

Isocyanide complexes of titanium: synthesis and X-ray crystal structure of *cis*-tetrachlorobis(2-trimethylsiloxyphenylisocyanide) titanium(IV) [☆]

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Abstract

The reaction of TiCl_4 with 2-trimethylsiloxyphenyl isocyanide **1** is described. At -10°C reaction of TiCl_4 with **1** in *n*-hexane yields the air-sensitive octahedral diisocyanide complex *cis*- $[\text{TiCl}_4(\textbf{1})_2]$ **2**. This complex crystallizes from *n*-hexane as solvate $2 \cdot \text{C}_6\text{H}_{14}$ and was characterized by X-ray crystallography. At room temperature TiCl_4 reacts with **1** in toluene to give an orange air-sensitive compound **3**, which was not completely characterized. Elemental analyses indicate the formation of a complex composed of one molecule of TiCl_4 and one molecule of **1**. IR spectroscopy shows that no isocyanide ligand is present in **3**.

Keywords: Isocyanide complex; Titanium; X-ray crystallography

1. Introduction

Recently we reported that the cleavage of the Si–O bond in complexes with coordinated 2-trimethylsiloxyphenyl isocyanides **1** [1] leads to mixtures of isocyanide and ylidene complexes depending on the electronic properties of the metal center (Scheme 1). After Si–O bond cleavage, the reaction stops at complex **A** with the 2-hydroxyphenyl isocyanide ligand if the isocyanide carbon is deactivated for nucleophilic attack by $(d \rightarrow p)\pi$ backbonding from the metal [2]. For electron-poor metal centers no stabilization by backbonding occurs and a subsequent intramolecular nucleophilic attack of the hydroxyl oxygen at the isocyanide carbon leads to complexes with the 1,2-dihydrobenzoxazol-2-ylidene ligand **B** [3]. The position of the equilibrium between complexes of types **A** and **B** can be shifted by changing the ability for backbonding of the metal center [2] or by reaction at the coordinated ligand [4]. For example, reaction of a mixture of complexes **A** and **B** with a strong base followed by reaction with an alkyl halide leads irreversibly to complex **C** with an

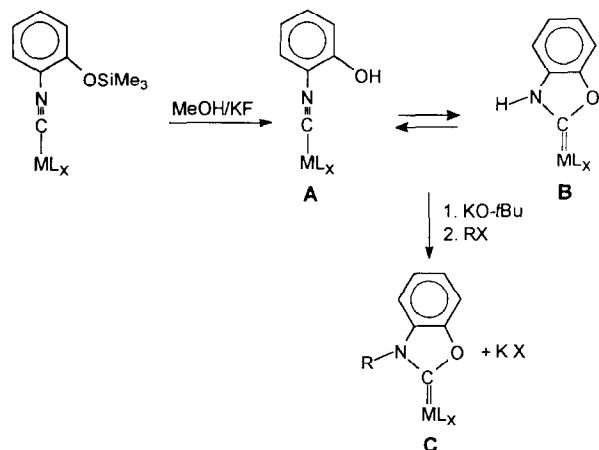
N-alkylated 1,2-dihydrobenzoxazol-2-ylidene ligand, even if the equilibrium between complexes **A** and **B** previously resided on the side of the isocyanide complex **A** [2b].

The reactivity of coordinated carbonyl or isocyanide ligands towards nucleophilic attack can be related to the wavenumber of stretching vibration or to the calculated force constant [5] of the CO or NC bond. The force constant expresses the amount of positive charge at the CO or CN carbon atom and is a measure of its susceptibility towards nucleophilic attack [6]. We have shown that with the 2-trimethylsiloxyphenyl isocyanide or the 2-hydroxyphenyl isocyanide ligands force constants below 1706 Nm^{-1} indicate stabilization of complexes of type **A** [2b]. If the force constant adopts a value higher than 1731 Nm^{-1} , the equilibrium between complexes **A** and **B** [2b] shifts mostly to the side of the ylidene complexes **B**.

Recently we became interested in ylidene and carbene complexes of the early transition metals in their highest oxidation state. Coordination of **1** to such an electron-poor metal center (e.g. Ti(IV)), which is unable to engage in $(d \rightarrow p)\pi$ backbonding, will give complexes with strongly activated isocyanides which upon cleavage of the Si–O bond should react to give complexes with the 1,2-dihydrobenzoxazol-2-ylidene ligand according to Scheme 1. In the case of the Ti(IV)

[☆] This paper is dedicated to Prof. Dr. H. Schumann on the occasion of his 60th birthday.

