15. Asymmetric *Diels-Alder* Reactions: X-Ray Crystal-Structure Analysis of [*N*-((*E*)-But-2-enoyl)bornane-10,2-sultam]tetrachlorotitanium[1])

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An X-ray diffraction analysis of the crystalline complex **2b** (ML_n = $TiCl_4$) shows a chelation of the carbonyl O-atom and the upper SO_2 O-atom by $TiCl_4$, a slightly pyramidal N-atom, and a π-face-stereoselective shielding of the C(α)-*Si* face by the $CH_2(3)$ group. The Ti-atom is in a pseudo-octahedral environment.

Introduction. – The antipodal, camphor-derived bornane-10,2-sultams have proved to be versatile chiral auxiliaries for asymmetric synthesis [1]. In particular, low-temperature, *Lewis*-acid-catalyzed inter- [2] and intramolecular [3] *Diels-Alder* reactions of *N*-enoylbornane-10,2-sultams **1** with 1,3-dienes display high *endo* and π-face stereoselectivities which have been applied to the enantioselective syntheses of (–)-1-*O*-methylloganin aglucone [4] and (–)-pulo'upone [5]. The corresponding additions of **1** and cyclopentadiene yielding **3** are exemplified in *Scheme 1* and *Table 1*. The rate enhancement and the

Scheme 1

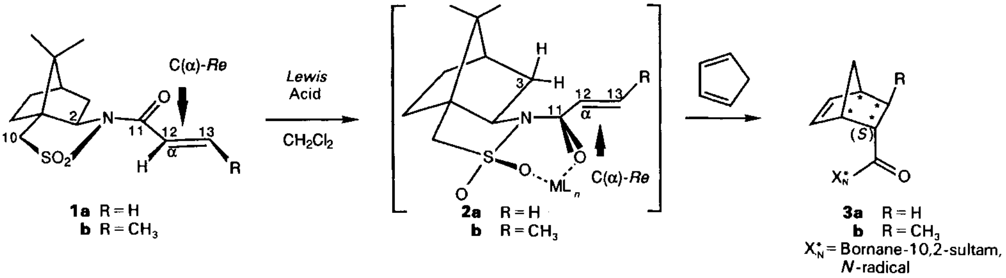

Table 1. *Asymmetric* Diels-Alder *Additions of Cyclopentadiene to* N-*Enoylsultams* **1** *Yielding* **3**

Entry	Series	R	*Lewis* acid (mol.-equiv.)		Reaction temp. [°] (time [h])	*endo* [%]	d.e. [%] of **3**	Yield [%] of **3**
1	**a**	H	none		+21 (72)	89	66	80
2	**b**	Me	none		+21 (96)	79	52	51
3	**a**	H	$BF_3 \cdot Et_2O$	(1.5)	–130 (6)	89	51	58
4	**a**	H	$TiCl_4$	(1.5)	–130 (6)	97	94	89
5	**a**	H	$EtAlCl_2$	(1.5)	–130 (6)	99.5	95	96
6	**b**	Me	$TiCl_4$	(0.5)	–78 (18)	99	93	98
7	**b**	Me	$EtAlCl_2$	(1.5)	–78 (18)	96	98	91

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[1]) Presented *(W.O.)* at the Annual Congress of the Royal Society of Chemistry, Canterbury, April, 1988.

high selectivity of the $TiCl_4$- and $EtAlCl_2$-promoted *Diels-Alder* reactions *(Entries 4–7)* were rationalized in terms of chelate **2** involving the dicoordinating *Lewis* acid ML_n, the carbonyl O-atom and the upper sulfonyl O-atom. Attack of the diene was then postulated to occur from the least hindered, lower, C(α)-*Re* face of the chelate **2** [2] *(Scheme 1)*. The lower diastereoselectivity observed with the monocoordinating $BF_3 \cdot Et_2O$ *(Entry 3)* is in accord with this argument.

The non-coordinated *N*-crotonoylbornane-10,2-sultam **1b**, however, was shown *via* an X-ray diffraction analysis to prefer a conformation where the NSO_2 and C=O groups are s-*trans* and the C=O/C(α)=C(β) bonds s-*cis* disposed [2] *(Fig. 1)*.

