



Synthesis and structural analysis of half-titanocenes containing 1,3-imidazolidin-2-iminato ligands: Effect of ligand substituents in ethylene (co)polymerization

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ARTICLE INFO

Article history:

Received 29 December 2014

Received in revised form

23 February 2015

Accepted 6 April 2015

Available online 25 April 2015

Keywords:

Titanium

Imidazolidin-2-iminato

Ethylene polymerization

Polymerization catalysts

ABSTRACT

A series of half-titanocenes containing 1,3-imidazolidin-2-iminato ligands of type, (*tert*-BuC₅H₄)TiCl₂[1,3-R₂(CH₂N)₂C=N] [R = *t*Bu (**2a**), cyclohexyl (Cy, **2b**), C₆H₅ (**2c**), 2,6-Me₂C₆H₃ (**2d**), 2,6-*i*Pr₂C₆H₃ (**2e**)] have been prepared and structures of **2a–d** have been determined by X-ray crystallography. Complex **2a** showed higher catalytic activity than the Cp analogue (**1a**) for ethylene polymerization but showed low catalytic activity in ethylene/1-hexene copolymerization under the similar conditions; the 2,6-Me₂C₆H₃ analogue (**2d**) showed moderate catalytic activity for the ethylene/1-hexene copolymerization. The copolymerization with styrene proceeded in a living manner under certain conditions, whereas the other complexes (**2a–c**) including the Cp analogues, CpTiCl₂[1,3-R₂(CH₂N)₂C=N] (**1a–d**), showed low catalytic activities and/or afforded a mixture of polymers (copolymer, and homopolymers) under the similar conditions.

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Introduction

Design of efficient molecular catalysts for precise olefin polymerization attracts considerable attention in the field of organometallic chemistry, catalysis, and of polymer chemistry [1–4]. Half-sandwich titanium complexes (half-titanocenes) containing anionic donor ligands of type, Cp'TiX₂(Y) (Cp' = cyclopentadienyl group; X = halogen, alkyl; Y = aryloxo, ketimide, phosphinimide etc., exemplified in Chart 1), are promising candidates [3,5–12], especially in terms of syntheses of new polymers by ethylene copolymerizations as demonstrated by the aryloxo and the ketimide analogues [3b–d,5,8c,d,9–12]. We already demonstrated that an efficient catalyst for the desired ethylene copolymerizations with α -olefin [5b–d], styrene [9,10], norbornene [11] as well as with the other cyclic olefins [12] can be tuned by the ligand modifications

(Cp', Y); the anionic ligand (Y) strongly affects the comonomer incorporation and the copolymerization behavior [3b,c].

Imidazolidin-2-iminato modified half-titanocenes, CpTiX₂[1,3-R₂(CH₂N)₂C=N] [X = CH₂Ph, Cl; R = *t*Bu (**1a**), cyclohexyl (**1b**), C₆H₅ (**1c**), 2,6-Me₂C₆H₃ (**1d**)] exhibited high catalytic activity for ethylene polymerization in the presence of cocatalysts [7], the *t*Bu analogue (**1a**) showed the highest catalytic activity in ethylene polymerization, and ethylene/1-hexene copolymerization with moderate comonomer incorporation affording the copolymer with uniform molecular weight distribution [7b]. Since *tert*-BuC₅H₄ analogues containing ketimide [12b] and imidazolin-2-iminato [8c] ligands showed higher catalytic activities in ethylene polymerization [8c], ethylene/cyclopentene copolymerization [12b], also since CpTiCl₂(N=C^{*t*}Bu₂) showed much higher catalytic activity than CpTiCl₂(N=CPh₂) in ethylene polymerization [13], we thus present synthesis of the *tert*-BuCp analogues containing imidazolidin-2-iminato ligands, (*tert*-BuC₅H₄)TiCl₂[1,3-R₂(CH₂N)₂C=N] [R = *t*Bu (**2a**), cyclohexyl (Cy, **2b**), C₆H₅ (**2c**), 2,6-Me₂C₆H₃ (**2d**), 2,6-*i*Pr₂C₆H₃ (**2e**)], and explored a possibility as the catalyst precursors for ethylene (co)polymerization in the presence of MAO [14].

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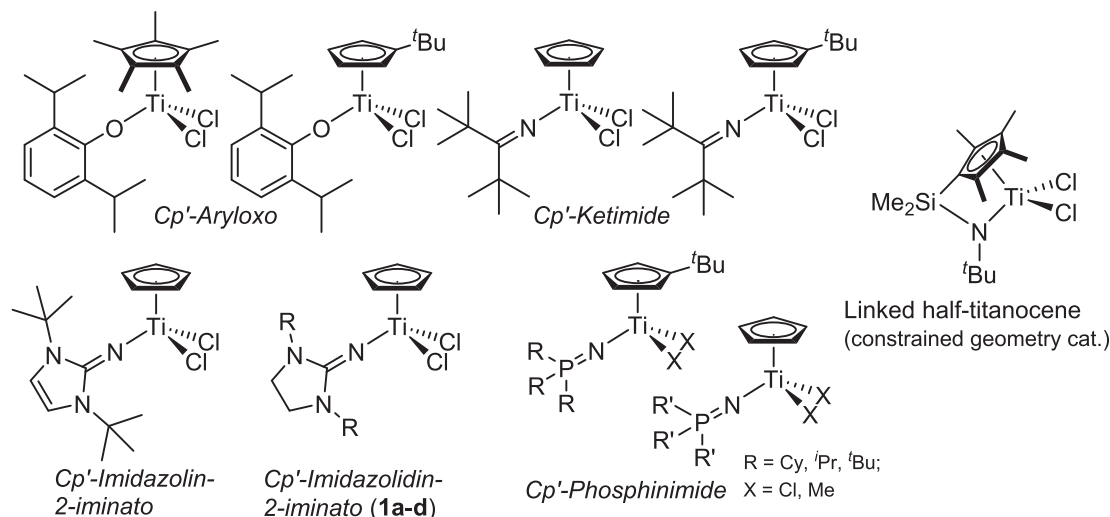