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Scheme 1. Reactions of coordinated 2-trimethylsiloxyphenyl isocyanide after Si–O bond hydrolysis.

complex this would lead to the first transition metal d^0 ylidene complex. Carbene complexes of the lanthanides were recently obtained by Schumann et al. [8] and by Arduengo et al. [9] by addition of a stabilized free carbene ligand (imidazol-2-ylidene type) to lanthanide precursors. The conversion of coordinated **1** into an ylidene ligand might prove advantageous compared to the direct synthesis of carbene complexes with imidazol-2-ylidene ligands [8,9] because the isocyanide route gives a N,O-stabilized carbene which is a better π -acceptor compared to a coordinated imidazol-2-ylidene [10] and because the 1,2-dihydrobenzoxazol-2-ylidene ligand can still be deprotonated and alkylated at the nitrogen atom [2b,3,4] of the five membered ring. The latter property can be used in a template synthesis to obtain complexes with multidentate carbene ligands, a type of complex recently synthesized by deprotonation of 1,1'-methylene-3,3'-dialkyldiimidazolium salts and reaction of the resulting dicarbene ligand with PdI₂ [11].

The first step in the synthesis of ylidene complexes of Ti(IV) according to Scheme 1 is the preparation of Ti(IV) complexes with the isocyanide **1**. In this contribution we describe the reaction of TiCl₄ with **1** at different temperatures and report the X-ray crystal structure of *cis*-[TiCl₄(**1**)₂] · C₆H₁₄.

2. Experimental section

All operations were carried out in dried freshly distilled solvents (dichloromethane over CaCl₂, *n*-hexane over LiAlH₄, toluene over sodium metal) in an argon atmosphere. Analytical data were obtained by using the following instruments: IR, Perkin-Elmer Model 983; NMR (¹H and ¹³C), Bruker AM 250 and AM 270; elemental analyses, Vario EL elemental analyzer at the Institut für Anorganische und Analytische Chemie der FU Berlin. The X-ray diffraction data were collected on

an Enraf-Nonius CAD-4 diffractometer fitted with a nitrogen cooling device for data collection at –100(2)°C. 2-Trimethylsiloxyphenyl isocyanide **1** was synthesized from benzoxazol (Aldrich) according to the method of Jutzi [12]. Freshly distilled commercial (Merck, 99.5%) TiCl₄ was used for all reactions.

2.1. Reaction of **1** with TiCl₄ at low temperature, synthesis of *cis*-tetrachlorobis(2-trimethylsiloxyphenyl isocyanide)titanium(IV) (**2**)

1.0 g (5.2 mmol) of **1** was dissolved in 15 ml of dry *n*-hexane in a Schlenk flask under argon. The colorless solution was cooled to –10°C and 0.49 g (2.6 mmol, 0.29 ml) of TiCl₄ was added dropwise. Upon addition of **1** the yellow complex **2** began to precipitate. After the addition was complete (10 min) the resulting suspension was stirred for an additional 10 min. The yellow precipitate was separated by filtration and washed with a little *n*-hexane. Recrystallisation of the solid from toluene/hexane (v:v, 1:3) gave air-sensitive (loss of *n*-hexane) crystalline **2** · C₆H₁₄. The hexane molecule can be removed in vacuo. Analytical data are for the solvent-free **2**. Yield: 1.34 g (90%). Anal. Calc. for C₂₀H₂₆Cl₄N₂O₂Si₂Ti (M = 572.30): C, 41.97; H, 4.58; N, 4.89. Found: C, 42.41; H, 4.72; N, 4.48. ¹H NMR (250 MHz, CDCl₃): δ 7.4–6.9 (m, 4 H, Ar-H); 0.33 (s, 9 H, Si-CH₃). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 152.65, 134.16, 132.93, 128.08, 121.81, 120.49 (Ar-C); 0.21 (Si-CH₃); the signal for the isocyanide carbon could not be observed. IR (CHCl₃): ν = 2200 (s, CN) cm^{–1}.

