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Novel Aryltitanium(IV) Complexes Containing η^3-NCN-Pseudofacial- and η^3-NCN-Meridional-Bonded $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (Abbreviated as NCN) Ligands. The Crystal Structures of $[TiCl_2(\eta^3\text{-}fac\text{-NCN})(O\text{-}i\text{-Pr})]$, $[TiCl(\eta^3\text{-}mer\text{-NCN})(O\text{-}i\text{-Pr})(OTf)]$ Containing an η^1-O-Bonded Triflate Anion, and the Seven-Coordinated $[Ti(\eta^3\text{-}mer\text{-NCN})(O\text{-}i\text{-Pr})(OTf)_2]$ Containing η^1-O- and η^2-O,O′-Bonded Triflate Anions

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Titanium(IV) derivatives of the chelating monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (abbreviated as NCN) are prepared by treating $[TiCl_3(OR)]$ (R = *i*-Pr, C_6H_4-OMe-4) with $[Li(NCN)]_2$. $[TiCl_2(NCN)(O\text{-}i\text{-Pr})]$ is smoothly methylated by methyllithium in toluene to give $[TiClMe(NCN)(O\text{-}i\text{-Pr})]$ and $[TiMe_2(NCN)(O\text{-}i\text{-Pr})]$. Enhancement of the Lewis acidity of the titanium center has been studied by substituting chloro ligands for triflato ligands to give $[TiCl(NCN)(O\text{-}i\text{-Pr})(OTf)]$ and $[Ti(NCN)(O\text{-}i\text{-Pr})(OTf)_2]$. X-ray studies of the dichloride and triflate complexes feature η^3-pseudofacial and η^3-meridional bonding modes for the NCN ligand, respectively. These different NCN bonding modes are explained in terms of the *trans* influence of the alkoxy and triflato ligands. A rare example of an organo titanium(IV) complex with a seven-coordinate titanium center is observed in the bis(triflate) complex as a result of bidentate O,O′-bonding mode of the triflato anion to one titanium center that is unprecedented in early transition metal chemistry. The triflato ligands exhibit a strong covalent bonding to titanium both in the solid state and in solution; the latter is demonstrated by the observation that cationic species are not formed upon addition of Lewis bases like THF, acetonitrile, and 1,2-bis(dimethylamino)ethane.

Introduction

Group 4 based bent metallocene complexes are important catalyst precursors for a variety of oligomerization and polymerization processes, of which homogeneous Ziegler−Natta type α-olefin polymerization is probably the most important.[1] To achieve better control over the properties of the resulting polymer, new catalyst systems have been developed through ligand modifications of the ancillary cyclopentadienyl ligand(s).[2] There is also an increased interest in the development of new ancillary ligands which can be used as alternatives for the cyclopentadienyl (abbreviated as Cp) ligand systems. Among the systems that have been developed are alkoxides,[3] aryloxides,[4] amides,[5] porphyrins,[6] benzamidinates,[7] β-diketiminates,[8] carboranes,[9] and amidodiphosphines.[10]

Both the Cp and non-Cp ligand systems affect the coordinative unsaturation and the Lewis acidity of the metal center. An enhanced Lewis acidic metal center is expected to increase the polymerization activity for α-olefins.[11] The linked amido−cyclopentadienyl ligands introduced by Bercaw and Shapiro[2a−e] are an example of a modified ligand system that provided complexes with enhanced Lewis acidity as compared to metal-

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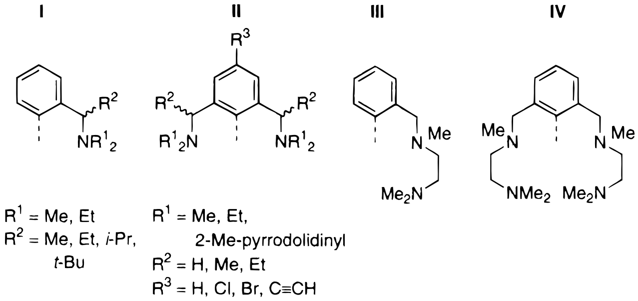

Figure 1. Examples of monoanionic arylamine ligands.

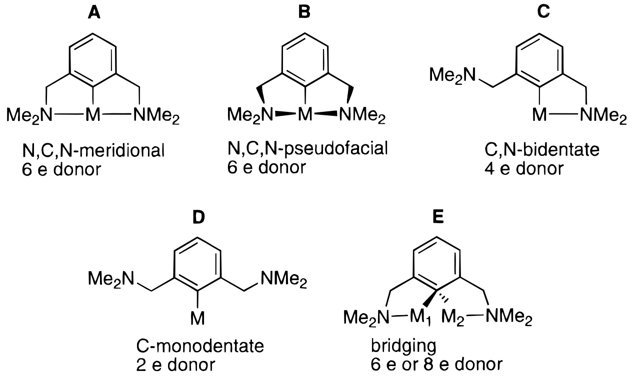

Figure 2. Previously reported bonding modes for NCN.

locenes. In fact, the first examples of homogeneous single-component living α-olefin polymerization catalysts are represented by the corresponding scandium complexes $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)ScR]$.[2d] Furthermore, the stereoselectivity of propylene insertion was shown to increase when cationic ethylene-bridged bis(indenyl)zirconium systems are used.[12]

Research in our group is focused on the use of ligand systems that combine a hard anionic (*cf.* Cp) aryl carbon atom with additional coordinating nitrogen donor atoms (Figure 1). It has been shown that the monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (abbreviated as NCN, Figure 1, **II** with $R^1 = Me$, $R^2 = R^3 = H$) can coordinate to a variety of metal centers with different bonding modes (Figure 2).[13] The additional NMe_2 units can interact with the metal center thereby leading to control of the coordinative unsaturation of the metal center. This is in contrast to Cp ligands, which can only change their coordination mode by ring slippage (η^5, η^3, and η^1). The unique properties of the NCN ligand led to new organometallic complexes with interesting catalytic activities different from those of the analogous Cp complexes.[13a,b] For example, the tantalum(V) complex $[TaCl({=}CCMe_3)(NCN)(O\text{-}t\text{-}Bu)]$ showed a reactivity with simple alkenes that varies from nonselective (probably reductive rearrangement) reactions to very clean alkene metathesis reactions.[14]

In this paper we present our initial results on the use of the NCN ligand in titanium(IV) organometallic chemistry. The synthesis and characterization of a range of (NCN)titanium(IV) complexes is described together with the molecular structures of $[TiCl_2(NCN)(O\text{-}i\text{-}Pr)]$, $[TiCl(NCN)(O\text{-}i\text{-}Pr)(OTf)]$, and $[Ti(NCN)(O\text{-}i\text{-}Pr)(OTf)_2]$.

Results and Discussion

Our initial attempts to prepare (NCN)titanium(IV) complexes involved the reactions of $TiCl_4$ or $TiCl_4(THF)_2$ with $[Li(NCN)]_2$ in 2:1 molar ratios in toluene at −78 °C. Immediately a color change to dark green was observed with the concomitant formation of a precipitate (LiCl). After complete addition, the color of the reaction mixture had turned to black/brown. Unfortunately, from these reaction mixtures no (NCN)titanium complexes could be isolated in significant yield. We there-

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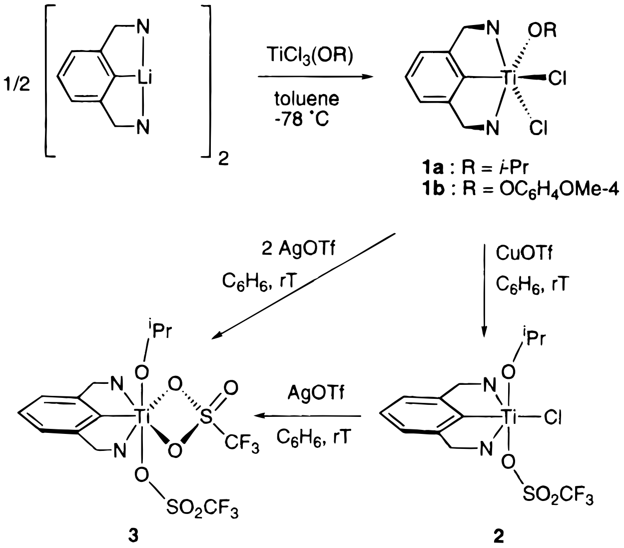
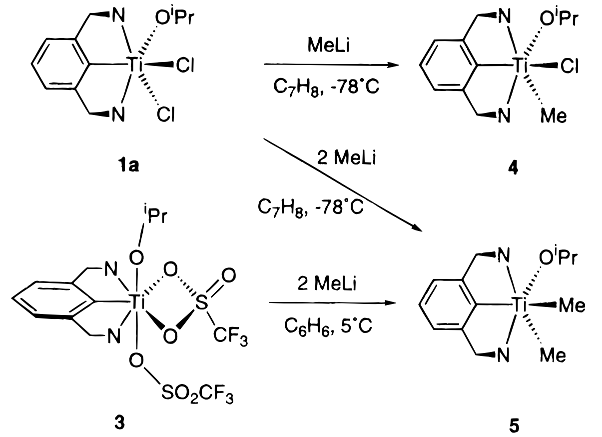
Scheme 1. Synthesis of [TiCl$_2$(NCN)(OR)] [R = *i*-Pr (1a), C$_6$H$_4$OMe-4 (1b)], [TiCl(NCN)(O-*i*-Pr)(OTf)], 2, and [Ti(NCN)(O-*i*-Pr)(OTf)$_2$], 3 (N = NMe$_2$)



