

Preliminary communication

Unexpected open-chain molecular structure of a titanocenyl-substituted dimethyl ether

Gerhard Erker*

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (F.R.G.)

Rüger Schlund and Carl Krüger

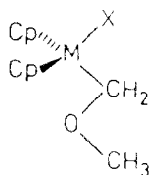
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a.d. Ruhr (F.R.G.)

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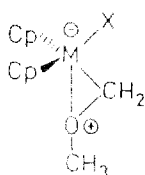
Abstract

Reaction of $(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{TiCl}_2$ with $\text{CH}_3\text{OCH}_2\text{MgCl}$ yielded $(\eta\text{-C}_5\text{H}_4\text{-CH}_3)_2\text{Ti}(\text{Cl})\text{CH}_2\text{OCH}_3$ (**2a**). Complex **2a** crystallizes in space group $P2_1/n$ with cell constants a 8.162(1), b 11.004(2), c 15.297(2) Å, β 96.40(1)°. In contrast to the three-membered metallacyclic zirconium compound of analogous composition $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{Cl})\text{CH}_2\text{OCH}_3$ (**1**), the titanocenyl-substituted ether **2a** has an open-chain (η^1 -/"O-outside") type structure.

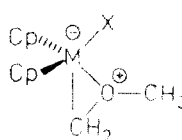
Theoretical descriptions of $\text{Cp}_2\text{M}(\text{X})\text{-A-B}$ systems (M = actinide or group 4 transition metal, A-B = σ -bound ligand with a donor group B such as CH_2PR_2 , CH_2NR_2 , acyl, formyl, or $\text{CR}_2\text{OR}'$) all agree on the existence of three local minima on the potential surface [1]. With stereochemically active ligands positioned in the Cp-M-Cp bisecting major plane of the bent metallocene system, these can be described as being of structural type **A** (open-chain, η^1 -donor outside), **B** (three-membered metallacycle, η^2 -donor outside), or **C** (η^2 -donor inside) for α -metallated dimethyl ether $\text{Cp}_2\text{M}(\text{X})\text{CH}_2\text{OCH}_3$:



A



B



C

Isolated examples have provided some information on each structural type. In addition, the interconversion of η^2 -coordinated geometrical isomers (**B** \rightleftharpoons **C**) has been studied in a few cases [2]. For the system $\text{Cp}_2\text{M}(\text{Cl})\text{CH}_2\text{OCH}_3$ we here report

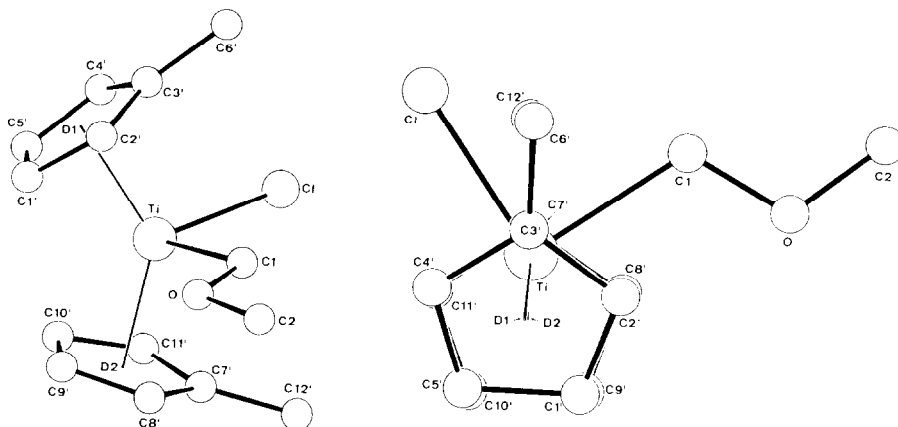


Fig. 1. Two views of the molecular geometry of **2a** as determined by X-ray diffraction.

the change of the preferred molecular geometry from η^2 -inside (C) (M = Zr, **1**) [3 *] to η^1 -outside (M = Ti, **2**). To the best of our knowledge this is the first example for which this type of geometrical isomerization has been manifested by X-ray diffraction studies on two appropriate species derived by a single systematic variation.

Reaction of $(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{TiCl}_2$ with excess $\text{CH}_3\text{OCH}_2\text{MgCl}$ (1.9 equiv.) in a 1/3 dimethoxymethane (“methylal”)/tetrahydrofuran mixture at -30°C yielded $(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ti}(\text{Cl})\text{CH}_2\text{OCH}_3$ (**2a**, 73%). Complex **2a** exhibits somewhat different spectroscopic features ($^1\text{H}/^{13}\text{C}$ NMR: δ 3.55/102.4 (140 Hz) CH_2 ; 3.13/61.8 ppm (140 Hz) CH_3) from those of the three-membered metallocyclic $\text{Cp}_2\text{Zr}(\text{Cl})\text{CH}_2\text{OCH}_3$ (**1**). (δ 2.59/71.5 (150 Hz) CH_2 ; 3.29/64.8 ppm (146 Hz) CH_3).

