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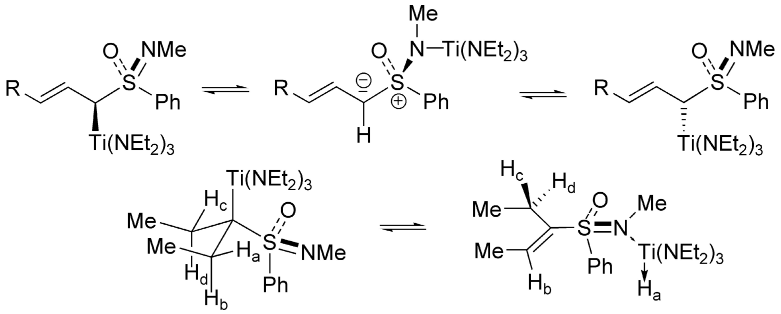

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Abstract: Variable-temperature ^{1}H and ^{13}C NMR spectroscopy of the sulfonimidoyl-substituted allyltitanium(IV) complexes *E*-**1a**−**c** and *Z*-**1a**−**c**, which carry diethylamino groups at the Ti atom, revealed a fast 1,3-C,N-shift of the Ti atom, leading to an equilibrium between the epimeric Cα-titanium allyl complexes **A** and **C** and the *N*-titanium allyl aminosulfoxonium ylide **B**. Based on these findings a model for the reactions of *E*-**1a**−**c** and *Z*-**1a**−**c** with aldehydes is proposed, which features regio- and diastereoselective reactions of the *N*-titanium ylide **B** at the α-position and the Cα-titanium complex **A** at the γ-position. Model ab initio calculations of the methylene and allyl (dimethylamino)sulfoxonium ylides **10** and **14**, respectively, revealed short Cα−S bonds, a stabilization by both electrostatic interaction and negative hyperconjugation, and a low Cα−S rotational barrier. The ylides preferentially adopt Cα−S and Cα−N conformations in which the lone pair orbital at the Cα atom is periplanar to the S═O bond and that at the N atom periplanar to the Cα−Ph bond. Variable-temperature NMR spectroscopy of the sulfonimidoyl-substituted alkyltitanium(IV) complex **16**, which carries diethylamino groups at the Ti atom, revealed a dynamic behavior leading to a complete topomerization of all four methylene hydrogens of the Cα-ethyl groups. Two fast processes are held responsible for the topomerization of the hydrogens of **16**. The first one is a reversible intramolecular β-hydride elimination/alkene-Ti−H insertion with the intermediate formation of a complex between (Et$_2$N)TiH and a 1-alkenyl sulfoximine, and the second one consists of a reversible 1,3-C,N-shift of the Ti atom in combination with a Cα−S bond rotation. Interestingly, the room-temperature NMR spectra of the corresponding sulfonimidoyl-substituted alkyltitanium(IV) complex **17**, which carries isopropoxy groups at the Ti atom, give no indication of a similar dynamic behavior of this complex.

Introduction

Chiral allyltitanium complexes have emerged as valuable reagents for the enantioselective allylation of aldehydes and imines.[1,2] Particularly useful are allyltitanium complexes that carry a heteroatom substituent since they allow the transfer of both an allyl moiety and a functional group, amenable to further synthetic transformations. Noteworthy examples are the sulfonimidoyl-substituted allyltitanium(IV) complexes **I** and **IV**[3] (Scheme 1), which have found application in the asymmetric synthesis of a number of compounds including γ,δ-unsaturated α-amino acids,[4a] bicyclic α-amino acids,[4b,c] γ-hydroxy β-amino

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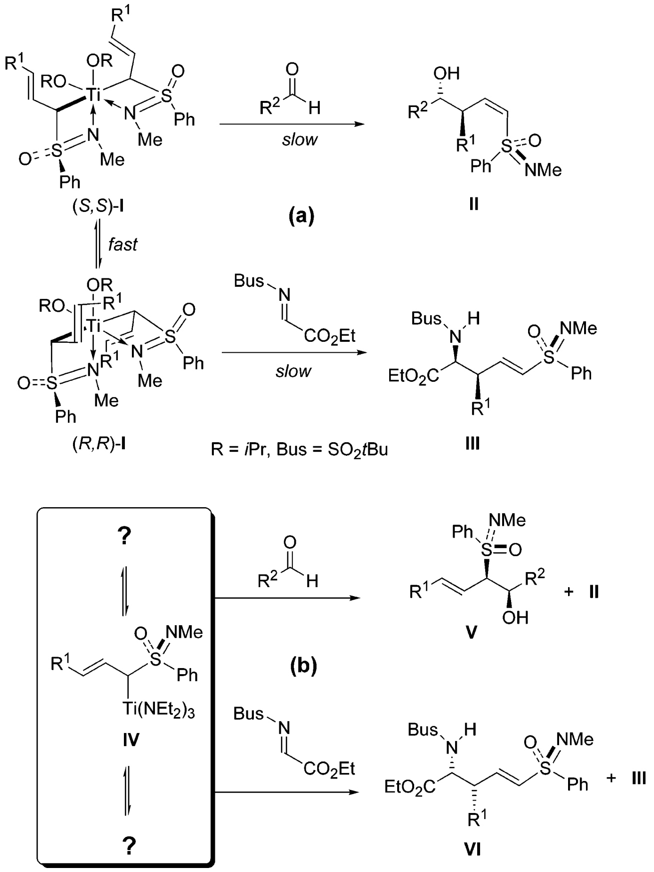
Scheme 1 (a) Reactivity Model for Bis(allyl)titanium Complexes **I**, Aldehydes, and *N*-Bus Imino Esters, and (b) Reactivity of the Mono(allyl)titanium Complexes **IV** toward Aldehydes and *N*-Bus Imino Esters



acids,[4d,e] 2,3-dihydrofurans,[4f] tetrahydrofurans,[4f] cycloalkenyl oxiranes,[4g] homopropargylic alcohols,[4h] homoallyl alcohols,[4i] and unsaturated prolines.[4j,5] Complexes **I** and **IV**, which owe their synthetic versatility primarily to the almost unique features of the sulfonimidoyl group,[1c,f] show a synthetically very useful and mechanistically interesting diversity in the regio- and diastereoselectivities of their reactions with aldehydes[3a−c,e,4e−i] and *N*-sulfonyl imino esters.[3d,4a−c,j,6a] The bis(allyl)titanium(IV) complexes **I** react with both aldehydes and *N*-*tert*-butylsulfonyl (Bus) imino ester, independent of the substitutents R^1 and R^2, with high diastereo- and regioselectivities at the γ-position to give the *anti*-configured homoallyl alcohols **II** and the *syn*-configured homoallyl amines **III**, respectively (Scheme 1a). Structural studies of **I** had revealed octahedral complexes with a η^2-coordination of the allylsulfoximine ligands via the C and N atom to the Ti atom.[3c] Complexes **I** have a low configurational stability of the Cα atoms, giving rise to a mixture of the diastereomers (*S*,*S*)-**I** and (*R*,*R*)-**I**. These features of **I** and in particular the coordination of the Ti atom to the Cα atom led to the proposal of a reactivity scheme, the key elements of which are highly regio- and diastereoselective reactions of (*S*,*S*)-**I** with aldehydes, similarly selective reactions of (*R*,*R*)-**I** with the *N*-Bus imino ester, and a fast equilibration of the diastereomeric titanium complexes.[3c]

In contrast, the mono(allyl)titanium(IV) complexes **IV** react with aldehydes with high diastereoselectivity at the α-position to afford the regioisomeric *syn*-configured homoallyl alcohols **V** (Scheme 1b). Remarkably, the regioselectivity is characteristically dependent on the size of both substituents R^1 and R^2. While in the case of larger substituents a highly regio- and diastereoselective α-hydroxyalkylation of **IV** with formation of **V** occurs, smaller substituents result in both a highly diastereoselective α- and γ-hydroxyalkylation with formation of **V** and **II**, respectively. However, complexes **IV** that contain a *Z*-configured double bond do not show such a substituent dependency of their regioselectivity. Instead they afford, irrespective of the substituents R^1 and R^2, the corresponding *Z*-configured homoallyl alcohols **V** with high regio- and diastereoselectivities. In all reactions of **IV** and its *Z*-configured isomers at the α-position the configuration of the double bond is fully retained in the homoallyl alcohols. Finally, the reactions of complexes **I** and **IV** with the *N*-Bus imino ester are characterized by a dichotomy not in regio- but diastereoselectivity. Complexes **IV** deliver the diastereomeric *syn*-configured homoallyl amines **VI** together with small amounts of **III**, both, however, with high diastereoselectivities.[6b]

The complementary diversity of the reactivity of **I** and **IV** and the substituent dependency of the regioselectivity of the reactions of **IV** with aldehydes pointed to a structure and dynamics of the mono(allyl)titanium complexes being different from those of the bis(allyl)titanium complexes. A preliminary NMR spectroscopic investigation of **IV** (R^1 = *i*Pr)[3b] gave a hint of a dynamic behavior of the mono(allyl)titanium complex, involving several unidentified equilibrium species. On the basis of the observation of an equilibrium between (*S*,*S*)-**I** and (*R*,*R*)-**I**, which ought to involve a sort of a reversible C,N-shift of the Ti atom, it was speculated that the Ti atom of **IV** could perhaps undergo a shift between the Cα, Cγ, N, and O atom with formation of the corresponding isomeric allyltitanium complexes.[3c] Unfortunately, with the exception of **I**, direct information on the structure and dynamics of heteroatom-substituted allyltitanium complexes including a possible C,-heteroatom-shift of the Ti atom, which could have served as an example for **IV**, is not available.[1,2] Given the high synthetic importance of these titanium complexes, this void is somewhat surprising. Therefore, a study of **IV** was desirable in order to gain information about their structure and dynamics and to eventually develop a reactivity model for the mono(allyl)-titanium complexes of the type formulated for **I**.

In this article we describe an NMR spectroscopic investigation of the allyltitanium(IV) complexes **IV**, which led to the detection of a metallotropic shift of these complexes and gave information on the structure of the equilibrium components, one of which is a novel *N*-titanium allyl aminosulfoxonium ylide. These results were supplemented by model ab initio calculations of allyl and alkyl (dimethylamino)sulfoxonium ylides. It is furthermore described that an extension of the studies of the allyl

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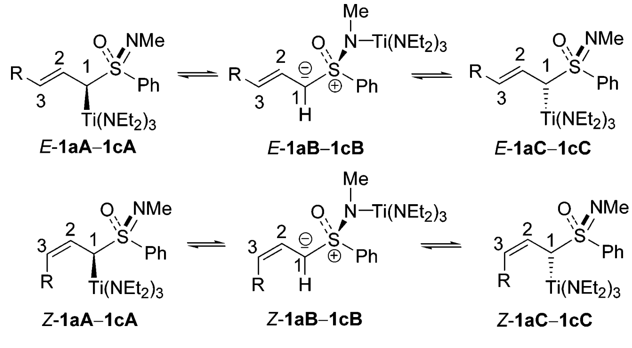
(5) For the synthesis of chiral sulfonimidoyl-substituted allyl tris(isopropoxy)-titanium(IV) complexes, which carry a further chiral substituent at the N atom, and their highly successful application in asymmetric synthesis, see: (a) Reggelin, M.; Weinberger, H. *Angew. Chem.* **1994**, *106*, 489−491; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 444−446. (b) Reggelin, M.; Weinberger, H.; Gerlach, M.; Welcker, R. *J. Am. Chem. Soc.* **1996**, *118*, 4765−4777. (c) Reggelin, M.; Weinberger, H.; Heinrich, T. *Liebigs Ann./Recl.* **1997**, 1881−1886. (d) Reggelin, M.; Heinrich, T. *Angew. Chem.* **1998**, *110*, 3005−3008; *Angew. Chem., Int. Ed.* **1998**, *37*, 2883−2886. (e) Reggelin, M.; Gerlach, M.; Vogt, M. *Eur. J. Org. Chem.* **1999**, 1011−1031.

(6) (a) Cyclic complexes of type **I** and **IV**, whose double bond is embedded in a carbocyclic ring, show the same diversity in reactivity. (b) Gais, H.-J.; Babu, G. S., unpublished.

