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A highly efficient titanium-based olefin polymerisation catalyst with a monoanionic iminoimidazolidide π -donor ancillary ligand†‡

Winfried P. Kretschmer,* Chris Dijkhuis, Auke Meetsma, Bart Hessen and Jan H. Teuben
Dutch Polymer Institute/Centre for Catalytic Olefin Polymerisation, Stratingh Institute of Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.
E-mail: kretschmer@chem.rug.nl

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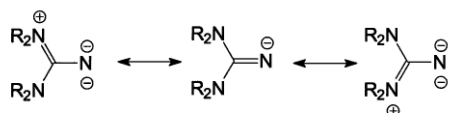
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The titanium complex $\text{Cp}[1,3-(2',6'\text{-Me}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{Ti}(\text{CH}_2\text{Ph})_2$, with a monoanionic η^1 -iminoimidazolidide ancillary ligand, is shown to be a highly efficient catalyst for olefin polymerisation when activated with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$.

Since the development of highly efficient group 4 metallocene catalysts for the polymerisation of olefins in the 1980–1990s,¹ recent research efforts into the design of new single-site olefin polymerisation catalysts have increasingly turned to non-metallocene systems.² Cationic mono(cyclopentadienyl) titanium alkyl complexes with an additional monoanionic π -donor ancillary ligand form a group of very interesting catalysts for the homo- and copolymerisation of olefins. Typical π -donor ancillary ligands that have been used in these catalysts are substituted phenoxides $2,6\text{-R}_2\text{C}_6\text{H}_3\text{O}^-$,³ ketimides $\text{R}_2\text{C}=\text{N}^-$,⁴ and phosphinimides $\text{R}_3\text{P}=\text{N}^-$.⁵ The latter are especially effective, which is possibly due to an improved π -donor capability through the availability of a zwitterionic resonance structure, increasing the negative charge on the nitrogen atom. Another system that, for similar reasons, may be expected to be an efficient ancillary ligand is the monoanionic 1,1,3,3-tetra-substituted η^1 -guanidinate group, $(\text{R}_2\text{N})_2\text{C}=\text{N}^-$ (Scheme 1).

We have used a 1,1,3,3-bis(pentamethylene) guanidinate anion (**A**) and a sterically protected guanidinate-type ligand, the 1,3-diarylinoimidazolidide anion (**B**), as ancillary ligands in mono(cyclopentadienyl) titanium olefin polymerisation catalysts. A comparison with catalysts supported by the related bis-Bu^t-ketimide (**C**) and tris-Bu^t-phosphinimide ligands (**D**) shows that especially the 1,3-diarylinoimidazolidide complex is a highly efficient catalyst for olefin homo- and copolymerisation, with good thermal stability and good resistance towards alkylaluminium scavengers.

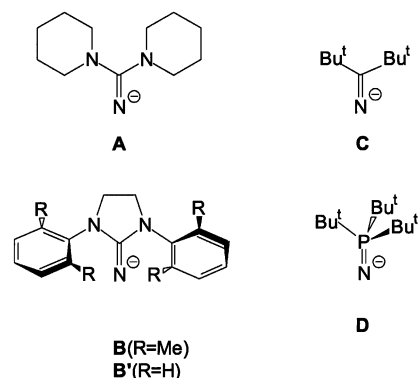
The lithium[1,1,3,3-bis(pentamethylene)guanidinate] $\text{Li}[\text{A}]$ was prepared *in situ* by reaction⁶ of piperidyl lithium with 1-piperidinecarbonitrile, while the 1,3-diarylinoimidazolidines $1,3\text{-Ar}_2(\text{CH}_2\text{N})_2\text{C}=\text{NH}$, with $\text{Ar} = \text{Xy}$ ($\text{Xy} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\text{H}[\text{B}]$), Ph ($\text{H}[\text{B}']$) were prepared from 1,2-dianilinoethanes and cyanogen bromide in toluene according to literature procedures.⁷ The corresponding cyclopentadienyl titanium dichloride complexes $\text{Cp}\{[(\text{CH}_2)_5\text{N}]_2\text{C}=\text{N}\}\text{TiCl}_2$ (**1a**) and $\text{Cp}[\text{Ar}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2$ (**1b**, **1b'**) were prepared by reaction of CpTiCl_3 with the Li-salts of the ligands. The titanium dibenzyl complexes $\text{Cp}\{[(\text{CH}_2)_5\text{N}]_2\text{C}=\text{N}\}\text{Ti}(\text{CH}_2\text{Ph})_2$



Scheme 1 Resonance structures in 1,1,3,3-tetra-substituted guanidinate anions.