Scheme 2. Synthesis of [TiClMe(NCN)(O-*i*-Pr)], 4, and [TiMe$_2$(NCN)(O-*i*-Pr)], 5 (N = NMe$_2$)



fore turned to other titanium(IV) salts, *i.e.*, trichlorotitanium(IV) alkoxide reagents.

The reaction of [Li(NCN)]$_2$ with 2 equiv of [TiCl$_3$(OR)] (R = *i*-Pr, C$_6$H$_4$OMe-4) in toluene at −78 °C gave the new (diaminoaryl)titanium(IV) complexes [TiCl$_2$(NCN)(OR)] (**1a**, **b**) [R = *i*-Pr (**1a**), C$_6$H$_4$OMe-4 (**1b**)] (Scheme 1). Due to the low solubility of the phenoxide complex **1b** in common polar or nonpolar solvents further studies on (NCN)titanium(IV) complexes were focused on the (isopropoxy)titanium(IV) complex **1a**.

As a potential route to enhance the Lewis acidity of the metal center, we explored the preparation of (NCN)titanium(IV) triflate complexes. The reaction of **1a** with either 1 equiv of CuOTf or 2 equiv of AgOTf in benzene at room temperature resulted in the formation of the mono- and bis(triflate) complexes **2** and **3**, respectively (Scheme 1). The preparation of **3** can also be accomplished by reacting **2** with 1 equiv of AgOTf under the same conditions.

To explore the preparation of (NCN)titanium(IV) alkyl species the corresponding mono- and dimethyl complexes have been prepared (Scheme 2). The reaction of a solution of **1a** in toluene with 1 or 2 equiv of MeLi (solution in Et$_2$O) at −78 °C resulted in the almost quantitative isolation of the mono- and dimethyl−(NCN)titanium(IV) complexes **4** and **5**, respectively. Alternatively, **5** is also accessible by reacting a solution of **3** in benzene with 2 equiv of MeLi at 5 °C. The dichloride complex **1a** was also reacted with 1 or 2 equiv of *n*-BuLi under conditions similar to those used for the preparation of **4** and **5**. Upon addition a color change of the reaction mixture to dark brown/black was observed, but we were unable to isolate pure material from these reactions.

The (NCN)titanium(IV) complexes **1**−**5** are air and moisture sensitive materials with discrete melting points of which the bis(triflate) complex **3** and the dimethyl complex **5** melt with decomposition. In the solid state, complexes **1**−**4** can be stored for months in an inert atmosphere. This is in contrast with the stability of the dimethyl complex **5**, which is stable for longer periods only below 0 °C. At room temperature **5** slowly decomposes to protonated NCN and unidentified products which hampered the microanalysis of this complex.

The complexes **1**−**3** are soluble in aromatic solvents and ethers but are sparingly soluble in saturated hydrocarbons, while the methyl complexes **4** and **5** readily dissolve in both polar and nonpolar solvents. Solutions of **1** in toluene can be refluxed for several hours without decomposition, whereas toluene solutions of the triflate and methyl complexes **2**−**5** decompose to give protonated NCN and products that have not been identified.

Molecular weight determinations (cryoscopy in benzene) of **1a**, **2**, **4**, and **5** showed these complexes to exist as monomeric species in this solvent. A concentration dependent molecular weight varying from 1.0 ($c = 6$ *m*) to 1.6 ($c = 55$ *m*) was observed for the bis(triflate) complex **3**, which points to a monomer−dimer equilibrium. Molecular weight determination of **1b** failed due to its low solubility in benzene.

The ^{1}H and ^{13}C{^{1}H} NMR data of the (NCN)titanium(IV) complexes (Table 1) confirmed their proposed composition. The NCN resonances are observed at chemical shift positions which are commonly encountered in (NCN)metal complexes.[13] The Ti−*Me* resonances in **4** (δ 0.95) and **5** (δ 0.68) have chemical shifts similar to those observed for [Cp$_2$TiMeR][15] ($\delta = 0.61$−1.00) and [TiMe(O-*i*-Pr)$_3$][15b] ($\delta = 0.98$).

At low temperature (220 K), the dichloride (**1**), methyl chloride (**4**), and dimethyl (**5**) complexes display four N−*Me* resonances in both the ^{1}H and ^{13}C{^{1}H} NMR spectra. This indicates that at this temperature these complexes have C_1 molecular symmetry. In addition, it indicates that both the NMe$_2$ units are coordinated to the titanium center as bidentate C,N-coordination of NCN would result in three N−*Me* resonances in a 1:1:2 ratio and monodentate C-coordination of NCN in only one N−*Me* resonance. Assuming a regular octahedral coordination for these complexes, a number of geometries can be considered which have either η^3-(pseudo)-facially or η^3-meridionally coordinated NCN ligands (Figure 3). It should be noted that in solutions of η^3-meridionally bonded (NCN)metal complexes, low energy barriers are found for the ring-flippage of the two five-membered chelate rings.[13]

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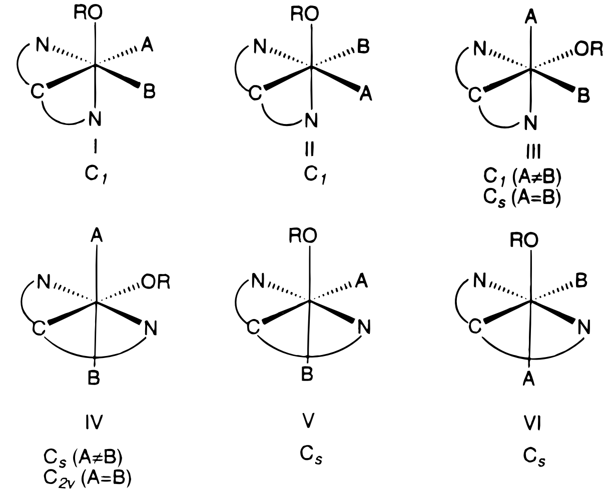
Table 1. Relevant ^{1}H and ^{13}C{^{1}H} NMR Data of the Dichloro, Triflato, and Methyl(NCN)titanium(IV) Complexes 1−5[a]

		^{13}C{^{1}H} NMR data		^{1}H NMR data	
complex	*T* (K)	CH$_2$N	NMe$_2$	CH$_2$N	NMe$_2$
[TiCl$_2$(NCN)(O-*i*-Pr)], **1a**	297[b]	68.4	50.3, 46.6	4.7, 2.6	2.8, 2.1
	220[c]	68.8, 67.4	50.6, 50.1, 47.0, 46.1	4.7, 4.5, 2.38, 2.39	3.0, 2.6, 2.2, 1.6
[TiCl$_2$(NCN)(OC$_6$H$_4$OMe-4)] **1b**	297[b]	69.0	50.6, 45.4	4.5, 2.7	2.8, 2.25
	220[c]	*d*	*d*	4.8, 4.35, 2.5[e]	3.0, 2.55, 2.2, 1.8
[TiCl(NCN)(O-*i*-Pr)(OTf)], **2**	297[b]	71.5	52.1, 50.7	3.79, 3.44	2.61, 2.37
[Ti(NCN)(O-*i*-Pr)(OTf)$_2$], **3**	297[b]	71.5	52.0, 49.6	3.8, 3.3	2.6, 2.3
[TiClMe(NCN)(O-*i*-Pr)], **4**	297[b]	*d*	*d*	3.6[e]	2.3
	220[c]	64.3, 62.8	44.7, 44.6, 41.6, 40.7	4.8, 4.4, 2.5[e]	2.75, 2.38, 2.20, 1.68
[TiMe$_2$(NCN)(O-*i*-Pr)], **5**	297[b]	68.1	46.8	3.6	2.25
	220[c]	68.3, 67.4	49.0, 46.4, 45.8, 45.7	4.45, 4.35, 2.62[e]	2.50, 2.25, 2.15, 2.12

[a] Chemical shifts in δ are indirectly referenced to SiMe$_4$ using solvent signals. [b] In benzene-d_6. [c] In toluene-d_8. [d] Not measured. [e] Two overlapping doublets each of 1H intensity, assigned by selective ^{1}H irradiation.