Scheme 2. Fluxional Behavior of the *E*- and *Z*-Configured Allyltitanium Complexes *E*-**1a**−**c** and *Z*-**1a**−**c**, Respectively



a: R = *i*Pr, **b**: R = *c*C_6H_{11}, **c**: R = Me

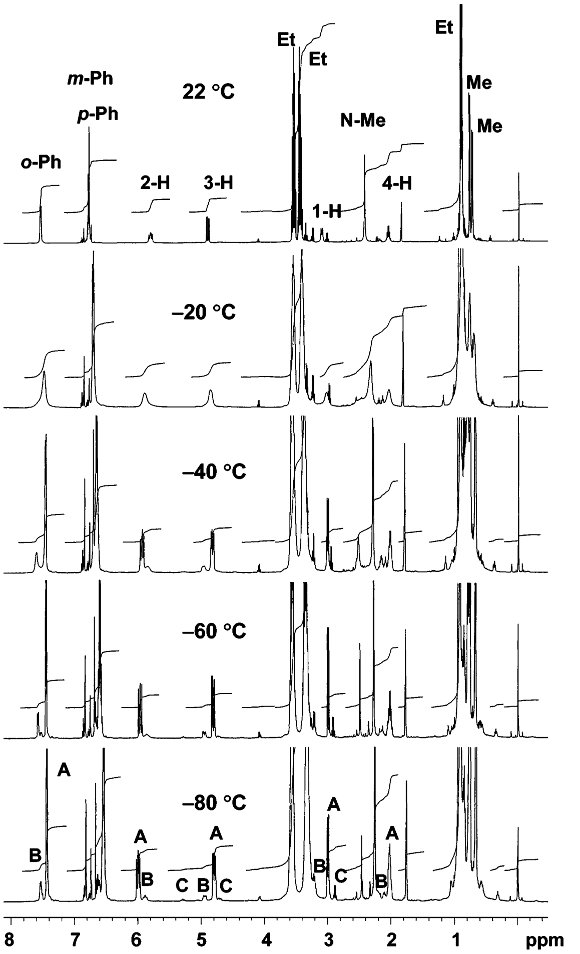


Figure 1. Temperature-dependent 500 MHz ^{1}H NMR spectra of the allyltitanium complex *E*-**1a** in [D_8]-toluene.

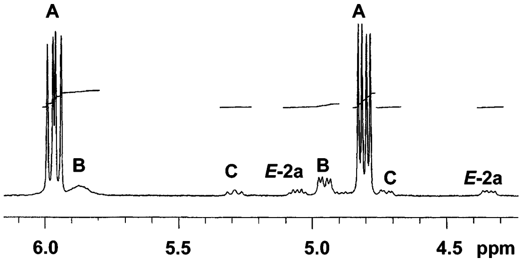


Figure 2. 500 MHz ^{1}H NMR spectrum of the double-bond hydrogen region of the titanium complex *E*-**1a** in [D_8]-toluene at −60 °C.

complexes **IV** to sulfonimidoyl-substituted alkyltitanium(IV) complexes led to the NMR spectroscopic observation of a further interesting dynamic behavior which is believed to be an example of a reversible intramolecular β-Ti−H elimination/reinsertion of an alkyltitanium(IV) complex.

Results and Discussion

I. Allyltitanium(IV) Complexes. Synthesis. The isopropyl-, cyclohexyl-, and methyl-substituted titanium complexes *E*-**1a**−**c** and *Z*-**1a**−**c**,[3a,c,7] respectively, were selected for the present study (Scheme 2). The reactivity of these complexes toward aldehydes and the *N*-Bus imino ester had already been determined,[3,4] and the variation of the substituent of the double bond should serve to delineate its influence upon the structure and dynamic behavior of the mono(allyl)titanium complexes. Treatment of the corresponding lithiated allyl sulfoximines with 1.1 equiv of $ClTi(NEt_2)_3$ first at −78 °C and then at room temperature gave the titanium complexes *E*-**1a**−**c** (see Scheme S1, Supporting Information). Solutions of complexes *E*-**1a**−**c** in [D_8]-toluene and [D_8]-tetrahydrofuran ([D_8]-THF) were prepared by decanting the ethereal solutions of the complexes from LiCl, removal of the solvent in a vacuum, and dissolving the residue in the deuterated solvent. Similarly, solutions of the *Z*-configured titanium complexes *Z*-**1a**−**c** in [D_8]-toluene and [D_8]-THF were prepared from the corresponding lithiated allyl sulfoximines through titanation with $ClTi(NEt_2)_3$. In some cases the solutions of *E*-**1a**−**c** and *Z*-**1a**−**c** contained small amounts of the corresponding starting allyl sulfoximine. However, this did not hamper the structural investigation.

NMR Spectroscopy of *E*-Configured Complexes. The isopropyl-substituted complex *E*-**1a** was investigated as a role model in more detail. The ^{1}H NMR spectra of complex *E*-**1a** in [D_8]-toluene (Figure 1) and [D_8]-THF (not shown) at room temperature showed only one set of sharp signals corresponding to an *E*-configured η^1-mono(allyl)titanium(IV) complex, the Ti atom of which is attached to the C-1 atom.[1f,3a,c,d] All signals were assigned by ^{1}H,^{1}H COSY experiments. Upon cooling the solution of *E*-**1a** in [D_8]-toluene gradually to −80 °C, a line-broadening occurred and several fully reversible coalescence phenomena were observed. At −20 °C all signals were significantly broadened, and two sets of signals appeared at −40 °C. Finally, three sets of signals were observed at −60 °C (Figure 2). The three signal sets were assigned to the Cα-titanium allyl complex *E*-**1aA**, the *N*-titanium allyl ylide *E*-**1aB**, and the epimeric Cα-titanium allyl complex *E*-**1aC**, respectively, on the basis of the ^{1}H chemical shifts, coupling constants, integral ratios (Table 1), and the ^{13}C NMR data described later. EXSY experiments of *E*-**1a** at −60 °C showed that *E*-**1aA**, *E*-**1aB**, and *E*-**1aC**, which were present in a ratio of 84:13:3 (Table 2), were in equilibrium with each other. The low-temperature NMR spectra indicated the presence of further species in trace amounts, the structures of which could, however, not unambiguously be assigned.

The signal assignment for *E*-**1aA**, *E*-**1aB**, and *E*-**1aC** was carried out at −80 °C by ^{1}H,^{1}H COSY experiments. These experiments also allowed the determination of the chemical shift for 1-H of *E*-**1aB**, the signal of which is hidden under the signals of the ethyl groups. The decisive chemical shifts and the coupling constants of the allyl moieties of the three equilibrium components are listed in Table 1. The variable-temperature ^{1}H NMR spectroscopy of *E*-**1a** in the potentially coordinating solvent [D_8]-THF also revealed the existence of the three

Table 1. Selected ^{1}H NMR Data (500 MHz) of the Equilibrium Components **A**−**C** of the Allyltitanium(IV) Complexes *E*-**1a**−**c** in [D$_8$]-Toluene at Low Temperatures[a]

		A			B			C		
complex	R	1-H	2-H	3-H	1-H	2-H	3-H	1-H	2-H	3-H
E-**1a**[b]	*i*Pr	3.26	6.26	5.07	3.5	6.15	5.21	3.26	5.55	4.97
		11.0	*14.8, 11.0*	*14.8, 6.9*	*c*	*13.9, 12.2*	*13.9, 5.8*	*c*	*14.4, 12.8*	*14.4, 5.7*
E-**1a**[d]	*i*Pr	3.12	5.81	4.94	3.52	5.83	4.94	3.30	5.82	4.94
		10.6	*15.2, 10.6*	*15.2, 7.0*	*c*	*c*	*c*	*10.4*	*c*	*c*
E-**1b**[e]	*c*C$_6$H$_{11}$	3.25	6.24	5.07	*f*	6.16	5.18	*f*	5.57	4.99
		10.7	*15.0, 10.7*	*15.0, 7.3*		*14.8, 12.0*	*14.8, 6.4*		*14.7, 11.1*	*14.7, 6*
E-**1c**[g]	Me	3.23	6.20	5.03	*f*	6.2	5.07	*f*	*f*	*f*
		10.6	*14.6, 11.0*	*14.6, 6.5*		*c*	*c*			

[a] Numbers in italics are averaged coupling constants. [b] At −80 °C. [c] Not determined. [d] In [D$_8$]-THF at −80 °C. [e] At −75 °C. [f] Not detected. [g] At −60 °C.

Table 2. Composition of the Equilibrium Components **A**−**C** of the Allyltitanium(IV) Complexes *E*-**1a**−**c** and *Z*-**1a**−**c** at Low Temperatures

complex	R	*T* (°C)	**A** (%)	**B** (%)	**C** (%)
E-**1a**	*i*Pr	−60	84	13	3
E-**1b**	*c*C$_6$H$_{11}$	−75	86	12	2
E-**1c**	Me	−60	82	12	6
Z-**1a**	*i*Pr	−78	36	64	*a*
Z-**1b**	*c*C$_6$H$_{11}$	−60	33	67	*a*
Z-**1c**	Me	−60	34	66	*a*

[a] Not observed.

equilibrium species *E*-**1aA**, *E*-**1aB**, and *E*-**1aC**. The chemical shift differences were, however, smaller than those in [D$_8$]-toluene, and the determination of all relevant spectral parameters was thus not possible. Therefore, the further NMR investigations of complexes *E*-**1a**−**c** were carried out in [D$_8$]-toluene. The ^{1}H NMR spectra of the cyclohexyl- and methyl-substituted complexes *E*-**1b** and *E*-**1c**, respectively, in [D$_8$]-toluene at room temperature each also showed only one set of sharp signals indicative of a *E*-configured η^{1}-mono(allyl)-titanium(IV) complex, the Ti atom of which is attached to the C-1 atom.[1f,3a,c,d] The signals in the ^{1}H NMR spectra of both complexes were assigned by ^{1}H,^{1}H COSY experiments. Variable-temperature ^{1}H NMR spectroscopy of complexes *E*-**1b** and *E*-**1c** also revealed in these cases the existence of equilibria composed of the three species *E*-**1bA**, *E*-**1bB**, and *E*-**1bC** in a ratio of 86:12:2 and of *E*-**1cA**, *E*-**1cB**, and *E*-**1cC** in a ratio of 82:12:6, respectively. Determination of the chemical shifts for 1-H of the equilibrium components *E*-**B** and *E*-**C** of complexes *E*-**1b** and *E*-**1c** was not carried out at low temperatures by ^{1}H,^{1}H COSY experiments because of their sufficient characterization by the other NMR data. Further long-term NMR experiments at low temperature were not undertaken for the determination of the other NMR parameters of *E*-**B** and *E*-**C** because of the similarity between complexes *E*-**1a**, *E*-**1b**, and *E*-**1c** and the slow but complicating *E*/*Z* isomerization of the later complex (vide infra).