2.2. Reaction of **1** with TiCl₄ at room temperature, synthesis of the Ti(IV) complex (**3**)

For this synthesis the order of addition of the reagents was reversed compared to the preparation of **2**. In addition a 1:1 stoichiometry of the reagents was used. A 0.5 g (2.6 mmol) sample of **1** was added dropwise to a solution of 0.29 ml (2.6 mmol, 0.29 ml) TiCl₄ in 20 ml of toluene at room temperature. Approximately 5 min after the addition was complete the red reaction mixture brightened and an orange solid precipitated. The solution was filtered and the residue washed with 10 ml of *n*-hexane. Drying in vacuo left an air-sensitive orange powder **3**. Yield: 0.59 g. Anal. Calc. for a complex composed of TiCl₄ and one equivalent of **1** C₁₀H₁₃Cl₄NOSiTi (M = 381.00): C, 31.53; H, 3.44; N, 3.68. Found: C, 31.61; H, 3.46; N, 3.72. ¹H NMR (250 MHz, CDCl₃): δ 7.5–6.9 (m, 4 H, Ar-H); 0.41 (s, 9 H, Si-CH₃). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 150.12, 129.81, 126.39, 122.07, 119.38, 119.18 (Ar-C); 0.21 (Si-CH₃); the signal for the former isocyanide carbon atom could not be observed. IR (KBr): ν = 3260 (s, br) cm^{–1}; no absorption was found between 3000

and 1650 cm^{-1} , the region where an isocyanide stretching vibration absorption should appear. If the reaction was carried out in CH_2Cl_2 an orange material, identical to **3**, was isolated. Addition of more than one equivalent of **1** to a toluene solution of TiCl_4 led to a darker red solution from which again only **3** precipitated.

2.3. X-ray crystal structure determination of $2 \cdot \text{C}_6\text{H}_{14}$ [13]

Air-sensitive yellow crystals of $2 \cdot \text{C}_6\text{H}_{14}$ were obtained by recrystallization from toluene/hexane (1:3, v:v) at -20°C . Selected crystallographic details: size of data crystal $0.35 \times 0.21 \times 0.15\text{ mm}$, formula $\text{C}_{26}\text{H}_{40}\text{Cl}_4\text{N}_2\text{O}_2\text{Si}_2\text{Ti}$, $M = 658.48\text{ amu}$, monoclinic, space group $C2/c$, $a = 10.1233(12)$, $b = 20.657(4)$, $c = 15.777(2)\text{ Å}$, $\beta = 96.201(12)^\circ$, $V = 3279.9(15)\text{ Å}^3$, $Z = 4$, $\rho_{\text{exp}} = 1.32$, $\rho_{\text{calc}} = 1.333\text{ g cm}^{-3}$, Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ Å}$, monochromator graphite), $\mu(\text{Mo } K\alpha) = 6.83\text{ cm}^{-1}$. 2827 symmetry independent diffraction data were measured at $-100(2)^\circ\text{C}$ in the 2θ range $2\text{--}50^\circ$. Structure solution with Patterson and Fourier methods. The asymmetric unit contains 1/2 molecule of $\text{cis}[\text{TiCl}_4(\mathbf{1})_2]$ (located about a twofold axis, Ti on a special position) and 1/2 molecule *n*-hexane. The methyl carbon atoms of the hexane molecule (C100 and C105) reside on special positions on the twofold axis (site occupancy 0.5). Four general positions for methylene carbon atoms were identified in the asymmetric

unit. The positional parameters for these atoms were refined with site occupancy factors of 0.5. In addition, the methylene carbon position appears to be disordered. No attempts were made to resolve the disorder. Thus, the asymmetric unit contains 1/2 $\text{cis}[\text{TiCl}_4(\mathbf{1})_2]$ and 1/2 *n*-hexane, giving a total of $Z = 4$ units of $\text{cis}[\text{TiCl}_4(\mathbf{1})_2] \cdot \text{C}_6\text{H}_{14}$ in the unit cell. Positional parameters for all atoms (except for the hexane molecule) were refined with anisotropic thermal parameters. Hydrogens were added on calculated positions (no hydrogen positions were calculated for the hexane molecule) [$d(\text{C-H}) = 0.95\text{ Å}$] [14] with $B_{\text{eq(H)}} = 1.3B_{\text{eq(C)}}$. $R = 4.72$, $R_w = 7.63$, $\text{GOF} = 1.472$ for 2151 structure factors $F_o^2 \geq 3\sigma(F_o^2)$ and 162 refined parameters (no absorption correction was applied to the data). Neutral atomic scattering factors [15] were used and all scattering factors were corrected for anomalous dispersion [15]. All calculations were carried out with the MolEN program package [16]. Positional and equivalent thermal parameters for non-hydrogen atoms are listed in Table 1. A plot of the $\text{cis}[\text{TiCl}_4(\mathbf{1})_2]$ molecule is presented in Fig. 1.

