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Imidazolin-2-iminato titanium complexes: synthesis, structure and use in ethylene polymerization catalysis

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Received 17th August 2005, Accepted 28th September 2005
First published as an Advance Article on the web 28th October 2005
DOI: 10.1039/b511752f

Published on 28 October 2005. Downloaded by University of California - Santa Cruz on 26/10/2014 19:44:25.

The Staudinger reaction of the imidazolin-2-ylidenes, 1,3-di-*tert*-butylimidazolin-2-ylidene (**1a**), 1,3-diisopropylimidazolin-2-ylidene (**1b**), 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (**1c**), 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (**1d**) and 1,3-bis(2,6-diisopropylphenylimidazolin-2-ylidene (**1e**), with trimethylsilyl azide furnishes the corresponding *N*-silylated 2-iminoimidazolines **2a–e**, which react with [(η-C_5H_5)$TiCl_3$] to afford half-sandwich cyclopentadienyl titanium complexes of the type [CpTi(L)Cl_2] (**3**) (L = imidazolin-2-iminato ligand). Similarly, the reactions of 1,3-di-*tert*-butyl-2-(trimethylsilylimino)imidazoline (**2a**) with [(η-*t*BuC_5H_4)$TiCl_3$] results in the formation of [(η-*t*BuC_5H_4)Ti(L)Cl_2] (**4**) (L = 1,3-di-*tert*-butylimidazolin-2-imide). Bis(1,3-di-*tert*-butylimidazolin-2-iminato)titanium dichloride (**5**) is obtained from the reaction of two eq. of **2a** with $TiCl_4$. Treatment of **5** with methyllithium results in the formation of the corresponding dimethyl complex [$L_2Ti(CH_3)_2$] (**6**), whereas [CpTi(L)$(CH_3)_2$] (**7**) is similarly obtained from **3a**. The molecular structures of **3a**, **3b**, **3c**, **3e**·C_7H_8, **4** and **7** are reported revealing linearly coordinated imidazolin-2-iminato ligands together with very short Ti–N bond distances. All dichloro complexes (**3a–e**, **4** and **5**) can be activated with methylaluminoxane (MAO) to give active catalysts for ethylene homopolymerization. In most cases, moderate to high activities are observed together with the formation of high (HMWPE) or even ultra high molecular weight polyethylene (UHMWPE).

Introduction

Non-metallocene systems are nowadays playing a key role in the quest for novel, highly efficient olefin polymerization catalysts.[1] Among other systems, monocyclopentadienyl titanium complexes of the type CpTi(L)X_2, containing an additional monoanionic ancillary ligand L, represent an important class of precatalysts for the homo- and copolymerization of olefins. Typical ligands L include π-donors such as aryloxides,[2] ketimides,[3] phosphoraneimides[4] and guanidinates,[5] which can be regarded as monodentate analogues to cyclopentadienyls, C_5R_5, due to their capability to act as 2σ,4π-electron donors. We have recently established a general method for the synthesis of related imidazolin-2-iminato ligands,[6,7] which can be described by the two limiting resonance structures **IA** and **IB** (Fig. 1), indicating that the ability of the imidazolium ring to effectively stabilize a positive charge should lead to highly basic ligands with a strong electron donating capacity.

Our preparative route is based on the observation that stable carbenes of the imidazolin-2-ylidene type undergo a Staudinger reaction[8] upon treatment with trimethylsilyl azide to furnish *N*-silylated 2-iminoimidazolines,[9] which can be directly used for the synthesis of transition-metal imidazolin-2-iminato complexes from metal halides or oxides, respectively.[6,7] Previous work[10] in this area is rather limited and had been confined to the use of the ligand precursor 2-imino-1,3-dimethylimidazoline obtained by a multi-step protocol from 2-aminoimidazole.[11] In contrast, the coordination chemistry of related phosphoraneiminato ligands has been extensively studied producing a large number of structurally diverse main group and transition-metal complexes.[12] Since it can be envisaged that the chemistry of imidazolin-2-iminato ligands could develop into an equally flourishing area of research, we have started a program to study their coordination chemistry as well as their application as ancillary ligands for the design and preparation of novel homogeneous catalysts. In this regard, we wish to present herein the preparation of titanium complexes of the type CpTi(L)X_2 and L_2TiX_2 (L = imidazolin-2-imide, X = Cl, CH_3) and their use in ethylene polymerization catalysis. A preliminary report on the synthesis of a limited number of such titanium complexes has been published previously.[6]

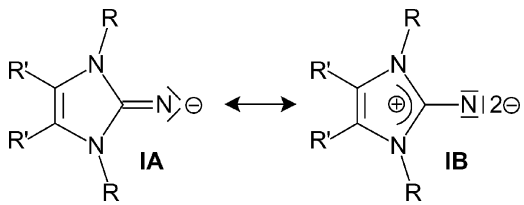

Fig. 1 Mesomeric structures for imidazolin-2-iminato ligands **I**.

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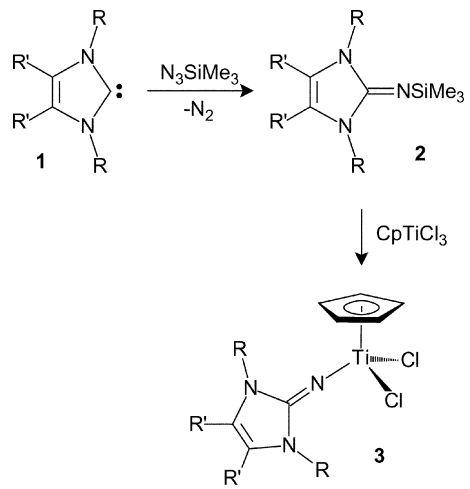
Results and discussion

Preparation and characterization of *N*-silylated 2-iminoimidazolines

As previously described,[6,7] the 2-(trimethylsilylimino)imidazolines **2** are generally accessible from the reaction of the imidazolin-2-ylidenes **1** with trimethylsilyl azide in boiling toluene (Scheme 1). **2a** (R = *t*Bu, R′ = H), **2d** (R = Mes, R′ = H) and **2e** (R = Dipp, R′ = H) are obtained as pale yellow solids, which can efficiently be recrystallized from hexane. In contrast, brownish oils are isolated from the reactions of the *N*-diisopropylimidazolin-2-ylidenes **1b** and **1c** with Me_3SiN_3, and the resulting *N*-silylated imines **2b** (R = *i*Pr, R′ = H) and **2c** (R = *i*Pr, R′ = CH_3) can be purified by bulb-to-bulb distillation at 180 °C/9 mbar. The conversion of the carbenes bearing 4,5-hydrogen atoms (**1a**, **1b**, **1d**, **1e**) can easily be followed by ^{1}H NMR spectroscopy as pronounced high-field shifts of about −0.70 ppm are observed for the resonances of the NCH hydrogen atoms upon formation of the corresponding imines. For the conversion of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (**1c**) into the corresponding imine **2c** on the other hand, a marked low-field shift of the septet CH resonance from 3.95 to 4.61 ppm is indicative of product formation. In contrast, this resonance remains almost unchanged when 1,3-diisopropylimidazolin-2-ylidene (**1b**) is employed. In the ^{13}C NMR spectra of all imines **2**, the resonances of the former carbene carbon atoms are found around 140 ppm, which is approximately 90 ppm up-field from the corresponding resonances in the free carbenes **1**. According to their ^{1}H and ^{13}C NMR spectra, the imines **2** exhibit pseudo-C_{2v} symmetry in solution implying that rotation around the N1–C1 axis is fast on the NMR time scale. It should be noted that the C1–N1–Si angle in **2a** was found to be close to linearity [169.3(2)°];[6,7] depending on the substitution pattern, however, significantly smaller angles can be observed, *e.g.* C1–N1–Si = 147.2(1)° in **2d**.[13]



a, R = *t*Bu, R' = H
b, R = *i*Pr, R' = H
c, R = *i*Pr, R' = Me
d, R = Mes, R' = H
e, R = Dipp, R' = H

Scheme 1 Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl.