† Electronic supplementary information (ESI) available: experimental, spectroscopic and polymerisation details. See <http://www.rsc.org/suppdata/cc/b1/b111343g/>

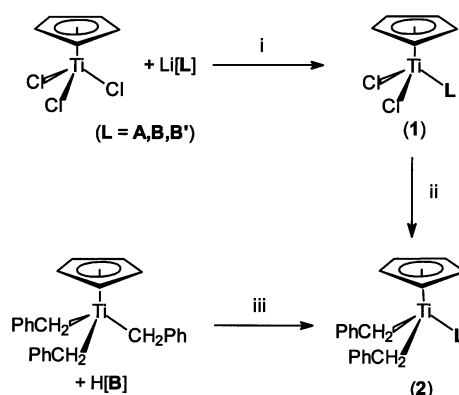
‡ Netherlands Institute for Catalysis Research (NIOK) publication no. RUG 01-4-05.



(**2a**) and $\text{Cp}[\text{Xy}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{Ti}(\text{CH}_2\text{Ph})_2$ (**2b**) were prepared through reaction of the corresponding dichlorides with two equiv. of benzyl Grignard, while the latter was also accessible by reaction of $\text{CpTi}(\text{CH}_2\text{Ph})_3$ with the neutral iminoimidazolidide (Scheme 2).

A crystal structure determination of the dichloride complex $\text{Cp}[\text{Ph}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2$ (**1b'**, Fig. 1)§ reveals a monomeric, three-legged piano-stool structure.⁸ The Ti–N(1) distance is short (1.792(2) Å), suggesting substantial π -donation to the metal centre, although the C(6)–N(1)–Ti arrangement is slightly bent (152.9(2)°). The distances of N(2) and N(3) to the central carbon atom C(6) are 0.1 Å shorter than those to the backbone carbons C(7/8), and both nitrogens are essentially planar (the sums of the angles around each N atom are 358.4 and 359.8° respectively), indicating substantial delocalisation in the N_2CN -fragment. A similar short Ti–N distance (1.78 Å) was found in a complex of another strong π -donating ligand, $\text{Cp}(\text{Ph}_3\text{P}=\text{N})\text{TiCl}_2$, whereas the ketimide complex $\text{Cp}(\text{Bu}^n\text{-Bu}^t\text{C}=\text{N})\text{TiCl}_2$ has a longer Ti–N distance of 1.872 Å.⁹ While structures of η^2/η^3 -bonded guanidinate complexes are well documented,¹⁰ **1b'** represents a rare example of a structurally characterised transition metal complex with a non-bridging η^1 -bonded guanidinate ligand.¹¹

Reaction of the dibenzyl complex **2b** with the Lewis acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$ leads to smooth abstraction of one benzyl



Scheme 2 Reagents and conditions: i, –80 to 25 °C, thf, 2 h; ii, 2 equiv. PhCH_2MgBr , –20 to 25 °C, Et_2O , 12 h; iii, 50 °C, toluene, 2 h.