1: A = B = Cl
2: A = Cl, B = OTf
3: A = B = OTf
4: A = Cl, B = Me
5: A = B = Me

Figure 3. Possible molecular geometries in regular octahedral complexes containing an η^3-N,C,N-bonded NCN ligand.

For **1** and **5** only geometries I, III, IV, and V need to be considered. Structures III, IV, and V can be excluded on the basis of symmetry (C_s, C_{2v}, and C_s, respectively), leaving only one possible structure, *i.e.*, I, in which the NCN ligand is facially coordinated and the alkoxy ligand is positioned *trans* to one of the NMe$_2$ units. Similar arguments apply to **4**, leading to structures I, II, and III as possible geometries, all with facially coordinated NCN ligands. For **1a** the structural assignment presented above was confirmed by an X-ray diffraction study (*vide infra*).

The triflate complexes **2** and **3** display only two NMe resonances in their NMR spectra, indicative of a higher symmetry of these complexes compared to **1**, **4**, and **5**. Considering that the triflato ligand can occupy either one or two coordination sites at the metal center (*vide infra*) and the fact that fluxional behavior cannot be excluded *a priori*, a structural assignment is more difficult. However, X-ray diffraction data revealed that mononuclear **2** and **3** have (distorted) octahedral structures (when the η^2-O,O′-bonded triflato ligand in **3** is considered as one of the vertices) with meridionally coordinated NCN ligands (*vide infra*), *i.e.*, structure V for both **2** and **3**. This is in full agreement with the NMR data since in solution these structures are expected to have time-averaged C_s symmetry as a result of rapid ring-flippage of the two five-membered chelate rings.

Fluxional Behavior of the (NCN)titanium(IV) Complexes in Solution. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**−**5** show temperature dependent characteristics, involving the N−*Me*, methylene, and aromatic protons of the NCN ligand, the isopropoxy protons, and the Ti−*Me* protons in **5**, consistent with these species being fluxional in solution. Experiments at variable concentrations (for **3**, concentrations lower than 10 *m* were used to prevent dimer formation) showed these fluxionalities to be concentration independent, indicating that intramolecular processes are operative. The energy barriers ($\Delta G^\ddagger$) of the fluxional processes in **1**−**5** (calculated from the Eyring equation and the coalescence temperature T_c)[16a] are presented in Table 2a. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of the fluxional processes in **1a** and **3** (determined from an Eyring plot)[16b] are presented in Table 2b.

In both the dichloride complexes (**1**), a low-energy and a high-energy fluxional process are observed. In contrast, in the methyl chloride (**4**) and dimethyl (**5**) complexes, which contain an η^3-pseudofacially bonded NCN ligand, only one fluxional process is observed. The high-energy process in **1** and the fluxional processes in **4** and **5** are associated with the coalescence of the N−*Me*, methylene, and, for **5**, Ti−*Me* signals. One possible explanation that would lead to this coalescence pattern is a simple process involving the association and dissociation of the Ti−N dative bond, thereby allowing low-energy pyramidal inversion to take place at the nitrogen atom. This conclusion is consistent with a calculated positive $\Delta S^\ddagger$ value for the process in **1a** (Table 2b) and the observation in the NMR spectra of N−*Me* resonances for the NCN ligand which are, at the fast exchange limit, at a position comparable to that for protonated NCN. In addition, this type of process has been proposed in many other (NCN)metal complexes.[13]

The lower energy process observed in the dichloride complexes **1a**,**b** is associated with (Figure 4) the coalescence of four N−*Me* signals to two signals and two AX patterns of the methylene protons to one AX pattern. Simultaneously, the coalescence of the alkoxy methyl

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(16) Eyring equation: $\Delta G^\ddagger = -RT_c \ln[2\pi h(\Delta\nu)/kT_c\sqrt{3}]$ with $\Delta G^\ddagger$ = free energy of activation (J), T_c = coalescence temperature (K), and $\Delta\nu$ = chemical shift difference (Hz); the other symbols have their usual meanings. (b) Eyring plot: $\ln(k/T) = C + \Delta S/R + (-\Delta H/R)(1/T)$, with k = rate constant (s^{-1}), T = temperature (K), C = 23.758, ΔS = entropy value (J mol^{-1} K^{-1}), R = 8.314 J mol^{-1} K^{-1}, ΔH = enthalpy value (J mol^{-1}).

Table 2

(a) Calculated[a] Energy Barriers (±2 kJ mol^{-1}) for the Observed Fluxional Processes in the Dichloro, Triflato, and Methyl (NCN)titanium(IV) Complexes **1**–**5**

complex	$\Delta G^{\ddagger}$ (T_c) (kJ mol^{-1}1 (K))			
	NMe$_2$	CH$_2$	OCH*Me*$_2$	Ti–*Me*
[TiCl$_2$(NCN)(O-*i*-Pr)], **1a**	56 (278)	56 (262)	56 (265)	*b*
	64 (324)	63 (335)	*b*	*b*
[TiCl$_2$(NCN)(OC$_6$H$_4$OMe-4)], **1b**	52 (269)	52 (266)	*b*	*b*
	60 (300)	59 (318)	*b*	*b*
[TiCl(NCN)(O-*i*-Pr)(OTf)], **2**	66 (310)	64 (318)	*b*	*b*
[Ti(NCN)(O-*i*-Pr)(OTf)$_2$], **3**	69 (330)	69 (342)	*b*	*b*
[TiClMe(NCN)(O-*i*-Pr)], **4**	52 (262)	51 (275)	52 (267)	*b*
[TiMe$_2$(NCN)(O-*i*-Pr)], **5**	43 (220)	45 (238)	43 (215)	43 (230)

(b) Calculated[c] Activation Parameters for the Observed Fluxional Processes in the Dichloride and Bis(triflate) Complexes **1a** and **5**

complex	coalescing groups	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
[TiCl$_2$(NCN)(O-*i*-Pr)], **1a**	aromatic protons	41 ± 4	−52 ± 10
	CH$_2$[d]	36 ± 4	−74 ± 10
	CH$_2$[e]	74 ± 2	28 ± 5
[Ti(NCN)(O-*i*-Pr)(OTf)$_2$], **3**	NMe$_2$	86 ± 4	63 ± 10

[a] Reference 16a. [b] Not Observed. [c] Reference 16b. [d] Low-temperature coalescence. [e] High-temperature coalescence.

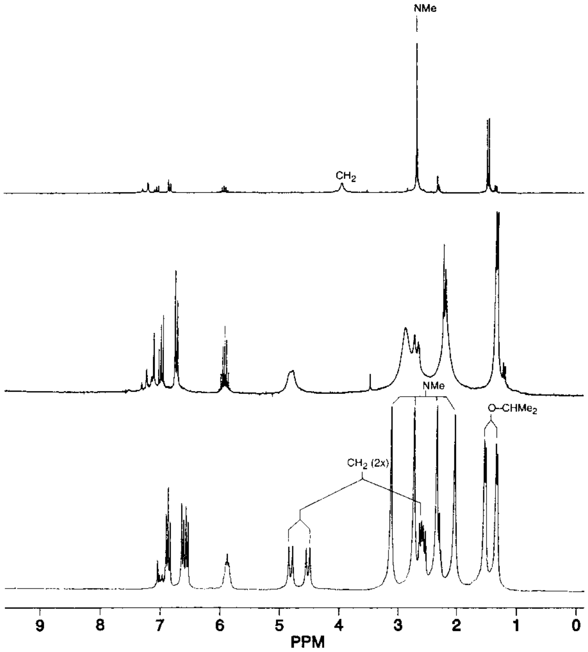

Figure 4. ^{1}H NMR spectra of **1a** showing the coalescence behaviour of **1a** in solution.

protons in **1a** and the aromatic protons H(3) and H(5) is observed.