Preparation and characterization of cyclopentadienyl-titanium imidazolin-2-iminato complexes

Silylated iminophosphophosphoranes have been widely used for complexation reactions with various metal halides or oxides to yield phosphoraneiminato complexes together with the elimination of trialkylsilyl halides or hexaalkyldisiloxanes, respectively.[12] Accordingly, half-sandwich complexes of the type $CpTi(L)Cl_2$ (**3**) can be isolated as red crystalline solids in high yields from the reaction of $[(\eta\text{-}C_5H_5)TiCl_3]$ with the 2-(trimethylsilylimino)imidazolines **2** in toluene overnight (Scheme 1). In general, desilylation and coordination to the titanium atom does not have a significant impact on the resonances observed for the hydrogen and carbon atoms of the heterocyclic imidazoline moiety. For the *N*-alkylated derivatives **3a–c**, the Cp hydrogen resonances are observed at about 6.5 ppm, whereas the *N*-arylated derivatives **3d** and **3e** exhibit the corresponding resonances at higher field at about 6.0 ppm due to shielding by the aryl substituents. The Cp carbon resonances for all complexes **3** are found in the range between 114 and 116 ppm.

The molecular structure of **3a** has been previously reported.[6] To compare the structural changes upon variation of the imidazoline substituents, the structures of **3b**, **3c** and **3e**·C_7H_8 have additionally been established by X-ray diffraction analyses. The structural parameters are assembled in Table 1, and ORTEP presentations are depicted in Fig. 2 (**3b**, **3c**) and Fig. 3 (**3e**), respectively. In

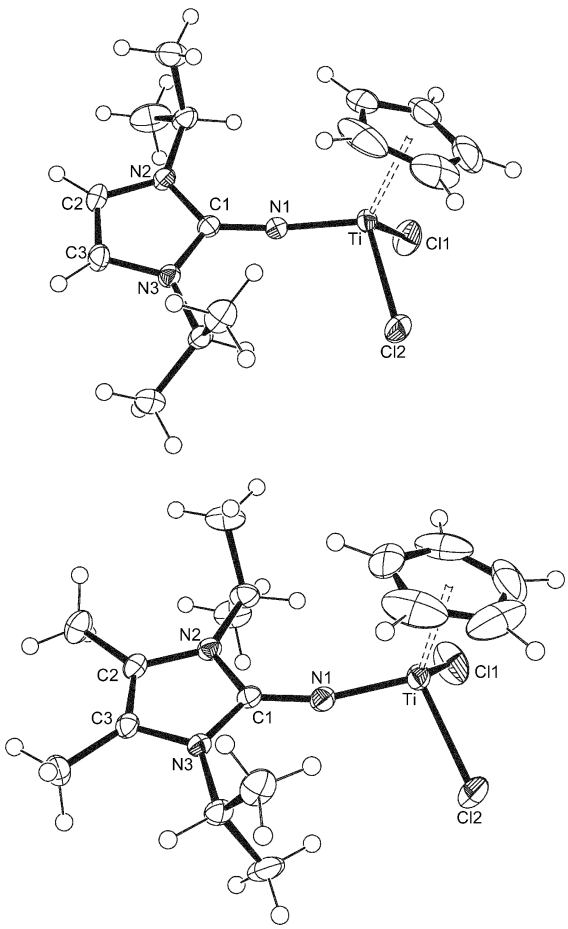


Fig. 2 ORTEP drawings of **3b** (top) and **3c** (bottom) with thermal ellipsoids drawn at 50% probability.

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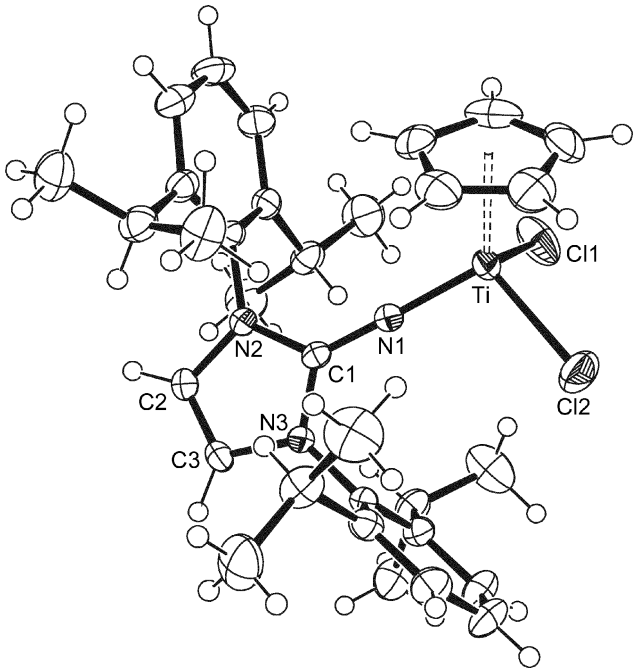

Fig. 3 ORTEP drawing of **3e** in **3e**·C_7H_8 with thermal ellipsoids drawn at 50% probability.

all cases, a three-legged piano-stool structure is observed with the titanium atom adopting a pseudo-tetrahedral geometry. Due to the steric requirements of both the cyclopentadienyl and of the respective imidazolin-2-iminato ligand, the angles at titanium between the Cp centroid and the nitrogen atom N1 are significantly larger than the corresponding Cp–Ti–Cl angles or the N–Ti–Cl and Cl–Ti–Cl angles, respectively (Table 1). In **3a**, the molecule resides on a crystallographic mirror plane, and the five-membered imidazoline ring consequently adopts a perfectly perpendicular orientation toward the pseudo mirror plane containing N1, Ti and the centroid of the cyclopentadienyl ring (dihedral angle = 90°).[6] In contrast, **3b** (61.7°), **3c** (75.4°) and **3e** (52.4°) exhibit significantly smaller torsion angles, and these considerable deviations from regular horizontal conformations suggest that mainly crystal packing forces account for the orientation of the imidazolin-2-iminato ligands. Further evidence for a relatively shallow potential energy surface of complexes **3** with respect to the orientation of the imidazoline moiety stems from temperature-dependent ^{1}H NMR spectroscopy, since a stable horizontal conformation would render the isopropyl methyl groups in **3b** and **3c** diastereotopic. In the temperature range between −80 and 20 °C, however, only one isopropyl CH_3 hydrogen resonance can be observed revealing that rotation about the Ti–N1–C1 axis is fast on the NMR time-scale even at low temperature.