The chemical shifts recorded for the equilibrium components *E*-**A** and *E*-**C** of complexes *E*-**1a**−**c** compare favorably with those of the bis(allyl)titanium(IV) complexes **6**[3b,c] and **7**[3d] and the mono(allyl)titanium(IV) complex **8**[1f] (Table 3), all of which exhibit a Cα−Ti bond. Table 1 shows similar chemical shifts for the allyl moieties of all three equilibrium components *E*-**A**, *E*-**B**, and *E*-**C** of complexes *E*-**1a**−**c**. A comparison of the NMR data of the titanium complexes *E*-**1aA**, *E*-**1aB**, and *E*-**1aC** with those of sulfoximine *E*-**2a** and the lithiated sulfoximines *E*-**3a**, **4**, and **5** reveals similar changes in the chemical shifts upon replacement of 1-H of the starting allyl sulfoximines by a Li atom and a Ti atom.[1f,8] The only major exemption is the chemical shift of 3-H. While the hydrogens at the 3-position of *E*-**2a**, *E*-**1aA**, *E*-**1aB**, and *E*-**1aC** have similar chemical shifts, the chemical shift for 3-H of the lithium salt *E*-**3a**, is significantly smaller. These chemical shift differences indicate that there exists in the titanium derivatives *E*-**1aA** and *E*-**1aC**, in contrast to the lithium derivatives *E*-**3a**, **4**, and **5**, no significant delocalization of the negative charge in the allyl moieties because of the lower polarity of the C−Ti bond. The absence of an upfield shift of the signal for 3-H of the ylide *E*-**1aB** as compared to the lithiated sulfoximines *E*-**3a**, **4**, and **5** may perhaps be ascribed to the powerful electron-withdrawing/polarizing effect the *N*-titanium aminosulfoxonium group exerts.[9] While the C-1 atoms of complexes *E*-**A** and *E*-**C** should have a tetrahedral coordination geometry, those of the allyl ylides *E*-**B** are expected to have a coordination geometry being close to planar (vide infra). This difference in the coordination geometry of the complexes is reflected in a low-field shift of 1-H of the ylides *E*-**B** as compared to the tetrahedral complexes *E*-**A** and *E*-**C**. Interestingly, while the chemical shifts for 1-H and 3-H of complexes *E*-**A** and *E*-**C** in [D$_8$]-toluene are very similar, those for 2-H are significantly different. It will be shown later how this difference can be used for an assignment of their configuration. Not only the chemical shifts but also the magnitudes of the coupling constants of the equilibrium components *E*-**A**, *E*-**B**, and *E*-**C** compare favorably with those of the model compounds *E*-**2a**, **4**, **5**, **6**, **7**, and **8** (cf. Tables 1 and 3). While ylides *E*-**B** have ^{3}J(1-H,2-H) values of 12.0−12.2 Hz, those of *E*-**2a**, **4**, and **5** are 10.4 and 11.0 Hz. Ab initio calculations and X-ray crystal structure analysis of the lithium salt **5** have revealed an almost planar coordination geometry of C-1 and an *s-trans* conformation in regard to the C1−C2 bond. According to model ab initio calculations of an allyl aminosulfoxonium ylide (vide infra), it is to be expected that ylide *E*-**B** also has a coordination geometry of C-1 that is close to planar and adopts the *s-trans* conformation around the C1−C2 bond. The *C*-titanium species *E*-**A** and *E*-**C** have ^{3}J(1-H,2-H) values ranging from 10.6 to 12.8 Hz, and the model compounds **6**, **7**, and **8** are characterized by values of 10.1−11.9 Hz. According to the X-ray crystal structure analysis

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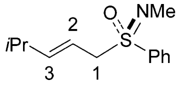
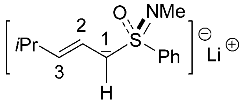
Table 3. Selected ^{1}H NMR and ^{13}C NMR Data of the Allyl Sulfoximine *E*-**2a**, the Lithiated Allyl Sulfoximines *E*-**3a**, **4**, and **5**, the Bis(allyl)titanium Complexes **6** and **7**, and the Mono(allyl)titanium Complex **8**[a]



E-**2a**



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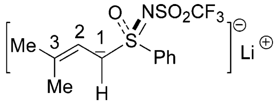

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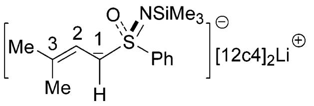

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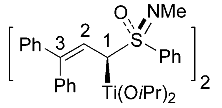

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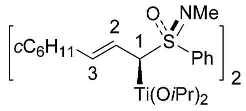

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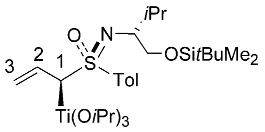


8

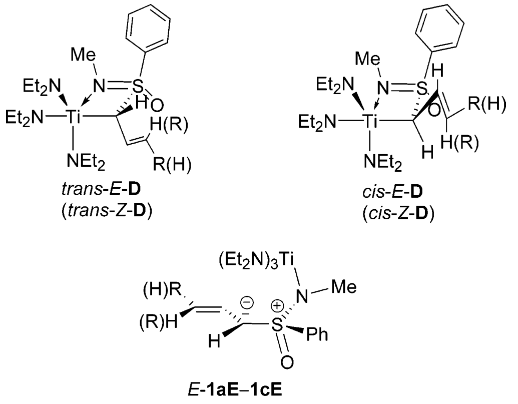
	^{1}H NMR			^{13}C NMR		
compound	1-H	2-H	3-H	C-1	C-2	C-3
E-**2a**	3.53[b]	5.26	4.96	55.11[c]	114.75	144.50
	14.0, 7.5	*15.4, 7.5, 1.2*	*15.4, 6.9, 1.2*	*139*	*166*	*155*
E-**3a**	3.09[d]	5.93	4.37	54.68[e]	127.34	113.65
	10.4	*15.1, 10.4, 0.9*	*15.1, 6.7*	*155*	*143*	*144*
4	3.48[f]	5.53		55.22[g]	119.8	111.0
	11.0	*11.0*		*169*	*148*	
5[h]	3.07	5.74		61.40	126.36	99.23
	10.7	*10.7*		*161*	*143*	-
6	3.75/4.30[h]	6.74/6.61		55.7/68.4[i]	127.6	131.8/138.9
	11.9/11.9	*11.9/11.9*		*147/142*	*j*	
7[k]	3.45[h]	4.86	5.22	69.6[i]	123.6	134.3
	10.1	*15.0, 10.1, 0.9*	*15.0, 6.7*	*142*	*168*	*j*
8[l]	3.77	6.04	4.64	65.6	132.7	118.5
	10.9	*m*	*11.0*	*144*	*m*	*m*

[a] Numbers in italics are averaged coupling constants. [b] 400 MHz in [D$_8$]-toluene at 22 °C. [c] 100/125 MHz in [D$_8$]-toluene at 22 °C. [d] 500 MHz in [D$_8$]-toluene at 22 °C. [e] 75 MHz in [D$_8$]-toluene at 22 °C. [f] 500 MHz in [D$_8$]-THF. [g] 125 MHz in [D$_8$]-THF. [h] 500 MHz in [D$_8$]-THF at −70 °C. [i] 125 MHz in [D$_8$]-THF at −70 °C. [j] Not determined. [k] In the presence of Ti(O*i*Pr)$_4$ and ClTi(O*i*Pr)$_3$. [l] In [D$_8$]-THF. [m] Not reported.

of **5**, the allyl group adopts a C1−C2 conformation in which 1-H and 2-H are in *trans* position. This suggests that *E*-**A** and *E*-**B** also adopt such a C1−C2 conformation.

The *S*-configuration was tentatively assigned to the major isomer *E*-**A** and the *R*-configuration to the minor isomer *E*-**C**. This assignment rests on the following observations and assumptions. The Ti atoms of complexes *E*-**A** and *E*-**C** are only tetracoordinated and thus contain vacant coordination sites. Therefore, it seems very likely that they adopt the structures of the cyclic four-membered η^2-complexes *trans*-*E*-**D** and *cis*-*E*-**D**, the sulfonimidoyl group of which is coordinated via the N atom to the Ti atom (Figure 3).

An intramolecular Ti−N coordination of this type had been previously observed for a complex of type **I**, carrying two phenyl groups at the 3-position, in the crystal and in solution (cf. Scheme 1).[3c] While the Ti atoms of *trans*-*E*-**D** and *cis*-*E*-**D** ought to have a trigonal-bipyramidal coordination geometry, the Ti atom of **I** is coordinated in a distorted octahedral fashion. In the *S*-configured complex *trans*-*E*-**D** the phenyl and alkenyl group are in *trans* position, and in the *R*-configured complex *cis*-*E*-**D** the two groups are in *cis* position. The hydrogen at the 2-position of complex *cis*-*E*-**D** points toward the center of the phenyl group. It should thus experience an upfield shift because of the anisotropic effect of the phenyl group. An inspection of the NMR data of the complexes *E*-**1aA**, *E*-**1aC**, *E*-**1bA**, and *E*-**1bC** listed in Table 1 reveals indeed a significant upfield shift of 2-H of the minor complex *E*-**C** as compared to the major complex *E*-**A**. The assumption of a η^2-coordination for the complexes *E*-**A** and *E*-**C** would also allow a rationalization of their different stabilities. Because of the *cis* position of the alkenyl group and the phenyl group complex, *cis*-*E*-**D** should be less stable than the corresponding complex *trans*-*E*-**D**, the alkenyl and phenyl groups of which are in the sterically less encumbered *trans* position.



trans-*E*-**D**
(*trans*-*Z*-**D**)

cis-*E*-**D**
(*cis*-*Z*-**D**)

E-**1aE**−**1cE**
(*Z*-**1aE**−**1cE**)

Figure 3. Structures of the allyltitanium complexes **A**, **B**, and **C**.

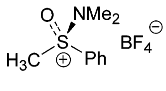
Ylide **B** most likely adopts a structure of type **E**, the Ti atom of which is attached to the N atom, which is not only more nucleophilic but also more Brønsted and Lewis basic than the O atom.[1c,f] This is in accordance with model ab initio calcula-

Table 4. Selected ^{13}C NMR (125 MHz) Data of the Equilibrium Components **A** and **B** of the Allyltitanium(IV) Complexes *E*-**1a**−**c** in [D$_8$]-Toluene at −70 °C[a]

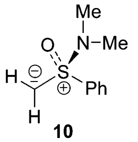
		A			B		
complex	R	C-1	C-2	C-3	C-1	C-2	C-3
E-**1a**	*i*Pr	60.28	123.74	131.58	57.21	118.41	*b*
		141	*159*	*159*	*171*	*158*	
E-**1b**	*c*C$_6$H$_{11}$	60.28	124.07	*b*	57.42	115.30	*b*
		137	*156*		*172*	*148*	
E-**1c**	Me	61.08	127.15	119.22	57.14	*b*	111.58
		138	*c*	*152*	*169*		*156*

[a] Numbers in italics are coupling constants. [b] Not detected. [c] Not determined.

Table 5. Selected ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Data of the Sulfoxonium Salt **9** and the Sulfoxonium Ylide **10** at Room Temperature[a]



9



10

compound	group	^{1}H	^{13}C
9[b]	CH$_3$	4.40	38.84
			144
10[c]	CH$_2$	1.66	23.20
			168

[a] Numbers in italics are coupling constants. [b] In [D$_6$]-DMSO. [c] In [D$_8$]-toluene in the presence of LiBF$_4$.

tions of an aminosulfoxonium ylide, which show that a (*N*,*N*-dimethylamino)sulfoxonium ylide is thermodynamically much more stable than the isomeric *O*,*S*-dimethyl aminosulfoxonium ylide (vide infra). However, the question as to which atom the Ti atom is attached is perhaps only an apparent one since both the N atom and the O atom might be coordinated to the Ti atom.[10] According to model ab initio calculations of an allyl dimethylaminosulfoxonium ylide (vide infra), the ylide **E** should adopt C1−S and C1−C2 conformations as shown because of stabilizing $n_C-\sigma_{SO}^*$ and $n_C-\pi^*$ interactions, respectively.

Because of the general similarity of the ^{1}H NMR data of *E*-**A**−**C**, a further unambiguous structural proof for the equilibrium components was sought. It was hoped that low-temperature ^{13}C NMR spectroscopy of *E*-**1a**−**c** would give additional structural information. The coordination geometries of C-1 of complexes **A**/**C** and **B** are significantly different. Thus the magnitude of the ^1J(C,H) values should also differ significantly because of their known dependency on the hybridization of the C atom.[11] Low-temperature ^{13}C NMR spectroscopy of the complexes *E*-**1a**−**c** in [D$_8$]-toluene also revealed in all cases fully reversible dynamic phenomena. For all three complexes, two sets of signals corresponding to the equilibrium species *E*-**A** and *E*-**B** were observed at −80 °C (Table 4). Because of the low concentration, in no case could signals corresponding to the minor equilibrium components *E*-**C** unambiguously be identified. Assignment of the signals was done by ^{1}H,^{13}C HMQC and ^{1}H,^{13}C HETCOR experiments, and the coupling constants were determined by HET2DJ experiments. The coupling constants for the ylides *E*-**B** were determined by long-term gated decoupling experiments at low temperatures. The ^{13}C NMR data of *E*-**A** and *E*-**B** give strong support to the structural assignment of the equilibrium species made on the basis of their ^{1}H NMR data. Of particular relevance are the magnitudes of ^1J(C,H) and the chemical shifts for C-1, C-2, and C-3 of the complexes *E*-**A** and the ylides *E*-**B**. The ^1J(C,H) values of 137−141 Hz for C-1 of complexes *E*-**A** are of a magnitude typical for tetrahedral alkyltitanium compounds,[12] as exemplified by complexes **6**−**8**, the ^1J(C,H) values of which are 142−147 Hz. The ylides *E*-**B**, however, are characterized by ^1J(C,H) values of 169−172 Hz for C-1, which are much higher than those for C-1 of complexes *E*-**A**. The higher ^1J(C,H) values of the ylides *E*-**B** are mainly a reflection of their different coordination geometry, which is expected to be close to planar, an assumption that is supported by the ab initio calculations of an allyl aminosulfoxonium ylide (vide infra). In addition to the dependency of ^1J(C,H) on the coordination geometry, the strong electron-withdrawing effect of the aminosulfoxonium group will, to a minor extent, also contribute to the magnitude of the coupling constant. This can be seen by comparing the two lithiated allyl sulfoximines *E*-**3a** and **4**, which differ in the substituent at the N atom but both have almost planar trigonal coordinated C1 atoms. While the *N*-methyl derivative *E*-**3a** has a ^1J(C,H) value of 155 Hz, the value for C-1 of the *N*-SO$_2$CF$_3$ derivative **4**, which carries the stronger electron-withdrawing sulfonimidoyl group, is 169 Hz.[8] Since relevant NMR data and other structural information of allyl and alkyl aminosulfoxonium ylides are not available, the ylide **10**, which was prepared from the aminosulfoxonium salt **9**[13] as a solution in [D$_8$]-toluene together with LiBF$_4$, was studied by NMR spectroscopy.[14] Ylide **10** showed for the methylene group a ^1J(C,H) value of 168 Hz (Table 5), which is similar in magnitude to those recorded for ylides *E*-**B**. The notion of a change in the coordination geometries of C-1 on going from the salt **9** to the ylide **10** is supported by the ab initio calculations of **10** (vide infra**)**.