Using a NOESY NMR experiment (at 205 K) of a sample of **1a** we could assign the N–*Me* resonances of each of the two NMe$_2$ units of **1a**. From this assignment it was evident that the observed coalescence pattern is obtained by rendering a N–*Me* group of one NMe$_2$ unit homotopic with a N–*Me* group of the other NMe$_2$ unit. Therefore, a process involving complete M–N dissociation can be excluded as this process would result in the coalescence of N–*Me* resonances of the same NMe$_2$ unit through pyramidal inversion at the nitrogen atom. The strongly negative $\Delta S^{\ddagger}$ value calculated for this process (Table 2b) is in agreement with such a nondissociative process. However, a process involving partial elongation of the Ti–N dative bond, possibly leading to tbp-like intermediates, cannot be excluded.

From these observations we conclude that a nondissociative, intramolecular isomerization process must be operative. A similar conclusion was also made about the fluxional processes in adducts of methyltitanium trichloride with bidentate ligands as, for example, dimethoxyethane or 1,2-bis(dimethylamino)ethane.[17] The isomerization process in **1a** probably involves either (i) a change in the NCN coordination mode from η^3-pseudofacial to η^3-meridional or (ii) site-exchange processes of the alkoxy and chloro ligands. Site-exchange processes which have been proposed in hexa-coordinate species are (i) the trigonal or Bailar twist,[18] (ii) the rhombic or Ray–Dutt twist,[19] and (iii) the edge inversion process.[20]

No evidence could be obtained that provided unequivocal evidence about which process is operative. A tentative assumption is that the operative process involves the change in the NCN coordination mode from η^3-pseudofacial to η^3-meridional. An argument in favor of this is that stable η^3-pseudofacially bonded (NCN)-titanium(IV) complexes have been prepared, *i.e.*, the triflate complexes **2** and **3** (*vide infra*).

In the triflate complexes **2** and **3** (with an η^3-meridionally bonded NCN ligand) only one fluxional process is observed, associated with the coalescence of the N–*Me* and methylene signals. For this process a positive $\Delta S^{\ddagger}$ was determined (Table 2b) in agreement with a dissociative process. A likely explanation that would lead to the observed coalescence phenomena is a simple process involving Ti–N dissociation/association. This process is also observed in **1**, **4**, and **5** (*vide supra*) and many other (NCN)metal complexes.[13]

The NMR data provided unambiguous information about the coordination mode of NCN in **1** and **5**, but not for **2**, **3**, and **4**, nor about the coordination mode of the triflato ligands in **2** and **3**. We therefore subjected single crystals of **1a**, **2**, and **3** to X-ray diffraction studies. Attempts to crystallize the methyl derivatives **4** and **5** failed because of their high solubility in common polar and nonpolar solvents while crystallization of the

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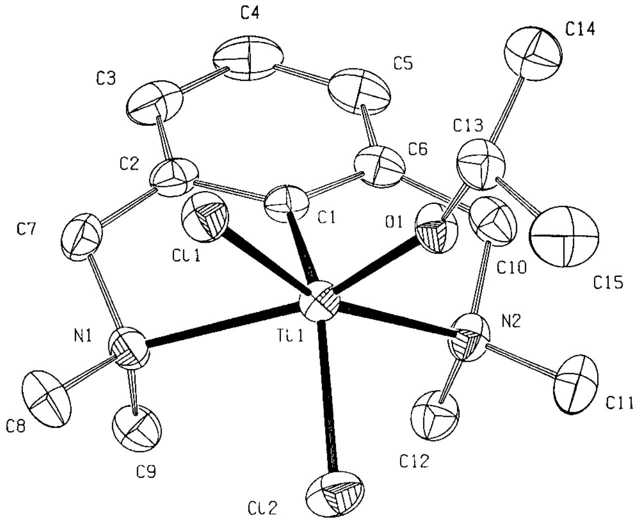

Figure 5. ORTEP drawing of complex **1a** at the 30% probability level. The hydrogen atoms are omitted for clarity.

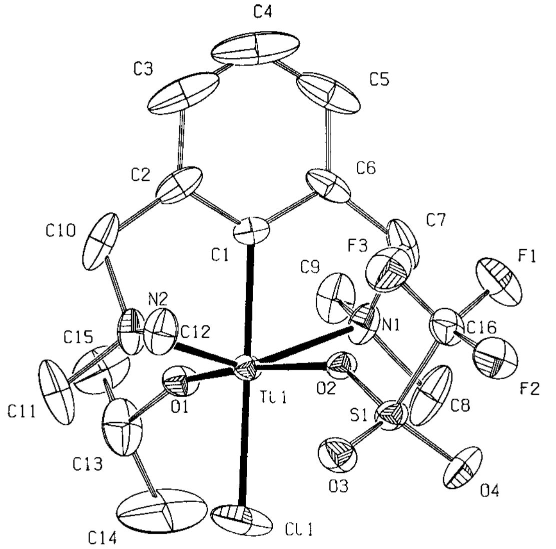

Figure 6. ORTEP drawing of complex **2** at the 30% probability level. The hydrogen atoms are omitted for clarity.

phenoxide complex **1b** was hampered by its low solubility in these solvents.

Molecular Structures of [TiCl$_2$(η^3-*fac*-NCN)(O-*i*-Pr)], 1a, [TiCl(η^3-*mer*-NCN)(O-*i*-Pr)(OTf)], 2, and [Ti(η^3-*mer*-NCN)(O-*i*-Pr)(OTf)$_2$], 3, in the Solid State. The molecular structures of **1a**, **2**, and **3** are shown in the Figures 5, 6, and 7, respectively, while selected bond distances and angles can be found in Table 3. The coordination sphere of the titanium center in the dichloride complex **1a** (Figure 5) can best be described as antiprismatic, which is a common geometry for d^0 metal complexes.[21]

The N(1)–Ti–N(2) angle (113.23(10)°) points to an η^3-pseudofacial coordination of the NCN ligand in accord with the NMR data (Table 1) (*vide supra*). This coordination mode for the NCN ligand has recently been observed in several main group and transition metal complexes.[13a,i–m] The η^3-pseudofacial coordination places the NMe$_2$ moieties in closer proximity of each other as compared to an η^3-meridionally bonded NCN ligand. Consequently, the smaller chloro ligand (Cl(2)), as compared to the alkoxy ligand, is placed in between the two NMe$_2$ moieties. In addition, this coordination places the alkoxy ligand (almost) *trans* to one of the NMe$_2$ moieties. Interestingly, the arrangement of the terdentate NCN and monodentate alkoxy and chloro ligands around the metal center renders the titanium atom in **1a** a stereogenic center. Both enantiomers are found in the unit cell of which the TPR-6-C[22] is shown in Figure 5.

The monotriflate complex [TiCl(NCN)(O-*i*-Pr)(OTf)], **2**, is likewise a mononuclear species but with an η^3-meridionally bonded NCN ligand, in accord with the NMR data (*vide supra*), and a distorted octahedral geometry (Figure 6). Typical for an η^3-meridionally

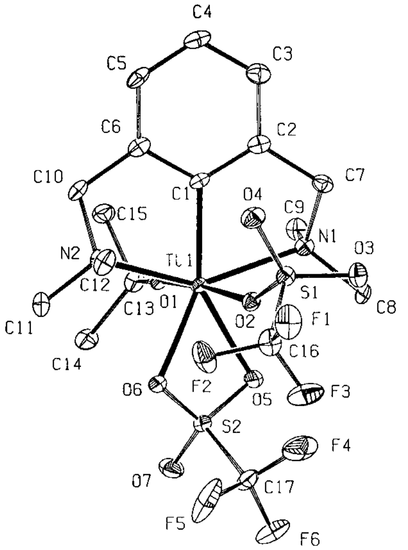

Figure 7. ORTEP drawing of complex **3** at the 30% probability level. The hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) Found in [TiCl$_2$(NCN)(O-*i*-Pr)], 1a, [TiCl(NCN)(O-*i*-Pr)(OTf)], 2, and [Ti(NCN)(O-*i*-Pr)(OTf)$_2$], 3

