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Preliminary communication

Studies on organolanthanide complexes

XLII *. Synthesis of the unsolvated monomeric complexes $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Ln}$ ($\text{Ln} = \text{La}, \text{Pr}$) and X-ray structure of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Pr}$

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Abstract

$(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Ln}$ ($\text{Ln} = \text{La}, \text{Pr}$) complexes have been synthesized by reaction of LnCl_3 with $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Na}$ in THF at room temperature. A single-crystal X-ray diffraction study shows that the complex $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Pr}$ is monomeric in structure, and that the coordination number of the central Pr atom is 11. This is the first example of unsolvated monomeric La and Pr metallocene complexes with the largest possible coordination number of the metal.

The solid-state structures of tris-(cyclopentadienyl) compounds of the light lanthanides (La, Pr, Nd), for example $(\text{C}_5\text{H}_5)_3\text{La}$ [1], $(\text{C}_5\text{H}_5)_3\text{Pr}$ [2] and $(\text{C}_5\text{H}_5)_3\text{Nd}$ [3], are polymers with two terminal C_5H_5 groups η^5 -bonded to the metal and a third C_5H_5 group bridging two metal centers in a η^5 and η^2 fashion, forming a zigzag polymer. Generally, the molecular structures of the trivalent lanthanide metallocenes are dependent on the lanthanide metals as well as on the size of the substituents on the cyclopentadienyl rings. $(\text{MeC}_5\text{H}_4)_3\text{La}$ [4] and $(\text{MeC}_5\text{H}_4)_3\text{Nd}$ [5] are tetrameric while $(\text{C}_5\text{H}_5)_3\text{La}$ and $(\text{C}_5\text{H}_5)_3\text{Nd}$ are polymers. $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ is tetrameric while $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ are monomers [6]. Although solvated monomeric lanthanum and praseodymium metallocenes with

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* For Part XLI see ref. 13.

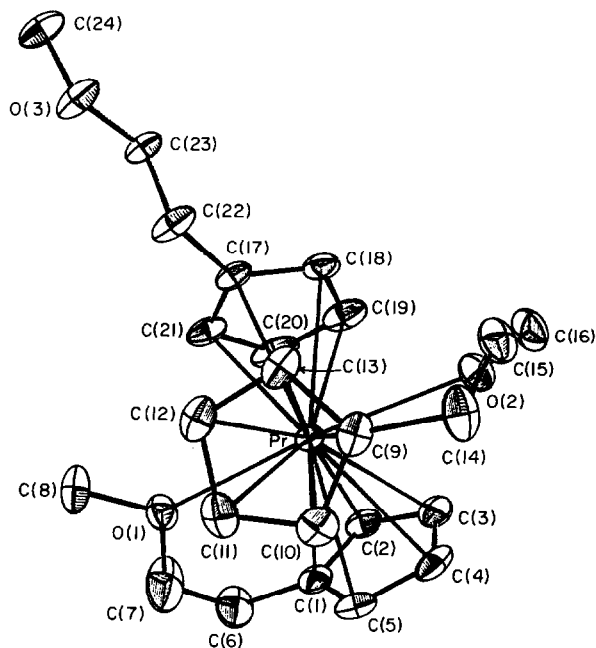
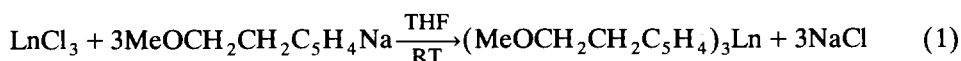


Fig. 1. Molecular structure and atom numbering scheme for complex 2. Selected bond distances (Å) and angles (deg) are as follows: Pr–O(1) 2.740(3), Pr–O(2) 2.836(3), Pr–Cp(1) 2.542 (Cp(1) = centroid of C1–C5 ring), Pr–Cp(2) 2.548 (Cp(2) = centroid of C₉–C13 ring), Pr–Cp(3) 2.569 (Cp(3) = centroid of C17–C21 ring), O(1)–Pr–O(2) 174.8(1), O(1)–Pr–Cp(1) 86.4(2); O(2)–Pr–Cp(2) 84.6(5), Cp(1)–Pr–Cp(2) 119.00(1), Cp(2)–Pr–Cp(3) 121.67(1), Cp(1)–Pr–Cp(3) 119.28(2).

two solvent molecules have been reported [7,8], we selected $\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_5$ as the ligand [9], because this permits formation of an intramolecular coordination bond between oxygen and the metal atom took place, resulting in an increase in the coordination number of the central metal atom. This satisfies the need of light lanthanide metals for coordination saturation. As a result, we have succeeded in synthesizing unsolvated monomeric light-lanthanide metallocenes.

