N(1)–Ti–Cl(1)	90.07(9)
N(2)–Ti–Cl(2)	86.99(10)	N(1)–Ti–Cl(2)	93.63(11)
N(2)–Ti–C(1)	87.93(14)	N(1)–Ti–C(1)	75.71(13)
N(2)–Ti–N(1)	77.82(12)	Ti–O(1)–C(13)	172.4(2)
N(2)–Ti–O(1)	171.13(13)		



$$E^{\text{rel}} = 0 \text{ kJ.mol}^{-1} \quad E^{\text{rel}} = 13 \text{ kJ.mol}^{-1} \quad E^{\text{rel}} = 22 \text{ kJ.mol}^{-1}$$

Fig. 3. Three possible stereoisomers of **1** containing an η^3 -pseudofacially bonded CNN ligand. The total energy of geometry I is defined to be 0 kJ mol⁻¹.

tion is thus more favourable for the CNN ligand than for the NCN ligand.

In addition, an elongated Ti–C^{*ipso*} bond distance is observed for **1a** (2.153(4) Å) as compared with the corresponding distance in **2** (2.090(3) Å) [36]. This effect is counter-balanced by a stronger Ti–O-*i*-Pr interaction in **1a** (cf. Ti–O–C = 172.4(2)°, Ti–O = 1.733(3) Å vs. Ti–O–C = 149.22(18)°, Ti–O = 1.765(2) Å in **2**).

Two sets of resonances with relative intensity ratio 3:2 (labeled **A** and **B**, respectively) are observed in the room temperature ¹H NMR spectra of **1**, corresponding to each of the two isomers. Characteristic overlapping low field resonances for the aromatic *ortho* protons at $\delta = 8.06$ are indicative of metalated aryl rings [47–49]. No coalescence of signals of diastereotopic OCHMe₂ and NMe₂ protons are observed up till 360 K, indicating that Ti–N dissociation is either not taking place at all or is at least slow on the NMR time scale. Above 360 K both isomers of **1** start to decompose.³ On the basis of the NMR data it was not possible to assign one of the sets **A** or **B** to **1a**.

Assuming distorted octahedral geometries for **1b**, two geometries have to be considered, i.e., geometries **II** and **III** (Fig. 3) with the O-*i*-Pr function positioned either *trans* to the internal amine donor or *trans* to C^{*ipso*} of the CNN ligand. Geometry **I** corresponds to **1a**. Semiempirical molecular modelling calculations (using the ZINDO approach with INDO/1 parameter set) were performed on all three structures and it was found that **I**, corresponding to **1a**, is the most stable stereoisomer. Isomers **II** and **III** were calculated to be 13 kJ mol⁻¹ and 22 kJ mol⁻¹ higher in energy, respectively, suggesting that geometry **II** is the more likely structure for **1b**.

The molecular structure of **1a** is similar to the tantalum(V) alkylidene complex [TaCl₂(=CH-*t*-Bu)(CNN)] (**3**) [50]. In both complexes the CNN ligand is η^3 -pseudofacially coordinated, the metal center is stereogenic and multiple stereoisomers are found (¹H NMR). Based on NMR and molecular mechanics studies of **3**, it was

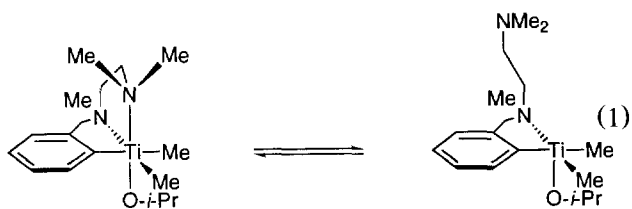
³ Characteristic resonances of protonated CNN are observed along with signals of other unidentified products.

proposed that the stereoisomers differ in the mutual positions of the chloro and alkylidene ligands [50].

2.1. Reactivity of $[\text{TiCl}_2(\text{CNN})(\text{O-}i\text{-Pr})]$, **1**

As NCN–titanium(IV) methyl complexes are easily accessible in high yields and show interesting catalytic activity we were interested in preparing the analogous CNN–titanium(IV) complexes. Reaction of mixture **1** with two equivalents of MeLi at -78°C afforded the dimethyl complex $[\text{TiMe}_2(\text{CNN})(\text{O-}i\text{-Pr})]$ (**4**). Complex **4** was isolated as an air-sensitive, dark red oil, which was soluble in polar and nonpolar solvents. Attempts to crystallize **4** failed due to its high solubility. Complex **4** was shown by ^1H NMR spectroscopy to be contaminated with small amounts of toluene and protonated CNN that could not be removed under reduced pressure.