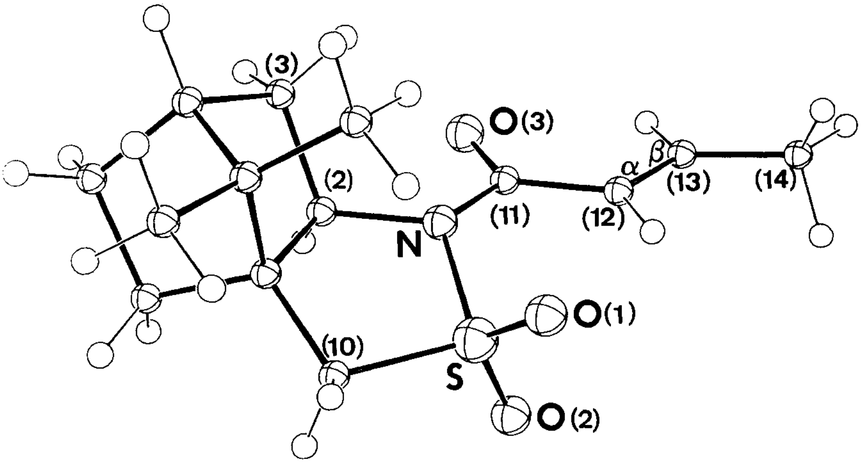

Fig. 1. *X-Ray crystal structure of non-coordinated sultam* **1b** [2]. Arbitrary numbering.

This preferred s-*trans* arrangement of the C=O and NSO_2 groups presumably results from minimization of dipole repulsions and has been found in all X-ray structure analyses of *N*-enoyl- and *N*-acylbornane-10,2-sultams studied to date [5–7]. ^{1}H-NMR measurements of **2b** in the presence of $[Eu(fod)_3]$ also show a predominant NSO_2/C=O s-*trans* and C=O/C(α)=C(β) s-*cis* disposition in solution [8].

Therefore, formation of the postulated chelate requires rotation about the N–C(O) amide bond to place the NSO_2 and C=O s-*cis* with respect to each other. Until now, this postulate was based on the following evidence. Addition of $TiCl_4$ (1 mol-equiv.) to **1b** in CH_2Cl_2 resulted in characteristic changes in the IR (particularly the asym. S=O stretching vibration) and ^{1}H-NMR spectra as displayed in *Table 2*. The ^{13}C-NMR spectrum revealed

Table 2. *IR- and ^{1}H-NMR-Spectral Comparison of* **1b** *and its* in-situ-*Prepared Chelate* **2b** ($ML_n = TiCl_4$)

Compound	IR (CH_2Cl_2; $\tilde{\nu}$ [cm^{-1}])		^{1}H-NMR (CD_2Cl_2; δ [ppm])[a])			
	C=O	SO_2 (asym.)	CH(13)	CH(12)	CH(2)	CH(10)
1b	1680	1132	7.05	6.50	3.90	3.45
2b ($ML_n = TiCl_4$)	1528	1110	7.69	6.28	4.15	3.76

[a]) Arbitrary numbering.

downfield shifts of 8 and 13 ppm for the carbonyl C-atom and C(13), respectively, whilst the C-resonance due to C(12) exhibited a 2.1 ppm upfield shift. These changes are in accord with previous spectroscopic studies on the effect of *Lewis* acids on other enone substrates [9].

It became important to verify the existence of such a chelate **2** in the light of highly π-face-selective additions of H_2 [10], OsO_4 [11], methylidenecyclopropane [12], and particularly, nitrile oxides [13] to enoylsultams **1** which proceed from the C(α)-*Re* face in the *absence* of a *Lewis* acid[2]. Chelates involving a SO_2 group are not known, whereas two X-ray-diffraction analyses of $TiCl_4$-chelated dicarbonyl compounds [14] [15] as well as limited evidence on the *Lewis* basicity of sulfones [16] have been reported.

We describe here the X-ray crystal-structure analysis of the 1:1 chelate **2b** formed by the addition of 1 mol-equiv. of $TiCl_4$ to a CH_2Cl_2 solution of *N*-crotonoylbornane-10,2-sultam **1b**. Suitable crystals of **2b**, obtained from CH_2Cl_2 either with or without slow addition of hexane (by diffusion) were grown and handled under an inert atmosphere due to their rapid decomposition on exposure to air.