	1a	**2**	**3**
Ti–C(1)	2.090(3)	2.086(5)	2.098(5)
Ti–N(1)	2.420(3)	2.235(5)	2.338(4)
Ti–N(2)	2.379(2)	2.252(5)	2.301(4)
Ti–Cl(1)	2.3439(10)	2.365(2)	
Ti–Cl(2)	2.3006(12)		
Ti–O(1)	1.765(2)	1.731(3)	1.730(3)
Ti–O(2)		2.096(3)	2.093(3)
Ti–O(5)			2.324(3)
Ti–O(6)			2.243(3)
N(1)–Ti–N(2)	113.23(10)	147.86(18)	147.26(15)
Ti–O(1)–C(13)	149.22(18)	157.2(4)	172.4(3)
Ti–O(2)–S(1)		147.2(2)	150.7(2)
Ti–O(5)–S(2)			93.91(16)
Ti–O(6)–S(2)			97.04(18)
O(5)–Ti–O(6)			61.70(12)
O(5)–S(2)–O(6)			106.40(19)

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[22] For the trigonal prismatic system, the configuration index is derived from the CIP rank numbers of the ligating atoms opposite the triangular face containing the greater number of ligating atoms of highest CIP rank. The chirality symbol is assigned by viewing the trigonal prism from above the prefered triangular face and noting the direction of progression of the priority sequence for the less-preferred triangular face. Leigh, G. J., Ed. *Nomenclature of Inorganic Chemistry. Recommendations 1990*; International Union of Pure and Applied Chemistry; Blackwell Scientific Publications: Oxford, 1990.

bonded NCN ligand[13a,c–h] the N(1), N(2), Ti, and C^{ipso} atoms are almost in one plane (maximum deviation from least-squares plane 0.009(1) Å). The two nitrogen atoms are in apical positions with a N(1)–Ti–N(2) bond angle amounting to 147.86(18)°. The angular deviation from perfect *trans* coordination is a result of the small N–Ti–C(1) bite angles in the two five-membered chelate rings, fused over the Ti–C^{ipso} bond (74.21(18) and 73.66(18)°), and is a general phenomenon observed in η^3-meridionally bonded (NCN)metal complexes.[13a,c–h] The triflato anion is placed *trans* to the alkoxy ligand with an O(2)–Ti–O(1) bond angle of 170.91(15)°, leaving the chloro ligand to be placed *trans* to C^{ipso}. The Ti–C bond distance in **2** is not affected by the substitution of one of the chloro ligands for a triflato ligand (*cf.* 2.086(5) Å in **2** with 2.090(3) Å in **1a**).

The mononuclear, bis(triflate) complex [Ti(NCN)(O-*i*-Pr)(OTf)$_2$], **3**, contains an η^3-meridionally bonded NCN, η^1-O-bonded alkoxy and triflato ligands, and, surprisingly, an η^2-O,O′-bonded triflato ligand (Figure 7). The geometry of **3** can best be described as pentagonal bipyramidal with the η^3-meridionally bonded NCN and the η^2-O,O′-bonded triflato ligands forming the equatorial plane (maximum deviation from the least-squares plane is 0.227(3) Å) while the alkoxy and the η^1-O-bonded triflato ligands occupy apical positions (O(1)–Ti–O(2) = 172.89(14)°). The η^1-O-bonded alkoxy ligand shows a remarkable almost linear Ti–O(1)–C(13) bond angle of 172.4(3)°. The Ti–C bond distance in **3** is again unaffected by the substitution of the chloro ligand for the triflato ligand, *i.e.*, a distance of 2.098(5) Å is found, which is comparable to this distance found in **1b** and **2** (*vide supra*).

To the best of our knowledge **3** is the first structurally characterized titanium(IV) complex containing an η^2-O,O′-bonded triflato ligand. In addition, the bidentate bonding mode of the triflato ligand renders the metal center as a rare example of an organo titanium(IV) complex containing a seven-coordinate titanium(IV) center. Only a few other organo titanium complexes with seven-coordinate metal centers have been reported.[23] In addition, several inorganic titanium complexes with seven-coordinate titanium centers are known as, for example, the dimeric titanium tartrate complex [Ti$_2$(DIPT)$_3${ON(CH$_2$Ph)$_2$}$_2$] (DIPT) = (*R*,*R*)-diisopropyltartrate), prepared and characterized by Sharpless *et al.*[24]

The Ti–O(alkoxy) bond distances in **1a** (1.765(2) Å), **2** (1.731(3) Å), and **3** (1.730(3) Å) are comparable to these distances found in related complexes (*e.g.*, 1.750(2) Å in [{CpTiCl$_2$}$_2$(OCMe$_2$CMe$_2$O)][25] and 1.77(2) Å in [{CpTiCl$_2$}$_2$O][26]). However, it is worthwhile noting that the Ti–O(alkoxy) bond distance in **2** and **3** is significantly shorter than this distance in **1a** and other related complexes (more than 10σ). An obvious difference between **1a**, **2**, and **3** is the Ti–O–C bond angles, which vary from 149.22(18) to 157.2(4) and 172.4(3)°, respectively. As has been proposed,[27] the M–O bond distance and, in particular, the M–O–C bond angle in group 4 metal alkoxide complexes give an indication of the degree of M–O dπ–pπ multiple bond character in the alkoxy–metal bond. The M–O–C bond angle is influenced by the hybridization of the oxygen atom, *i.e.*, M–O–C bond angles of 109, 120, and 180° are expected for sp^3-, and sp^2-, and sp-hybridized oxygen atoms, respectively. The sp- and sp^2-hybridized oxygen atoms can π-donate four and two additional p-electrons, respectively, into empty d orbitals of the metal center.

It is obvious that the M–O–C bond angles in **1a**, **2**, and **3** point to a hybridization of the oxygen atom between sp^2 and sp. However, the increase of the M–O–C bond angle in the series **1a**, **2**, and **3** indicates that the consecutive replacement of a chloro ligand for a triflato ligand increases the s character in the hybridization of the oxygen atom of the alkoxy ligand, *i.e.*, the dπ–pπ interaction between the titanium and oxygen atoms increases in this series. This increase of the M–O–C bond angle and thereby the M–O dπ–pπ interaction reflects the enhanced Lewis acidity of the titanium center as a result of the replacement of chloro ligands for less electron donating triflato ligands. Finally, the almost linear M–O–C bond angle found in the bis(triflate) complex **3** renders this complex formally a 18-electron species, which is in line with the enhanced stability of **3** toward air compared to the stability of other (NCN)titanium(IV) complexes.

The substitution of the chloro ligands by triflato ligands in going from **1a** to **3** also causes a change in coordination mode of NCN from η^3-pseudofacial (**1a**) to η^3-meridional (**2** and **3**). The electronic factors which affect the molecular geometry of **1a**, **2**, and **3** are illustrated by the position of the alkoxy ligand and the variation of the Ti–N bond distance. A strong M–O-(alkoxy) interaction is obtained by a position of the alkoxy ligand *trans* to the ligated atom with the weakest electron-donating capacity. This leads in the dichloride complex **1a** to the alkoxy ligand being observed *trans* to one of the ligated nitrogen atoms and, as a result of this orientation, to an η^3-pseudofacially coordinated NCN ligand.

In the triflate complexes **2** and **3** the alkoxy ligand is positioned *trans* to an electron-withdrawing triflato ligand, allowing for a stronger M–O(alkoxy) interaction as compared with **1a** (*cf.* M–O–C bond angles of 149.22(18)° in **1a** and 157.2(4)° and 172.4(3)° in **2** and **3**, respectively). A *trans* alkoxy–triflato orientation can only be accommodated by the titanium center when NCN is η^3-meridionally coordinated. In addition, an η^3-meridional bonding mode generally allows shorter M–N bond distances, *i.e.*, 2.24 Å (mean) and 2.32 Å (mean) in **2** and **3**, respectively, *vs* 2.40 Å (mean) in **1a**, which is in line with an enhanced Lewis acidic titanium(IV) center in **2** and **3**. In contrast to these substantial changes in the Ti–N bond distances, the Ti–C^{ipso} distance seems unaffected (Table 3). Similar observa-

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tions have been made earlier in other NCN-containing compounds.[13a]

Besides electronic factors, also steric factors affect the molecular geometry of these complexes. To accommodate the triflato ligand, a sterically more demanding ligand as compared with a chloro ligand, a more obtuse N−Ti−N bond angle is observed in **2** and **3** (Table 3), resulting in an η^3-meridionally coordinated NCN ligand. The substitution of the second chloro ligand for a triflato ligand places the NMe_2 moieties of **3** in close proximity to the oxygen atoms of the η^2-O,O′-coordinated triflato ligand. This is obvious from the short *N*-methyl C−H···O contacts (H···O = 2.31 Å (mean), C···O = 2.80 Å (mean)) and the C−H···O bond angle of 109° (mean) found in **3**. The latter interactions could explain the slightly longer Ti−N distances in **3** (2.32 Å (mean)) as compared to these distances in **2** (2.24 Å (mean)).