The dimethyl complex **4** shows fluxional behaviour in the ^1H NMR spectrum. At low temperature (220 K) the NMR data are similar to **1**, i.e., indicative of two stereoisomeric species with η^3 -pseudofacially coordinated CNN ligands. At room temperature, the ^1H NMR spectrum reveals one coalesced NMe_2 signals ($T^{\text{coal}} = 230\text{ K}$, $\Delta G^\ddagger = 46\text{ kJ mol}^{-1}$),⁴ one resolved AX pattern for the benzylic protons and two Ti–Me signals. This observation points to the presence of one asymmetric species, in which a fluxional process is operative involving the methyl groups of the NMe_2 unit. A possible fluxional process could be an association–dissociation process involving the Ti– NMe_2 bond, a process which has been observed in other CNN–metal complexes [51–53]. Dissociation of the Ti– NMe_2 bond provides a pentacoordinate η^2 -C,N-bonded CNN–titanium(IV) species (Eq. (1)). This coordination mode of the CNN ligand has also been observed for $[\text{M}(\text{CNN})(\text{cod})]$ (M = Rh, Ir) in solution [53]. The fact that the benzylic protons as well as the Ti–Me groupings are still diastereotopic, indicates that the η^2 -C,N bonding is rigid on the NMR timescale, i.e., the Ti–N(Me_2) on–off process leaves the stereochemistry at the Ti center and the N(Me) donor site unaffected.



Eq. (1) shows the proposed formation of a pentacoordi-

⁴ Eyring equation: $\Delta G^\ddagger = -RT_c \ln[2\pi h(\Delta\nu)/kT_c\sqrt{3}]$ with $\Delta G^\ddagger =$ free energy activation (J), $T_c =$ coalescence temperature (K), $\Delta\nu =$ chemical shift difference (Hz), the other symbols have their usual meaning.

nate species through dissociation of the NMe_2 unit of the CNN ligand.

Preliminary experiments indicate that CNN–titanium(IV) complexes are catalytically active in, e.g., Ziegler–Natta-type α -olefin polymerizations. Further studies regarding the structure, scope and activity of these complexes are currently under investigation.

3. Experimental

All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were provided by Dornis U. Kolbe, Mülheim a.d., Ruhr, Germany. The molecular modelling calculations were performed with CAChe Scientific; Oxford Molecular Group software. ^1H (200 or 300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (50 or 75 MHz) NMR spectra were recorded on Bruker AC200 or AC300 spectrometers at ambient temperature unless otherwise stated. The following abbreviations have been used: s, singlet; d, doublet; t, triplet; m, multiplet; sp, septet; br, broad signal. $[\text{Li}(\text{CNN})]_2$ [49] was prepared according to a literature procedure. All other reagents were obtained commercially and used as such.

3.1. Preparation of $[\text{TiCl}_2\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}(\text{OCHMe}_2)]$, **1**

To a stirred solution of TiCl_4 (20.78 mmol) in toluene (150 ml) $\text{Ti}(\text{O-}i\text{-Pr})_4$ (6.93 mmol) was added. The resulting yellow solution was stirred for 15 min at room temperature after which it was cooled to -78°C . At this temperature a solution of $[\text{Li}(\text{CNN})]_2$ (13.9 mmol) in toluene (100 ml) was added dropwise in 1 h. The formed brown/red mixture was allowed to warm to room temperature in 1 h and stirred at this temperature for another 30 min. The crude product was isolated by centrifugation of the reaction mixture and decantation of the toluene fraction. The remaining solid was extracted with C_6H_6 ($4 \times 75\text{ ml}$) after which the solvent from the combined organic fractions was evaporated in vacuo. The obtained red/brown powder was washed with pentanes ($3 \times 25\text{ ml}$) and dried in vacuo to give **1** as a dark red powder (7.87 g, 77%). Red needles suitable for X-ray analysis were obtained by cooling a saturated solution of **1** in toluene to -30°C for three days. Mp $122\text{--}125^\circ\text{C}$. Anal. calc. for $\text{C}_{15}\text{H}_{26}\text{Cl}_2\text{N}_2\text{OTi}$: C, 48.80; H, 7.10; N, 7.59; found C, 48.71; H, 6.98; N, 7.43. Cryoscopy $\text{MW}(\text{calc}) = 369.07$, $\text{MW}(\text{obs}) = 385$ (by cryoscopy in benzene). ^1H NMR (C_6D_6): stereoisomer **A**: δ 8.06 (m, 1H, *o*-ArH), 6.99 (m, 2H, ArH), 6.75 (m, 1H, ArH), 4.76 (sp, $^3J = 6.18\text{ Hz}$, 1H, OCH), 4.08 (d, $^2J = 14.0\text{ Hz}$, 1H, ArCH₂N), 3.37 (m, 1H,