Structure of the Chelate 2b ($ML_n = TiCl_4$). – The X-ray-diffraction analysis of **2b** ($ML_n = TiCl_4$) revealed the structure depicted in the ORTEP diagrams *(Fig. 2)*.

The Ti-atom is in a pseudooctahedral environment consisting of 4 Cl-atoms (two axial, two equatorial), the carbonyl O-atom and the upper, pseudoequatorial sulfone O-atom. The two axial Cl-atoms are bent towards the camphor moiety (Cl(3)–Ti–Cl(4) = 167.9(1)°) resulting in the distorted octahedral environment about the Ti-atom. The C(12)=C(13) bond is synperiplanar with the C=O group (torsional angle C(13)–C(12)–C(11)–O(3) = –9.0(1)°) which is, in turn s-*cis* with respect to the NSO_2 group. In contrast, the C=O and NSO_2 groups are s-*trans*-disposed in the parent *N*-crotonoylbornane-10,2-sultam **1b** (see above, *Fig. 1*). The N-atom in **2b** is slightly pyramidal as defined by its height above the plane of the remaining atoms which form the pyramid (C(11), C(2), and S)[3]. For the chelate **2b** ($ML_n = TiCl_4$), this height is calculated as 0.15 Å compared to 0.23 Å for non-coordinated **1b** and 0.51 Å for an ideal sp^3-hybridized N-atom (in the same environment with all the bond angles defined as 109.5°). An angle of 18.5° is observed between the lone pair on the N-atom (defined by a line perpendicular to the C(2), C(11), S plane) and the $2p_z$ orbital of the carbonyl group (defined by the line perpendicular to the N,O(3), C(12) plane). An almost identical value (18.1°) is found for the parent *N*-crotonoylbornane-10,2-sultam **1b** indicating a similar interaction between the N lone pair and the enoyl system in the chelate **2b** ($ML_n = TiCl_4$). Apparently, due to the constraint of the five-membered sultam ring, the lone pair on the N-atom does *not* bisect the O–S–O angle. This bisection is postulated to afford maximum delocalization over a sulfonamide linkage [18] and has been frequently observed in X-ray studies of conformationally flexible sulfonamides [19].

Table 3 shows a comparison of selected bond angles and distances of the chelate **2b** ($ML_n = TiCl_4$) *versus* the parent enoylsultam **1b**. Of note is the lengthening of the C=O bond (0.04 Å) and the shortening of the N–C(11) bond (0.03 Å) in the chelate **2b** ($ML_n = TiCl_4$) indicative of electron withdrawal by the Ti-atom and in accord with the ^1H- and ^{13}C-NMR shifts previously discussed. The S–N–C(11) valence angle is

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[2] For a discussion of this topicity and its possible stereoelectronic origin, see [8] [13].

[3] For an alternative approach to estimate the pyramidality of the N-atom, see [17].