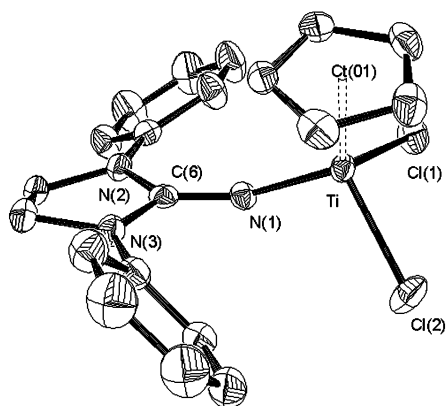


Fig. 1 Molecular structure of $\text{Cp}[\text{Ph}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2$ **1b'** (hydrogen atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): Ti–Cl(1) 2.3045(7), Ti–Cl(2) 2.2902(7), Ti–N(1) 1.792(2), N(1)–C(6) 1.305(3), N(2)–C(6) 1.359(3), N(2)–C(7) 1.465(3), N(3)–C(6) 1.362(3), N(3)–C(8) 1.467(4); Ti–N(1)–C(6) 152.9(2), Cl(1)–Ti–Cl(2) 100.90(2), Cl(1)–Ti–N(1) 104.92(6), Cl(2)–Ti–N(1) 105.55(6).

group to yield the ionic complex $\{\text{Cp}[\text{Xy}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{Ti}(\eta^2\text{-CH}_2\text{Ph})_2\}^+[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$. As seen by NMR spectroscopy ($\text{C}_6\text{D}_5\text{Br}$ solvent),¹² the anion is non-coordinating and the cationic metal centre is stabilised by an η^2 -bonding of the remaining metal-bound benzyl group.¹³

In order to compare their efficiency in olefin polymerisation catalysis, all the complexes $\text{Cp}(\text{L})\text{Ti}(\text{CH}_2\text{Ph})_2$ (**2a–2b**), with **L** = $[(\text{CH}_2)_5\text{N}]_2\text{C}=\text{N}^-$ (**A**), $\text{Xy}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}^-$ (**B**), $\text{Bu}_2\text{C}=\text{N}^-$ (**C**) and $\text{Bu}_3\text{P}=\text{N}^-$ (**D**) were synthesised, and tested for ethene homopolymerisation with $\text{B}(\text{C}_6\text{F}_5)_3$ activator, both in the absence and presence of partially hydrolysed tris(isobutyl)aluminium (TIBAO)¹⁴ as impurity scavenger. The results of these experiments are listed in Tables 1 and 2 respectively.

From these data it can be seen that the catalyst with the iminoimidazolide ligand **B** is highly efficient, both with and without TIBAO scavenger. Under the applied conditions this catalyst performs even better than the catalyst with the phosphinimide ligand **D**. The catalysts with the ketimide **C** and guanidinate **A** ancillary ligands are less efficient, with the guanidinate being especially susceptible to deactivation by TIBAO scavenger. The steric protection imparted by the xylyl substituents in the iminoimidazolide catalyst apparently makes the system much more robust, while retaining the favourable electronic properties of the $\text{N}_2\text{C}=\text{N}$ ligand core. The

Table 1 Ethene homopolymerisation with $\text{Cp}(\text{L})\text{Ti}(\text{CH}_2\text{Ph})_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalysts (10 μmol Ti, 1.1 equiv. $\text{B}(\text{C}_6\text{F}_5)_3$, 210 ml toluene, 5 bar ethene, 80 °C, 15 min run time)

Ligand L	PE yield/g	Productivity/ kg(PE) mol(Ti) ⁻¹ h ⁻¹ bar ⁻¹	10 ⁻³ M_w	M_w/M_n
A	4.7	376	406	1.9
B	11.2	896	361	1.9
C	4.4	353	543	1.9
D	10.6	848	518	2.2

Table 2 Ethene homopolymerisation with $\text{Cp}(\text{L})\text{Ti}(\text{CH}_2\text{Ph})_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalysts and TIBAO scavenger (10 μmol Ti, 1.1 equiv. $\text{B}(\text{C}_6\text{F}_5)_3$, Al/Ti = 20, 260 ml toluene, 5 bar ethene, 80 °C, 15 min run time)

