

Indenyl effect in d^0 -transition metal complexes: synthesis, molecular structure and lactone polymerization activity of $[\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})]$ \star

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Abstract

The titanium methoxo complex $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$, prepared from the trichloro complex $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_3$, was found to polymerize ϵ -caprolactone with ring opening significantly more efficiently than analogous cyclopentadienyl derivatives. The crystal structure of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$ was determined and shows a C_s -symmetric piano-stool conformation with the strongly π -donating methoxo group trans to the six-membered ring.

1. Introduction

Mono(cyclopentadienyl)titanium complexes of the type $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{X}_3$ ($\text{C}_5\text{R}_5 = \text{C}_5\text{H}_5$, substituted and functionalized cyclopentadienyl; X = monoanionic ligand) exhibit a variety of interesting polymerization activities including syndiospecific styrene [1], ethylene and α -olefin [2], 1,3-diene [3] as well as living alkyl isocyanate polymerization [4]. Recently, we have demonstrated that titanium alkoxo complexes of the general formula $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{X}_2(\text{OR}')$ are capable of polymerizing ϵ -caprolactone (CL) under ring opening in a living manner [5]. In the course of these studies, we noted that the polymerization activity depends on the cyclopentadienyl ring substitution pattern and also that β -butyrolactone is not polymerized by these complexes [5b]. Herein we wish to report that the indenyl derivative, $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$, is by far the most active initiator in this series.

2. Results and discussion

When the indenyl trichloro complex $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_3$ [6] is treated with lithium methoxide in dichloromethane–hexane at -40°C and slowly warmed to room temperature, moisture-sensitive red crystals of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$ can be isolated with a 50% yield. Analytical, IR, ^1H and ^{13}C NMR spectroscopy as well as mass spectrometry (MS) data are consistent with a piano-stool configuration with C_s symmetry (see Fig. 1). Thus the ^1H and ^{13}C NMR chemical shifts for the indenyl ligand are recorded at significantly higher field than those of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_3$. The methoxo group gives rise to a singlet at 4.37 ppm in the ^1H and at 71.6 ppm in the ^{13}C NMR spectrum. As we have noted earlier for the complexes of the type $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{X}_2(\text{OMe})$, these values are not very sensitive to the nature of ring substitution [5d].

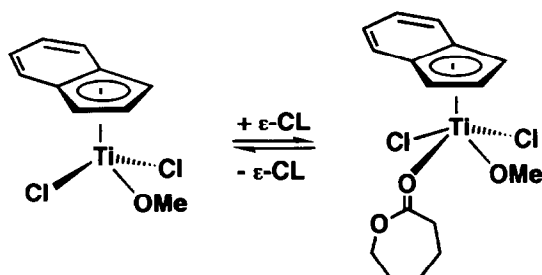
Polymerization of CL with a monomer : initiator ratio of 34 : 1 and an initiator concentration of 0.03 mol l^{-1} in toluene at 100°C was almost complete within 60 min. This activity is by far the highest observed so far for the mononuclear titanium complexes of this series (Table 1). While characterization of the isolated polycaprolactone is in progress, preliminary analyses appear to

\star Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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support a well-defined polymerization mode. Interestingly, upon addition of CL to a solution of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$, all signals become significantly broad in the ^1H NMR spectrum but sharpen once the polymerization has started. In agreement with our proposed mechanism for the ring-opening polymerization [5], we regard this as evidence for the reversible complexation of the lactone at the d^0 -titanium center according to

Equation 1



So far, we have been unable to observe such an equilibrium with other mono(cyclopentadienyl)titanium complexes [8].

A single-crystal X-ray diffraction analysis of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$ [9] revealed the expected piano-stool configuration with the indenyl penta-hapto bonded to the tetravalent titanium center with a ring centroid bond distance of 197.6 pm (Fig. 1). The molecule resides on a crystallographic mirror plane. As in many transition metal indenyl complexes with penta-hapto coordination [12] the distance from the titanium to the carbon atoms shared by the five- and six-membered rings is significantly longer (247.9(1) pm compared with 231.6(4) and 232.7(3) pm). The methoxy group is coordinated as a pronounced π donor, as evidenced by the short

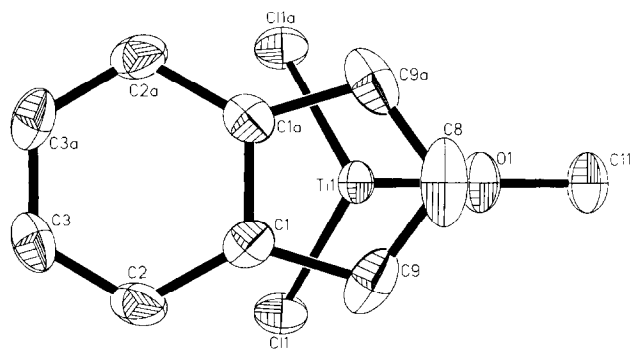


Fig. 1. Molecular structure of $\text{Ti}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_2(\text{OMe})$. Selected bond distances and an angle are as follows: Ti–Cl, 227.4(1) Å; Ti–Cl, 247.9(2) Å, Ti–O(8), 231.6(4) Å; Ti–O(9), 232.7(3) Å, Ti–O, 173.2(2) Å; Ti–Cp(centroid), 197.6 Å; Ti–O–C(11), 163.3(1). Thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms have been omitted for clarity.