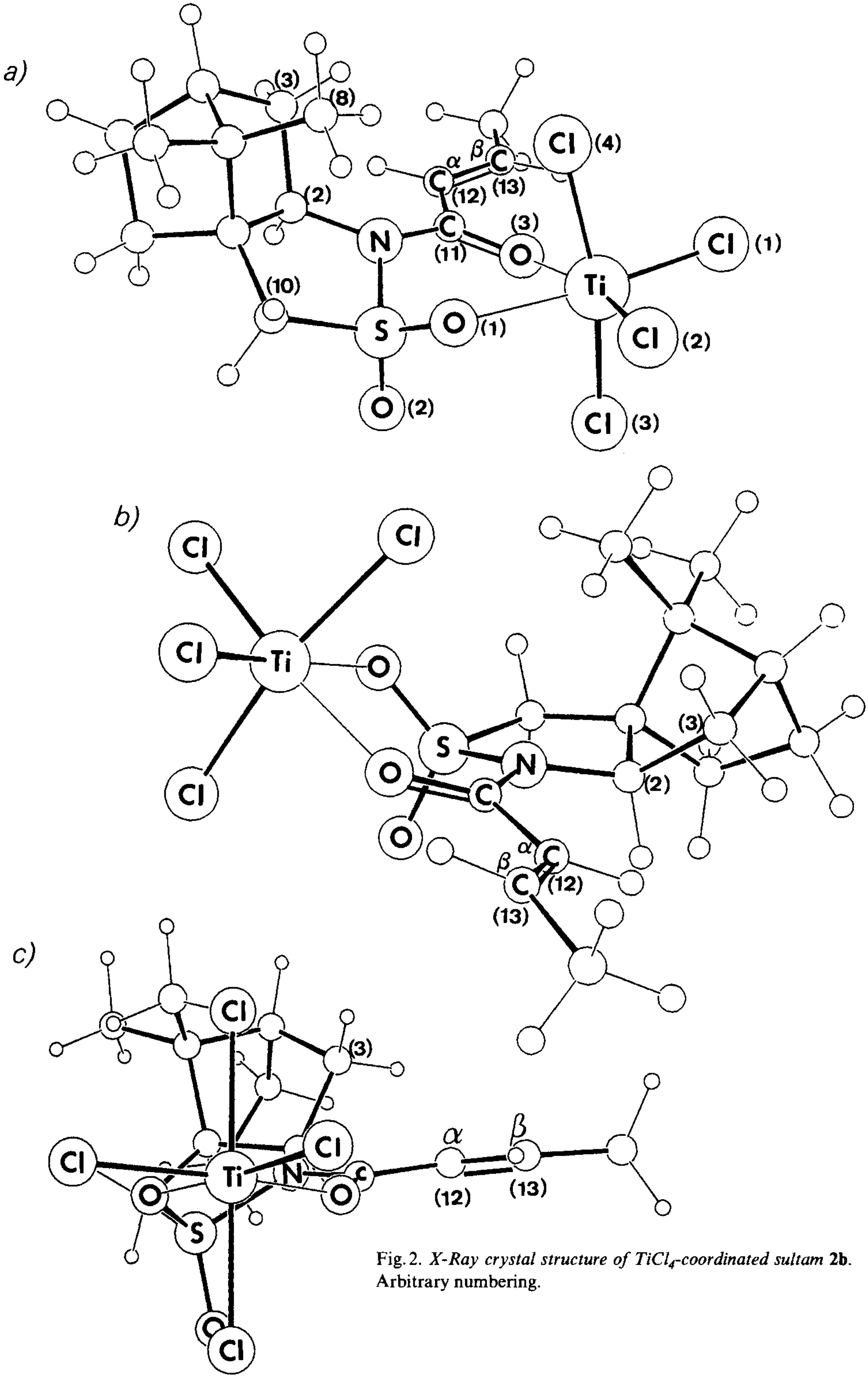


Fig. 2. *X-Ray crystal structure of $TiCl_4$-coordinated sultam* **2b**. Arbitrary numbering.

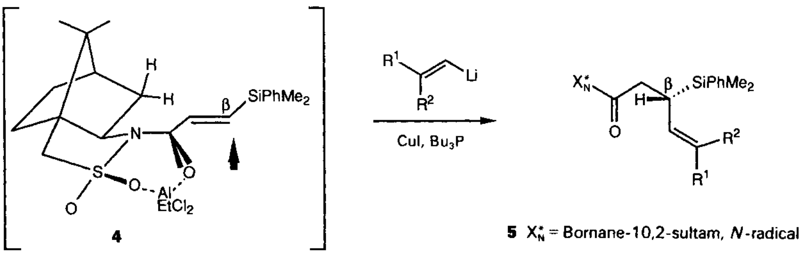
Table 3. *Comparison of Selected Bond Lengths and Bond Angles Between* N-*((*E*)-But-2-enoyl)bornane-10,2-sultam* **1b** *and its $TiCl_4$ Complex* **2b**