NMR Spectroscopy of *Z*-Configured Complexes. The ^{1}H NMR spectra of the *Z*-configured complexes *Z*-**1a**, *Z*-**1b**, and *Z*-**1c** in [D$_8$]-toluene at room temperature each showed only one set of sharp signals corresponding to a *Z*-configured η^1-mono(allyl)titanium(IV) complex, the Ti atom of which is attached to the C-1 atom.[1f,3a,c,d] The low-temperature ^{1}H and ^{13}C NMR spectroscopy of *Z*-**1a**, *Z*-**1b**, and *Z*-**1c** in [D$_8$]-toluene revealed

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(10) For the intramolecular 1,4-coordination of a sulfonyl O atom to a Ti atom, see: (a) Gais, H.-J.: Vollhardt, H. J.: Lindner, H. J.; Paulus, H. *Angew. Chem.* **1988**, *100*, 1598−1600; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1540−1542. (b) Royo, E.; Betancort, J. M.; Davis, T. J.; Carroll, P.; Walsh, P. J. *Organometallics* **2000**, *19*, 4840−4851.

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(13) Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc*. **1973**, *95*, 7418−7423.

(14) For NMR data of sulfur ylides, see: (a) Schmidbaur, H.; Kammel, G. *Chem. Ber*. **1971**, *104*, 3234−3240. (b) Barbella, G.; Dembech, P.; Garbesi, A. *Tetrahedron Lett.* **1980**, *21*, 2109−2112. (c) Pörschke, K.-R. *Chem. Ber.* **1987**, *120*, 425−427. (d) Aggarwal, V. K.; Schade, S.; Taylor, B. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2811−2813.

Table 6. Selected ^{1}H NMR Data (500 MHz) of the Equilibrium Components **A** and **B** of the Allyltitanium(IV) Complexes *Z*-**1a**−**c** in [D$_8$]-Toluene at Low Temperatures[a]

		A			**B**		
complex	R	1-H	2-H	3-H	1-H	2-H	3-H
Z-**1a**[b]	*i*Pr	3.55	6.18	5.18	3.72	6.17	4.97
		c	*9*	*9*	*c*	*9*	*9*
Z-**1b**[d]	*c*C$_6$H$_{11}$	*c*	6.14	5.07	*d*	6.13	4.94
			10	*9*		*10*	-
E-**1c**	Me	*c*	6.20	5.22	*c*	6.2	5.07
			9	*e*		*9*	*e*

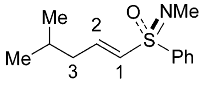
[a] Numbers in italics are coupling constants. [b] At −78 °C. [c] Not observed. [d] At −75 °C. [e] Not determined.

Table 7. Selected ^{13}C NMR (125 MHz) Data of the Equilibrium Components **A** and **B** of the Allyltitanium(IV) Complexes *Z*-**1a**−**c** in [D$_8$]-Toluene at −70 °C[a]

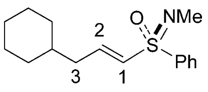
		A			**B**		
complex	R	C-1	C-2	C-3	C-1	C-2	C-3
Z-**1a**	*i*Pr	55.69	118.25	*c*	56.65	123.57	*b*
		b	*b*		*b*	*b*	
Z-**1b**	*c*C$_6$H$_{11}$	55.46	122.26	*c*	55.60	118.25	*c*
		136	*155*		*170*	*150*	
Z-**1c**	Me	55.57	126	117.27	55.57	121.31	108.97
		∼140[d]		*162*	*∼160*[d]	*b*	*159*

[a] Numbers in italics are coupling constants. [b] Not determined. [c] Not detected. [d] The precise magnitude of the coupling constant cannot be given because of the identical chemical shifts for C-1 of **A** and **B**. The values were estimated on the basis of the HET2DJ spectrum.

Table 8. Selected ^{1}H NMR and ^{13}C NMR Data of the Vinyl Sulfoximines *E*-**11** and *E*-**12** in CDCl$_3$[a]



E-**11**



E-**12**

	^{1}H (400 MHz)			^{13}C (125 MHz)		
compound	1-H	2-H	3-H	C-1	C-2	C-3
E-**11**	6.31	6.83	2.10	130.79	145.65	40.47
	15.1, 1.3	*15.1, 7.3*	*b*	*179*	*155*	*129, 131*
E-**12**	6.30	6.84	2.11	130.77	145.66	39.32
	14.3	*14.3, 7.4*	*b*	*176*	*156*	*127*

[a] Numbers in italics are coupling constants. [b] Not determined.

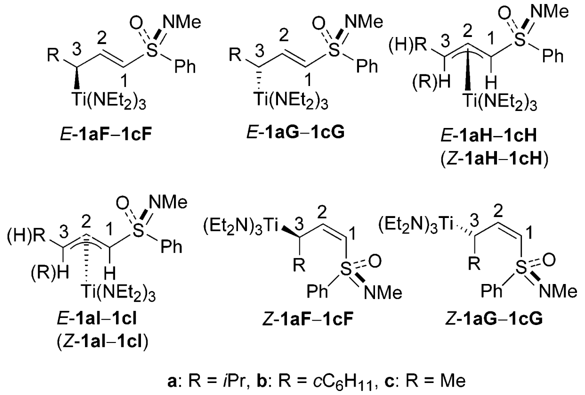


Figure 4. Alternative structures for the equilibrium components **A**, **B**, and **C** of the titanium complexes *E*-**1a**−**c** and *Z*-**1a**−**c**.

in all cases fully reversible dynamic phenomena. For all three complexes, two sets of signals corresponding to the *Z*-configured C-titanium allyl complex *Z*-**A** and the *N*-titanium allyl ylide *Z*-**B** in ratios of 36:64, 33:67, and 34:66 (cf. Table 2), respectively, were observed at −60 to −78 °C. In no case could signals be detected corresponding to the complexes *Z*-**C**. Thus in the case of the *Z*-configured complexes *Z*-**1a**−**c** the ylide *Z*-**B** and not the C-titanium complex *Z*-**A** is the major equilibrium component. Assignment of the signals was made by ^{1}H,^{1}H COSY, ^{1}H,^{13}C HMQC, and ^{1}H,^{13}C HETCOR experiments. The coupling constants were determined by HET2DJ and long-term gated decoupling experiments at low temperatures. Structural assignment of *Z*-**A** and *Z*-**B** was made on the basis of the chemical shifts, coupling constants, and integral ratios.

The NMR data of the *Z*-configured equilibrium components *Z*-**A** and *Z*-**B** (Table 6 and Table 7) favorably compare with those of the corresponding *E*-configured species *E*-**A** and *E*-**B**. Particularly supportive for the structural assignment are the magnitudes of ^{1}J(C,H) for the C-1 atoms. While the value for the C-titanium complex *Z*-**1bA** is 136 Hz, that for the ylide *Z*-**bB** amounts to 170 Hz.

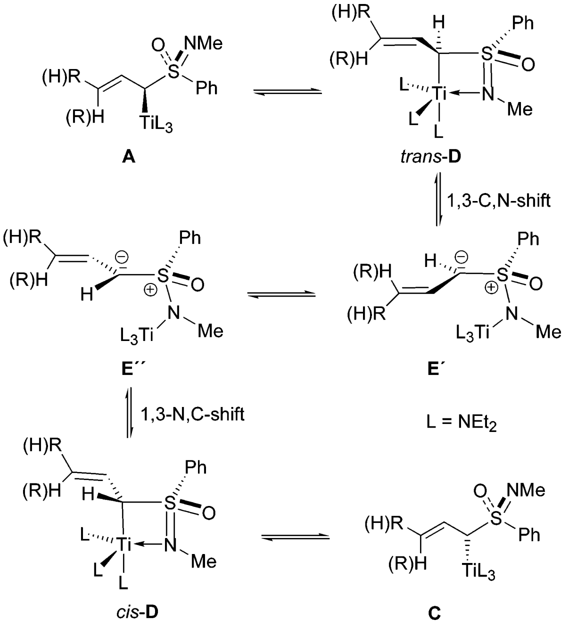
The *Z*-configured complexes *Z*-**A** were tentatively also assigned the *S*-configuration. The presence of the epimeric complexes *Z*-**C** could, however, not be detected. On the basis of the assumption that complexes *Z*-**A** and *Z*-**C** preferentially adopt the structures of the η^{2}-complexes *trans*-*Z*-**G** and *cis*-*Z*-**G** (cf. Figure 3), respectively, a shift of the equilibria to the side of the ylides *Z*-**B** would be conceivable because of unfavorable steric interactions resulting from the *Z*-configured double bond.

The variable-temperature ^{1}H NMR spectra of *E*-**1a**−**c** and *Z*-**1a**−**c** showed a further interesting feature. Two sharp multiplets were always observed for the methylene hydrogens of the ethyl groups at the N atoms of the equilibrium components irrespective of the temperature. This shows that the methylene hydrogens are diastereotopic, a phenomenon that can only occur if the tris(diethylamino)titanium group of the various equilibrium species remains attached to the chiral allylsulfoximine moieties in all of the dynamic processes that take place.

Alternative Structures. A comparison of the ^{1}H NMR data of the *E*- and *Z*-configured complexes **A**, **B**, and **C** with those of the 1-alkenyl sulfoximines *E*-**11** and *E*-**12** (Table 8) shows that the alternative structures of the η^{1}-allyltitanium complexes **F** and **G** (Figure 4) for the equilibrium species of **1a**−**c** can be excluded. Sulfoximines *E*-**11** and *E*-**12** should be reasonably good NMR spectroscopic models for complexes **F** and **G** because of the minor effect the Ti atom is expected to exert upon the double bond of the latter. For example, if one would propose that two of the three equilibrium species adopt the structure **F** or **G** rather than **A**, **B**, and **C**, chemical shifts of 3.12−3.72 and of 4.94−5.22 would have to be assigned to 1-H and 3-H, respectively, of **F** or **G**. This does, however, not concur with the NMR data of the known allyltitanium(IV) complexes including those of complexes **6**−**8**.[1f,3,12] A comparison of the ^{13}C NMR data of the equilibrium species *E*-**A** and *E*-**B** with those of the 1-alkenyl sulfoximines *E*-**11** and *E*-**12** also shows, in agreement with the ^{1}H NMR data (vide supra), that the alternative structures **F** and **G** for the equilibrium species of complexes *E*-**1a**−**c** can be excluded. In particular δ values of 55.46−61.08 and ^{1}J(C,H) values of 137−141 Hz for C-1 would be incompatible with structures **F** and **G**.

Although the NMR data strongly favor structures **A** and **C** of the C-titanium complexes, the alternative structure of the η^{3}-allyl complexes **H** and **I** cannot be entirely excluded.