Interestingly, the structural features of the η^1-coordinated triflato ligand in **2** and **3** strongly resemble those of the bonding arrangement in the free anion.[28] The S−O(3) and S−O(4) bond distances (1.43 Å mean) are similar to the corresponding three sulfur−oxygen bond distances in the free anion (1.43 Å mean). The longer S−O(2) bond distance of 1.47 Å of the η^1-bonded oxygen atom falls in the range 1.44−1.50 Å observed for this bond distance in other structurally related complexes with η^1-*O*-triflato bonding modes.[29] The elongated S−O(2) bond distance compared to the bond distances found for S−O(3) and S−O(4) points to a reduction in the S−O(2) bond order and hence in an increase in the Ti−O(triflato) bond order. This increase in bond order together with a Ti−O(triflato) bond distance which is significantly shorter than the sum of the van der Waals radii[30] points to a covalently bonded triflato ligand to the titanium center. Although the Ti−O(triflato) bond distance (2.093(3) Å) is slightly longer than that found in $[(1,3\text{-}C_5H_3(SiMe_3)_2)Ti(CF_3COCHCOCF_3)_2OTf]$ (2.018(5) Å)[31] and $[Cp_2Ti(OTf)_2]$ (2.003(7) Å),[32] and therefore does not seem to support this conclusion, a rather covalent Ti−O(triflato) bond would explain the observation that our attempts to replace the triflato ligands in **2** and **3** by other Lewis bases were not successful (*vide infra*).

Similar arguments apply for the η^2-O,O′-bonded triflato anion in **3**, which likewise cannot be substituted by other nucleophiles (*vide infra*), indicating that this η^2-O,O′-bonded triflato ligand is covalently bonded to the titanium(IV) center as well. The results of the molecular weight determinations of **2** and **3** also corroborate this conclusion. Whereas **2** is mononuclear, **3** seems to exist in benzene as a monomer at low concentration while a monomer−dimer equilibrium exists at higher concentrations. Dimer formation most likely involves η^2-bridging triflato ligands, thereby creating two seven-coordinate titanium centers (Figure 8). This bimetallic η^2-O,O′-bridging bonding mode of triflato ligands has been encountered for example in $[\{Cu_4(OH)_4(OTf)_2(N(C_5H_5N)_3)_4\}^{2+}]$[33] and $[Me_2Sn(OTf)_2]$.[34] All other bond distances and angles found in the η^2-O,O′-bonded triflato ligand are comparable to those found in the η^1-O-bonded triflato ligand.

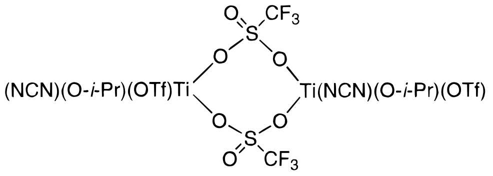

Figure 8. Proposed dimeric structure bis(triflato)(NCN)-titanium(IV) complex **3**.

Reactivity of NCN−Titanium Complexes. It was shown by Thewalt *et al.* that the dissolved triflate complexes $[Cp_2Ti(OTf)_2]$ and $[(C_5Me_5)_2Ti(OTf)_2]$ readily form cationic species upon addition of Lewis bases like THF, acetonitrile, DMF, or bipy.[32] In contrast to these observations, the (NCN)titanium(IV) triflate complexes **2** and **3** showed (^{1}H NMR) no interaction with any of these Lewis bases. Also mixtures of the dichloride complex **1a** and the bis(triflate) complex **3** in a 1:1 molar ratio in polar or nonpolar solvents did not comproportionate to the monotriflate complex **2**. This leads us to conclude that the (triflato)(NCN)titanium(IV) complexes **2** and **3** do not form cationic species in solution. Apparently, the triflato ligands in **2** and **3** are strongly bonded to titanium, which is in line with a high Lewis acidity of the metal center.

Preliminary studies have been performed to investigate the reactivity of the new (NCN)titanium(IV) complexes as catalysts or catalyst precursors in well-known titanium-mediated or -catalyzed organic reactions. As the (NCN)titanium(IV) complexes were shown to be Lewis acids with a stable and defined geometry, they might be interesting precursors for Lewis acid catalyzed organic reactions. The dichloride complex **1a**, the bis(triflate) complex **3**, and the methyl complex **4** were shown to be catalytically active in the 1,2-addition reaction of Et_2Zn to benzaldehyde in toluene at room temperature. After 3 h, **3** showed full conversion of benzaldehyde into 1-phenyl-1-propanol while **1a** and **4** gave full conversion after 5 h.[35] This is in line with the enhanced Lewis acidity of **3** as compared with **1a** and **4**. The nontransferability of the NCN ligand and the presence of organometallic species during the catalytic reaction became evident when the reaction mixture was quenched with D_2O. After acidic workup of the aqueous phase, all NCN was recovered as its monodeuterio derivative.

No activity was observed for these neutral (NCN)-titanium(IV) complexes in the Ziegler−Natta polymerization of α-olefins.[36]

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[36] Piloting experiments indicate that analogous (NCN)titanium(III) complexes, derived from **1a** by a reduction with magnesium amalgam, are active as catalyst precursors in the polymerization of ethene and propene.

Conclusions

The results presented in this paper show that with the terdentate-bonded NCN ligand new (NCN)titanium(IV) complexes containing chloro, methyl, or triflato ligands are easily accessible in high yields. The versatile bonding properties of the NCN ligand were illustrated by the isolation of (NCN)titanium(IV) complexes containing either an η^3-meridionally or η^3-pseudofacially bonded NCN ligand.

The η^3-meridional bonding mode of NCN led to the isolation of novel (NCN)titanium(IV) triflate complexes in which not only an η^1-O-bonded triflato ligand was observed but also an η^2-O,O′-bonded triflato ligand, unprecedented in early transition metal complexes. The latter complex is, to the best of our knowledge, the first structurally characterized seven-coordinate aryltitanium(IV) complex. The preparation of the (NCN)titanium(IV) bis(triflate) shows that the use of NCN can lead to new complexes which exhibit interesting novel structural features due to the complementary behavior of the coordination chemistry of NCN compared to Cp. Both (NCN)titanium(IV) triflate complexes were shown to have enhanced Lewis acidic metal centers resulting in remarkably strong covalently bonded triflato ligands. As a result of this strong binding, no cationic species were formed upon addition of Lewis bases.

Test experiments showed the (NCN)titanium(IV) complexes to be catalytically active in the 1,2-addition reaction of Et_2Zn to benzaldehyde. As the NCN ligand is acting as a nontransferable ligand and was shown to be chemically inert during catalysis, new enantioselective catalysts are accessible with the use of chiral NCN analogues.

The (NCN)titanium(IV) dichloride complex **1a** was also shown to be a starting complex for the preparation of related (NCN)titanium(III) complexes.[36] Further investigations are underway to identify these species and investigate their scope and activity in Ziegler–Natta α-olefin polymerization reactions. Results of these investigations will be the subject of forthcoming publications.

Experimental Section

General Comments. All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany; ^1H (200 or 300 MHz) and $^{13}C\{^1H\}$ (50 or 75 MHz) NMR spectra were recorded on Bruker AC200 or AC300 spectrometers at ambient temperature unless stated otherwise. The following abbreviations have been used: s, singlet; d, doublet; t, triplet; m, multiplet; sp, septet; br, broad signal. $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$[37] was prepared according to a literature procedure. All other reagents were commercially obtained and used as such.