$\text{NCH}_2\text{CH}_2\text{N}$ (A or B), 3.00 (s, 3H, $\text{N}(\text{CH}_3)$), 2.85 (d, $^2J = 14.0$ Hz, 1H, ArCH_2N), 2.60 (s, 3H, $\text{N}(\text{CH}_3)$), 2.05 (s, 3H, $\text{N}(\text{CH}_3)$), 1.6–1.2 (m, $\text{NCH}_2\text{CH}_2\text{N}$), 1.2 ($2 \times$ d, $^3J = 6.18$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$); stereoisomer **B**: δ 8.06 (m, 1H, *o*-ArH), 6.99 (m, 2H, ArH), 6.75 (m, 1H, ArH), 5.07 (sp, $^3J = 6.19$ Hz, 1H, OCH), 4.62 (d, $^2J = 14.3$ Hz, 1H, ArCH_2N), 3.12 (d, $^2J = 14.2$ Hz, 1H, ArCH_2N), 3.10 (s, 3H, $\text{N}(\text{CH}_3)$), 2.50 (s, 3H, $\text{N}(\text{CH}_3)$), 1.65 (s, 3H, $\text{N}(\text{CH}_3)$), 1.6–1.2 (m, $\text{NCH}_2\text{CH}_2\text{N}$), 1.5 ($2 \times$ d, $^3J = 6.19$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): stereoisomer **A**: δ 200.0 ($\{\text{Ar}\}\text{CTi}$), 142.9, 141.1, 126.7 and 125.4 ($\{\text{Ar}\}\text{C}$), 85.7 (OCH), 70.6 (ArCH_2), 57.7 and 56.7 ($\text{NCH}_2\text{CH}_2\text{N}$), 52.3, 51.8 and 50.0 (NCH_3 and $\text{N}(\text{CH}_3)_2$), 25.3, 24.4 and 24.3 ($\text{OCH}(\text{CH}_3)_2$) (A + B); stereoisomer **B**: δ 205.4 ($\{\text{Ar}\}\text{CTi}$), 140.7, 135.9, 122.9 and 122.8 ($\{\text{Ar}\}\text{C}$), 84.6 (OCH), 70.1 (ArCH_2), 58.0 and 56.8 ($\text{NCH}_2\text{CH}_2\text{N}$), 53.3, 51.2 and 50.4 (NCH_3 and $\text{N}(\text{CH}_3)_2$).

3.2. Preparation of $[\text{TiMe}_2\{\text{C}_6\text{H}_4(\text{CH}_2\text{-N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}(\text{OCHMe}_2)]$, **4**

To a solution of **1** (2.52 mmol) in 50 ml of toluene a solution of MeLi (5.04 mmol) in Et_2O was added at -78°C . The reaction mixture was allowed to warm to room temperature in one hour during which the colour of the reaction mixture changed to dark red and a precipitate (LiCl) was formed. The crude product was isolated by centrifugation of the reaction mixture followed by decantation of the organic layer. After extracting the remaining solid with pentanes (2×25 ml) the solvent of the combined organic fractions was evaporated in vacuo to give 1.62 g (78%) of **4** as a red oil. ^1H NMR (C_6D_6 , 297 K): δ 8.00 (m, *o*-ArH), 7.4–7.0 (m, 3H, ArH), 5.13 (sp, $^3J = 6.2$ Hz, 1H, OCH), 4.40 (d, $^2J = 13.7$ Hz, 1H, ArCH_2), 3.29 (d, $^2J = 14.0$ Hz, 1H, ArCH_2), 2.75 (m, 1H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.58 (s, 3H, NCH_3), 1.73 (br s, 6H, $\text{N}(\text{CH}_3)_2$), 2.0–1.5 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.56 (2 d, $^3J = 6.05$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$), 0.72 (s, 6H, TiCH_3), 0.60 (s, 6H, TiCH_3). ^1H NMR (C_7D_8 , 220 K): stereoisomer **I**: δ 8.0 (m, 1H, *o*-ArH), 7.3–6.9 (m, 3H, ArH), 5.18 (sp, $^3J = 5.7$ Hz, 1H, OCH), 4.62 (d, $^2J = 13.7$ Hz, 1H, ArCH_2), 3.33 (d, $^2J = 13.9$ Hz, 1H, ArCH_2), 2.8 (s, 3H, NCH_3), 2.0–1.0 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.7 (s, 3H, $\text{N}(\text{CH}_3)_2$), 1.5–1.6 (m, 6H, $\text{OCH}(\text{CH}_3)_2$), 1.25 (s, 3H, $\text{N}(\text{CH}_3)_2$), 0.7 (br s, 3H, Ti-CH_3), 0.35 (br s, 3H, Ti-CH_3); stereoisomer **II**: δ 8.0 (m, 1H, *o*-ArH), 7.3–6.9 (m, 3H, ArH), 4.32 (sp, $^3J = 5.7$ Hz, 1H, OCH), 4.18 (d, $^2J = 14.4$ Hz, 1H, ArCH_2), 3.1 (d, $^2J = 14.6$ Hz, 1H, ArCH_2), 2.33 (s, 3H, NCH_3), 2.0–1.0 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.9 (s, 3H, NCH_3), 1.5–1.6 (m, 6H, $\text{OCH}(\text{CH}_3)_2$), 1.08 (s, 3H, $\text{N}(\text{CH}_3)_2$), 0.7 (br s, 3H, Ti-CH_3), 0.35 (br s, 3H, Ti-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 220 K): 196.1 ($\{\text{Ar}\}\text{CTi}$), 143.1, 137.3, 128.3,