Short Ti–N1 distances ranging from 1.765(3) Å in **3a** to 1.778(2) Å in **3e** are observed together with almost linear geometries about the N1 atom, which is indicative of efficient ligand-to-metal π-donation confirming that the ligand can be regarded as a six-electron donor. Thereby, the isopropyl derivatives

Table 1 Selected bond lengths (Å) and angles (°)

	3a	**3b**	**3c**	**3e**·C_7H_8	**4**	**7**
Ti–Cp_{av}	2.372	2.361	2.355	2.374	2.400	2.405
Ti–Cp_{ct}	2.064	2.045	2.048	2.058	2.085	2.092
Ti–Cp_{range}	2.338(5)–2.414(3)	2.336(3)–2.381(2)	2.333(2)–2.374(4)	2.334(2)–2.419(3)	2.327(3)–2.501(2)	2.383(2)–2.428(2)
Ti–N1	1.765(3)	1.768(2)	1.762(2)	1.778(2)	1.774(2)	1.805(1)
Ti–Cl1	2.3253(6) × 2[b]	2.3118(6)	2.3187(7)	2.3088(7)	2.3197(8)	
Ti–Cl2		2.3184(6)	2.3028(7)	2.2977(8)	2.3199(8)	
Ti–C_{Me1}						2.161(2)
Ti–C_{Me2}						2.161(2)
N1–C1	1.332(4)	1.324(2)	1.324(2)	1.309(2)	1.331(3)	1.310(2)
N2–C1	1.373(2)	1.366(2)	1.366(2)	1.371(2)	1.375(3)	1.389(2)
N2–C2	1.382(3)	1.389(2)	1.399(3)	1.394(2)	1.383(3)	1.387(2)
C2–C3	1.331(3)[b]	1.342(3)	1.349(3)	1.333(3)	1.335(4)	1.333(2)
N3–C3		1.385(2)	1.393(2)	1.391(2)	1.389(3)	1.388(2)
N3–C1		1.361(2)	1.357(3)	1.366(2)	1.375(3)	1.386(2)
Ti–N1–C1	170.7(2)	163.3(1)	164.6(1)	175.8(1)	172.6(2)	176.0(1)
N1–Ti–Cl1	103.47(5) × 2[b]	105.61(5)	103.09(6)	104.17(5)	101.37(7)	
N1–Ti–Cl2		102.02(5)	102.93(5)	104.15(5)	103.33(7)	
N1–Ti–C_{Me1}						103.63(7)
N1–Ti–C_{Me2}						104.73(7)
N1–C1–N2	126.9(1)	128.0(2)	126.2(2)	128.9(2)	126.8(2)	127.5(1)
Cp_{Ct}–Ti–N1	121.37	119.66	118.02	119.72	122.83	124.35
C1–N2–C2	108.7(2)	108.7(1)	109.0(2)	109.4(2)	108.5(2)	108.8(1)
N2–C2–C3	108.2(2)	107.9(2)	107.1(2)	107.6(2)	108.4(2)	108.5(2)
Cl1–Ti–Cl2	102.10(3)[b]	99.22(2)	104.04(3)	100.49(3)	102.29(3)	
Cp_{Ct}–Ti–Cl1	112.16 × 2[b]	113.92	111.92	113.04	112.89	
Cp_{Ct}–Ti–Cl2		113.87	115.20	113.11	111.73	
C_{Me1}–Ti–C_{Me2}						95.92(8)
Cp_{Ct}–Ti–C_{Me1}						112.77
Cp_{Ct}–Ti–C_{Me2}						111.45
Interplanar angle[a]	90	61.7	75.4	52.4	89.3	89.8

[a] Angle between the least-squares planes containing the heterocycle (C1, C2, C3, N2, N3) and Ti, N1 and the Cp centroid, respectively. [b] Molecule **3a** resides on a crystallographic mirror plane.

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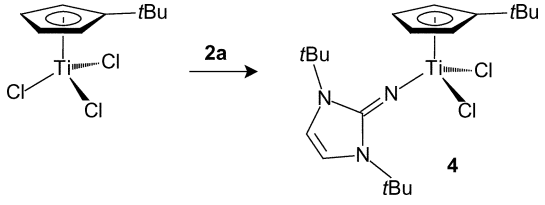
3b [163.3(1)°] and **3c** [164.6(1)°] exhibit the smallest Ti–N1–C1 angles, whereas considerably larger angles are produced by the sterically more demanding ligands in **3a** [170.7(2)°] and **3e** [175.8(1)°]. In agreement with a strong contribution of canonical form **IB** to the ground-state electronic structure of the imidazolin-2-iminato ligands in complexes **3** (Fig. 1), the observation of short Ti–N1 distances goes along with a pronounced elongation of the corresponding N1–C1 distances, which in the case of **3a** [1.332(4) Å], **3b** and **3c** [both 1.324(2) Å] adopt an intermediate position between the values expected for a typical N–C_{sp^2} single (1.38 Å) and double bond (1.28 Å), respectively.[14] Consequently, the shortest N1–C1 distance is observed for the diarylated derivative **3e** [1.309(2) Å], which at the same time exhibits the longest Ti–N1 bond length (*vide supra*, Table 1).

Comparable structural parameters about the titanium atom have been observed for complexes of the type $CpTi(NPR_3)Cl_2$ (R = *cyclo*-C_6H_{11}, *i*Pr, *t*Bu) containing strong π-donating trialkylphosphoraneiminato ligands with Ti–N distances ranging between 1.750(3) and 1.775(11) Å.[4a] The structural characterization of a closely related guanidinate complex with a saturated 1,3-diphenyl-4,5-dihydroimidazolin-2-iminato ligand reveals a similarly short but nevertheless notably longer Ti–N distance [1.792(2) Å] and a stronger deviation from a linear Ti–N–C orientation [152.9(2)°].[5] These findings indicate that hydration and saturation of the C–C double bond leads to a decreased π-electron release capability in comparison with the unsaturated imidazolin-2-iminato ligands presented in our study. In addition, it should be noted that ketimide complexes of the type $CpTi(N{=}CR_2)Cl_2$, which have also been employed in ethylene homopolymerization,[3] exhibit much longer Ti–N together with shorter N–C distances, *e. g.* Ti–N = 1.872(4) Å and N–C = 1.267(6) Å in $CpTi(N{=}CRR')Cl_2$ (R = *n*Bu, R′ = *t*Bu).[3d]

Finally, it should be noted that the Ti–N distances in the structurally characterized complexes **3** reported herein fall in the same range as the Ti–O separations in aryloxide complexes of the type $CpTi(OAr)Cl_2$ despite the larger size of the nitrogen atom. This further supports the strong π-donating ability of imidazolin-2-iminato ligands, which can be regarded as highly π-basic aryloxide analogues.[2l,m,15]

