

An Alternative Route for Preparing Tricyclopentadienyl Lanthanides [LnCp₃]

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Tricyclopentadienil lanthanídeos foram obtidos pelas reações entre metanossulfonatos de lanthanídeos(III) anidros [Ln(MS)₃] [Ln=Nd, Yb] e ciclopentadienieneto de sódio. Os compostos foram caracterizados através de análise elementar, espectrometria de emissão atômica com plasma de argônio induzido (ICP-AES) e espectro na região do infravermelho.

Tricyclopentadienyl lanthanides were obtained by a reaction between anhydrous lanthanide(III) methanesulphonates [Ln(MS)₃] [Ln=Nd, Yb] and sodium cyclopentadienide. They were characterized by elemental analysis, inductively coupled argon plasma atomic spectrometry (ICP-AES), and infrared spectroscopy.

Keywords: *methanesulphonate, lanthanide, cyclopentadienyl*

Introduction

The past twenty years have witnessed a period of vigorous activity in the field of lanthanide organometallic chemistry¹⁻⁷. This activity reflects, among other factors, the growing realization that lanthanides may possess a unique, interesting, and useful organometallic chemistry which, in the explosive growth of organotransition metal chemistry, has been largely and unjustifiably ignored.

Tricyclopentadienides were the first well-characterized lanthanide organometallics to be prepared⁸, and these compounds have been shown to undergo a variety of interesting reactions, such as catalysis of olefin polymerization or hydrogenation⁵⁻⁷.

Several methods for the preparation of tricyclopentadienyl lanthanides are described on the literature¹. The most commonly used is based in the reaction of anhydrous lanthanide chlorides (very air-sensitive compounds) with potassium or sodium cyclopentadienide in an organic solvent such as benzene diethyleter or tetrahydrofuran⁸⁻¹⁰. The method for preparing anhydrous lanthanide halides has been the subject of several investigations¹¹⁻¹³. The hydrated

salts are readily obtained by a reaction between the oxides, hydroallic acid solutions and ammonium halide. This process requires a special apparatus to sublime all of the ammonium halide, and must be heated *in vacuo* for 8 h at 430 °C¹¹.

In this work we describe the synthesis of tricyclopentadienyl lanthanides [LnCp₃] through the reaction between anhydrous lanthanide methanesulphonates [Ln(MS)₃] and an excess of sodium cyclopentadienide in tetrahydrofuran. The products were characterized by elemental analysis, inductively coupled argon plasma atomic spectrometry (ICP-AES) and infrared spectroscopy.

Experimental

All manipulations were performed under of pre-purified nitrogen or argon. Solvents were dried by standard techniques and thoroughly deoxygenated before use (using standard Schlenk techniques and vacuum line).

Elemental analyses (%C, %H) were performed by the Laboratório de Microanálise do Instituto de Química da USP. The lanthanide determinations (%Ln) were performed using ICP-AES by the Atomic Emission Spec-

trometry Laboratory, Chemistry Institute, USP. Infrared spectra were recorded on a Bomem spectrophotometer, FTIR-BOMEM, model MB-102, from 200 to 4000 cm^{-1} , using Nujol or fluorolube mulls between cesium iodide windows.

Sodium cyclopentadienide was prepared *in situ* by treating the freshly distilled monomer with sodium dispersion in tetrahydrofuran.

Tetrahydrofuran is used in large amounts in the preparation of this compound. Thus, it was most important to increase the speed of the purification of this solvent. The new method involves refluxing the solvent (500 mL) with potassium hydroxide, metallic sodium (2 g) and benzophenone (1 g) for 5 h. With this new method we can prepare 1500 mL in 12 h. The new purification method for tetrahydrofuran is easier and less time consuming, and the product is as good as that obtained by the method in the literature.

Synthesis of $[\text{Ln}(\text{MS})_3]$: the anhydrous lanthanide methanesulfonates were prepared by heating, under vacuum ($\sim 10^{-5}$ mmHg), for 4 h, the hydrated lanthanide methanesulfonates, which were previously prepared as described in the literature¹³.

