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Non-bridged amido cyclopentadienyl complexes of titanium: synthesis, characterization, and olefin polymerization catalysis

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Abstract

Alkylation of Ti(η^5-C_5Me_5)(NMe_2)Cl_2 gives thermally stable, crystalline dialkyl complexes Ti(η^5-C_5Me_5)(NMe_2)R_2 (R = Me, CH_2Ph, Ph). The molecular structure of the dibenzyl complex reveals an unprecedented conformation of the doubly bonded NMe_2 group which is turned parallel to the η^5-C_5Me_5 ligand, according to single-crystal X-ray diffraction studies. Treatment of the dibenzyl complex with $B(C_6F_5)_3$ in d^5-bromobenzene solution results in the quantitative formation of a thermally (> 10°C) unstable monobenzyl cation as solvent-separated ion pair $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)CH_2Ph]^+$ $[PhCH_2B(C_6F_5)_3]^-$ which efficiently polymerizes styrene syndiospecifically at 25°C. Ethylene is polymerized by Ti(η^5-C_5Me_5)(NMe_2)Cl_2–methylalumoxane with low activity. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Amido ligand; Half-sandwich complex; Benzyl cation; Styrene polymerization

1. Introduction

Titanium complexes featuring a linked amido-cyclopentadienyl ligand Ti(η^5:η^1-$C_5R'_4ZNR''$)X_2 [1] are considered to be the first non- or post-metallocene [2] catalysts for the homogeneous olefin polymerization by providing electrophilic 12-electron alkyl cations of the type $[Ti(\eta^5{:}\eta^1\text{-}C_5R'_4ZNR'')R]^+$ [3]. Whereas the variation of the substituents on the amido and cyclopentadienyl moieties R′ and R″ has been studied extensively in the recent past, the nature of the bridge Z was kept thus far, fairly constant ($SiMe_2$ [4], CH_2CH_2 [5,6b,c], $CH_2CH_2CH_2$ [5]). A short link such as $SiMe_2$ between the two ancillary ligands is assumed to be necessary for the polymerization catalysis to perform well [6]. This may be ascribed to the generation of a sterically more open reaction site by virtue of the chelate effect [7]. It has also become evident that only a specific combination of R′, R″ and Z leads to an enhanced activity, since the ligand sphere critically influences the cation–anion interaction and thus the accessibility of the monomer [5c]. We report here the synthesis and characterization of titanium amido half-sandwich complexes that lack any linking group between the cyclopentadienyl ligand and the amido function.

2. Results and discussion

When Ti(η^5-C_5Me_5)Cl_3 is reacted with one equivalent of $LiNMe_2$ in ethereal solution, the mono(amido) complex Ti(η^5-C_5Me_5)(NMe_2)Cl_2 can be isolated in 75% yield as dark red crystals [8]. In agreement with the presence of a doubly-bonded ($\sigma + p_\pi$–d_π) amido ligand with low barrier to rotation [9], only one temperature invariant signal is observed for the NMe_2 group by ^{1}H- and ^{13}C-NMR spectroscopy (δ 3.01 and 43.7, respectively). Reaction of the dichloro complex with the alkylating reagents LiMe, $Mg(CH_2Ph)_2(Et_2O)_2$, and LiPh gives the corresponding dialkyl complexes Ti(η^5-C_5Me_5)(NMe_2)R_2 (R = Me, CH_2Ph, Ph) in good yields as yellow (R = Me, Ph) or red (R = CH_2Ph) crystals.

The dibenzyl complex shows ^{1}H- and ^{13}C-NMR spectroscopic features similar to those of Ti(η^5-C_5Me_5)$(CH_2Ph)_3$ [10], Ti(η^5-$C_5Me_4SiMe_2NR$)$(CH_2Ph)_2$ [11] or Ti(η^5-$C_5Me_4CH_2C_6H_4O$)$(CH_2Ph)_2$ [12]. Thus the

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resonances for the benzyl AB protons appear at δ 1.87 and 2.24 ($^2J_{AB} = 10.8$ Hz) and the carbon resonance is recorded at δ 81.5 with $^1J_{CH} = 125$ Hz. The single-crystal X-ray structure analysis revealed a typical three-legged piano-stool configuration (Fig. 1) with one of the two benzyl groups showing a slight distortion, as judged by the increased angle at C13 of 120.9(2)°. Most notably, the NMe_2 ligand is not oriented perpendicular to the C_5Me_5 ring [9] as all other mono(amido) complexes of the type $Ti(\eta^5\text{-}C_5R'_5)(NR''_2)X_2$. Rather the plane containing the planar amido–nitrogen atom forms an angle of 26° with that of the C_5Me_5 ring. Given the low rotational barrier of the NMe_2 group, this feature is not surprising, but not encountered so far in related complexes. The competition between the amido ligand and one of the two benzyl groups for the empty d-orbital probably induces this distortion [9].