Recrystallization of **2a** from diethyl ether at -6°C produced red crystals suitable for an X-ray structure determination [4 *].

The Ti-center in **2a** is pseudo-tetrahedrally coordinated by two methyl-substituted Cp ligands (eclipsed conformation), a chloro- ($d(\text{Ti}-\text{Cl})$ 2.350(1) Å), and a methoxy-methyl group. The ligand atoms C(1), O, C(2), and Cl are oriented in the central $\text{Cp}'\text{-Ti-Cp}'$ bisecting plane such that O is located 0.02 Å below the plane defined by the atoms Ti, Cl and C(1). Most importantly, the CH_2OCH_3 ligand is clearly η^1 -coordinated ($\text{Ti}-\text{C}(1)$ 2.216(2), $\text{C}(1)-\text{O}$ 1.429(2), $\text{O}-\text{C}(2)$ 1.417(2) Å; the $\text{Ti}\cdots\text{O}$ separation (3.118(1) Å) clearly is far away from a bonding distance). The “O-outside” orientated ligand appears to adopt the sterically most favourable position in front of the bent metallocene unit (*anti*-conformation of CH_3 and Ti with respect to the $\text{C}(1)-\text{O}$ linkage; angle $\text{Ti}-\text{C}(1)-\text{O}$ 116.0(1) $^\circ$).

Complexes **1** and **2a** exhibit quite different chemical behaviour. Whereas the three-membered zirconacycle **1** can act as a methylene transfer agent to yield $\text{Cp}_2\text{Zr}(\text{Cl})\text{OCH}_3$ (**3**), thermolysis of the open-chain structured titanium system **2a** proceeds in a much more complicated way, finally yielding the cyclotetramer $[(\eta\text{-C}_5\text{H}_4\text{-CH}_3)\text{Ti}(\text{Cl})\text{OCH}_3]_4$ (**4**) [5 *].

The X-ray crystal structure analyses of **1** and **2a** have not revealed any obvious steric reason for the observed structural differences. Therefore, the drastic alteration

* Reference numbers with asterisks indicate notes in the list of references.

of the preferred structural type from **C** (η^2 -/*O*-inside) for zirconium to **A** (η^1 -/*O*-outside) for titanium may possibly simply reflect the higher Lewis acidity of the heavier group 4 transition metal in the bent metallocene unit. The results should make **1** and **2** ideal systems for testing the potential of advanced methods of theoretical calculations applied to organometallic systems.

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References and notes

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- For selected examples see: (a) N.E. Schore and H. Hope, *J. Am. Chem. Soc.*, 102 (1980) 4251; N.E. Schore, S.J. Young, and M.M. Olmstead, *Organometallics*, 2 (1983) 1769; H.H. Karsch, G. Müller, and C. Krüger, *J. Organomet. Chem.*, 273 (1984) 195; G. Erker, U. Dorf, J.L. Atwood, and W.E. Hunter, *J. Am. Chem. Soc.*, 108 (1986) 2251; (b) G. Fachinetti, C. Floriani, and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, (1977) 2207; G. Erker and F. Rosenfeldt, *Angew. Chem.*, 90 (1978) 640; *J. Organomet. Chem.*, 188 (1980) C1; (c) P.J. Fagan, J.M. Manriquez, S.H. Vollmer, C.S. Day, V.W. Day, and T.J. Marks, *J. Am. Chem. Soc.*, 103 (1981) 2206; 102 (1980) 5393. (d) A.S. Ward, E.A. Mintz, and M.R. Ayers, *Organometallics*, 5 (1986) 1585.
- G. Erker, R. Schlund, and C. Krüger, *J. Chem. Soc., Chem. Commun.*, (1986) 1403; selected structural parameters of **1** (numbering scheme analogous to compound **2a** in Fig. 1): Zr-C(1) 2.271(5) Å, Zr-O 2.204(3) Å, Zr-C(1)-O 69.0(2)°.
- Crystal data: C₁₄H₁₉ClOTi, *M* = 286.7, monoclinic, space group *P*2₁/*n* (No. 14), *a* 8.162(1), *b* 11.004(2), *c* 15.297(2) Å, β 96.40(1)°, *V* 1365.2 Å³, *Z* = 4, *D*_c 1.39 g cm⁻³, μ 7.99 cm⁻¹, 7380 reflections measured averaged to yield 3930 unique reflections, of which, 2926 were considered observed (*I* ≥ 2σ(*I*)) and were used in the solution and refinement of the structure. They were corrected for Lorentz and polarization effects. The structure was solved by the heavy atom method using the SHELX 86 structure solution program and refined by full-matrix least squares. All the hydrogen atoms were located by a difference-Fourier synthesis, and their positional parameters were included in the final refinement cycles. *R* = 0.030, *R*_w = 0.035. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- For details concerning the formation of **4** as well as its molecular structure see: G. Erker, C. Krüger, and R. Schlund, *Z. Naturforsch., B*, 42 (1987) 1009.