Chart 1. Selected examples for nonbridged half-titanocenes as catalyst precursors for olefin polymerization, and linked half-titanocene (constrained geometry catalyst, CGC) [3,5–8].

Results and discussion

Synthesis of half-titanocenes containing 1,3-imidazolidin-2-iminato ligands

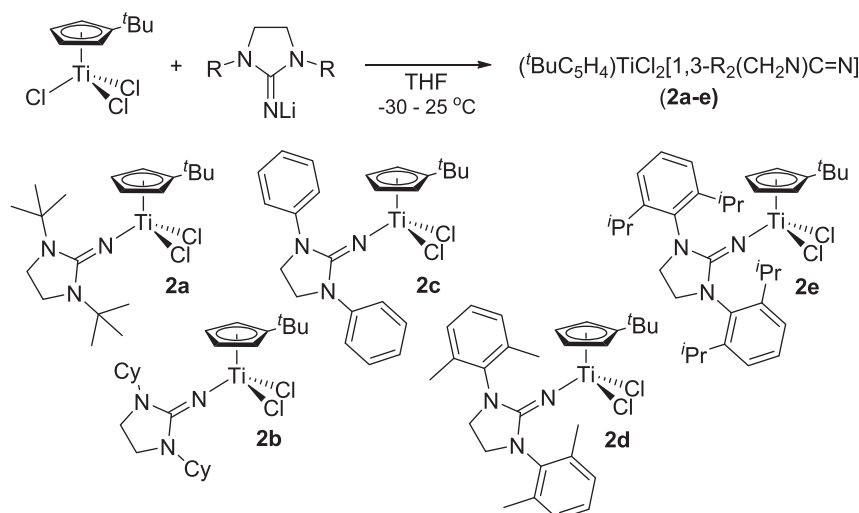
Half-sandwich titanium complexes containing substituted imidazolidin-2-iminato ligands, (*tert*-BuC₅H₄)TiCl₂[1,3-R₂(CH₂N)₂C=N] [R = *t*Bu (**2a**), cyclohexyl (Cy, **2b**), C₆H₅ (**2c**), 2,6-Me₂C₆H₃ (**2d**), 2,6-*i*Pr₂C₆H₃ (**2e**)], could be prepared from (*tert*-BuC₅H₄)TiCl₃ by treating with Li[1,3-R₂(CH₂N)₂C=N] (Scheme 1) according to the analogous method report previously for syntheses of the Cp (C₅H₅) analogues (**1a–d**) [7]. The resultant complexes (**2a–e**) were identified by NMR spectra and elemental analysis. The corresponding lithium iminoimidazolidide, Li[1,3-R₂(CH₂N)₂C=N] were prepared by the analogous procedure in the previous report by treating with ⁿBuLi in *n*-hexane [7,15]. However, our attempts for preparation of Cp^{*}TiCl₂[1,3-*t*Bu₂(CH₂N)₂C=N] were not successful, and recovered Cp^{*}TiCl₃ even under heating in toluene.

Yellow microcrystals of **2a–d** that are suitable for X-ray crystallographic analyses were grown from the chilled CH₂Cl₂ solution

(−30 °C) layered by *n*-hexane, and their structures are shown in Fig. 1. The selected bond distances and angles are summarized in Table 1 [16].

These complexes (**2a–d**) fold a distorted tetrahedral geometry around the titanium, and the Ti–N bond distances [1.7692(12)–1.8048(13) Å] are relatively similar to those in **1a–d** [1.7650(16)–1.7918(17) Å] [7], and are apparently shorter than those in (1,3-Me₂C₅H₃)TiCl₂[N(2,6-Me₂C₆H₃) (SiMe₃)] [1.898(2) Å] [17a], Cp^{*}TiCl₂[N(Me) (cyclohexyl)] [1.870(3) Å] [17b], and in Cp^{*}TiCl₂(N=CPh₂) [1.827(2) Å] [13]. These results thus suggest that both the titanium and nitrogen form σ-bond in addition to π-donation from the nitrogen, and the π-donation from nitrogen to Ti would be strong compared to the complexes exemplified above [13,17]. The distances are close or longer than those in half-sandwich titanium complexes containing imidazolin-2-iminato ligands, CpTiCl₂[1,3-R₂(CHN)₂C=N], [1.765(3), 1.768(2), and 1.778(2) Å in R = *t*Bu, *i*Pr, 2,6-*i*Pr₂C₆H₃, respectively] [8b].

The Ti–Cl bond distances and the Cl(1)–Ti(1)–Cl(2) bond angles in **2a–d** [2.2917(5)–2.3142(4) Å; 97.730(15)–103.585(17)°,



Scheme 1.

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