Reaction of the dibenzyl complex with $B(C_6F_5)_3$ in d^5-bromobenzene at −30°C results in the clean formation of the dark brown mono(benzyl) cation as a solvent-separated ion pair $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)]^+$ $[PhCH_2B(C_6F_5)_3]^-$ (Scheme 1). Characteristic NMR spectroscopic features for this assignment include the value for $\Delta\delta(p,m\text{-F})$ of 2.9 ppm [13] and the benzyl resonance at δ 92.2 with $^1J_{CH} = 146$ Hz in the ^{13}C-NMR spectrum. This ion pair decomposes above 0°C to give a mixture of yet unidentified products. The dimethyl complex also reacts analogously with $B(C_6F_5)_3$ to give the ion pair $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)Me]^+$ $[MeB(C_6F_5)_3]^-$ which, however, is engaged in a dissociative equilibrium with the starting materials.

Styrene is efficiently polymerized by a solution containing $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)R]^+$ $[RB(C_6F_5)_3]^-$ in toluene at 25°C to give highly syndiotactic polymer with $T_m = 273$°C. Under the same conditions, the linked amido–cyclopentadienyl derivative $[Ti(\eta^5\text{-}C_5Me_4SiMe_2NMe)(CH_2Ph)]^+$ $[PhCH_2B(C_6F_5)_3]^-$ is virtually inactive [14]. The methylalumoxane-activated dichloro complex $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)Cl_2$ polymerizes ethylene only sluggishly (70 g polymer mol^{-1} Ti·h·bar; toluene, 50°C, Ti:Al = 2000). These results clearly indicate the critical role of the covalent link between the amido and the cyclopentadienyl ligand in half-sandwich titanium catalysts [15]: the presence of the chelate ligand suppresses the formation of Ti(III) species responsible for the syndiospecific styrene polymerization [16], at the same time stabilizing the Ti(IV) alkyl cation for ethylene polymerization.

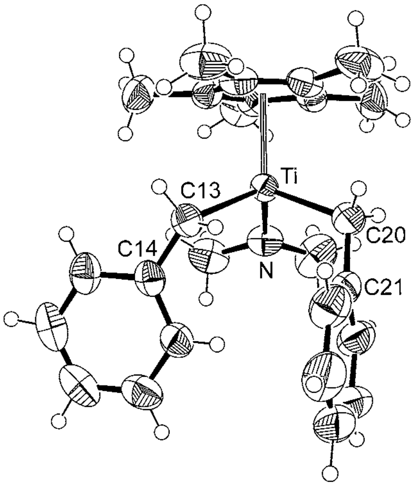
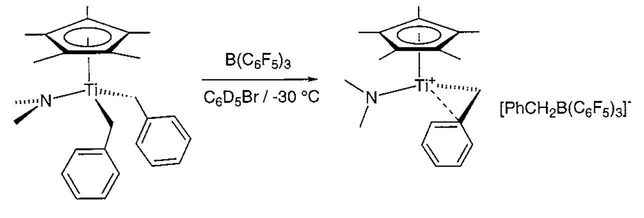


Fig. 1. ORTEP diagram of the molecular structure of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)_2$. Thermal ellipsoids are drawn at a 50% probability level. Selected bond lengths (Å) and angles (°): Ti–N, 1.887(2); Ti–C13, 2.159(2); Ti–20, 2.162(3); Ti–Cp(centroid), 2.079(2); Cp(centroid)–Ti–N, 122.2(1); C13–Ti–C20, 100.9(1); Ti–C13–C14, 120.9(2); Ti–C20–C21, 114.0(2).



Scheme 1.