Scheme 3. Mechanistic Scheme for the Metallotropic Shift of the Allyltitanium Complexes *E*-**1a**−**c** and *Z*-**1a**−**c**



Unfortunately, an unambiguous structural characterization of η^3-allyltitanium(IV) complexes has not yet been described, and thus NMR data for a comparison are not available.[15] However, the absence of an *E*/*Z* isomerization of complexes *E*-**1a**, *E*-**1b**, *Z*-**1a**, and *Z*-**1b** and the slowness of the *E*/*Z* isomerization of *E*-**1c** and *Z*-**1c** can be taken as further evidence speaking against structures **H** and **I**.

Metallotropic Shift. The components **A**, **B**, and **C** of complexes *E*-**1a**−**c** and *Z*-**1a**−**c** are in rapid equilibrium at low temperatures. As a consequence, these titanium complexes exhibit a low configurational stability at C-1. A possible mechanism for the rearrangement is depicted in Scheme 3. The η^2-complex *trans*-**D** suffers a metallotropic[16] 1,3-C,N-shift to give the ylide **E′**, the depicted Cα−S and S−N conformations of which are energetically favorable ones according to the model ab initio calculations. The cleavage of the C−Ti bond of *trans*-**D** and *cis*-**D** will be facilitated by the strong stabilization of the negative charge of the resulting ylides **E′** and **E″** by the aminosulfoxonium group. The carbanion stabilizing effect of the aminosulfoxonium group is much stronger than that of the sulfonimidoyl group.[9] For example, while *N*,*S*-dimethylphenylsulfoximine has a pK_a value of 33, that of the aminosulfoxonium salt **9** is 14.5. A further stabilization of the negative charge of ylides **E′** and **E″** is provided by the double bond, as indicated by model ab initio calculations of an allyl aminosulfoxonium ylide (vide infra). The cleavage of the Ti−C bond will also be facilitated by the diethylamino donor groups at the Ti atom. Rotation around the Cα−S bond of the ylide **E′** generates the isomeric ylide **E″**. According to the model ab initio calculations, it is to be expected that ylides **E′** and **E″** have a low Cα−S rotational barrier (vide infra).

The rearrangement is concluded by a cyclization of ylide **E″** with formation of the epimeric η^2-complex *cis*-**D**, which is perhaps in equilibrium with the η^1-complex **C**. In agreement with the proposed intramolecular course of the metallotropic shift and the epimerization is the observation of diastereotopic methylene hydrogens of the ethyl groups at the Ti atom in all of the variable-temperature NMR spectra of complexes *E*-**1a**−**c** and *Z*-**1a**−**c**.

***E*/*Z* Isomerization.** During the long-term NMR experiments with the *E*- and *Z*-configured methyl-substituted complexes *E*-**1c** and *Z*-**1c**, respectively, in [D$_8$]-toluene a slow *E*/*Z* isomerization of both complexes was observed. The synthesis of *E*-**1c** starting from the pure allyl sulfoximine *E*-**1c** at −78 °C gave a mixture of *E*-**1c** and *Z*-**1c** in a ratio of 15:1. After the mixture had been kept first for 4 weeks at −70 °C and then for 2 weeks at −22 °C, the ratio of the isomers had changed to 9:1. A further storage of the 9:1 mixture of *E*-**1c** and *Z*-**1c** at room temperature first for 9 h and then for 24 h saw a change of the ratio of the isomers first to 5.5:1 and then to 3.5:1. The time course of the isomerization of *Z*-**1c** was followed in less detail. The synthesis of *Z*-**1c** starting from the pure allyl sulfoximine *Z*-**2c** at −78 °C gave a mixture of *Z*-**1c** and *E*-**1c** in a ratio of 20:1 After the mixture had been kept for 24 h at −60 °C, the ratio of the isomers had changed to 13:1. Interestingly, an *E*/*Z* isomerization of the isopropyl- and cyclohexyl-substituted complexes *E*-**1a**, *E*-**1b**, *Z*-**1a**, and *Z*-**1b**, respectively, was not observed even at room temperature, and the synthesis of these complexes was not accompanied by a partial isomerization. Two mechanisms can be envisioned for the isomerization of *E*-**1c** and *Z*-**1c**: a series of consecutive metallotropic 1,3-C,N-, 1,5-N,C-, 1,5-C,N-, and 1,3-N,C-shifts or, alternatively, two consecutive metallotropic 1,3-C,C-shifts in combination with two metallotropic 1,3-C,N- and 1,3-N,C-shifts (see Schemes S2 and S3 and the discussion, Supporting Information). NMR spectroscopy of simple allyltitanium(IV) complexes having a terminal double bond had revealed a fast 1,3-C,C-shift of the Ti atom.[12,17] Whether a similar fast shift of the Ti atom also occurs in the case of allyltitanium(IV) complexes having a 3-alkyl- or 3-aryl-substituted internal double bond is not clear yet. If there is an equilibrium between the substituted allyltitanium isomers, it must be fast and shifted, according to the NMR data, almost completely to the side of the isomer carrying the internal double bond. However, direct information about the dynamics of substituted allyltitanium(VI) complexes is lacking.[12,17,18]

Reactivity Scheme for Aldehydes. Based on the observation of a fast equilibrium between the isomeric C-titanium complexes **IVA** and **IVC** and the N-titanium complex **IVB**, a reactivity model for the rationalization of the regio- and diastereoselectivities of the reactions of complexes **IV** with aldehydes is proposed in Scheme 4.

This model, which is based on the assumption of the operation of the Curtin−Hammett principle,[19] that is, the reactions of **IVA**,

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[15] For the X-ray crystal structure analyses of η^3-allyltitan(III) complexes, see: (a) Chen, J.; Kai, Y.; Kasai, N.; Yasuda, H. *J. Organomet. Chem.* **1991**, *407*, 191−205. (b) Greidanus, G.; McDonald, R.; Stryker, J. M. *Organometallics* **2001**, *20*, 2492−2504

[16] (a) Radius, U.; Sundermeyer, J.; Peters, K.; von Schnering, H.-G. *Eur. J. Inorg. Chem.* **2001**, 1617−1623. (b) Čermák, J.; St'astná, L.; Sýkora, J.; Císařová, I.; Kvíčala, J. *Organometallics* **2004**, *23*, 2850−2854.

[17] (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441−487. (b) Reetz, M. T.; Steinbach, R.; Westermann, J.; Peter, R.; Wenderoth, B. *Chem. Ber.* **1985**, *118*, 1441−1454. (c) Kasatkin, A.; Nakagawa, T.; Okamoto, S.; Sato, F. *J. Am. Chem. Soc.* **1995**, *117*, 3881−3882.

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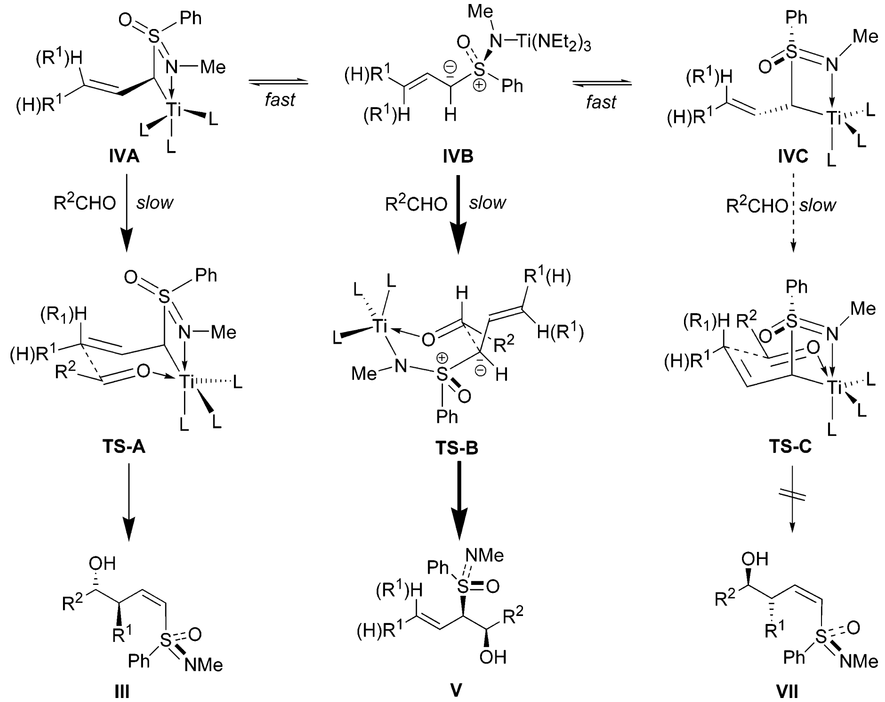
Scheme 4. Reactivity Model for the Mono(allyl)titanium Complexes **IV** and Aldehydes



IVB, and **IVC** with aldehydes are significantly slower than their isomerization, features the six-membered cyclic chair-like transition states **TS-A** and **TS-C** and the boat-like transition state **TS-B** for the reactions of **IVA**, **IVC**, and **IVB**, respectively. Key features of **TS-A** and **TS-C** are a coordination of the sulfonimidoyl N atom to the Ti atom. The boat-like transition state **TS-B** should be preferred over the corresponding chair-like transition state (not shown) because of the Cα−S and S−N conformations in which the lone pair orbitals at the Cα atom and the N atom are approximately periplanar to the S═O and Cα−Ph bonds, respectively. According to the ab initio calculations of aminosulfoxonium ylides (vide infra), this will allow for an efficient stabilization of the transition state by a 2-fold negative hyperconjugation, $n_C-\sigma_{SO}^*$ and $n_N-\sigma_{SPh}^*$ (vide infra).[20] Furthermore, in **TS-B** the lone pair orbitals at the Cα atom and the N atom are in an energetically favorable orthogonal position to each other. While **TS-B** has a pentacoordinated Ti atom with a trigonal-bipyramidal geometry, **TS-A** and **TS-C** contain hexacoordinated Ti atoms with an octahedral geometry.

Decisive factors that will primarily determine the energy difference between (*E*)-**TS-A** and (*E*)-**TS-B** are the steric interactions between R^1 and R^2 in the first and between R^2 and the alkenyl group in the second case. While these interactions are presumably of the same magnitude for $R^1 = R^2 = Me$, the interaction between R^1 and R^2 in (*E*)-**TS-A** will become more destabilizing with increasing size of the substituents than that between R^2 and the alkenyl group in (*E*)-**TS-B**. Thus with increasing size of the substituents (*E*)-**TS-B** is energetically more and more preferred over (*E*)-**TS-A**. In the case of the *Z*-configured complex (Z)-**IV** the transition state (*Z*)-**TS-A** will always be higher in energy than (*Z*)-**TS-B** because of a destabilizing interaction between R^1 and the sulfonimidoyl group. The *R*-configured C-titanium complex **IVC** should react with aldehydes via transition state **TS-C** to give the diastereomer **VII**. Formation of this isomer has, however, not been observed. This can be ascribed to an unfavorable steric interaction of the *endo*-positioned phenyl group with the aldehyde in transition state **TS-C**. In **TS-A** the phenyl group is located in the sterically less demanding *exo* position.

II. Ab Initio Calculation of (Dimethylamino)sulfoxonium Ylides. The crucial role the *N*-titanium allyl (amino)sulfoxonium ylide **B** plays in the dynamics and reactions of the mono(allyl)-titanium complexes **IV** with aldehydes prompted us to carry out model quantum-chemical ab initio calculations of the *N,N*-dimethyl ylide **10**, the isomeric *O,N*-dimethyl ylide **13**, and the allyl (*N,N*-dimethylamino)sulfoxonium ylide **14** (Figure 5).

Information was sought as to the Cα−S conformation, the relative stability, the coordination geometry of the Cα atom, and the Cα−S rotational barrier of the ylides. Further motives for the study of **10** and **14** were the synthetic importance of chiral ylides of this type, which have found application as nucleophilic alkylidene transfer reagents in asymmetric synthesis,[1c,f,4b,g,j,21] and the virtually complete lack of information about their structure.