Since variations of the substitution pattern not only of the monodentate but also of the cyclopentadienyl ancillary ligand often have a great impact on the level of catalytic activity,[1–4] we have synthesized complex **4** bearing a *tert*-butylcyclopentadienyl ($tBuC_5H_4$) ligand in addition to the cyclopentadienyl-titanium complexes **3** (Scheme 2). **4** could be readily obtained in high yield from the reaction of $[(\eta^5\text{-}tBuC_5H_4)TiCl_3]$ with **2a** in hexane overnight. Apart from the fact that additional ^1H and ^{13}C NMR resonances are observed for the substituted Cp ring, the spectroscopic characteristics of **4** are very similar to those observed for the corresponding complex **3a**. To evaluate structural changes upon the introduction of the sterically demanding *tert*-butyl group, crystals of complex **4** were subjected to an X-ray diffraction analysis, and the molecular structure is shown in Fig. 4. To minimize steric interaction, the imidazolin-2-iminato ligand and the *tert*-butyl Cp substituent adopt a *transoid* orientation, and an almost perfect horizontal conformation is observed for the heterocyclic five-membered ring with respect to the pseudo-mirror plane containing N1, Ti and the centroid of the cyclopentadienyl ring (dihedral angle = 89.3°). Due to the introduction of an additional *tert*-butyl group, the cyclopentadienyl ring in **4** is coordinated in a more asymmetric fashion than in **3a**, and the Ti–C distances range from 2.327(3) to 2.501(2) Å with the largest separation being observed between titanium and the quarternary *ipso*-carbon atom. Apart from the differences in Cp coordination, the bond distances and angles involving Ti, N1 and the two chlorine atoms as well as the structural parameters of the imidazolin-2-iminato ligand are very similar to those established for **3a** (Table 1).[6]



Scheme 2

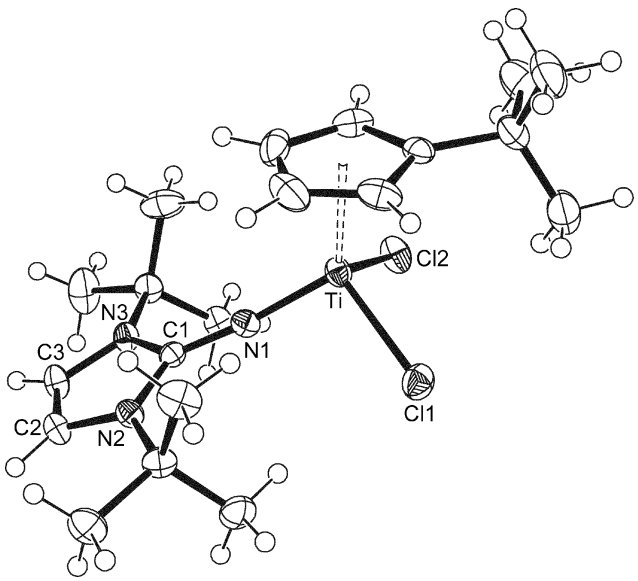


Fig. 4 ORTEP drawing of **4** with thermal ellipsoids drawn at 50% probability.

Preparation and characterization of bis(imidazolin-2-iminato) titanium complexes and alkylation reactions

As described previously,[6] bis(1,3-di-*tert*-butylimidazolin-2-iminato)titanium dichloride **5** can be obtained in almost quantitative yield as an orange crystalline solid from the reaction of $TiCl_4$ with two eq. of the silylated imine **2a** in boiling toluene for 48 h (Scheme 3). **5** could subsequently be converted into the yellow dimethyl complex **6** by treatment with methyllithium in diethyl ether. The alkylation can be easily followed by NMR spectroscopy, since characteristic CH_3 resonances are observed at 1.10 and 42.1 ppm in the ^1H and ^{13}C NMR spectra, respectively. The molecular structure of **6** was additionally established by X-ray diffraction analysis, and an ORTEP presentation is shown in Fig. 5. The complex exhibits the expected pseudo-tetrahedral geometry about titanium, and the Ti–N–C angles are close

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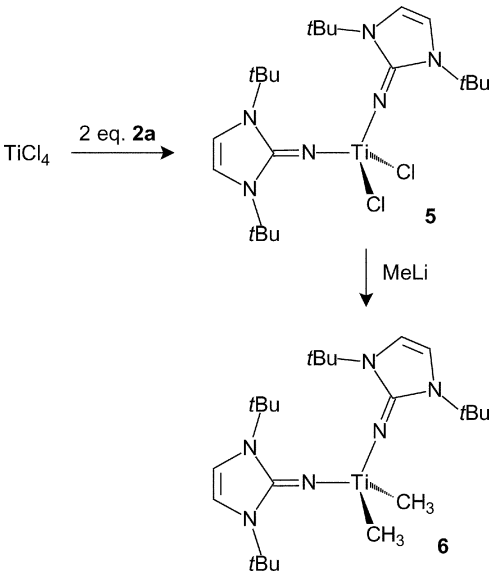


Scheme 3

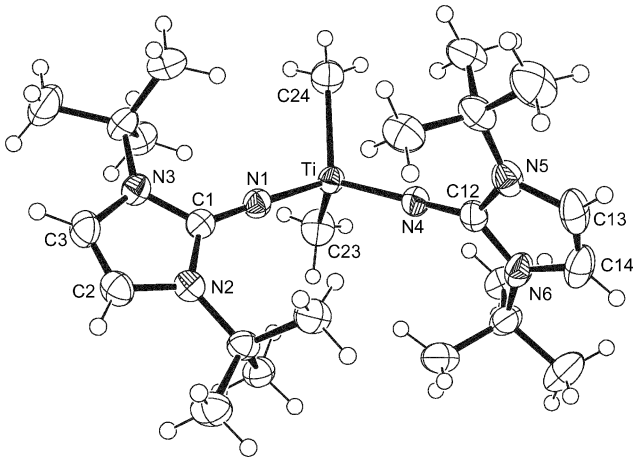
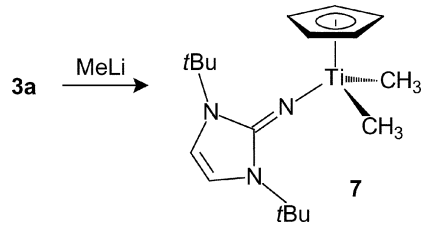


Fig. 5 ORTEP drawing of **6** with thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ti–C23 2.114(2), Ti–C24 2.110(2), Ti–N1 1.819(1), Ti–N4 1.828(1), N1–C1 1.300(2), N2–C1 1.388(2), N2–C2 1.388(2), C2–C3 1.325(3), N3–C3 1.390(2) N3–C1 1.383(2), N4–C12 1.299(2), N5–C12 1.388(2), N5–C13 1.396(2), C13–C14 1.312(3), N6–C14 1.381(2), N6–C12 1.390(2); Ti–N1–C1 176.1(1), N1–Ti–C23 105.75(8), N1–Ti–C24 109.69(7), N1–C1–N2 128.1(1), C1–N2–C2 108.9(1), N2–C2–C3 108.6(2), Ti–N4–C12 171.9(1), N4–Ti–C23 109.81(8), N4–Ti–C24 109.65(8), N4–C12–N5 127.2(2), C12–N5–C13 108.1(2), N5–C13–C14 108.9(2), N1–Ti–N4 116.36(6).