Synthesis of $[\text{Ln Cp}_3]$: the cyclopentadienyl lanthanides were prepared by a reaction between NaCp (60 mmol) in tetrahydrofuran and anhydrous lanthanide methanesulfonates (15 mmol). This mixture was heated under reflux for ca. 6 h, followed by filtration and concentration until dry. Purification by vacuum ($\sim 10^{-5}$ mmHg) and sublimation at 120–150 °C yielded the pure products. Yield: 30%. Anal. Calcd for $[\text{NdCp}_3]$: C, 53.04; H, 4.46; Nd, 42.50. Found: C, 52.48; H, 4.78; Nd, 42.29. Anal. Calcd for $[\text{YbCp}_3]$: C, 48.89; H, 4.11; Yb, 47.00. Found: C, 48.23; H, 4.45; Yb, 47.14.

Results and Discussion

The analytical data (presented in the Experimental Section) allow the compounds to be written as $[\text{LnCp}_3]$ (Ln = Nd, Yb; Cp = cyclopentadienyl). The Yb derivative is a dark green solid, while the Nd compound is a reddish-blue solid.

Infrared spectra of the compounds $[\text{Ln Cp}_3]$ (Ln = Nd, Yb) are typical of pentahaptocyclopentadienyl organometallic structures^{13–18}. They exhibit characteristic absorptions at the following frequencies: 770 (s, br), 1015 (m), 1140 (m) and 3095 (w). These correspond, under C_{5v} local symmetry, to A_1 and E_1 out-of-plane wagging, E_1 (C-H) in-plane wagging, E_1 (C-C) ring breathing and E_1 (C-H) stretching modes, respectively. These results also indicate σ -centered coordination of the anion Cp to the Ln (III) ions, with high ionic character.

Conclusions

In the process described here, we used anhydrous lanthanide methanesulfonate salts, which are easily obtained by heating the hydrated salts under vacuum for 4 h, as the starting material for the synthesis of $[\text{Ln}(\text{Cp})_3]$. As these salts are not very air-sensitive, this synthetic method for the preparation of $[\text{LnCp}_3]$ is easier and faster, and the product is as good as that obtained by the anhydrous lanthanide chloride route.

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References

1. T.J. Marks, *Prog. in Inorg. Chem.* **24**, 51 (1978).
2. T.J. Marks, *J. Organomet. Chem.* **227**, 317 (1982).
3. W.J. Evans, *Adv. Organomet. Chem.* **24**, 131 (1985).
4. B. Kanellakopulos and K.W. Baqual, *MTP International Review of Science, Inorg. Chem., Series One* **7**, 299 (1971).
5. P.L. Watson, *J. Am. Chem. Soc.* **104**, 337 (1982).
6. P.L. Watson and G.W. Parshall, *Acc. Chem. Res.* **18**, 51 (1985).
7. A.Z. Voskboinikov, *J. Organomet. Chem.* **385**, 289 (1990).
8. J. M. Birmingham and G. Silkinson, *J. Am. Chem. Soc.* **78**, 42 (1956).
9. E.O. Fisher and H. Fisher, *J. Organomet. Chem.* **3**, 181 (1965).
10. M. Tsutsui, T. Tukino and D.Z. Lorenz, *Naturforsch* **21**, 1 (1966).
11. M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.* **24**, 387 (1962).
12. J.H. Freeman and M.L. Smith, *J. Inorg. Nucl. Chem.* **7**, 224 (1958).
13. J.B. Reed, B.S. Hopkins and L.F. Audrieth, *J. Am. Chem. Soc.* **57**, 1159 (1935).
14. L.B. Zinner, *An. Acad. Brasil. Ciênc.* **52**, 715 (1980).
15. G. Davidson, *Organomet. Chem. Rev. Sect. A* **8**, 303 (1972).
16. H.P. Fritz, *Adv. Organomet. Chem.* **1**, 239 (1964).
17. W.J. Evans, *J. C. S. Chem. Comum.* 292. (1981).
18. G.W. Watt and E.W. Gillow, *J. Am. Chem. Soc.* **91**, 775 (1969).
19. C. Quian, *J. Organomet. Chem.* **247**, 161 (1983).
20. W.J. Evans and J.H. Meadows, *Organomet. Synthesis*, vol. 3, Elsevier 1 (1986).