	1b	**2b** ($ML_n = TiCl_4$)	Difference
Bond Lengths [Å]			
S–O(1)	1.430(5)	1.447(4)	+0.017
S–O(2)	1.423(5)	1.424(5)	+0.001
S–N	1.694(4)	1.701(5)	+0.007
S–C(10)	1.795(7)	1.772(7)	–0.023
O(3)–C(11)	1.218(6)	1.260(7)	+0.042
N–C(11)	1.384(6)	1.356(8)	–0.028
C(11)–C(12)	1.463(8)	1.435(9)	–0.028
C(12)–C(13)	1.333(7)	1.318(9)	–0.015
Bond Angles [°]			
O(1)–S–O(2)	117.6(4)	117.1(3)	–0.5
S–N–C(11)	121.3(3)	117.4(4)	–3.9
O(3)–C(11)–N	118.4(5)	118.7(5)	+0.3
N–C(11)–C(12)	117.6(4)	119.2(5)	+1.6
C(11)–C(12)–C(13)	121.1(5)	122.6(6)	+1.5
C(12)–C(13)–C(14)	125.0(5)	126.1(7)	+1.1

decreased by 3.9° owing to the chelation. It also appears from the proximity of the H-atoms bonded to C(12) and C(2) (2.31 Å; *Fig. 2b*) that C(α)-substituted *N*-enoylbornane-10,2-sultams would be unlikely to form conformationally analogous chelates.

Discussion. – The described data support our initial postulate that $TiCl_4$ ($EtAlCl_2$, Me_2AlCl)-mediated *Diels-Alder* reactions of *N*-enoylbornane-10,2-sultams proceed by attack of the diene to the lower C(α)-*Re* face of chelates **2**. This rationale also applies to π-face-selective conjugate additions to enoylsultams **1** which were observed in the presence of a metal having at least two vacant coordination sites [1]. For example, Et_2AlCl-promoted additions of phosphine-stabilized cuprates to *N*-(β-silylenoyl)sultams **1** (R = $SiPhMe_2$; →**5**) proceed most plausibly *via* the aluminium chelate **4** [1b][20] *(Scheme 2)*.

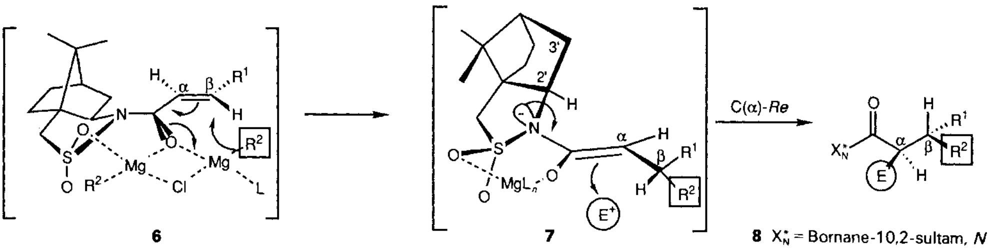
Scheme 2



5 X^{*}_{N} = Bornane-10,2-sultam, *N*-radical

Furthermore, Mg chelates **6** are probably involved in the 1,4-addition of *Grignard* reagents to enoylsultams **1** [7] *(Scheme 3)*. We, thus, assume that the second equiv. of R^2MgCl delivers R^2 to **6** from the bottom side. During this process, the C=O/C(α)=C(β) s-*cis* conformation apparently translates into the (*Z*)-configuration of 'enolate' **7**. Alkyla-

Scheme 3



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8 X^*_N = Bornane-10,2-sultam, *N*-rac

tion of the latter occurred again with high stereodifferentiation to give **8**, presumably *via* the depicted topicity. The origin of the π-face discrimination in this series of reactions remains to be defined.

Nevertheless, the X-ray crystal-structure analysis of the chelate **2b** ($ML_n = TiCl_4$) reveals that for the $TiCl_4$-mediated *Diels-Alder* reaction, the Cl-atoms play only a minor role in blocking the C(α)-*Si* face of the enoyl moiety[4]. More important seems to be the steric effect of the H_{exo}-C(3) which may interfere with the approach of a diene to the C(α) from the C(α)-*Si* face (*Fig. 2*). It is also possible that the two faces of the enoyl unit are rendered diastereotopic by virtue of the conformationally fixed N-atom lone pair and that the stereoselection observed is at least partially stereoelectronic in origin. The stereoelectronic effect of the N-atom lone pair in the stereoselective reactions of amide enolates and enamines with electrophiles has previously been invoked[2] [7] [21], but the extension of this postulate to *N*-enoyl systems has little precedent, and further work is underway in our laboratories to explore this effect.

