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Synthesis and characterization of chlorovinylcyclopentadienyl lanthanides

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Abstract

In this work the synthesis and characterization of a novel class of organolanthanide compounds: [Ln($C_5H_4CH{=}CH_2$)$_2$Cl], Ln=La, Sm, Eu, Gd, Dy, Er; [Ln($C_5H_4CH{=}CH_2$)Cl_2], Ln=Nd, Tb and [Dy($C_5H_4CH{=}CH_2$)$_3$] are presented. Compounds were characterized by elemental analyses, complexometric titration with EDTA, argentimetric titration, thermal analyses, magnetic susceptibility and vibrational spectra in the infrared region. According to the infrared spectra, a σ-centered bonding is assumed, corresponding to a local symmetry C_{5v}, for the vinylcyclopentadienyl anion. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organometallic polymers are useful in a variety of applications such as catalysts, UV absorbers, semiconductors, and antifouling agents [1–3]. In spite of their potential applications, very few η^5-vinylcyclopentadienyl organometallic monomers are known.

The first compound of this class to be obtained, vinylcyclopentadienyl-cyclopentadienyl iron(II), [Fe($C_5H_4CH{=}CH_2$)(C_5H_5)], was synthesized in 1955 by Arimoto and Haven [4].

In the beginning of the eighties Rausch and co-workers [5–10] developed new synthetic routes to obtain vinylcyclopentadienyls of transition elements and also presented the first structural studies.

The preparation of trivalent lanthanide organometallic compounds was widely investigated during the last years. In a recent review [11] one can see that most organolanthanide compounds studied contained the cyclopentadienyl ligand and some derivatives.

So, this work has as its main objective to contribute to the study of organolanthanide compounds, using and also adapting the synthesis described in the literature to obtain vinylcyclopentadienyl lanthanide(III), seeking applications as precursors for organometallic polymers and conducting polymers.

2. Experimental details

All manipulations were performed under prepurified argon. Solvents were dried by standard techniques and thoroughly deoxygenated before use (using standard Schlenk techniques and vacuum line).

The compounds were characterized by elemental analysis (%C and %H). Lanthanide determination (%Ln) was performed by complexometric titration with EDTA [12], Chloride determination (%Cl) was made by argentimetric titration on a Metrohm Instrument model-E636. Thermal analyses were recorded on a Shimadzu Thermogravimetric Analyzer-TGA-50. The heating rate was 20°C/min in air (flow rate, 50.0 ml/min) and 2–5 mg of sample were used in a platinum pan. Infrared spectra were recorded on a FTIR-BOMEM, model MB-102, from 200 to 4000 cm^{-1}, using Nujol or Fluorolube mulls between cesium iodide windows. Magnetic susceptibility measurements on powdered samples (weighed portions, 10 mg) were carried out on a Cahn-7500 electrobalance (Gouy method) with $HgCo(SCN)_4$ as standard at 27°C. The resulting molar susceptibilities (χ_M) were corrected for the diamagnetism of the anions.

2.1. Synthesis and characterization of compounds

2.1.1. [$LnCl_3$]

Anhydrous lanthanide chlorides were obtained by dehydration of hydrated lanthanide chlorides as described in the literature [13]. Approximately 100 ml of HCl (6.0 mol/l)

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were added to 1 mmol of Ln_2O_3. A clear solution was obtained after boiling for some minutes. Ammonium chloride was then added in molar ratio $6NH_4Cl$:$1LnCl_3$. After crystallization of the double salt, it was transferred to a Schlenk tube and placed in a tubular furnace. Dehydration was performed under vacuum (~10^{-5} mmHg) in two steps, 250°C for 2 h for elimination of the water and 300°C for 4 h for elimination of the excess of ammonium chloride and the remaining water. The anhydrous lanthanide chlorides were stored in a Schlenk tube under argon. Yield: 85–90%. Anal.Calcd. for [$LaCl_3$]: La, 56.63; Cl, 43.37. Found: La, 56.57; Cl, 43.52; for [$NdCl_3$]: Nd, 57.56; Cl, 42.44. Found: 57.81; Cl, 42.58; for [$SmCl_3$]: Sm, 58.57; Cl, 41.43. Found: Sm, 58.32; Cl, 41.60; for [$EuCl_3$]: Eu, 58.82; Cl, 58.67. Found: Eu, 41.17; Cl, 41.29; for [$GdCl_3$]: Gd, 59.65; Cl, 40.35. Found: Gd, 59.49; Cl, 40.53; for [$TbCl_3$]: Tb, 59.90; Cl, 40.09. Found: Tb, 59.68; Cl, 40.18; for [$DyCl_3$]: Dy, 60.44; Cl, 39.55. Found: Dy, 60.23; Cl, 39.76; for [$ErCl_3$]: Er, 61.13; Cl, 38.87. Found: Er, 61.01; Cl, 39.01.