to linearity [Ti–N1–C1 = 176.1(1)°, Ti–N4–C12 = 171.9(1)°]. The Ti–C distances of 2.114(2) and 2.110(2) Å as well as the Ti–N distances of 1.819(1) and 1.828(1) Å are very similar to those observed for the closely related bis(phosphoraneiminato) complex $[(t\mathrm{Bu_3PN})_2\mathrm{Ti(CH_3)_2}]$ [Ti–C = 2.121(3), 2.129(3) Å; Ti–N = 1.824(2), 1.830(2) Å].[4c]

As a representative example for the half-sandwich mono(imidazolin-2-iminato) complexes of the type $\mathrm{CpTi(L)Cl_2}$ (**3**), **3a** was also dialkylated by treatment with methyllithium to afford complex **7** as an orange crystalline solid in almost quantitative yield (Scheme 4). The ^{1}H and ^{13}C NMR resonances



Scheme 4

of the metal-coordinated methyl groups are observed at 0.74 and 27.9 ppm, respectively, significantly upfield from the corresponding resonances found for the $[\mathrm{L_2Ti(CH_3)_2}]$ analogue **6**. To evaluate structural changes upon methylation, **7** was characterized crystallographically as well, and the molecular structure is presented in Fig. 6. The Ti–C [both 2.161(2) Å] and Ti–N separations [1.805(1) Å] fall in the expected ranges and are similar to those in **6**. The imidazolin-2-iminato ligand is linearly bound [Ti–N1–C1 = 176.0(1)°], and the five-membered heterocycle adopts an almost perfect horizontal conformation with a torsion angle of 89.8° (Table 1). Comparison with the structural data of the corresponding dichloro complex **3a** reveals a longer Ti–N1 separation [1.805(1) *vs.* 1.765(3) Å] together with a shorter N1–2C1 separation [1.310(2) *versus* 1.332(4) Å], which indicates that methylation weakens the interaction between titanium and the imidazolin-2-iminato ligand. The successful preparation of complexes **6** and **7** implies that similar dimethyl derivatives might be involved as intermediate pre-catalysts in the homopolymerization of ethylene upon activation of complexes of type **3** and **4** with methylalumoxane (*vide infra*).

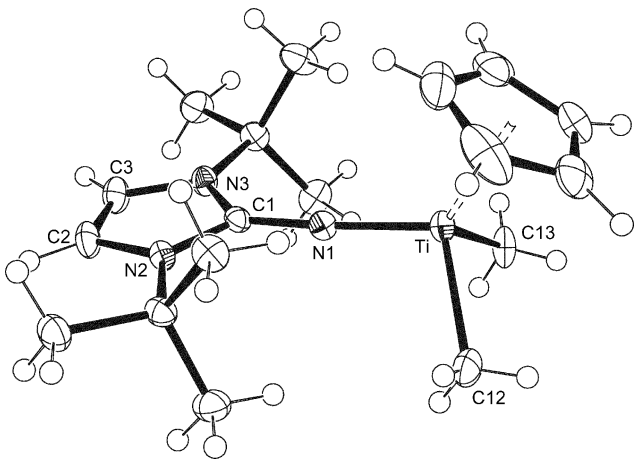


Fig. 6 ORTEP drawing of **7** with thermal ellipsoids drawn at 50% probability.

Ethylene polymerization catalysis

In order to compare their efficiency in olefin polymerization catalysis, the dichloro complexes **3a–e**, **4** and **5** were tested for ethylene homopolymerization. Upon activation with methylaluminoxane (MAO), all compounds give active catalysts, and the results are summarized in Table 2. The properties of the isolated polyethylene (PE) were determined by means of DSC and GPC techniques. Melting points of the polyethylene samples

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Table 2 Ethylene polymerisation data[a]

Pre-catalyst (*M*)	*m* (pre-cat.)/mg; *n* (pre-cat.)/mmol	Al/Ti[b]	Reaction time/min	Yield PE/g	Activity[c]	Mp/°C	M_w[f]	PDI[e,f]
3a (378.18)	20; 0.053	122/1	15	10.8	408	126	960 000	2.2
	20; 0.053	122/1	15	10.0	378	—	1 200 000	2.6
3b (350.12)	20; 0.057	113/1	60	3.0	26	120	2 400 000[d]	2.4
3c (378.18)	20; 0.053	122/1	50	2.6	30	127	2 700 000	2.4
3d (502.32)	20; 0.040	162/1	60	4.4	55	131	3 000 000	2.6
3e (586.48)	20; 0.034	189/1	30	4.5	132	126	1 200 000	5.1[g]
	20; 0.034	189/1	30	3.6	106	127	750 000	4.5[g]
4 (434.28)	20; 0.046	140/1	15	13.4	583	126	600 000	2.7
	20; 0.046	140/1	10	7.1	463	128	450 000	2.0
	20; 0.046	140/1	5	6.5	848	129	280 000	2.2
	20; 0.046	140/1	5	5.0	652	—	500 000	2.1
5 (507.38)	20; 0.039	164/1	20	0.2	8	123	1 800 000[d]	16.7[h,i]

[a] Reactions in toluene solution at 25 °C, 2 bar ethene. [b] 3.5 mL of a 10% [m/m] solution of MAO in toluene (EURECEN AL 5100-10-toluene from Crompton GmbH, Bergkamen; $\rho = 0.89$ g cm^{-3}) with an overall Al concentration between 4.60 and 5.60% [m/m]. [c] Activity = g(PE) mmol(pre-cat.)$^{-1}$ bar(ethene)$^{-1}$ h^{-1}. [d] ^{13}C{^{1}H} (1,2,4-trichlorobenzene–d_6-benzene, 350 K): δ 30.1 ppm. [e] The molecular weight distributions were determined by Prof. B. Rieger (Ulm); 1,2,4-trichlorobenzene at 145 °C. [f] PDI = M_w/M_n. [g] Bimodal distribution. [h] Multimodal distribution. [i] Highly asymmetric curve progression.

were found to be in the range 117–131 °C. Comparison of the results obtained for complexes **3a–3c** indicates that bulky substituents on the imidazoline nitrogen atoms are beneficial for the catalytic activity, which was found to be high for the *tert*-butyl derivative **3a** and moderate for the isopropyl derivatives **3b** and **3c**.[1a,c] Furthermore, substitution in 4,5-position of the imidazoline ring does not seem to have a significant impact on the activity. GPC data for the PE derived from complexes **3b** and **3c** show the formation of high molecular weight PE with M_w in the range of 2 500 000 g mol^{-1} and polydispersities of 2.4. The catalysts derived from the aryl substituted compounds exhibit moderate (**3d**) to high activities (**3e**).[1a,c] In the case of **3d**, linear polyethylene was obtained with an ultra high molecular weight of $M_w = 3\,000\,000$ g mol^{-1} (UHMWPE) and a polydispersity of 2.6. The introduction of a sterically demanding substituent on the cyclopentadienyl ring in compound **4** significantly improved the activity in comparison to the catalytic system **3a**/MAO. The catalyst derived from **4** represents the most active system within this series with an activity of up to 848 g (PE) mmol^{-1} (pre-cat.) h^{-1} bar^{-1}. For the non-metallocene complex **5**, only a low activity was observed, but also with this system, PE with high molecular weight (M_w = 1 800 000) was obtained. A limited activity in ethylene polymerisation was also reported for the structurally related phosphoraneiminato complex (tBu$_3$PN)$_2$TiCl$_2$ in combination with MAO as an activator.[4c]