Preparation of $[TiCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OCHMe_2)]$, 1a. To a stirred solution of $TiCl_4$ (37.50 mmol) in toluene (250 mL) was added Ti(O-*i*-Pr)$_4$ (12.50 mmol). The resulting yellow solution was stirred for 15 min at room temperature, after which it was cooled to −78 °C. At this temperature a solution of $[Li(NCN)]_2$ (25.0 mmol) in toluene (250 mL) was added dropwise in 1 h. The yellow/green mixture was allowed to warm to room temperature in 1 h and stirred at this temperature for another 30 min. The crude product was isolated by centrifugation of the reaction mixture and decantation of the toluene fraction. The remaining solid was extracted with C_6H_6 (4 × 75 mL), after which the solvent from the combined organic fractions was evaporated *in vacuo*. The obtained yellow/green powder was washed with pentanes (3 × 25 mL) and dried *in vacuo* to give **1a** as a pale yellow powder (13.57 g, 74%). Yellow needles, suitable for X-ray analysis, were obtained by cooling a saturated solution of **1a** in toluene to −20 °C for 3 days. Mp: 115 °C. Anal. Calcd for $C_{15}H_{26}Cl_2N_2OTi$: C, 48.80; H, 7.10; N, 7.59. Found: C, 48.88; H, 7.04; N, 7.49. ^1H NMR (C_6D_6): 6.88 (t, $^3J = 7.40$ Hz, 1H, Ar*H*), 6.61 (d, $^3J = 7.40$ Hz, 2H, Ar*H*), 5.88 (sp, $^3J = 6.22$ Hz, 1H, OC*H*), 1.22 (d, $^3J = 4.96$ Hz, 6H, OCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 206.5 ({Ar}*C*Ti), 128.9−122.6 ({Ar}C), 86.6 (O*C*H), 25.3 (OCH(*C*H$_3$)$_2$). In addition, see Table 1.

Preparation of $[TiCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OC_6H_4\text{-}OMe\text{-}4)]$, 1b. Following the same procedure as for **1a** using $TiCl_4$ (21.19 mmol), $Ti(OC_6H_4(OMe\text{-}4))_4$ (7.06 mmol), and $[Li(NCN)]_2$ (14.13 mmol) resulted in 10.27 g (84%) of **1b** as a dark red powder. Mp: 117−118 °C. Anal. Calcd for $C_{19}H_{26}Cl_2N_2O_2Ti$: C, 52.68; H, 6.05; N, 6.47. Found: C, 52.53; H, 6.08; N, 6.50. ^1H NMR (C_6D_6): 7.05 (d, $^3J = 6.78$ Hz, 2H, Ar*H*), 6.90 (t, $^3J = 7.09$ Hz, 1H, Ar*H*), 6.60 (m, 4H, OC$_6$*H*$_4$OCH$_3$), 3.24 (s, 3H, OC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 155.7 ({Ar}*C*O), 146.2 ({Ar}*C*), 129.6−127.6 ({Ar}*C*), 122.5, 120.6, and 114.3 ({Ar}*C*), 55.1 (O*C*H$_3$). In addition, see Table 1. The ({Ar}*C*Ti) carbon atom was not observed due to the low solubility of **1b** in benzene.

Preparation of $[TiCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OCHMe_2)(O_3SCF_3)]$, 2. To a vigorously stirred solution of **1a** (1.65 mmol) in C_6H_6 (25 mL) was added CuOTf (1.65 mmol), after which stirring was continued for 45 min. After centrifugation of the reaction mixture and decantation of the organic layer, the remaining solid was extracted with C_6H_6 (3 × 25 mL). The solvent from the combined organic fractions was evaporated *in vacuo* to give **2** as an orange powder (0.75 g, 94%). A saturated solution of **2** in toluene was cooled to −30 °C for 3 days to give orange needles of **2** suitable for X-ray analysis. Mp: 100−101 °C. The bis(triflate) **3** was always present in variable amounts in samples of **2**, hampering NMR and elemental analysis. The latter was corrected for the presence of 14% of **3**. Anal. Calcd for $C_{16}H_{26}ClF_3N_2O_4STi$: C, 38.98; H, 5.28; N, 5.64. Found: C, 38.88; H, 5.40; N, 5.63. ^1H NMR (C_6D_6): 6.87 (t, $^3J = 7.40$ Hz, 1H, Ar*H*), 6.59 (d, $^3J = 7.20$ Hz, 2H, Ar*H*), 4.77 (sp, 1H, OC*H*), 1.13 (d, $^3J = 7.18$ Hz, 6H, OCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 205.7 ({Ar}*C*Ti), 145.2 ({Ar}*C*), 125.7 and 122.1 ({Ar}*C*H), 84.7 (O*C*H), 24.9 (OCH(*C*H$_3$)$_2$). In addition, see Table 1.

Preparation of $[Ti\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OCHMe_2)(O_3SCF_3)_2]$, 3. To a solution of **1a** (2.52 mmol) in C_6H_6 (25 mL) was added AgOTf (5.04 mmol) with vigorous stirring. After 30 min of stirring at ambient temperature the crude product was isolated by centrifugation of the reaction mixture followed by decantation of the organic layer. The remaining silver salts were extracted with C_6H_6 (2 × 25 mL), after which the solvent of the combined organic fractions was evaporated *in vacuo* to give **3** as an orange solid (1.35 g, 90%). Crystals suitable for X-ray analysis were obtained by cooling a saturated solution of **3** in toluene to −30 °C. Mp: 127−128 °C dec. Anal. Calcd for $C_{17}H_{26}F_6N_2O_7S_2Ti$: C, 34.24; H, 4.39; N, 4.70. Found: C, 34.33; H, 4.31; N, 4.78. ^1H NMR (C_6D_6): 6.88 (t, $^3J = 7.55$, 1H, Ar*H*), 6.60 (d, $^3J = 7.5$ Hz, 2H, Ar*H*), 4.5 (sp, $^3J = 6.0$ Hz, 1H, OC*H*), 1.0 (d, $^3J = 5.97$ Hz, 6H, OCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 207.49 ({Ar}*C*Ti), 145.11 ({Ar}*C*), 122.04 and 129.31 ({Ar}*C*H), 87.67 (O*C*H), 24.67 (OCH(*C*H$_3$)$_2$). In addition, see Table 1.

Preparation of 3 Starting from 2. To a vigorously stirred solution of **2** (2.0 mmol) in C_6H_6 (25 mL) was added AgOTf (2.0 mmol) at room temperature. The reaction mixture was

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Table 4. Crystallographic Data for 1a, 2, and 3

	1a	**2**	**3**
	Crystal Data		
formula	$C_{15}H_{26}Cl_2N_2OTi$	$C_{16}H_{26}ClF_3N_2O_4STi$	$C_{17}H_{26}F_6N_2O_7S_2Ti$
molecular weight	369.17	482.79	596.40
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	10.0107(18)	15.5282(9)	14.614(2)
b, Å	10.3607(11)	16.4782(14)	9.618(2)
c, Å	17.8448(13)	16.9143(13)	17.483(2)
β, deg	94.424(12)		98.458(9)
V, $Å^3$	1845.3(4)	4328.0(6)	2430.6(7)
D_{calc}, g cm^{-3}	1.329	1.482	1.630
Z	4	8	4
F(000)	776	2000	1224
μ, cm^{-1}	65.9 (Cu Kα)	6.6 (Mo Kα)	6.1 (Mo Kα)
cryst size, mm	1.48 × 0.23 × 0.20	0.50 × 0.25 × 0.20	1.88 × 0.25 × 0.03
	Data Collection		
T, K	295	150	150
θ_{min}, θ_{max}, deg	2.5, 75.0	1.2, 25.0	1.4, 27.4
SET4 θ_{min}, θ_{max} deg	18.27, 23.42 (15 rflns)	11.64, 13.85 (25 rflns)	10.37, 13.82 (25 rflns)
wavelength, Å	1.541 84 [Cu Kα]	0.710 73 [Mo Kα]	0.710 73 (Mo Kα)
filter/monochromator	Ni filter	graphite mon	graphite mon
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$, deg	$0.50 + 0.14 \tan\theta$	$0.71 + 0.35 \tan\theta$	$0.55 + 0.35 \tan\theta$
horizontal vertical apertures, mm	3.00, 6.00	3.00, 4.00	1.88, 4.00
X-ray exposure time, h	49	22	19
linear instability, %	1	2	18
ref rflns	$\bar{2}20$, $\bar{2}\bar{2}0$, $\bar{1}3\bar{2}$	205, $\bar{4}\bar{2}4$, 042	$\bar{2}17$, $\bar{4}\bar{2}4$, $\bar{5}2\bar{2}$
data set	−12:9, −12:0, −22:22	−19:19, 0:20, 0:21	−18:13, 0:12, −22:22
total data	6546	7455	7825
total unique data	3804 ($R_{int} = 0.098$)	3807 ($R_{int} = 0.059$)	5517 ($R_{int} = 0.080$)
obsd data	2487 [$I > 2.5\sigma(I)$]	3807 [$I > -3\sigma(I)$]	5517 [$I > -3\sigma(I)$]
DIFABS corr range	0.660, 2.031		
	Refinement		
no. of refined params	210	259	319
final R^a	0.0417 [2487$I > 2.5\sigma(I)$]	0.0626 [2170$I > 2\sigma(I)$]	0.0715 [2937$I > 2\sigma(I)$]
final $R_w{}^b$	0.0458		
final $wR_2{}^c$		0.1582	0.1674
goodness of Fit	0.93	0.99	0.95
$w^{-1\ d}$	$\sigma^2(F) + 0.000265F^2$	$\sigma^2(F^2) + (0.0730P)^2$	$\sigma^2(F^2) + (0.0699P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.014, 0.077	0.000, 0.001	0.000, 0.000
min and max residual density, e $Å^{-3}$	−0.34, 0.29	−0.32, 0.44	−0.56, 0.52