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Experimental Part

General. All manipulations involving the preparation of **2b** ($ML_n = TiCl_4$) were carried out under N_2 in a glove box. Solvents were dried by distillation under N_2 from drying reagents (CH_2Cl_2(CaH_2, then P_2O_5), hexane(Na)) and were thoroughly degassed prior to introduction into the glove box. M.p.: *Kofler* hot stage; uncorrected. UV: *Kontron Uvikon 820*. IR: *Matteson Instruments Polaris* FT Spectrometer. ^{1}H-(200 MHz) and ^{13}C-NMR (50 MHz): standard tetramethylsilane (δ = 0 ppm).

*[*N*-((*E*)-But-2-enoyl)bornane-10,2-sultam]tetrachlorotitanium* (**2b**, $ML_n = TiCl_4$). *Method A. N*-((*E*)-2-Butenoyl)bornane-10,2-sultam (**1b**; prepared according to [11]; 300 mg, 106 mmol) was dissolved in CH_2Cl_2 (10 ml) in one of two cylindrical flasks which were linked at the top by a sinter tube. Addition of $TiCl_4$ (116 µl, 1 mol-equiv.) at r.t. gave a clear yellow soln. Hexane (10 ml) was placed in the other half of the apparatus which was then stoppered (*Teflon* rings) and allowed to stand at r.t. for several days. Slow diffusion of the solvents resulted in the formation of fine yellow crystals of **2b** ($ML_n = TiCl_4$).

Method B. $TiCl_4$ (38.7 µl, 1 mol-equiv.) was added at r.t. to a soln. of **1b** (100 mg, 0.35 mmol) in CH_2Cl_2 (2.0 ml) within an ampoule to give a clear yellow soln. The ampoule was removed from the glove box and immediately sealed under a stream of Ar. After several days at –5°, fine yellow crystals of **2b** ($ML_n = TiCl_4$) had formed. The crystals decomposed immediately on exposure to air. M.p. 175° (dec.). UV (sat. soln. in hexane): 213, 223, 260. IR (CH_2Cl_2): 2980*m*, 1639*s*, 1528*m*, 1350*s*, 1110*m*. ^{1}H-NMR (CD_2Cl_2): 0.99 (*s*, 3 H); 1.14 (*s*, 3 H); 1.32–1.60 (2 H);

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[4] For an X-ray structure analysis of tetrachloro[ethyl-*O*-acryloyllactate]titanium which indicates a stereoface-selective shielding of the dienophilic bond by a Cl-ligand, see [14].

1.92–2.20 (5 H); 2.14 (*dd*, J = 7, 1, 3 H); 3.76 (br. *s*, 2 H); 4.15 (br. *dd*, J = 7.5, 5.0, 1 H); 6.28 (br. *d*, J = 14.5, 1 H); 7.69 (br. *m*, 1 H). ^{13}C-NMR (CD_2Cl_2): 172.04 (*s*); 159.80 (*d*); 119.93 (*d*); 66.14 (*d*); 53.07 (*d*); 48.64 (*s*); 45.62 (*s*); 39.44 (*t*); 33.16 (*t*); 26.44 (*t*); 21.23 (*q*); 20.42 (*q*); 19.91 (*q*).

X-Ray Crystal-Structure Analysis of **2b** ($ML_n = TiCl_4$). A yellow crystal was transferred to a glass capillary and sealed under Ar. Cell parameters and reflection intensities were measured at r.t. on a *Philips-PW1100*

Table 4. *Crystal Data, Intensity Measurements, and Structure Refinement for* **2b** ($ML_n = TiCl_4$)