The relatively narrow polydispersities of the PE derived from complexes **3a–d** and from **4** indicate the operation of single-site catalysts. In contrast, bimodal or even multimodal molecular weight distributions are observed for the polymers obtained by use of **3e** and **5**, respectively, which might reveal the presence of more than one active site. Although the mechanism of pre-catalyst activation by MAO can not be fully explained at this stage, the possibility to isolate stable dimethyl complexes such as **6** and **7** suggests the formation of similar dialkyl intermediates upon reaction with the MAO. It remains to be investigated whether subsequent methyl abstraction affords the presumed active catalysts of type [CpTi(L)Me]$^+$ or leads to the additional formation of other species. To further elucidate the pathway of catalyst generation, future work in this field will focus on the use of single-component activators such as the borane B(C$_6$F$_5$)$_3$, or the trityl and anilinium salts [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], respectively, for the activation of imidazolin-2-iminato titanium dialkyl complexes.

Experimental

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-GX 270 (270 MHz) and JEOL-GX 400 (400 MHz) instruments. The syntheses of compounds **3a** and **5** have been previously communicated.[6] for reason of comparison their characterization is also included here. [(η^5-C$_5$H$_5$)TiCl$_3$],[16] [(η^5-tBuC$_5$H$_4$)TiCl$_3$],[17] the imidazolin-2-ylidenes **1a–e**[18,19] and the 2-(trimethylsilylimino)imidazolines **2a**, **2c** and **2d**[7] were prepared according to literature procedures.

Preparations

General procedure for the preparation of 2-(trimethylsilylimino)-imidazolines 2. A solution of the respective imidazolin-2-ylidene **1** (10 mmol) in toluene (20 mL) was treated dropwise with trimethylsilyl azide (14 mmol in case of **1a** and **1c–e**; 10 mmol in case of **1b**) at ambient temperature, and the resulting reaction mixture was subsequently heated in boiling toluene for 72 h. Filtration and evaporation of the solvent afforded the imines as yellowish solids (**2a**, **2d** and **2e**) or as a brownish oils (**2b** and **2c**), respectively, of which the latter can be purified by bulb to bulb distillation at 180 °C/9 mbar.

2a. Yield: 88% (Found: C, 62.63; H, 11.09; N, 15.57%. Calc. for C$_{14}$H$_{29}$N$_3$Si: C, 62.86; H, 10.93; N, 15.71%); δ_H (400 MHz, C$_6$D$_6$) 6.03 (2 H, s, NCH), 1.36 (18 H, s, CCH$_3$) and 0.52 (9 H, s, SiCH$_3$); δ_C (100.52 MHz, C$_6$D$_6$) 139.7 (NCN), 107.5 (NCH), 54.2 (N*C*Me), 28.1 (C*C*H$_3$) and 4.4 (SiCH$_3$).

2b. Yield: 60%; δ_H (400 MHz, C$_6$D$_6$) 5.89 (2H, s, NCH), 4.40 (2H, sept, CHMe), 0.98 (12 H, d, CCH$_3$) and 0.43 (9 H, s, SiCH$_3$); δ_C (100.52 MHz, C$_6$D$_6$) 143.2 (NCN), 106.8 (NCH), 44.3 (*C*HMe), 21.9 (CH*Me*) and 4.5 (SiCH$_3$). It should be noted that the reaction of **2b** with Me$_3$SiN$_3$ is accompanied by the formation

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of the disilylated product 1,3-diisopropyl-2-(trimethylsilylimino)-4-trimethylsilylimidazoline, for which the following ^{1}H NMR spectroscopic data were obtained: δ_H (400 MHz, C_6D_6) 6.18 (1H, s, NCH), 4.27 (1H, sept, CHMe), 3.95 (1H, sept, CHMe), 1.54 (6 H, d, CCH_3), 0.97 (6 H, d, CCH_3), 0.44 (9 H, s, $SiCH_3$) and 0.15 (9 H, s, $SiCH_3$).

2c. Yield: 92% (Found: C, 62.55; H, 11.10; N, 15.34%. Calc. for $C_{14}H_{29}N_3Si$: C, 62.86; H, 10.93; N 15.71%); δ_H (400 MHz, C_6D_6) 4.59 (2H, sept, CHMe), 1.71 (6H, s, CH_3), 1.18 (12 H, d, CH_3) and 0.44 (9 H, s, $SiCH_3$); δ_C (100.52 MHz, C_6D_6) 144.4 (NCN), 113.9 (N*C*Me), 45.0 (*C*HMe), 21.3 (CH*Me*), 10.0 (NC*Me*) and 4.3 ($SiCH_3$).

2d. Yield: 80% (Found: C, 72.55; H, 8.16; N, 10.58%. Calc. for $C_{24}H_{31}N_3Si$: C, 73.61; H, 8.49; N, 10.73%); δ_H (400 MHz, C_6D_6) 6.78 (4H, s, *m*-H), 5.76 (2H, s, NCH), 2.21 (12H, s, *o*-CH_3), 2.10 (6 H, s, *p*-CH_3) and −0.09 (9 H, s, $SiCH_3$). δ_C (100.52, C_6D_6) 140.7 (NCN), 137.6 (*ipso-C*), 136.2 (*p-C*Me), 134.5 (*o-C*Me), 128.9 (*m-C*H), 112.1 (*C*H), 20.8 (*p*-C*Me*), 18.0 (*o*-C*Me*) and 3.1 ($SiCH_3$).

2e. Yield: 94% (Found: C, 76.13; H, 9.37; N, 8.83%. $C_{30}H_{45}N_3Si$ requires C, 75.73; H 9.53; N, 8.83%); δ_H (400 MHz, C_6D_6) 7.21 (4H, m, *m*-H), 7.14 (2H, s, *p*-H), 5.95 (2H, s, NCH), 3.18 (4H, sept, CHMe), 1.38 (12H, d, CH_3), 1.20 (12 H, d, CH_3) and −0.16 (9 H, s, $SiCH_3$). δ_C (67.93 MHz, C_6D_6) 148.0 (*o-C*), 141.3 (NCN), 135.2 (*ipso-C*), 129.4 (*p-C*H), 123.9 (*m-C*H), 113.8 (*C*H), 28.9 (*C*HMe), 24.4 (CH*Me*), 23.5 (CH*Me*) and 3.5 ($SiCH_3$).

General procedure for the preparation of complexes [(η-C_5H_5)Ti(L)Cl_2] (3) (L = imidazolin-2-iminato ligand). These compounds were prepared employing very similar procedures, and thus only one representative example is detailed. To a solution of 615 mg (2.80 mmol) of [(η-C_5H_5)$TiCl_3$] in toluene (13 mL) was added at room temperature a solution of 750 mg (2.80 mmol) of **2a** in toluene (10 mL). The reaction mixture was stirred overnight, and the solvent was evaporated. The residue was washed several times with hexane and dried *in vacuo*.