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma[w(||F_o| - |F_c||)^2]/\Sigma[w(F_o{}^2)]]^{1/2}$. [c] $wR_2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$. [d] $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$.

stirred for 1 h at room temperature, after which the same workup procedure was used as for the preparation of **3** starting from **1a**.

Preparation of [TiClMe{$C_6H_3(CH_2NMe_2)_2$-2,6}(OCHMe$_2$)], 4. A solution of **1a** (4.60 mmol) in toluene (50 mL) was cooled to −78 °C, after which MeLi (2.9 mL of a 1.6 M solution in Et_2O; 4.60 mmol) was added. The reaction mixture was allowed to warm to room temperature in 1 h. The solvent of the reaction mixture was removed *in vacuo*. Extraction of the obtained brown solid with hexanes (3 × 25 mL), followed by removal of the solvent *in vacuo* from the combined organic fractions, gave 1.58 g of **4** (98%) as a yellow solid. Mp: 104−106 °C. Anal. Calcd for $C_{16}H_{29}ClN_2OTi$: C, 55.10; H, 8.38; N, 8.03. Found: C, 54.95; H, 8.30; N, 8.06. ^1H NMR (C_6D_6): 6.95 (t, $^3J = 7.68$ Hz, 1H, Ar*H*), 6.71 (d, $^3J = 7.34$ Hz, 2H, Ar*H*), 5.65 (sp, $^3J = 6.20$ Hz, 1H, OC*H*), 1.35 (d, $^3J = 6.16$ Hz, 6H, OCH(CH_3)$_2$), 0.95 (s, 3H, Ti(CH_3)). $^{13}C\{^1H\}$ NMR (C_7D_8, 220 K): 196.7 ({Ar}*C*Ti), 141.7 ({Ar}*C*), 139.6, 118.0, and 117.3 ({Ar}O*C*H), 77.4 (*C*H), 49.6 (Ti(*C*H_3)), 21.33 and 21.27 (OCH(*C*H_3)$_2$). In addition, see Table 1.

Preparation of [TiMe$_2${$C_6H_3(CH_2NMe_2)_2$-2,6}(OCHMe$_2$)], 5. Following the same procedure as for **4** using **1a** (4.09 mmol) and MeLi (5.1 mL of a 1.6 M solution in Et_2O; 8.18 mmol) gave **5** (3.60 mmol, 88%) as a yellow, green powder. Mp: 110−112 °C dec. ^1H NMR (C_6D_6): 7.0 (t, $^3J = 6.62$ Hz, 1H, Ar*H*), 6.8 (d, $^3J = 7.3$ Hz, 2H, Ar*H*), 5.3 (sp, $^3J = 6.15$ Hz, 1H, OC*H*), 1.42 (d, $^3J = 6.14$ Hz, 6H, OCH(CH_3)$_2$), 0.68 (s, 6H, Ti(CH_3)). $^{13}C\{^1H\}$ NMR (C_7D_8, 215 K): 197.3 ({Ar}*C*Ti), 147.7 and 144.4 ({Ar}*C*), 127.5, 122.9, and 123.1 ({Ar}*C*H), 77.6 (O*C*H), 56.0 and 48.4 (Ti(*C*H_3)), 26.9 (OCH(*C*H_3)$_2$). In addition, see Table 1.

The 1,2-Addition Reaction of Et_2Zn to Benzaldehyde Catalyzed by 1a. To a solution of **1a** (5 mol %) and benzaldehyde (2.74 mmol) in toluene (25 mL) was added Et_2Zn (2.74 mmol), and the mixture was stirred at room temperature for 5 h for complete conversion (as indicated by GC−MS analysis of a sample of the reaction mixture). The reaction mixture was hydrolyzed with 50 mL of a 4 M HCl solution. The organic layer was separated, the water layer was extracted with Et_2O (3 × 25 mL), and the combined organic fractions were dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash distillation and identified by comparing the NMR, GC, and MS data with those of authentic samples. Yield: 0.40 g (93%). **1-Phenyl-1-propanol:** GC−MS (relative intensity) *m*/*z* 136 (M^+, 8); 118 ($M^+ - H_2O$, 8); 107 ($M^+ - C_2H_5$, 100). ^1H NMR ($CDCl_3$): 7.4 (m, 5H, Ar*H*), 4.6 (t, 1H, ArC*H*), 2.7 (br s, 1H, O*H*), 1.8 (dq, 2H, CH_2), 0.95 (t, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 144.8 ({Ar}*C*), 128.5, 127.6, and 126.3 ({Ar}*C*H), 76.0 (Ar*C*H), 32.2 (*C*H_2), 10.0 (*C*H_3).

The 1,2-Addition Reaction of Et_2Zn to Benzaldehyde Catalyzed by 3. A similar procedure as for the **1a**-catalyzed 1,2-addition reaction was used, but starting with benzaldehyde (2.01 mmol), 5 mol % of **3**, and Et_2Zn (2.01 mmol) in toluene (25 mL), the reaction mixture was stirred for 3 h for complete conversion (as indicated by GC−MS analysis of a sample of the reaction mixture). The workup procedure is identical to that for the **1a**-catalyzed 1,2-addition reaction, with identical NMR, GC, and MS data for the product 1-phenyl-1-propanol. Yield: 0.30 g (92%).

The 1,2-Addition Reaction of Et_2Zn to Benzaldehyde Catalyzed by 4. A similar procedure as for the **1a**-catalyzed 1,2-addition reaction was used, but starting with benzaldehyde (4.0 mmol), 5 mol % of **4**, and Et_2Zn (4.0 mmol) in toluene (25 mL), the reaction mixture was stirred for 5 h for complete conversion (as indicated by GC−MS analysis of a sample of the reaction mixture). The workup procedure is identical to that for the **1a**-catalyzed 1,2-addition reaction, with identical NMR, GC, and MS data for the product 1-phenyl-1-propanol. Yield: 0.62 g (88%).

Crystal Structure Determination of 1a, 2, and 3. Crystals suitable for X-ray structure determination were either sealed in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-F sealed tube diffractometer (**1a**) or glued to the top of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode (**2** and **3**). The crystal of **1a** consisted of two individuals rotated by 4.5° with respect to each other. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of well-centered reflections (SET4[38]). The unit-cell parameters were checked for the presence of higher lattice symmetry.[39] Crystal data and details on data collection are given in Table 4.

Data were corrected for *Lp* effects and for the linear decay of three periodically measured reference reflections during X-ray exposure time. For compound **1a** the standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.021I)^2$.[40] An empirical absorption correction (DIFABS[41]) was applied for compound **1a**.

All structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[42]). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76[43]) for compound **1a**. The other compounds were refined on F^2 using full-matrix least-squares techniques (SHELXL-93[44]); no observance criteria were applied during refinement of F^2.

Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl hydrogen atoms were refined as a rigid group, allowing for rotation around the N−C or C−C bonds. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of **1a** were refined with two overall isotropic displacement parameters. The hydrogen atoms of the other compounds were included in the refinement with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms.

For compound **1a** the neutral atom scattering factors were taken from Cromer and Mann,[45] anomalous dispersion corrections from Cromer and Liberman.[46] For the other compounds neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*.[47] Geometrical calculations and illustrations were performed with PLATON.[48] All calculations were performed on a DECstation 5000.

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Supporting Information Available: Further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters for **1a**, **2**, and **3** (18 pages). Ordering information is given on any current masthead page.

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