3. Results and discussion

Addition of TiCl_4 to a solution of the isocyanide **1** in *n*-hexane yields the diisocyanide complex $\text{cis}[\text{TiCl}_4(\mathbf{1})_2]$ **2** in good yield (90%). This complex crys-

Table 1
Positional and equivalent isotropic thermal parameters for $2 \cdot \text{C}_6\text{H}_{14}$ ^a

Atom	x	y	z	$B_{\text{eq}} (\text{Å}^2)$
Ti	0.500	0.10766(4)	0.250	1.80(2)
Cl1	0.3633(1)	0.17186(5)	0.16737(6)	3.82(2)
Cl2	0.3590(1)	0.09341(5)	0.35139(6)	2.65(2)
Si	0.3144(1)	-0.13741(5)	0.39210(6)	2.04(2)
O	0.3515(3)	-0.1137(1)	0.2954(2)	2.46(5)
N	0.3523(3)	-0.0287(1)	0.1684(2)	1.73(6)
C1	0.3970(4)	0.0197(2)	0.1917(2)	1.79(7)
C2	0.3025(4)	-0.0909(2)	0.1495(2)	1.80(7)
C3	0.2564(4)	-0.1076(2)	0.0670(2)	2.00(7)
C4	0.2065(4)	-0.1692(2)	0.0502(2)	2.27(7)
C5	0.2057(4)	-0.2131(2)	0.1161(3)	2.44(8)
C6	0.2538(4)	-0.1966(2)	0.1987(2)	2.38(8)
C7	0.3024(4)	-0.1342(2)	0.2178(2)	2.03(7)
C8	0.4109(5)	-0.2108(2)	0.4241(3)	3.01(9)
C9	0.3680(4)	0.3487(2)	0.1127(3)	3.36(9)
C10	0.1338(5)	0.4321(2)	0.0390(3)	2.82(8)
C100	0.000	0.1291(9)	0.250	12.3(5)*
C101	0.024(2)	0.0584(8)	0.2152(9)	7.4(4)*
C102	0.026(1)	0.0483(8)	0.1019(9)	6.9(3)*
C103	0.022(2)	0.0932(9)	0.138(1)	8.4(4)*
C104	0.995(1)	0.0272(7)	0.3575(9)	6.3(3)*
C105	0.000	0.0095(9)	0.250	11.8(4)*

^a Estimated standard deviation are given in parentheses. The equivalent isotropic thermal parameter B_{eq} is defined as $8/3\pi^2[\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]$; starred atoms were refined with isotropic thermal parameters; C100–C105 are the positional parameters for the hexane molecule; Ti, C100 and C105 reside on special positions on the twofold axis.

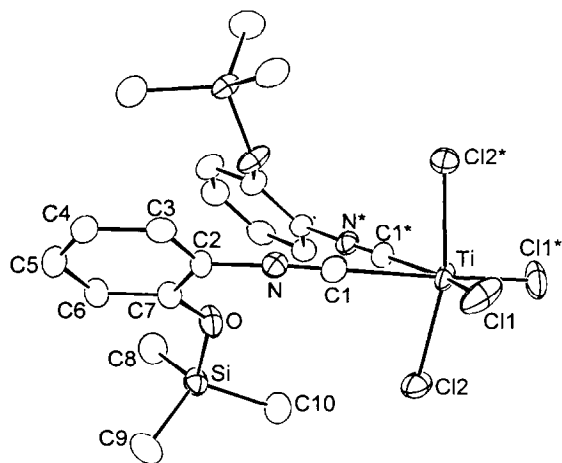


Fig. 1. ORTEP drawing of **2** in $2 \cdot \text{C}_6\text{H}_{14}$ showing 50% probability thermal ellipsoids and the atomic numbering scheme. Starred atoms represent transformed coordinates of the type $-x, y, 1/2 - z$. The titanium atom is located on a special position on the twofold axis.

tallizes with one molecule of *n*-hexane as $2 \cdot \text{C}_6\text{H}_{14}$. Its molecular structure was established by X-ray diffraction (Fig. 1). In **2**, the titanium atom is coordinated in a distorted octahedral fashion by four chlorine and two isocyanide carbon atoms in *cis*-positions.