3a. Yield: 1.03 g, 97% (Found: C, 50,18; H, 6.54; N, 10,73%. Calc. for $C_{16}H_{25}Cl_2N_3Ti$: C, 50.82; H, 6.66; N, 11.11%); δ_H (400 MHz, C_6D_6) 6.42 (5 H, s, C_5H_5), 5.69 (2H, s, NCH) and 1.33 (18 H, s, CH_3); δ_C (100.52, $CDCl_3$) 146.6 (s, NCN), 115.6 (C_5H_5), 109.2 (NCH), 59.0 (*C*Me) and 29.8 (C*Me*).

3b. Yield: 99% (Found: C, 47.88; H, 6.09; N, 11.46%. $C_{14}H_{21}Cl_2N_3Ti$ requires C, 48.02; H, 6,05; N, 12.00%); δ_H (400 MHz, C_6D_6) 6.44 (5H, s, C_5H_5), 5.52 (2H, s, NCH), 4.66 (2H, sept, CHMe) and 0.86 (12 H, d, CH_3); δ_C (100.52 MHz, C_6D_6) 114.6 (C_5H_5), 108.9 (NCH), 47.3 (*C*HMe) and 22.0 (CH*Me*); the NCN resonance could not be detected.

3c. Yield: 89% (Found: C, 50.26; H, 6.69; N, 10.83%. $C_{16}H_{25}Cl_2N_3Ti$ requires C, 50,81; H, 6,66; N, 11.11%); δ_H (400 MHz, C_6D_6) 6.46 (5H, s, C_5H_5), 4.70 (2H, m, CHMe), 1.32 (6H, s, $NCCH_3$) and 1.10 (12 H, d, CH_3); δ_C (100.52 MHz, C_6D_6) 116.7 (N*C*Me), 114.3 (C_5H_5), 47.6 (*C*HMe), 21.3 (CH*Me*) and 9.1 (NC*Me*); the NCN resonance could not be detected.

3d. Yield: 87% (Found: C, 60.62; H, 5.95; N, 7.94%. $C_{26}H_{29}Cl_2N_3Ti$ requires C, 62.17; H, 5.82; N, 8.36%); δ_H (400 MHz, C_6D_6) 6.79 (4H, s, *m*-H), 5.97 (5H, s, C_5H_5), 5.41 (2H, s, NCH), 2.16 (12H, s, *o*-CH_3) and 2.08 (6 H, s, *p*-CH_3). δ_C (100.52 MHz, C_6D_6) 142.9 (NCN), 139.7 (*ipso-C*), 136.2 (*p-C*Me), 132.0 (*o-C*Me), 129.6 (*m-C*H), 114.5 (C_5H_5), 114.1 (NCH), 21.0 (*p*-C*Me*) and 17.9 (*o*-C*Me*).

3e. Yield: 100% (Found: C, 64.25; H, 7.09; N, 6.62%. $C_{32}H_{41}Cl_2N_3Ti$ requires C, 65.53; H 7.05; N, 7.16%); δ_H (400 MHz, C_6D_6) 7.23 (4H, m, *m*-CH), 7.14 (2H, s, *p*-CH), 5.94 (5H, s, C_5H_5), 5.77 (2H, s, NCH), 2.95 (4H, sept, CHMe), 1.49 (12H, d, CH_3) and 1.07 (12 H, d, CH_3). δ_C (67.93 MHz, C_6D_6) 146.7 (*o-C*), 143.3 (NCN), 132.5 (*ipso-C*), 130.9 (*p-C*H), 124.6 (*m-C*H), 115.5 (NCH), 115.0 (C_5H_5), 29.3 (*C*HMe), 24.7 (CH*Me*) and 23.4 (CH*Me*).

Preparation of [(η-*t*BuC_5H_4)Ti(L)Cl_2] (4) (L = 1,3-di-*tert*-butylimidazolin-2-imide). To a solution of 206 mg (0.75 mmol) of [(η-*t*BuC_5H_4)$TiCl_3$] in hexane (10 mL) was added a solution of 200 mg (0.75 mmol) of **2a** in hexane (8 mL). The reaction mixture was stirred overnight. The solvent was evaporated to yield 291 mg of complex **4** (0.67 mmol, 89%) (Found: C, 55.52; H, 7.91; N, 9.52%. $C_{20}H_{33}Cl_2N_3Ti$ requires C, 55.31; H, 7.66; N, 9.68%); δ_H (400 MHz, C_6D_6) 6.51 (2H, t, $C_5H_4CMe_3$), 6.26 (2H, t, $C_5H_4CMe_3$), 5.71 (2H, s, NCH), 1.60 (9H, s, $C_5H_4CCH_3$) and 1.36 (18 H, s, CH_3); δ_C (67.93 MHz, C_6D_6) 161.4 ($C_4H_4CCMe_3$), 115.7 ($CHCCMe_3$), 111.4 ($CHCHCCMe_3$), 109.2 (NCH), 58.6 (*C*Me), 33.5 ($C_5H_4CMe_3$), 31.5 ($C_5H_4CMe_3$) and 29.5 (C*Me*); the NCN resonance could not be detected.

Preparation of [L_2TiCl_2] (5) (L = 1,3-di-*tert*-butylimidazolin-2-imide). To a solution of 266 mg (1.40 mmol) of $TiCl_4$ in toluene (5 mL) was added a solution of 750 mg (2.80 mmol) of **2a** in toluene (10 mL). This mixture was heated to 110 °C for 48 h. Orange crystalline **5** was isolated by filtration and dried under vacuum (613 mg, 1.20 mmol, 86%) (Found: C; 51.66, H; 7.99, N; 16.08%. Calc. for $C_{22}H_{40}Cl_2N_6Ti$: C, 52.08; H, 7.95; N, 16.56%); δ_H (400 MHz, C_6D_6) 5.82 (4H, s, NCH) and 1.60 (36H, s, CH_3); δ_C (100.52 MHz, C_6D_6) 142.9 (NCN), 107.7 (NCH), 57.0 (*C*Me) and 28.8 (C*Me*).

Preparation of [$L_2Ti(CH_3)_2$] (6) (L = 1,3-di-*tert*-butylimidazolin-2-iminato ligand). 116 mg (0.23 mmol) of **5** were suspended in diethyl ether (6 mL) and 0.29 mL (0.46 mmol) of a 1.6 M solution of MeLi in diethyl ether was added by a syringe. The mixture was stirred at room temperature for 45 min, whereupon the colour changed from red to yellow. The solvent was removed under reduced pressure. The solid residue was taken up in 5 mL of toluene to give a cloudy, bright yellow suspension, which was filtered. The solvent was removed under vacuum yielding 93 mg (0.20 mmol, 87%) of **6** as a shiny yellow solid (Found: C, 61.81; H, 9.76; N, 17.29%. $C_{24}H_{46}N_6Ti$ requires C, 61.78; H, 9.94; N, 18.01%); δ_H (400 MHz, C_6D_6) 5.97 (4H, s, NCH), 1.63 (36H, s, CH_3) and 1.10 (6H, s, $TiCH_3$); δ_C (100.52 MHz, C_6D_6) 140.5 (NCN), 106.8 (NCH), 56.0 (N*C*Me), 42.1 (Ti*C*H_3) and 28.4 (C*C*H_3).