Methylene Ylides. A conformational search at the HF/6-31+G* level of theory resulted in two stationary points for **10**, **10a**, and **10b** (Figure 6) (see Table S1, Supporting Information) and five for **13**, **13a**, and **13b** (Figure 7) (see Table S1, Supporting Information) and **13c**−**e** (see Figure S1, Supporting Information). Calculation of the normal frequencies showed that they all are local minima. Starting from these structures further geometry optimizations have been performed with the same basis set but now including correlation energy by means of Møller−Plesset perturbation theory to the second-order

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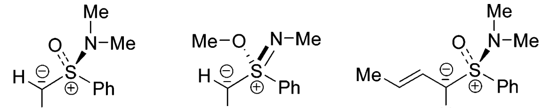
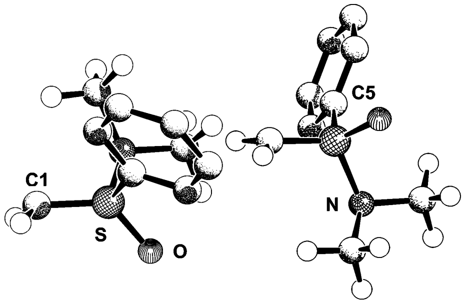
(19) Seeman, J. L. *Chem. Rev.* **1983**, *83*, 83−134.

(20) Previously we had proposed a chair-like TS for the reaction of **IVB** with aldehydes.[3c] On the basis of the model ab initio calculations of the aminosulfoxonium ylides we now consider the boat-like TS to be more likely. In the boatlike TS there is a $n_C-\sigma_{SO}^*$ interaction, which is much more stabilizing than the $n_C-\sigma_{SPh}^*$ interaction (cf. Figures 8 and 9) in the chair-like TS.



10 **13** **14**

Figure 5. (Dimethylamino)sulfoxonium ylides.

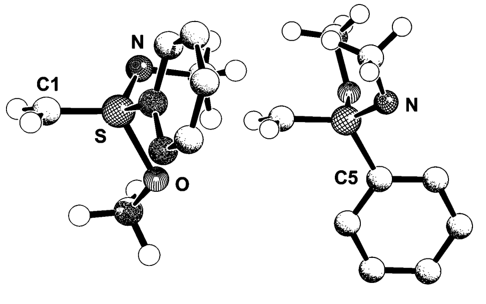


0.0 *+1.7*
10a **10b**

Figure 6. Two local minima of the *N*,*N*-dimethyl ylide **10**. The numbers are the energies in kcal/mol relative to the most stable conformer isomer **10a** calculated at the ZPE+MP2/ 631+G*//MP2/6-31+G* level.

(MP2/6-31+G*).[22] The relative energies, which are also given in Figure 6 and Figure 7, have been obtained by adding the zero-point energy calculated at the HF/6-31+G* level and multiplied by 0.95 to the correlated total energies. At this level of theory the most stable *N*,*N*-disubstituted aminosulfoxonium ylide **10a** is 25.7 kcal/mol lower in energy than the most stable *O*,*N*-disubstituted ylide **13a**. At a sum of bond angles of 347.1° the formally negatively charged carbon atom of **10a** is strongly pyramidalized. The S−C1 bond length is 1.628 Å and, therefore, significantly shorter than a typical S−C single bond as in Me_2S at the same level of theory (1.806 Å).[23]

An NBO analysis[24,25] of the wave function revealed a lone pair of approximately 90% p character and an occupation number of about 1.7 e at C-1. While the S−C1 bond lengths of conformers **10a** and **10b** are almost the same, the pyramidalization of the C1 atom of the latter is smaller ($\sum\angle$C1 356.2°). The H−C1−S=O dihedral angles in **10a** are 80.5° and −60.8°. Therefore the lone pair at C-1 (n_C) is in an almost ideal position for negative hyperconjugation with the σ* orbital of the S=O bond.[26] If the CH_2 group of **10a** in its frozen minimum structure is rotated about the S−C1 bond into a position where the lone pair at the carbon atom is approximately orthogonal to the S=O bond and the remaining geometry is optimized, the S−C1 bond is only slightly longer (1.631 Å) than in **10a**. Similarly the S=O bond in the rotated structure (1.479 Å) is only slightly shorter than in the fully optimized geometry (1.494 Å). The S−C1 bond is highly polar, and the Merz−Singh−Kollman (MDK) charges are +0.94 e at the S atom and −1.15 e at the C1 atom. At +2.18 e the natural charge at the S atom is much stronger, while that at C-1 of −1.17 e is quite similar to the MSK value. Due to the high polarity of the S−C1 bond, it is therefore conceivable that electrostatics contribute significantly to the shortening of this bond.



+25.7 *+27.4*
13a **13b**

Figure 7. Two local minima of the *O*,*N*-dimethyl ylide **13**. The numbers are the energies in kcal/mol relative to the most stable *N*,*N*-dimethyl isomer **10a** calculated at the ZPE+MP2/ 631+G*//MP2/6-31+G* level.

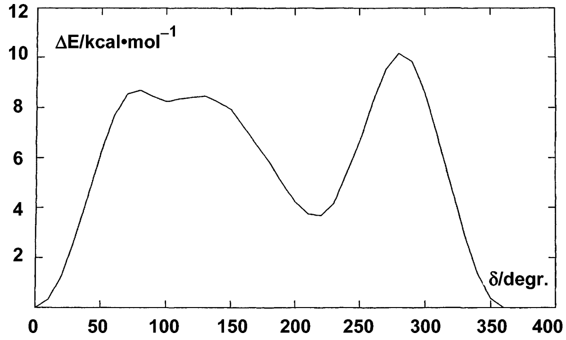


Figure 8. Potential energy function describing the rotation about the S−C1 bond of ylide **10a**.

The barrier to rotation about the S−C1 bond of **10a** was calculated in a semirigid approximation. Starting from the fully optimized geometry of **10a** the structure of the CH_2 group was kept frozen and the dihedral angle (ϑ) was increased between one hydrogen of the methylene group and the sulfur-bonded C5 atom in steps of $\delta = 10°$. For each of these points we then performed a geometry optimization of all remaining structural parameters at the MP2/6-31+G* level. The resulting potential curve is shown in Figure 8.

The curve has maxima of $\Delta E = 8.5$, 8.7, and 10.2 kcal/mol at $\delta = 80°$, 130°, and 280°, respectively and minima of 0.0, 8.2, and 3.7 kcal/mol at $\delta = 0°$, 100°, and 220°, respectively. In all of the relative minima the lone pair at C-1 (n_C) is approximately *trans* periplanar to one of the S−X (X = O, N, C) bonds and can, therefore, interact with the corresponding σ_{SX}* orbital (Figure 9). As already mentioned above, the lowest energy has been obtained for X = O followed by X = N at $\Delta E = 3.7$ kcal/mol and finally for X = C at $\Delta E = 8.2$ kcal/mol. The energy lowering due to the $n-\sigma_{SX}$* interaction can be estimated using an energy expression derived from second-order perturbation theory, $\Delta E_{n\sigma^*}^{(2)} = -q_n \cdot \langle n|\mathbf{F}|\sigma^*\rangle^2/(\epsilon_{\sigma^*} - \epsilon_n)$,

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(23) Wiberg, K. B.; Castejon, H. *J. Am. Chem. Soc.* **1994**, *116*, 10489−10497.

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(26) Raabe, G.; Gais, H.-J.; Fleischhauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 4622−4630, and references therein.

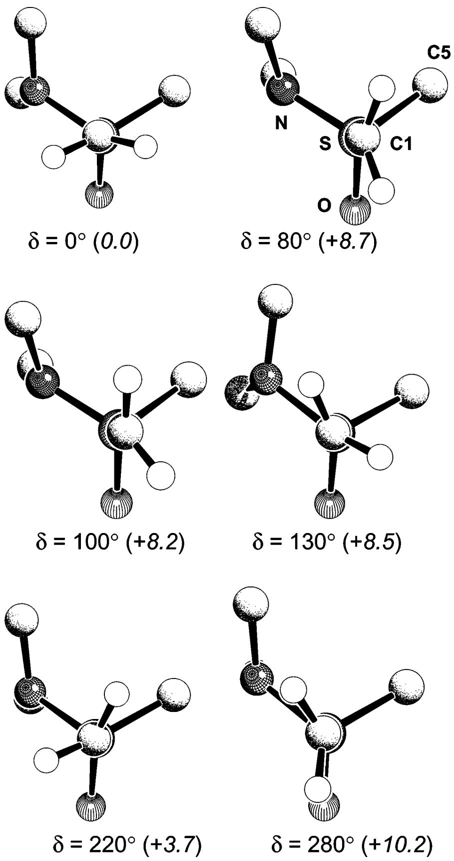
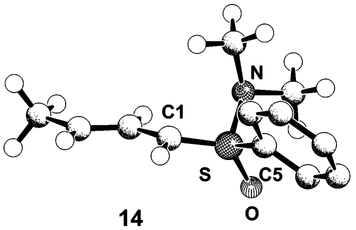


Figure 9. Relative orientation of the CH_2 group and the S−X (X = O, N, C) bonds of ylide **10a** together with the corresponding energies relative to the most stable rotamer ($\delta = 0°$) in the minima (above) and the maxima (below) of the potential energy function describing the rotation about the S−C1 bond of the ylide.

where **F** is the Fock operator of the molecule, q_n is the occupation number of the lone pair, and ϵ_{σ^*} and ϵ_n are the NBO orbital energies of the σ^* and the nonbonding orbital, respectively.[24,25] The stabilization energies are −59 kcal/mol for X = N, −45 kcal/mol for X = O, and −44 kcal/mol for X = C. It is, therefore, obvious that the shape of the potential curve is not completely determined by negative hyperconjugation between n_C and σ_{SX}^*. Another fact that has to be considered is the interaction of the nitrogen lone pair (n_N) with the σ^* orbitals of the S═O bond, the S−C5 linkage, and the *trans*-oriented C−H bonds of the two methyl groups. While the $n_N - \sigma_{CH}^*$ interaction is quite similar not only at $\delta = 0°$, 100°, and 220 but also at 280° (~ −18 to −19 kcal/mol), stabilization due to $n_N - \sigma_{SC}^*$ interaction is most and least effective at $\delta = 0°$ (−12.2 kcal/mol) and $\delta = 280°$ (−7.7 kcal/mol), respectively. The values at $\delta = 220°$ (−9.5 kcal/mol) and 100° (−8.0 kcal/mol) lie in between. At values between −1 and −5 kcal/mol for the points of the potential curve given above the stabilizing $n_N - \sigma_{SO^*}$ interaction is relatively weak. Thus the $n_N - \sigma_{CH}^*$ interaction is small but nevertheless significant. The fact that the energy of the relative minimum at $\delta = 100°$ is relatively high despite an $n_C - \sigma_{SC}^*$ interaction that is as stabilizing as that between n_C and σ_{SO}^* seems to be surprising. However, a closer inspection of the structure shows that in this conformer n_N and n_C are oriented approximately parallel and the resulting repulsion energy will cancel most of the energy lowering caused by delocalization of n_C into σ_{SC}^*. In contrast n_N and n_C are almost orthogonal at $\delta = 220°$ and the repulsive interaction will be much lower in this case. Combined with the effective $n_C - \sigma_{SN}^*$ interaction (vide supra) this leads to a minimum only 3.7 kcal/mol above the energetically lowest point of the potential curve. The point of highest energy was obtained at $\delta = 280°$. Here n_N and n_C are in an energetically favorable *anti* orientation. However, in this structure the conformation about the S−C1 bond can be described as fully eclipsed, resulting in a rise of the energy which obviously outnumbers the energy lowering caused by the *anti* orientation of n_N and n_C.



14

Figure 10. Local minimum obtained for the allyl ylide **14** at the MP2/6-31+G* level.

Allyl Ylide. Starting from ylide **10a** a structure was defined where one of the hydrogen atoms at C-1 was replaced by the *E*-configured 2-propenyl group resulting in the structure of the allyl ylide **14**. The structure of **14** optimized at the MP2/6-31+G* level is shown in Figure 10 (see Table 1, Supporting Information).