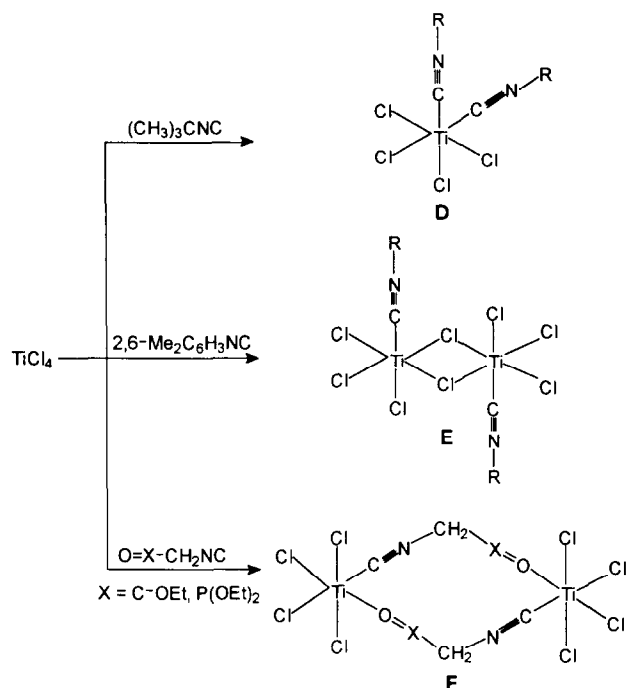
The reaction of isocyanides with TiCl_4 has been studied by Floriani et al. during their investigations of the Passerini reaction [17,18]. They found that this reaction, in contrast to previous reports [19], yields exclusively hexacoordinated isocyanide adducts of TiCl_4 . No isocyanide insertion into the Ti–Cl bond was observed. The isocyanide adducts belong, depending on the substitution of the isocyanide, to the structure types **D–F** (Scheme 2). Our investigations corroborate these results. Complex **2** belongs to structure type **D**. The formation of 1:2 (type **D**) and 1:1 (type **E**) adducts was attributed to steric factors, while the formation of complexes of type **F** results from the substitution of the isocyanide with an oxygen donor function. In our hands, reaction of 2 equivalents of **1** with TiCl_4 always gives the diisocyanide complex **2**. No 1:1 adduct was found and the formation of a complex of type **F** via coordination of the oxygen atom of the isocyanide to a titanium atom appears precluded owing to steric factors.

Bond length and angles in **2** fall in the range previously observed for isocyanide adducts of TiCl_4 . The Ti–C1 distance [2.242(4) Å, Table 2] compares well with the corresponding distances in complex **D** [2.240(8), 2.256(6) Å] [17] and **E** [2.235(6) Å] [18]. The C1–Ti–C1* angle in **2** is significantly smaller than 90°,

Table 2
Selected bond distances (Å) and angles (°) for $2 \cdot \text{C}_6\text{H}_{14}$ ^a

Atom	Atom	Distance	Atom	Atom	Atom	Angle
Ti	Cl1	2.2324(12)	Cl1	Ti	Cl1*	107.11(8)
Ti	Cl2	2.2752(10)	Cl1	Ti	Cl2	95.22(4)
Ti	Cl	2.242(4)	Cl1	Ti	Cl2*	93.60(4)
Si	O	1.684(3)	Cl1	Ti	Cl	90.60(10)
Si	C8	1.844(5)	Cl1	Ti	Cl*	162.25(10)
Si	C9	1.862(4)	Cl2	Ti	Cl2*	165.13(7)
Si	C10	1.843(4)	Cl2	Ti	C1	83.34(9)
O	C7	1.338(5)	Cl2	Ti	C1*	84.62(9)
N	C1	1.142(5)	C1	Ti	C1*	71.7(2)
N	C2	1.400(5)	O	Si	C8	108.9(2)
C2	C3	1.379(5)	O	Si	C9	109.0(2)
C2	C7	1.401(5)	O	Si	C10	103.3(2)
C3	C4	1.384(6)	C8	Si	C9	112.2(2)
C4	C5	1.381(6)	C8	Si	C10	111.7(2)
C5	C6	1.385(6)	C9	Si	C10	111.2(2)
C6	C7	1.400(5)	Si	O	C7	129.7(2)
			C1	N	C2	173.2(4)
			Ti	C1	N	172.9(3)
			N	C2	C3	120.5(3)
			N	C2	C7	116.9(3)
			C3	C2	C7	122.6(4)
			C2	C3	C4	119.4(4)
			C3	C4	C5	119.4(4)
			C4	C5	C6	121.1(4)
			C5	C6	C7	120.6(4)
			O	C7	C2	118.0(3)
			O	C7	C6	125.1(3)
			C2	C7	C6	116.8(4)