Preparation of [(η-C_5H_5)Ti(L)$(CH_3)_2$] (7) (L = 1,3-di-*tert*-butylimidazolin-2-iminato ligand). To a suspension of 405 mg (1.07 mmol) of **3a** in toluene (15 mL) was added at room temperature 1.34 ml (2.14 mmol) of a 1.6 M solution of MeLi in diethyl ether. The colour of the solution immediately turned from red to yellow. After stirring for 16 h, the reaction mixture was filtered through Celite to give a clear orange solution. Removal of all volatiles gave 340 mg (1.01 mmol, 94%) of **7** as an orange solid (Found: C, 62.47; H, 9.09; N, 11.82%. $C_{18}H_{31}N_3Ti$ requires C, 64.08; H, 9.26; N, 12.46%); δ_H (400 MHz, C_6D_6) 6.42 (5H, s, C_5H_5), 5.90 (2H, s, NCH), 1.38 (18H, s, CH_3) and 0.74 (6H, s, $TiCH_3$); δ_C (67.93 MHz, C_6D_6) 111.4 (C_5H_5), 107.6 (NCH), 44.3

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(*C*Me), 28.5 (C*Me*) and 27.9 (Ti*C*H_3); the NCN resonance could not be detected.

Single-crystal X-ray crystal structure determinations

General procedure. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling system at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Raw data were corrected for Lorentz polarization, and, arising from the scaling procedure, for latent decay and absorption effects. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The final difference-Fourier map showed no striking features.

CCDC reference numbers 281530 (**3b**), 281531 (**3c**), 281532 (**3e**), 281533 (**4**), 281534 (**6**) and 281535 (**7**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511752f

3b. $C_{14}H_{21}Cl_2N_3Ti$, $M_r = 350.11$, red fragment (0.38 × 0.46 × 0.69 mm), monoclinic, space group $C2/c$ (no. 15), $a = 17.8609(2)$, $b = 8.3732(1)$, $c = 23.1179(2)$ Å, $\beta = 97.3494(3)°$, $V = 3428.95(6)$ Å^3, $Z = 8$, $D_c = 1.356$ g cm^{-3}, $F_{000} = 1456$, $\mu = 0.805$ mm^{-1}, $T = 123$ K, $R_1 = 0.0298$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0791$ [all data], GOF = 1.034, $\Delta e_{min/max} = +0.54/-0.25$ e Å^{-3}.

3c. $C_{16}H_{25}Cl_2N_3Ti$, $M_r = 378.16$, red needle (0.23 × 0.25 × 0.66 mm), orthorhombic, space group *Pbca* (no. 61), $a = 18.0659(2)$, $b = 11.2730(1)$, $c = 18.2918(2)$ Å, $V = 3725.25(7)$ Å^3, $Z = 8$, $D_c = 1.349$ g cm^{-3}, $F_{000} = 1584$, $\mu = 0.746$ mm^{-1}, $T = 123$ K, $R_1 = 0.0346$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0848$ [all data], GOF = 1.029, $\Delta e_{min/max} = +0.43/-0.44$ e Å^{-3}.

3e·C_7H_8. $C_{39}H_{49}Cl_2N_3Ti \cdot C_7H_8$, $M_r = 678.58$, red needle (0.43 × 0.46 × 1.07 mm), monoclinic, space group $P2_1/n$ (no. 14), $a = 12.8096$ (1), $b = 18.5630(2)$, $c = 15.5127(2)$ Å, $\beta = 90.8894(5)°$, $V = 3688.24(7)$ Å^3, $Z = 4$, $D_c = 1.222$ g cm^{-3}, $F_{000} = 1440$, $\mu = 0.407$ mm^{-1}, $T = 173$ K, $R_1 = 0.0444$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0934$ [all data], GOF = 1.120, $\Delta e_{min/max} = +0.30/-0.26$ e Å^{-3}.

4. $C_{20}H_{33}Cl_2N_3Ti$, $M_r = 434.26$, red needle (0.08 × 0.10 × 0.51 mm), monoclinic, space group $P2_1/c$ (no. 14), $a = 8.8141(1)$, $b = 17.2213(2)$, $c = 15.1835(2)$ Å, $\beta = 104.3295(5)°$, $V = 2233.00(5)$ Å^3, $Z = 4$, $D_c = 1.292$ g cm^{-3}, $F_{000} = 920$, $\mu = 0.632$ mm^{-1}, $T = 173$ K, $R_1 = 0.0445$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0916$ [all data], GOF = 1.110, $\Delta e_{min/max} = +0.74/-0.25$ e Å^{-3}.

6. $C_{24}H_{46}N_6Ti$, $M_r = 466.54$, yellow plate (0.08 × 0.25 × 0.31 mm), orthorhombic, space group *Pbca* (no. 61), $a = 18.4995(1)$, $b = 16.2737(1)$, $c = 18.6379(1)$ Å, $V = 5611.04(5)$ Å^3, $Z = 8$, $D_c = 1.105$ g cm^{-3}, $F_{000} = 2032$, $\mu = 0.325$ mm^{-1}, $T = 173$ K, $R_1 = 0.0358$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0984$ [all data], GOF = 1.053, $\Delta e_{min/max} = +0.32/-0.25$ e Å^{-3}.

7. $C_{18}H_{31}N_3Ti$, $M_r = 337.33$, orange fragment (0.28 × 0.36 × 0.46 mm), monoclinic, space group $P2_1/n$ (no. 14), $a = 11.0252(1)$, $b = 10.1497(1)$, $c = 16.7456(2)$ Å, $\beta = 90.3793(5)°$, $V = 1873.83(3)$ Å^3, $Z = 4$, $D_c = 1.196$ g cm^{-3}, $F_{000} = 728$, $\mu = 0.458$ mm^{-1}, $T = 123$ K, $R_1 = 0.0311$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0796$ [all data], GOF = 1.024, $\Delta e_{min/max} = +0.24/-0.31$ e Å^{-3}.

Ethene polymerization reactions

A Büchi laboratory autoclave BEP 280, equipped with a BPC Büchi pressflow gas controller and a pressure-proofed dropping funnel, was charged with 200 mL of toluene and saturated with ethene (2 bar) for 10 min at 25 °C, controlled by the flow meter. The catalyst was dissolved in 3.5 mL of a 10% [m/m] solution of MAO in toluene ($\rho = 0.89$ g cm^{-3}) and injected into the autoclave using the dried dropping funnel. The polymerization reaction was stopped by quenching with 20 mL of aqueous HCl/methanol (1 : 1 v/v). The resulting polymer was collected by filtration, washed subsequently with HCl, water, tetrahydrofuran, and acetone, and dried at 80 °C *in vacuo* overnight. Melting points of the polyethylene samples were measured using a DSC 2010 TA instrument, $^{13}C\{^1H\}$ NMR spectra were recorded on a AC 200 P Bruker spectrometer at 350 K and the molecular weight determination was performed using HT-GPC (Waters Alliance GPC 2000), 1,2,4-trichlorobenzene; 145 °C; universal calibration to polystyrene and relative to polyethylene standards).

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG Ta 189-6/1).

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