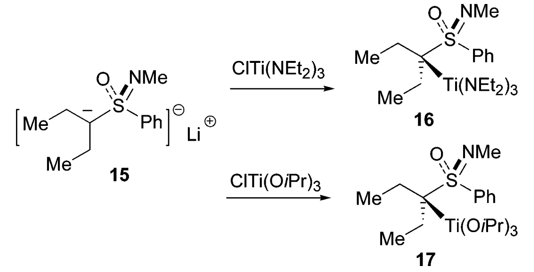
At a sum of bond angles of 356.3° the C1 atom of **14** has an almost planar coordination geometry and its pyramidalization is thus much less pronounced than in **10a**. Accordingly, the lone pair at C-1 (occupancy: 1.6 e) has a stronger p character (~96%) than that of n_C in **10a**. Moreover, the MSK charges at the C1 atom (−0.66 e) and at the S atom (+0.74 e) are significantly lower than in **10a**, resulting in a less polar S−C1 bond. At 2.19 e the natural charge at the S atom of **14** is essential identical with the corresponding value in **10a**, while a clearly lower value of −0.90 e is obtained for the charge at the C1 atom because of the interaction of its lone pair orbital with the double bond. While the length of the S−C1 bond is 1.632 Å and therefore only slightly longer than in **10a**, the lengths of the C1−C2 and C2−C3 bonds are 1.452 and 1.352 Å, respectively. In **14** the stabilization energy due to a delocalization of n_C into σ_{SO}^* is −41 kcal/mol and, therefore, only 4 kcal/mol less favorable than in **10a**. At a second-order energy of −42 kcal/mol the interaction of n_C with the π^* orbital of the CC double bond is of essentially equal importance.

III. Alkyltitanium(IV) Complexes. NMR Spectroscopy. The observation of a fast 1,3-C,N-shift of the Ti atom of the allyltitanium complexes *E*-**1a**−**c** and *Z*-**1a**−**c** prompted us to study the alkyltitanium(IV) complexes **16** and **17** in order to see whether their Ti atom also undergoes a fast reversible 1,3-C,N-shift (Scheme 5).

Titanation of the lithiated sulfoximine **15** (see Scheme S4, Supporting Information) with $ClTi(NEt_2)_3$ and $ClTi(O\textit{i}Pr)_3$ afforded the titanium complexes **16** and **17**, respectively. While the isopropoxy-substituted complex **17** was stable at ambient temperatures in THF and toluene solution, the diethylamino-substituted complex **16** started to decompose slowly at 0 °C. The complexes **16** and **17** were configurationally stable at the S atom, as shown by their hydrolysis, which afforded the corresponding enantiomerically pure sulfoximine.

Surprisingly, the ^{1}H NMR spectrum of **16** in [D_8]-THF at 20 °C featured only one very broad signal for the four

Scheme 5. Synthesis of Sulfonimidoyl-Substituted Alkyltitanium Complexes



15

16

17

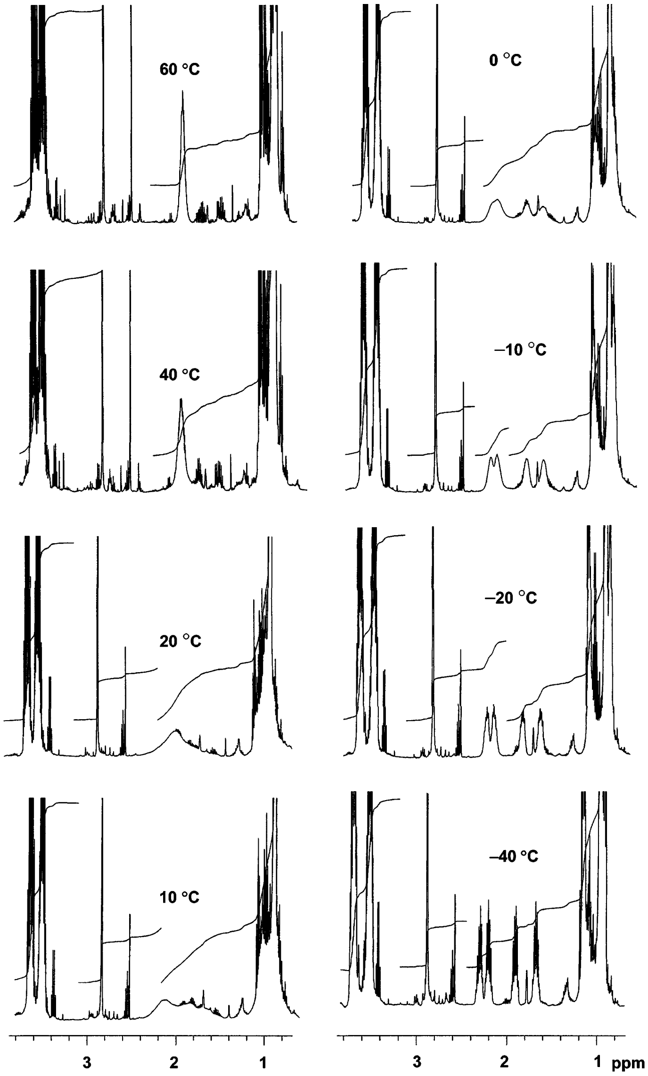


Figure 11. Temperature-dependent 500 MHz ^{1}H NMR spectra of the Cα-ethyl, *N*-ethyl, and *N*-methyl hydrogen region of the titanium complex **16** in [D$_8$]-THF. The upper parts of the *N*-ethyl and *N*-methyl signals have been cut off.

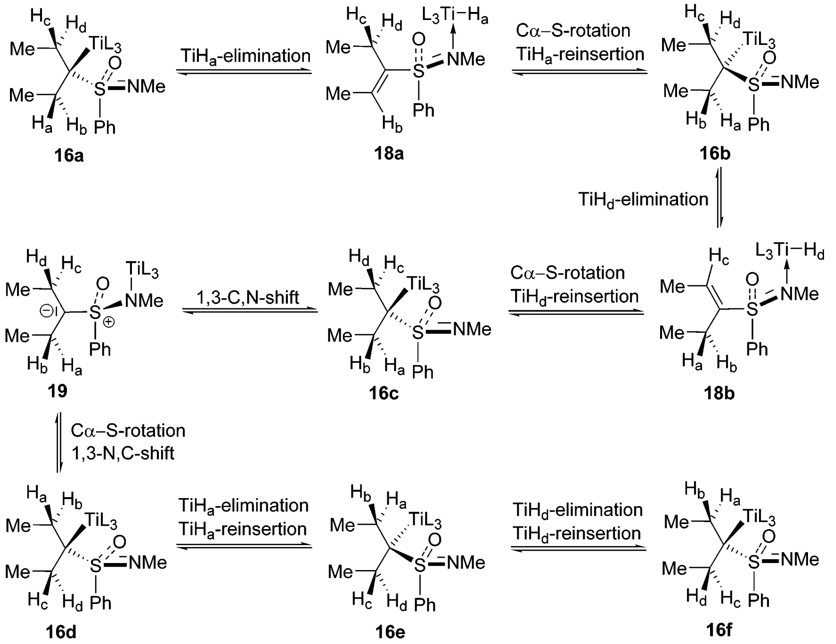
diastereotopic hydrogens of the methylene groups and only one broad signal for the methyl hydrogens of the ethyl groups at the Cα atom (Figure 11). These signals became sharper at 40 °C, and finally at 60 °C the methylene hydrogens resolved into a broad multiplet and the methyl hydrogens into a sharp triplet. Upon cooling the solution of **16** in [D$_8$]-THF gradually from room temperature to −40 °C and lower, the very broad signal initially observed for the four methylene hydrogens was first split into two broad signals at approximately 10 °C, and each broad signal was further split into two broad signals at approximately 0 °C. Four sharp doublets of quartets appeared for the four hydrogens of the methylene groups at approximately −40 °C, and two triplets evolved for the hydrogens of the two methyl groups. The two consecutive coalescence phenomena involving all four Cα-methylene hydrogen signals were fully reversible, and an equilibrium with one of the decomposition products was not observed. Assignment of the signals of the hydrogens of each methylene group was made by ^{1}H,^{1}H COSY and ^{1}H,^{13}C HMQC experiments. Accordingly, the signals at $\delta = 1.51$ and at $\delta = 1.74$ ppm are for the hydrogens of one of the methylene groups, and those at $\delta = 2.04$ and $\delta = 2.13$ ppm belong to the hydrogens of the other methylene group. Thus upon raising the temperature from −40 °C to room temperature, each pair of signals of the methylene hydrogens collapses into one broad signal. Finally, it seems important to note that the variable-temperature ^{1}H NMR spectra of **16** always exhibited two sharp multilplets for the methylene hydrogens of the ethyl groups at the N atoms.

The ^{13}C NMR spectrum of **16** in [D$_8$]-THF at room temperature showed a broad signal for the Cα atom, two extremly broad signals for the methylene C atoms, one sharp signal for the methyl C atoms of the ethyl groups at the Cα atom, and two sharp signals for the ethyl groups at the N atoms. The broad signals became significantly sharper at 40 °C, and the two broad signals for the methylene C atoms resolved into one broad signal. Finally at 60 °C there was one sharp signal for the Cα atom, one less broadened signal for the methylene C atoms, one sharp signal for the methyl C atoms of the ethyl groups at the Cα atom, and two sharp signals for the *N*-ethyl groups. Upon cooling the solution of **16** gradually from room temperature to −78 °C, fully reversible coalescence phenomena were observed. A sharp signal for the Cα atom was recorded, the two broad signals for the methylene C atoms each turned into a sharp signal, and the signal for the methyl C atoms was split into two sharp signals. Signal assignment was made by ^{1}H,^{13}C HMQC experiments.

The variable-temperature ^{1}H and ^{13}C NMR spectra of **16** in the less polar solvent [D$_8$]-toluene showed in all aspects similar features as in the more polar and coordinating solvent [D$_8$]-THF.

In summary, the results of the variable-temperature ^{1}H and ^{13}C NMR experiments of complex **16** in the two different solvents [D$_8$]-toluene and [D$_8$]-THF unequivocally show that (1) the diastereotopic hydrogens of the Cα-methylene groups suffer a topomerization *within* and *between* the Cα-methylene groups and (2) the C-ethyl groups experience a diastereotopomerization. The operation of two different intramolecular processes is proposed in order to account for the experimental observations (Scheme 6). The first process is composed of a reversible intramolecular *β*-hydride elimination and alkene-titanium hydride insertion. Accordingly, a *β*-hydride(H$_a$) elimination of **16a** gives **18a**, a complex between (Et$_2$N)$_3$TiH$_a$ and a 1-alkenyl sulfoximine. Rotation around the Cα−S bond of **18a** and a subsequent intramolecular Ti−H$_a$ alkene insertion at the *Si-Re* face of the double bond of **18a** affords complex **16b**. A similar Ti−H$_d$ elimination/reinsertion of **18b** affords via the 1-alkenyl sulfoximine Ti−H complex **18b** the complex **16c**. These series of events leads to a topomerization of the hydrogens within the methylene groups. The second process consists of a 1,3-C,N-shift of the Ti atom followed by a consecutive Cα−S

Scheme 6. Mechanistic Scheme for the Complete Topomerization of the Cα-Ethyl Methylene Hydrogens of the Alkyltitanium Complex **16**



bond rotation and 1,3-N,C-shift of the Ti atom. Accordingly, a 1,3-C,N-shift of **16c** furnishes the ylide **19**, which experiences a Cα–S bond rotation followed by a 1,3-N,C-shift of the Ti atom to deliver complex **16d**. This process causes a topomerization of the hydrogens between the methylene groups. The complete topomerization of all four methylene hydrogens is achieved by two further Ti–H elimination/reinseration sequences involving complexes **16d** and **16e**, which deliver complex **16f**.

The second process also leads to a topomerization of the two Cα-ethyl groups, as revealed by the temperature-dependent ^{13}C NMR spectra of **16**. Particularly important factors for the rapid establishment of the equilibria depicted in Scheme 6 should be (1) the formation of donor-stabilized titanium hydrides as intermediates, (2) the intramolecular β-H elimination, and (3) the intramolecular hydridotitanation of the double bond. The observation of diastereotopic methylene hydrogens of the tris(diethyl)amino group in all of the variable-temperature NMR spectra of complex **16** is consistent with the proposed intramolecular course of both processes. The regioselectivity of the insertion of the Ti–H bond into the alkene could be determined by the coordination of the titanium hydride to the sulfonimidoyl group and the intramolecular course of the reactions.