2.1.2. 6-Methylfulvene

6-Methylfulvene was obtained by adapting methods previously described by McCain [14]. The 6-methylfulvene was stored in a Schlenk tube under argon. Yield 26%. Anal. Calcd.: C, 91.25; H, 8.75. Found: C, 91.15; H, 8.72. Freezing point: −69°C.

2.1.3. [Li ($C_5H_4CH{=}CH_2$)]

Vinylcyclopentadienyl lithium was prepared by methods described by Ogasa et al. [7] and Macomber and coworkers [9,15], and was stored in a Schlenk tube under argon. Yield 80%. Anal. Calcd.: C, 85.72; H,7.19; Li, 7.08. Found: C, 85.55; H,7.28; Li, 6,98; IR, 1676 s (νC=C) (vinyl), 1594 s (νC=C) (Cp), 1067 s (νasC–C), 1027 sh (γCH), 960 w (δCH), 865 w (δCH_2) (vinyl), 730 s (γCH).

2.1.4. [$Ln(C_5H_4CH{=}CH_2)_xCl_{3-x}$]

To a Schlenk flask of 250 ml coupled to a reflux condenser, was added 150 ml of THF and 0.80 g of anhydrous lanthanide chloride. Vinylcyclopentadienyl lithim was added in different molar ratio [$LnCl_3$]:[$Li(C_5H_4CH{=}CH_2)$] of 1:1 or 1:2, in an attempt to prepare different compounds, respectively [$Ln(C_5H_4CH{=}CH_2)Cl_2$], Ln=La, Sm, Eu, Gd, Dy, Er and [$Ln(C_5H_4CH{=}CH_2)_2Cl$], Ln=Nd, Tb. The mixture was refluxed for 3 h. The precipitate obtained was filtered in a sintered glass funnel, washed with THF and dried under vacuum. These compounds were stored in a Schlenk tube under argon. Yield: 50–60%. Calc. Anal. for: [$La(C_5H_4CH{=}CH_2)_2Cl$]: C, 47.15; H, 3.96; Cl, 9.94; La, 38.95. Found: C, 46.31; H, 3.78; Cl, 10.21; La, 39.41; For: [$Nd(C_5H_4CH{=}CH_2)Cl_2$]: C, 27.45; H, 2.30; Cl, 23.16; Nd, 47.09. Found: C, 26.26; H, 2.28; Cl, 22.78; Nd, 47.61; For [$Sm(C_5H_4CH{=}CH_2)_2Cl$]: C, 45.67; H, 3.83; Cl, 9.63; Sm, 40.85. Found: C, 44.62; H, 3.72; Cl, 9.70; Sm, 41.12; For [$Eu(C_5H_4CH{=}CH_2)_2Cl$]: C, 45.48; H, 3.82; Cl, 9.59; Eu, 41.10; Found: C, 44.91; H, 3.73; Cl, 9.78, Eu, 41.88; For [$Gd(C_5H_4CH{=}CH_2)_2Cl$]: C, 44.84; H, 3.76; Cl, 9.45; Gd, 41.93.Found: C, 44.18; H, 3.84; Cl, 9.78; Gd, 42.33; For [$Tb(C_5H_4CH{=}CH_2)Cl_2$]: C, 26.19; H, 2.20; Cl, 22.09; Tb 49.51. Found: C 25.28, H 2.38, Cl 21.83, Tb 50.01; For [$Dy(C_5H_4CH{=}CH_2)_2Cl$]: C 44.22, H 3.71; Cl, 9.32; Dy, 42.73; Found: C, 43.43; H, 3.62; Cl, 9.10; Dy, 43.03; For [Er ($C_5H_4CH{=}CH_2)_2Cl$]: C, 43.67; H, 3.66; Cl, 9.21; Er, 43.44. Found: C, 42.58; H, 3.60; Cl, 9.21; Er, 42.92.

2.1.5. [$Dy((C_5H_4CH{=}CH_2)_3$]

2.1.5.1. Bis(vinylcyclopentadienyl)mercury(II)

Bis(vinylcyclopentadienyl)mercury(II) was prepared by adapting a method described by West et al. [16], and was obtained as a gray solid. Yield: 56%. IR, 1595 s (νC=C) (vinyl), 1540 s (νC=C) (Cp), 1067 s (νasC–C), 1027 sh (γCH), 960 w (δCH), 851 w (δCH_2) (vinyl), 730 s (γCH).