Formula	$C_{14}H_{21}NO_3S\cdot TiCl_4$	$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.60
Molecular weight	473.1	No. of measured reflections	2082
Crystal system	Orthorhombic	No. of observed reflections	1670
Space group	$P2_12_12_1$	Criterion for observed	$\lvert F_o\rvert > 4\sigma(F_o)$
Crystal size [mm]	0.22 × 0.22 × 0.40	No. of parameters	217
a [Å]	7.8993(12)	Refinement (on F)	full-matrix
b [Å]	12.273(3)	Weighting scheme	$\omega = 1$
c [Å]	20.567(5)	H-atoms	calculated
V [Å^3]	1993.9(5)	Max. and average Δ/σ	0.016, 0.003
Z	4	Max. and min. $\Delta\rho$ [eÅ^{-3}]	0.40, −0.48
D_c [g·cm^{-3}]	1.58	S	1.32
F_{000}	968	R [%]	3.8
μ [mm^{-1}]	1.078		

Table 5. *Selected Bond Lengths* [Å], *Bond Angles, and Torsional Angles* [°] *for* **2b** ($ML_n = TiCl_4$)

Ti–Cl(1)	2.198(2)	S–C(10)	1.772(7)
Ti–Cl(2)	2.234(2)	O(3)–C(11)	1.260(7)
Ti–Cl(3)	2.256(2)	N–C(11)	1.356(8)
Ti–Cl(4)	2.314(2)	C(1)–C(2)	1.544(9)
Ti–O(1)	2.330(5)	C(1)–C(10)	1.525(10)
Ti–O(3)	2.027(4)	C(11)–C(12)	1.435(9)
S–O(1)	1.447(4)	C(12)–C(13)	1.318(9)
S–O(2)	1.424(5)	C(13)–C(14)	1.473(11)
S–N	1.701(5)		
Cl(1)–Ti–Cl(2)	99.74(8)	Ti–O(3)–C(11)	141.8(4)
Cl(1)–Ti–Cl(3)	96.31(8)	O(1)–S–O(2)	117.1(3)
Cl(1)–Ti–Cl(4)	93.34(8)	O(1)–S–N	107.3(3)
Cl(1)–Ti–O(1)	174.77(14)	O(1)–S–C(10)	112.7(3)
Cl(1)–Ti–O(3)	97.84(14)	O(2)–S–N	110.6(3)
Cl(2)–Ti–Cl(3)	93.26(8)	O(2)–S–C(10)	110.9(3)
Cl(2)–Ti–Cl(4)	92.24(8)	N–S–C(10)	96.2(3)
Cl(2)–Ti–O(1)	83.52(12)	S–N–C(2)	111.6(4)
Cl(2)–Ti–O(3)	162.38(14)	S–N–C(11)	117.4(4)
Cl(3)–Ti–Cl(4)	167.92(9)	C(2)–N–C(11)	128.0(5)
Cl(3)–Ti–O(1)	87.54(13)	O(3)–C(11)–N	118.7(5)
Cl(3)–Ti–O(3)	86.06(14)	O(3)–C(11)–C(12)	122.1(5)
Cl(4)–Ti–O(1)	82.41(13)	N–C(11)–C(12)	119.2(5)
Cl(4)–Ti–O(3)	85.44(14)	C(11)–C(12)–C(13)	122.6(6)
O(1)–Ti–O(3)	78.85(17)	C(12)–C(13)–C(14)	126.1(7)
Ti–O(1)–S	121.4(3)		
O(1)–S–N–C(11)	63.5(5)	C(2)–N–C(11)–C(12)	−5.4(9)
O(2)–S–N–C(11)	−65.3(5)	C(10)–C(1)–C(2)–N	−27.0(7)
C(10)–S–N–C(11)	179.7(5)	C(2)–C(1)–C(10)–S	14.4(7)
S–N–C(2)–C(1)	28.7(6)	O(3)–C(11)–C(12)–C(13)	−8.7(10)
S–N–C(11)–O(3)	−25.6(7)	N–C(11)–C(12)–C(13)	172.8(6)
S–N–C(11)–C(12)	153.0(5)	C(11)–C(12)–C(13)–C(14)	174.1(7)

diffractometer (MoK_α). The structure was solved by direct methods (MULTAN 84) [22] and refined by full-matrix least-squares analysis (XTAL) [23]. The crystal data, intensity measurements, and structure refinement are given in *Table 4*. *Table 5* describes selected bond lengths, bond angles, and torsional angles some of which are compared with those of non-coordinated **1b** (*Table 3*). Crystallographic data have deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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