Single steps of the processes depicted in Scheme 6 and the possible existence of the hydrido complexes **18a** and **18b** are supported by literature precedents. For example, it is has been shown that (1) alkyltitanium(IV) complexes decompose by a β-hydride elimination with formation of alkenes[27] and (2) titanium(IV) hydride complexes that carry O and/or N atom based ligands at the Ti atom[28a–d] undergo an alkene insertion in the Ti–H bond.[28c,d] Furthermore the isolation of a stable (ArO)$_3$TiH/PMe$_3$ complex, which may serve as a model for the hydrido complexes **18a** and **18b**, had been reported.[28b] The low-temperature ^{1}H NMR spectra of **16** did not show the characteristic Ti–H signals expected[28] for hydrido complexes of type **18a** and **18b**. This does, however, not speak against the existence of these complexes because of the possibility of their presence in only minute amounts. Finally it should be noted that while a reversible β-hydride elimination and alkene-hydride insertion of alkylmetal complexes are well documented and have been directly observed for a number of transition metals, the NMR spectroscopic detection of such a process of an alkyltitanium(IV) complex has apparently not been described before.[29–31]

The 1,3-C,N-shift of the Ti atom of the alkyltitanium complex **16** is expected to be less facile than the corresponding shift of the Ti atom of the allyl titanium complexes **A** and **B** because of the absence of the stabilization of the negative charge by the double bond. In principle, the second process of Scheme 6 (**16c** → **19** → **16d** and vice versa), leading to a crossover topomerization of the hydrogens, could also proceed via a reversible dissociation of **16** with the formation of a contact ion pair of type $[Ti(NEt_2)_3]^+/[PhS(O)(NMe)CEt_2]^-$. However,

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[27] (a) Akita, M.; Yasuda, H.; Nagasuna, K.; Nakamura, A. *Bull. Chem. Soc. Jpn*. **1983**, *56*, 554–558. (b) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc*. **1983**, *105*, 1136–1143. (c) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc*. **1997**, *119*, 8630–8641. (d) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc*. **1999**, *121*, 7822–7836. (e) de Meijere, A.; Kozhushkov, S. I.; Savchenko, A. I. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002; pp 390–434.

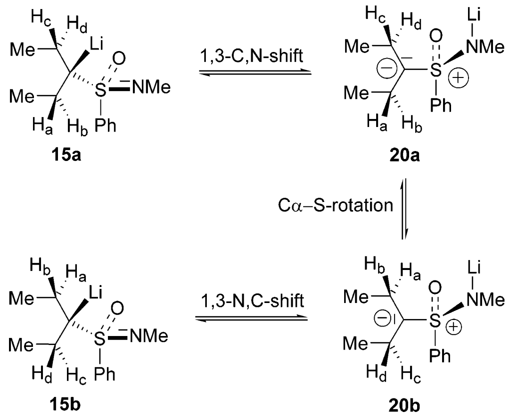
[28] (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452–1454. (b) Nöth, H.; Schmidt, M. *Organometallics* **1995**, *14*, 4601–4610. (c) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc*. **1997**, *119*, 10696–10719. (d) Turculet, L.; Tilley, T. D. *Organometallics* **2004**, *23*, 1542–1553.

[29] (a) Schrock, R. R.; Parshall, G. W. *Chem. Rev*. **1976**, *76*, 243–268. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev*. **1976**, *76*, 219–242. (c) Reetz, M. *Organotitanium Reagents in Organic Synthesis;* Springer-Verlag: Berlin, 1986. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Brookhart, M.; Green, M. L. H.; Wong, L.-L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1988; Vol. 36, pp 1–124. (f) Bochmann, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, 1995; Vol. 4, pp 273–421.

[30] (a) Green, M. L. H.; Sella, A.; Wong, L.-L. *Organometallics* **1992**, *11*, 2650–2659. (b) Tempel, D.; Brookhart, M. *Organometallics* **1998**, *17*, 2290. (c) Umezawa-Vizzini, K.; Lee, T. R. *Organometallics* **2004**, *23*, 1448–1452.

[31] For the observation of a reversible alkene extrusion upon reaction of an alkyltitanium(III) complex with alkenes, which proceeds via an intermediate titanium(III) hydride, see: Luinstra, G. A.; Voegelzang, J.; Teuben, J. H. *Organometallics* **1992**, *11*, 2273–2281.

Scheme 7. Mechanistic Scheme for the Crossover Topomerization of the Ethyl Hydrogens of the Lithiated Sulfoximine **15**



the formation of a trisdiethylaminotitanium cation would not be compatible with the observation of diastereotopic methylene hydrogens for the *N*-ethyl groups in the ^{1}H NMR spectrum of **16** even at room temperature and can thus be excluded.

The complete topomerization of the Cα-methylene hydrogens of the titanium complex **16** cannot alone be brought about by a 1,3-C,N-shift of the Ti atom and a Cα−S bond rotation. Such processes lead only to a crossover topomerization of hydrogens between the Cα-methylene groups (cf. Scheme 6 and vide infra). The topomerization of the hydrogens within the methylene groups can be accomplished only by a reversible cleavage of the C−H bonds. On the basis of this consideration it was of interest to investigate the corresponding sulfonimidoyl-substituted alkylithium derivative **15** (Scheme 7) by NMR spectroscopy.

Previous studies of lithioalkyl sulfoximines had revealed a 1,3-C,N-coordination of the Li atom as shown in **15a** and a low configurational stability of the Cα atom.[8a,b,32] The later feature is due to a fast 1,3-shift of the Li atom in **15a** and **15b** and a low barrier for rotation around the Cα−S bond of **20a** and **20b**.[33] In this respect the lithioalkyl sulfoximine **15** resembles the titanium complex **16**. However, unlike the facile reversible Ti−H elimination/reinsertion of **16**, a reversible Li−H elimination of **15** is a process not likely to occur at room temperature.[34] Thus the dynamic processes of **15** depicted in Scheme 7 should lead only to a topomerization of H_a and H_d and of H_b and H_c and vice versa but not to an exchange of the hydrogens within the methylene groups at the Cα atom as observed for **16**. Indeed, the ^{1}H NMR spectrum of **15** in [D$_8$]-THF at room temperature showed two sharp multiplets for the methylene hydrogens and one sharp triplet for the methyl hydrogens of the ethyl groups at the Cα atom. The ^{13}C NMR spectrum of **15** in [D$_8$]-THF at room temperature featured for both methylene C atoms and both methyl C atoms one sharp signal each.

Finally, it seems interesting to note that the ^{1}H NMR spectrum of the isopropoxy-substituted complex **17** (cf. Scheme 5) at room temperature in [D$_8$]-THF shows four sharp well-separated multiplets for the methylene hydrogens of the ethyl groups and the ^{13}C NMR spectrum features two signals for the methylene groups and two signals for the methyl groups. Thus in the case of the isopropoy-substituted complex **17** the Ti−H elimination and the 1,3-C,N-shift of the Ti atom are less facile processes than in the case of the diethylamino-substituted complex **16**. This observation points to an important role played by the diethylamino groups of **16** in its dynamics.

Conclusion

N-Methylsulfonimidoyl-substituted allyl tris(diethylamino)-titanium(IV) complexes undergo a fast intramolecular 1,3-C,N-shift of the Ti atom. This leads to the formation of an equilibrium mixture of Cα-titanium allyl complexes and *N*-titanium allyl ylides, the equilibrium composition depending on the configuration of the double bond. As a consequence, these complexes exhibit a low configurational stability at the Cα atom. The equilibrium complexes generally have a configurationally stable double bond except in the case of the methyl-substituted complexes, which experience a slow *E*/*Z* isomerization. Whether this is caused by a 1,3-C,C-shift of the Ti atom cannot be told on the basis of the present data.

The observation of a fast equilibrium between the Cα-titanium allyl complexes and the *N*-titanium allyl ylide allowed the development of a reactivity model for the regio- and stereoselective reaction of the complexes with aldehydes. This model, which is based on the Curtin−Hammett principle, features selective reactions of aldehydes with the *N*-titanium allyl ylide and the *S*-configured Cα-titanium complex via six-membered boat-like and chair-like cyclic transition states at the α- and the γ-position, respectively. The increase in regioselectivity with increasing size of the substituents is attributed to a greater steric interaction between R^1 and R^2 in the chair-like transition state than between R^2 and the alkenyl group in the boat-like transition state.

On the basis of the observation of two coalescence phenomena in the ^{1}H and ^{13}C NMR spectra of **16** in [D$_8$]-THF and [D$_8$]-toluene solution, it is concluded that the *N*-methylsulfonimidoyl-substituted alkyl tris(diethylamino)titanium(IV) carrying two ethyl groups at the Cα atom shows a dynamic behavior that is characterized by a complete topomerization of all of the diastereotopic hydrogens of the two Cα-ethyl groups. Two processes are proposed in order to account for this phenomenon. The first one involves a reversible intramolecular β-hydride elimination and alkene-Ti−H bond insertion with the intermediate formation of a donor complex between $(Et_2N)TiH$ and a 1-alkenyl sulfoximine, and the second one features a reversible 1,3-C,N-shift of the Ti atom together with a rotation around the Cα−S bond. Although precedent exists for the single steps of the β-hydride elimination and alkene Ti−H bond insertion, a reversible process of this type of an alkyltitanium(IV) complex has apparently not been observed by NMR spectroscopy before.

According to ab initio calculations, the methylene (dimethylamino)sulfoxonium ylide and the allyl (dimethylamino)sulfox-

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(32) (a) Gais, H.-J.; Erdelmeier, I.; Lindner, H. J.; Vollhardt, J. *Angew. Chem.* **1986**, *98*, 914−915; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 938−939. (b) Gais, H.-J.; Dingerdissen, U.; Krüger, C.; Angermund, K. *J. Am. Chem. Soc.* **1987**, *109*, 3775−3776. (c) Müller, J. F. K.; Batra, R.; Spingler, B.; Zehnder, M. *Helv. Chim. Acta* **1996**, *79*, 820−826. (d) Müller, J. F. K.; Neuburger, M.; Spingler, B. *Angew. Chem.* **1999**, *111*, 3766−3769; *Angew. Chem., Int. Ed.* **1999**, *38*, 3549−3552.

(33) The 1,3-C,N-shift of the Li atom of **15** could also take place within a cyclic eight-membered dimer of **15**, the Li atoms of which are each coordinated by a Cα atom and a N atom; see ref 32a. Alternatively, the topomerization of the hydrogens of the methylene groups could proceed within an ion pair formed through dissoziation of **15**.

(34) Schöllkopf, U. In *Methoden der Organischen Chemie* (*Houben-Weyl*); Müller, E., Ed.; Thieme: Stuttgart, 1970; Bd. XIII/1, pp 86−251.

onium ylide have rather short and highly polar Cα−S bonds. Stabilization of the ylides is provided by electrostatic interaction and negative hyperconjugation, two modes of stabilization that also operate in the case of α-sulfonimidoyl and α-sulfonyl carbanions.[8,26] Because of a maximization of the negative hyperconjugation and a minimization of the repulsion between the two lone pair orbitals at the Cα atom and the N atom, both ylides preferentially adopt Cα−S and Cα−N conformations in which the lone pair orbital at the Cα atom is periplanar to the S═O bond and that at the N atom is periplanar to the S−Ph bond. The methylene ylide and most likely also the allyl ylide have rather low Cα−S bond rotational barriers. All together these results are supportive of a metallotropic C,N-shift of the Ti atom in the mono(allyl) complexes **IV**.

Acknowledgment. Financial support of this work by the Deutsche Forschungsgemeinschaft (Collaborative Research Center “Asymmetric Synthesis with Chemical and Biological Methods”) is gratefully acknowledged.

Supporting Information Available: Scheme S1 showing the synthesis of *E*-**1a**−**c** and *Z*-**1a**−**c**; Scheme S4 showing the synthesis of **15** and **16**; Figure S1 showing the relative energies and structures of ylides **13c**−**e**; Schemes S2 and S3 showing a mechanistic rationalization of the *E*/*Z* isomerization of *E*-**1c** and *Z*-**1c**; discussion of Schemes S2 and S3; Table S1 showing the bonding parameters of **10a**, **13a**, **13b**, and **14**; experimental procedures and NMR data for *E*-**1a**, *Z*-**1a**, *E*-**1b**, *Z*-**1b**, *E*-**1c**, *Z*-**1c**, *E*-**2a**, *Z*-**2a**, *E*-**2b**, *Z*-**2b**, *E*-**2c**, *Z*-**2c**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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