We now describe the synthesis of the complexes $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Ln}$ where Ln = La, Pr and the X-ray crystallographic investigation of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Pr}$. $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{La}$ (1) was obtained by treating a solution of $\text{NaC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe}$ in THF with anhydrous LaCl_3 at room temperature, filtering and removing THF under vacuum. Moisture-sensitive white crystals of 1 were obtained by recrystallization from hexane at room temperature. Pale yellow crystals of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Pr}$ (2) were obtained in a similar manner. The reaction is represented by the following equation.



(1) Ln = La, 65% yield; (2) Ln = Pr, 75% yield.

* Reference number with asterisk indicates a note in the list of references.

The mass spectra [10*] of **1** and **2** showed evidence of the monomeric parent molecular ion and no larger fragments. In ^1H NMR analysis, all proton resonances of **1** were shifted to lower field compared with $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Na}$. The protons of CH_3O^- from three ligands gave two peaks with an integral ratio 2:1 in ^1H NMR at -112°C [10*]. This is in agreement with the result of the X-ray structure analysis of **2**.

The X-ray structure analysis [11*] showed that complex **2** is a monomer, in which the Pr atom is surrounded by three $\eta^5\text{-CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4$ groups. The molecular structure of **2** is shown in Fig. 1. It is noteworthy that only two oxygen atoms of the three ether substituents linked to the cyclopentadienyl rings coordinate to the central metal, giving a coordination number of 11 for Pr. The bond parameters indicate that the structure has a trigonal bipyramid geometry if the $\eta^5\text{-cyclopentadienyl}$ is regarded as occupying a single polyhedral vertex. The Pr-C (η^5) bond lengths range from 2.776 to 2.894 Å, and the average Pr-C (η^5) distance is 2.82 Å, similar to the values reported in $[(\text{C}_5\text{H}_5)_3\text{Pr}]_\infty$ (2.81 Å) and in $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{NCCCH}_3)_2$ (2.82 Å). The average Pr-O bond length is 2.79 Å, which is 0.23 Å longer than the Pr-O bond length of $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{thf})$ [12]. The bond angle of O(1)-Pr-O(2) is 174.8° in **2**, which is comparable with the bond angle of N-Pr-N' in $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{NCCCH}_3)_2$.

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- 10 Spectroscopic data, for **1**: MS(EI): 507(0.08), $[M-1]^+$; 385(100), $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ln}]^+$; 124(2.76), $[\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_5]^+$; 66(1.30), $[\text{C}_5\text{H}_6]^+$; ^1H NMR ($[\text{C}_5\text{H}_6]$)/THF, 25°C): δ 2.53 (t, 2H, $-\text{CH}_2-$), 3.33 (s, 3H, MeO-), 3.55 (t, 2H, MeOCH₂-), 5.59 (s, 4H, C₅H₄). ^1H NMR, (-112°C): δ 3.15 (s, 3H, MeO-), 3.45 (s, 6H, MeO-). For **2**: 509(0.09), 387(100), $[M-1]^+$ $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ln}]^+$; 66(3.99), $[\text{C}_5\text{H}_6]^+$.
- 11 Crystal data for **2**: $\text{C}_{24}\text{H}_{33}\text{O}_3\text{Pr}$, $M = 510.44$, monoclinic, space group $P2_1/n$, $a = 8.517(2)$, $b = 24.422(2)$, $c = 11.132(1)$ Å, $\beta = 95.73(1)^\circ$, $v = 2303.9$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 21.265$ cm⁻¹, $D_c = 1.471$ g cm⁻³, $F(000) = 1040$. 4156 unique reflections were measured to $2\theta_{\text{max}} 50^\circ$, 3054 reflections with $F^2 \geq 3\sigma(F^2)$ were used in the refinement, $R = 0.030$. All crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K α radiation ($\lambda = 0.7107$ Å). The data sets were corrected for Lorentz polarization effects and empirical absorption. The

structure was solved using Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method.

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