Ligand L	PE yield/g	Productivity/ kg(PE) mol(Ti) ⁻¹ h ⁻¹ bar ⁻¹	10 ⁻³ M_w	M_w/M_n
A	0.4	32	583	1.7
B	20.0	1600	663	2.2
C	5.8	464	—	—
D	14.1	1128	717	2.1

catalyst $\text{Cp}[\text{Xy}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{Ti}(\text{CH}_2\text{Ph})_2/\text{B}(\text{C}_6\text{F}_5)_3$ is also effective in ethene/1-alkene copolymerisation and propene homopolymerisation. Copolymerisation runs at 80 °C in 210 ml of toluene at 5 bar ethene pressure, with 20 ml of 1-hexene or styrene added, yielded the copolymers ethene/1-hexene (3960 kg mol⁻¹ h⁻¹, $M_w = 181 \times 10^3$, $M_w/M_n = 2.0$, 18 wt% 1-hexene incorporation) and ethene/styrene (1960 kg mol⁻¹ h⁻¹, $M_w = 179 \times 10^3$, $M_w/M_n = 2.1$, 10 wt% styrene incorporation). Propene homopolymerisation (50 °C, 3 bar propene, 210 ml toluene solvent) yielded polypropene (14360 kg mol⁻¹ h⁻¹, $M_w = 81 \times 10^3$, $M_w/M_n = 1.9$) that shows a significant enrichment in syndiotactic triads (60% rr, 23% mm).

In conclusion, we have established that the 1,3-bis(xylyl)iminoimidazolide anion is an excellent monoanionic ancillary ligand for monocyclopentadienyl titanium olefin polymerisation catalysts. The comparative ethene homopolymerisation experiments performed thus far suggest that, under the applied conditions, the catalyst is even more efficient than the corresponding catalyst with the successful tris(*tert*-butyl)phosphinimide ancillary ligand.

Notes and references

§ *Crystallographic data* for $\text{Cp}[1,3\text{-Ph}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2$ (**1b'**): $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{N}_3\text{Ti}$, $M = 420.15$, orthorhombic, space group $P2_12_12_1$, $a = 9.868(1)$, $b = 10.320(1)$, $c = 18.840(1)$ Å, $U = 1918.6(3)$ Å³, $T = 180$ K, $Z = 4$, $D_c = 1.455$ g cm⁻³, $\mu = 7.33$ cm⁻¹, Enraf-Nonius CAD-4F diffractometer, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 4401 unique reflections, final residuals $wR(F^2) = 0.0764$, $R(F) = 0.0316$ for 4018 reflections with $F_o \geq 4\sigma(F_o)$ and 311 parameters. CCDC reference number 176621. See <http://www.rsc.org/suppdata/cc/b1/b11343g/> for crystallographic data in CIF or other electronic format.

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- ¹H NMR ($\text{C}_6\text{D}_5\text{Br}$, 293 K): δ 2.23 (s, 12 H, CH_3), 2.73 (s, 2 H, $\text{C}_6\text{H}_5\text{CH}_2\text{Ti}$), 3.39 (s, br, 2 H, $\text{C}_6\text{H}_5\text{CH}_2\text{B}$), 3.51 (s, 4 H, NCH_2), 5.21 (s, 5H, C_5H_5), 6.29 (d, 2 H, $J_{\text{HH}} 7.7$ Hz, $\text{C}_6\text{H}_5\text{CH}_2$), 6.83 (t, 2 H, $J_{\text{HH}} 7.4$ Hz, $\text{C}_6\text{H}_5\text{CH}_2$), 6.90–7.25 (m, 12 H, $\text{Me}_2\text{C}_6\text{H}_3$, $\text{C}_6\text{H}_5\text{CH}_2$); ¹³C {¹H} NMR ($\text{C}_6\text{D}_5\text{Br}$, 293 K, all CF resonances were excluded): δ 18.4 (CH_3), 33.0 (br, BCH_3), 46.6 (CH_2CH_2), 69.9 (TiCH_2), 112.8 (C_5H_5), 117.4 (Ph), 122.5 (Ph), 123.4 (Ph), 127.8 (C_6H_3), 128.8 (Ph), 129.7 (C_6H_3), 130.6 (Ph), 134.3 (C_6H_3), 135.7 (Ph), 137.5 (C_6H_3), 149.6 (Ph), 152.4 (Ph), 160.6 (CN); ¹⁹F NMR ($\text{C}_6\text{D}_5\text{Br}$, 293 K): δ -131.1 (d, o-F), -164.4 (t, p-F), -167.2 (t, m-F); $\Delta\delta$ [p -F] - (m -F)] 2.8 ppm.
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