3. Experimental

3.1. Synthesis of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)_2$

To a cooled (−78°C) mixture of 1.55 g (5.20 mmol) of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)Cl_2$ and 1.84 g (5.19 mmol) of $Mg(CH_2Ph)_2(Et_2O)_2$, 40 ml of ether was added slowly. The mixture was stirred and warmed to room temperature within 3 h while the solution turned dark red. After an additional stirring for 30 min at room temperature, the ether was removed in vacuum leaving a dark red residue. The residue was stripped with 25 ml of pentane and extracted with 50 ml of pentane. Concentration of the dark red solution to 10 ml and slow cooling to −30°C afforded red crystals; yield: 1.43 g (3.49 mmol, 67%). ^{1}H-NMR (400.1 MHz, C_6D_6): δ 7.20 (t, $^3J_{HH} = 7.6$ Hz, 4H, *meta*-C_6H_5), 6.92 (t, $^3J_{HH} = 7.4$ Hz, 2H, *para*-C_6H_5), 6.88 (d, $^3J_{HH} = 7.2$ Hz, 4H, *ortho*-C_6H_5), 2.56 (s, 6H, NMe_2), 2.24 (d, $^2J_{AB} = 10.8$ Hz, 2H, CH_2Ph), 1.87 (d, $^2J_{AB} = 10.8$ Hz, 2H, CH_2Ph), 1.71 (s, 15H, C_5Me_5). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 152.16 (s, *ipso*-C_6H_5), 128.16 (d, $^1J_{CH} = 154.3$ Hz, *ortho*-C_6H_5), 126.61 (d, $^1J_{CH} = 154.6$ Hz, *meta*-C_6H_5), 121.80 (d, $^1J_{CH} = 158.0$ Hz, *para*-C_6H_5), 120.72 (s, C_5Me_5), 81.48 (t, $^1J_{CH} = 124.8$ Hz, CH_2Ph), 43.69 (q, $^1J_{CH} = 134.2$ Hz, NMe_2), 11.27 (q, $^1J_{CH} = 126.4$ Hz, C_5Me_5). Anal. Calc. for $C_{26}H_{35}NTi$: C, 76.27; H, 8.62; N, 3.42. Found: C, 75.65; H, 8.39; N, 4.39%. Crystal data: $C_{26}H_{35}NTi$, $M_r = 409.45$, crystal size $1.10 \times 0.48 \times 0.22$ mm, $V = 1164.5(2)$ Å^3, $D_{calc.}$ 1.168 Mg m^{-3}, triclinic, $P\bar{1}$, $a =$

8.0974(7), $b = 9.9735(6)$, $c = 14.648(1)$ Å, $\alpha = 94.114(5)$, $\beta = 99.131(7)$, $\gamma = 90.877(6)°$, $Z = 2$, $F(000) = 440$, 7219 reflections collected in $0 \leq h \leq 11$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$ measured in the θ range of 3–30°, 6777 [$R_{int} = 0.0158$] independent reflections, 5132 observed reflections, 359 parameters, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0554$, $wR_2 = 0.1338$, R indices (all data): $R_1 = 0.0850$, $wR_2 = 0.1673$, goodness-of-fit on F^2 1.109, largest difference peak and hole 0.591 and -0.893 e Å^{-3}.

3.2. Reaction of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)_2$ with $B(C_6F_5)_3$

Precooled (−30°C) solutions of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)_2$ (27 mg, 66 μmol) and $B(C_6F_5)_3$ (34 mg, 66 μmol) in 0.3 ml of C_6D_5Br were each mixed in the cold to give a dark yellow–brown solution. The combined solution was transferred quickly to a precooled NMR tube and the spectra were recorded at various temperatures. ^{1}H-NMR (400.1 MHz, C_6D_5Br, −20°C): δ 7.22 (m, 2H, BCH_2Ph), 7.10 (m, 1H, $TiCH_2Ph$ *para*-H), 7.07 (m, 2H, $TiCH_2Ph$ *meta*-H), 7.00 (m, 3H, BCH_2Ph), 6.51 (d, $^3J_{HH} = 6.0$ Hz, 2H, $TiCH_2Ph$ *ortho*-H), 3.39 (br, BCH_2), 2.79 (s, 2H, $TiCH_2$), 2.35 (s, 6H, NMe_2), 1.61 (s, 15H, C_5Me_5). ^{13}C-NMR (100.6 MHz, C_6D_5Br, −30°C): δ 148.68 (s, $BCH_2C_6H_5$-*ipso*), 148.44 (d, $^1J_{CF} = 239$ Hz, *ortho*-C_6F_5), 140.22 (d, $^1J_{CF} = 243.9$ Hz, *para*-C_6F_5), 136.63 (d, $^1J_{CF} = 258.1$ Hz, *meta*-C_6F_5), 132.85 (d, $^1J_{CH} = 156$ Hz), 132.36 (d, $^1J_{CH} = 160$ Hz), 132.17 (s, $TiCH_2C_6H_5$-*ipso*), 131.43 (d, $^1J_{CH} = 162$ Hz), 131.21 (d, $^1J_{CH} = 165$ Hz), 128.86 (d, $^1J_{CH} = 166$ Hz), 127.25 (s, C_5Me_5), 122.96 (d, $^1J_{CH} = 151$ Hz), 92.17 (t, $^1J_{CH} = 146$ Hz, $TiCH_2$), 44.91 (q, $^1J_{CH} = 137$ Hz, NMe_2), 33.0 (br, BCH_2), 11.71 (q, $^1J_{CH} = 128$ Hz, C_5Me_5). ^{19}F-NMR (376.5 MHz, C_6D_5Br, −30°C): δ -132.0 (*ortho*-C_6F_5), −164.5 (*para*-C_6F_5), −167.3 (*meta*-C_6F_5).

4. Supplementary material

Crystallographic data for the structural analysis of $Ti(\eta^5\text{-}C_5Me_5)(NMe_2)(CH_2Ph)_2$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 138218. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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