^a Estimated standard deviations of the last significant figure are given in parentheses; starred atoms represent transformed coordinates of the type $-x, y, 1/2 - z$.

Scheme 2. Isocyanide complexes of TiCl_4 .

a property noticed earlier in complexes of type **D** [17]. As expected for a d^0 complex, the isocyanide in **2** acts exclusively as σ -donor. This leads to a small *trans*-effect for the Ti–Cl distances [Ti–Cl1 2.2324(12), Ti–Cl2 2.2752(10) Å]. Similar shortening of the Ti–Cl bond *trans* to an isocyanide has been reported by Floriani et al. [17]. The isocyanide group in **2** deviates only slightly from linearity. Different structural features are observed for Ti(II) isocyanide complexes such as $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})(\text{CNCMe}_3)]$ [20]. The Ti–CN bond is shortened to 2.112(9) Å due to Ti–C ($d \rightarrow p$) π backbonding. In accordance with this observation, the backbonding causes the sp^2 character of the isocyanide nitrogen atom to increase and the C–N–C angle of the isocyanide deviates strongly from linearity [159.8(10)°] [20].

The fact that the isocyanide in **2** is a pure σ -donor is also reflected in the C–N stretching vibration frequency ($\nu = 2200 \text{ cm}^{-1}$). This value is significantly higher than for the free ligand ($\nu = 2120 \text{ cm}^{-1}$) [12]. For **2** we calculated a force constant [7] of 1843 Nm^{-1} , for the NC bond. This value is well above the value of 1731 Nm^{-1} which indicates immediate intramolecular nucleophilic attack and ylidene-formation if the Si–O bond is cleaved. Thus, the isocyanides in **2** are extremely activated for intra- or intermolecular nucleophilic attack.

Similar observations were made by Floriani et al., who noticed that exclusion of water is essential for the preparation of isocyanide adducts of TiCl_4 . Their complexes were also reactive towards intermolecular nucleophilic attack by water. The major difference between

complexes **D** and **2** is the fact that **2** is functionalized with a trimethylsiloxy group which can be hydrolyzed to allow controlled intramolecular nucleophilic attack of the thus liberated hydroxyl group at the isocyanide carbon as shown in Scheme 1. We have found that Si–O bond cleavage in complexes of type **2** does not require MeOH/KF but instead is achieved by reacting TiCl_4 with **1** at room temperature.

Addition of **1** to a toluene or dichloromethane solution of TiCl_4 causes formation of an orange product, **3**, which contains **1** and TiCl_4 in a 1 : 1 stoichiometry. The composition does not change if the isocyanide is added in a 2 : 1 ratio. Complex **3** is not an isocyanide complex, since no CN stretching vibration was observed in the IR spectrum. Microanalytical and spectroscopic data indicate the presence of a trimethyl and a benzoxazol group in **3**. The molecular structure of **3** has not been determined yet. In the absence of an isocyanide absorption in the IR spectrum it can be assumed that the Si–O bond was cleaved and that the liberated hydroxyl oxygen atom had attacked the isocyanide carbon atom. However, this does not necessarily lead to an ylidene complex. After the nucleophilic attack, the initially formed complex can rearrange to give a complex with an N-coordinated benzoxazol ligand, which we have already identified in reactions of $[\text{W}(\text{CO})_5(\mathbf{1})]$ [3a]. The trimethylsilyl group could be bound to the titanium atoms (in an octahedral complex) or have silylated the benzoxazol carbon atom. Since we cannot identify the signal for the benzoxazol or ylidene carbon atoms in the ^{13}C NMR spectrum of **3**, a definite statement about the molecular structure of this complex is not possible at this time. Further investigations, including ^{29}Si NMR investigations, are in progress.

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