Table 1. Relative activities of some titanium half-sandwich complexes of the type $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_2(\text{OMe})$ towards ϵ -caprolactone ring-opening polymerization

C_5R_5	Activity (min) ^a	$\delta(^{13}\text{C})$ of OCH_3 ^b (ppm)	$\delta(^{49}\text{Ti})$ of $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3$ ^c (ppm)
C_5H_5	315	72.6	–390
$\text{C}_5\text{H}_4(\text{SiMe}_3)$	120	72.5	–361
1,3- $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$	96	72.3	–332
C_6H_7	15	71.6	–267

^a Activity measured as time required for the reaction to reach 50% conversion at 100°C. Conditions: 0.051 mmol of the titanium complex was mixed with 1.342 mmol of CL lactone in a total solution volume of 0.75 ml of toluene- d_8 in a 5 mm NMR tube.

^b In CDCl_3 . ^c See [7].

titanium oxygen bond length of 173.2(2) pm and the obtuse angle at the oxygen of 163.3(1)°. The most notable feature of the crystal structure is that the molecule adopts a conformation in which the strongly π -donating methoxy group is trans to the annulated benzene ring of the indenyl ligand. Furthermore, the coordination of the $\text{TiCl}_2(\text{OMe})$ fragment at the indenyl ligand is characterized by a slip distortion of 17 pm (difference between the Ti–Cp(centroid) and Ti–Cp(normal) distances) as well as a fold angle for the five-membered ring of 5.2° [12].

Dramatic reactivity enhancements by substituting indenyl for the cyclopentadienyl ligand have precedents mainly for the electron-rich transition metal complexes such as rhodium complexes [13] although Group 4 metal complexes of bridged bis(indenyl) ligands generally appear also to be more reactive in the metallocene-catalyzed α -olefin polymerizations [6,14]. We are at present investigating whether the ligand effect in d^0 titanium complexes observed in the ring-opening polymerization activity may be correlated with electronic and steric effects of the five-membered ligand [15]. To this end, we are at present studying various ring-substituted indenyl derivatives of the general type $\text{Ti}(\eta^5\text{-C}_9\text{R}_7)\text{Cl}_2(\text{OMe})$ as initiators for the lactone polymerization.

3. Experimental section

All experiments were performed under argon using standard Schlenk techniques. (Indenyl)trichlorotitanium was synthesized according to a modified literature method [6] using freshly prepared (trimethylsilyl)indene and titanium tetrachloride. NMR spectra were recorded on a Bruker AC 300 spectrometer, and mass spectra on a Varian spectrometer CH7.

3.1. Dichloro(indenyl)methoxotitanium

A solution of *n*-butyllithium (2.4 ml of 1.5 M solution in hexane) was diluted with hexane (10 ml) and

treated with dry methanol (150 μ l, 119 mg, 3.7 mmol) at room temperature. After the end of gas evolution, the mixture was cooled to -40°C and treated with a solution of (indenyl)trichlorotitanium (1.0 g, 3.7 mmol) in dichloromethane (20 ml). The reaction mixture was slowly warmed to ambient temperature, filtered and concentrated. Layering with hexane and cooling to -78°C afforded red needles (yield in two crops, 500 mg (50%); melting point, 160°C (decomposition)). ^1H NMR (CDCl_3): δ 4.37 (s, 3 H, OCH_3), 6.82 (m, 1 H, H-2), 6.87 (m, 2 H, H-1, H-3), 7.45 (m, 2 H, H-4, 7), 7.80 (m, 2 H, H-5, 6) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 71.6 (OCH_3), 111.7 (C-1,3), 120.0 (C-2), 125.4 (C-4,7), 128.8 (C-5,6), 129.5 (C-8,9) ppm. IR (KBr): ν 3094 w, 2924 s, 2854 s, 1462 m, 1377 m, 1341 w, 1102 br m ($\nu(\text{C}-\text{O})$), 828 m, 744 m, 401 w cm^{-1} . MS (electron compact): m/z (%) 264 (8) [M^+], 233 (1) [$\text{M}^+ - \text{OCH}_3$], 229 (1) [$\text{M}^+ - \text{Cl}$], 198 (1) [$\text{M}^+ - 2\text{Cl}$], 115 (100) [C_8H_7^+], 83 (13) [TiCl^+]. Anal. Found: C, 45.00; H, 3.99. $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{OTi}$ calc.: C, 45.33; H, 3.80%.