Table 2

Crystal data and details of the structure determination for **1a**

Crystal data	
Empirical formula	$\text{C}_{15}\text{H}_{26}\text{Cl}_2\text{N}_2\text{OTi}$
Formula weight	369.17
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.128(2), 10.408(2), 12.980(2)
β (deg)	109.060(9)
<i>V</i> (Å ³)	1804.0(5)
<i>Z</i>	4
D_{calc} (g cm ⁻³)	1.359
$F(000)$ (electrons)	776
μ (Mo K α) (cm ⁻¹)	7.7
Crystal size (mm)	0.20 \times 0.55 \times 0.55
Data collection	
Temperature (K)	150
Radiation (Å) Mo K α (with monochromator)	0.71073
θ min–max (deg)	1.5, 27.5
Scan type, scan, (deg)	ω , 1.21 + 0.35 tan(θ)
Dataset	– 18:17; – 13:0; – 14:16
Total data, Unique data	6860, 4145
Observed data ($I > 2.0 \sigma(I)$)	2613
Refinement	
<i>N</i> ref, <i>N</i> par	4145, 195
<i>R</i> , wR^a , <i>S</i>	0.0573, 0.1383, 1.02
Max. and average shift/error	0.000, 0.000
Min. and max. residual density (e Å ⁻³)	– 0.43, 0.49

$$^a w = 1/(\sigma^2(F_o^2) + 0.0408P)^2 + 1.7449P, \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

125.2, 124.7 ($\{\text{Ar}\}\text{C}$), 78.0 (OCHMe_2), 71.6 (ArCH_2), 57.5 and 57.0 ($\text{NCH}_2\text{CH}_2\text{N}$), 49.2 ($\text{N}(\text{CH}_3)_2$), 48.7 ($\text{N}(\text{CH}_3)$), 27.0 (Ti-CH_3), 26.6 ($\text{OCH}(\text{CH}_3)_2$), 21.3 (Ti-CH_3).

3.3. Computational details

Results were obtained utilizing the ZINDO approach, as implemented in the CAChe WorkSystem, with standard INDO/1 semiempirical parameters. For geometry optimization of **I** crystallographically derived atom coordinates were used as input data. For geometries **II** and **III** coordinates were derived by changing the molecular geometry of **I** using the builder routine in the molecular modelling package.

3.4. Crystal structure determination of **1a**

Numerical details have been collected in Table 2. X-ray data were collected for a transparent yellowish crystal cut-to-size from a cluster on an Enraf-Nonius CAD4-T diffractometer on Rotating Anode (Mo K α -graphite monochromator, 6 kW) and using the inert oil mounting technique.

Unit-cell dimensions were derived from the SET4 [54] setting angles of 25 reflections and checked for higher symmetry with the program LEPAGE [55]. The structure was solved by automated Patterson techniques using DIRDIF [56] and refined on F^2 with SHELXL [57]. Data were corrected for absorption using the DI-FABS technique as implemented in PLATON [58] (Correction range 0.531:1). Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Geometrical calculations and the ORTEP illustrations were done with PLATON [58].

Full details may be obtained from one of the authors (ALS).

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