Acknowledgments

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References and notes

- [1] (a) N. Ishihara, M. Kuramoto and M. Uoi, *Macromolecules*, **21** (1988) 3356; (b) J.C.W. Chien and Z. Salajka, *J. Polym. Sci. A*, **29** (1991) 1243; (c) C. Pellecchia, P. Longo, A. Proto and A. Zambelli, *Makromol. Chem., Rapid Commun.*, **13** (1992) 265; (d) A. Kucht, H. Kucht, S. Barry, J.C.W. Chien and M.D. Rausch, *Organometallics*, **12** (1993) 3075.
- [2] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight and S.Y. Lai (Dow), *Eur. Pat. Appl. EP 416815-A2*, 13 March 1991; J.A. Canich (Exxon), *PCT Appl. WO 91-04257*, 4 April 1991; (b) C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics*, **12** (1993) 4473; (c) J.C. Flores, J.C.W. Chien and M.D. Rausch, *Organometallics*, **13** (1994) 4140; (d) A.N. Chernega, R. Gomez and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1993) 1415; (e) R. Quyoum, Q. Wang, M.-J. Tudoret and M.C. Baird, *J. Am. Chem. Soc.*, **116** (1994) 6435.
- [3] G. Ricci, S. Italia, A. Giarusso and L. Porri, *J. Organomet. Chem.*, **451** (1993) 67.
- [4] (a) T.E. Patten and B.M. Novak, *Macromolecules*, **26** (1993) 436; (b) S.M. Hoff and B.M. Novak, *Macromolecules*, **26** (1993) 4067, 5530.
- [5] (a) J. Okuda and I.L. Rushkin, *Macromolecules*, **26** (1993) 5530; (b) J. Okuda, I.L. Rushkin, S. Ngo and P. König, *Polymer Prepr., Am. Chem. Soc., Div. Polym. Chem.* **35** (1994) 524; (c) J. Okuda, *Makromol. Chem., Macromol. Symp.*, in press; (d) I.L. Rushkin, *Master's Thesis*, State University of New York at Albany, 1993.
- [6] T.E. Ready, R.O. Day, J.C.W. Chien and M.D. Rausch, *Macromolecules*, **26** (1993) 5822.
- [7] A. Hafner and J. Okuda, *Organometallics*, **12** (1993) 949.
- [8] In structurally characterized lactone adducts, see (a) W.J. Evans, J.L. Shreeve and R.J. Doedens, *Inorg. Chem.*, **32** (1993) 245; (b) I. Saura-Llamas, D.M. Dalton, A.M. Arif and J.A. Gladysz, *Organometallics*, **11** (1992) 683; (c) G. Brinkmann, O. Schupp, K. Peters, L. Walz and H.G. von Schnering, *J. Organomet. Chem.*, **438** (1992) 117.
- [9] The compound, obtained as red crystals by slow cooling of a hexane solution, crystallizes in the orthorhombic space group *Pnma*. Data collection in the range $3.0^{\circ} < \theta < 25.0^{\circ}$ was performed using ω scans on a Siemens P4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 71.073$ pm) at 213(2) K. Crystal data: $a = 1263.6(3)$ pm, $b = 1085.4(2)$ pm and $c = 809.3(2)$ pm; $V = 1.1100(4)$ nm³; $Z = 4$; $D_{\text{calc}} = 1.586$ Mg m⁻³. From 2112 measured reflections all 1024 independent reflections ($R(\text{int}) = 0.053$) were used and 918 parameters were refined by the full-matrix least-squares method on F_o^2 data (SHELXL-93) [10]. The structure was solved using direct methods (SHELXS-86) [11] and difference Fourier syntheses and refined with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located and refined isotropically. Refinements converged with residuals of $wR_2 = 0.1153$ for all F_o^2 data corresponding to $R = 0.0459$ for all observed reflections with $F_o^2 > 46(F)$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD401606, the names of the authors and the journal citation.
- [10] SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1993.
- [11] G.M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, 1986.
- [12] J.W. Faller, R.H. Crabtree and A. Habib, *Organometallics*, **4** (1985) 929.
- [13] (a) M.E. Rereck, L.-N. Ji and F. Basolo, *J. Chem. Soc., Chem. Commun.*, (1983) 1208; (b) M.E. Rereck and F. Basolo, *J. Am. Chem. Soc.*, **106** (1984) 5908; (c) A.K. Kakkar, N.T. Taylor, T.B. Marder, J.K. Shen, N. Halliman and F. Basolo, *Inorg. Chim. Acta*, **198–200** (1992) 1992; (d) F. Basolo, *Polyhedron*, **9** (1990) 1503.
- [14] P.C. Möhring and N.J. Coville, *J. Organomet. Chem.*, **479** (1994) 1, and references cited therein.
- [15] While this work was in progress, bis(indenyl)-samarium(II) was reported to be more active in CL polymerization than the bis(pentamethylcyclopentadienyl) analogue; see (a) W.J. Evans and H. Katsuma, *Macromolecules*, **27** (1994) 2330; (b) W.J. Evans, T.S. Gummersheimer, T.J. Boyle and J.W. Ziller, *Organometallics*, **13** (1994) 1281.