2.1.5.2. Reaction of bis(vinylcyclopentadienyl)mercury(II) with metallic dysprosium

Bis(vinylcyclopentadienyl)mercury(II) (0.5 g, 1 mmol) reacted with powdered dysprosium (0.14 g, 0.8 mmol) in THF. The mixture was refluxed for about 3 h. Then it was filtered to remove the metallic mercury that was formed, resulting in a yellow solution. The solvent was removed under vacuum and after addition of pentane, a yellow solid was formed. This mixture was filtered and the precipitate was dried under vacuum. Yield 40%. Calc. Anal. for: [$Dy(C_5H_4CH{=}CH_2)_3$]: C, 57.86; H, 4.85; Dy, 37.27. Found: C, 55.52; H, 4.62; Dy, 38.02. IR, 1622 s (νC=C) (vinyl), 1567 s (νC=C) (Cp), 1067 s (νasC–C), 1027 sh (γCH), 960 w (δCH), 840 w (δCH_2) (vinyl), 730 s (γCH).

3. Results and discussion

Anhydrous lanthanide chlorides, used here as starting material for preparation of organolanthanide compounds, are very difficult to obtain in a very high degree of purity. Several preparation methods are described in the literature [17,18], but only the method that uses dehydration with ammonium chloride, as described here (Section 2), is adequate for the production of absolutely pure lanthanide chlorides.

The synthetic routes used here for the preparation of the intermediate compounds 6-methylfulvene, vinylcyclopentadienyl lithium and bis(vinylcyclopentadienyl)mercury(II), based on methods described in the literature [9,14–16], led to pure compounds.

The analytical data (presented in Section 2) confirm the compounds as [$Ln(C_5H_4CH{=}CH_2)_2Cl$], Ln=La, Sm, Eu, Gd, Dy, Er; [Ln($C_5H_4CH{=}CH_2$)Cl_2], Ln=Nd, Tb and [Dy($C_5H_4CH{=}CH_2$)$_3$]. These compounds are practically insoluble in acetonitrile, methanol, nitromethane and tetrahydrofuran.

The thermal analyses studies were based on TG/DTG techniques. The processes of thermal decomposition for the organolanthanide compounds [Ln($C_5H_4CHCH_2$)$_2$Cl], Ln=La, Sm, Eu, Gd, Dy, Er; [Ln($C_5H_4CHCH_2$) Cl_2], Ln=Nd, Tb and [Dy($C_5H_4CH{=}CH_2$)$_3$] were almost the same. The compounds lost weight gradually with increasing temperature from ca. 30–850°C. At this temperature, Ln_2O_3 (Ln=La, Nd, Sm, Eu, Dy, Er) or Tb_4O_7 is formed. By knowing the weight loss percentage and the thermal decomposition product, it was possible to calculate the molecular weight of the compounds which were in agreement (2%) with that expected for the synthesized compounds.

Infrared spectra of the compounds [Ln($C_5H_4CH{=}CH_2$)$_2$Cl], Ln=La, Sm, Eu, Gd, Dy, Er; [Ln($C_5H_4CH{=}CH_2$)Cl_2], Ln=Nd, Tb (Table 1) and [Dy($C_5H_4CH{=}CH_2$)$_3$] (Section 2), exhibit characteristic absorption at the following frequencies: 1570 cm^{-1} assigned to the stretching mode of the double bonds in the cyclopentadienyl (Cp) ring (νC=C), 1670 cm^{-1} assigned to the stretching mode of the exocyclic vinyl group (νC=CH_2) and 850 cm^{-1} assigned to the out of plane deformations of the vinyl group (δ=CH_2) [19–21]. The presence of bands at 750, 1028, 1154 and 3080 cm^{-1}, assigned, 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, also indicated σ-centered coordination of the vinylcyclopentadienyl anion to the lanthanide(III) ions, with ionic character [19].

The molar magnetic susceptibilities obtained for the compounds [Er($C_5H_4CH{=}CH_2$)$_2$Cl] and [Nd($C_5H_4CH{=}CH_2$)Cl_2] were 40 723×10^{-6} cgsu (300 K) and 4347×10^{-6} cgsu (300 K), respectively. These values are close to those for other organolanthanide compounds [22,23] and it is possible to consider that in these compounds the metal to ring bonds are electrostatic in nature.

The vinyl organometallic compounds [Ln($C_5H_4CH{=}CH_2$)$_2$Cl], Ln=La, Sm, Eu, Gd, Dy, Er and [Ln ($C_5H_4CH{=}CH_2$)Cl_2], Ln=Nd, Tb, have been prepared in good yields by the reaction of vinylcyclopentadienyl lithium and anhydrous lanthanide chlorides in appropriate molar ratio. However, this route was inadequate to the synthesis of tris(vinylcyclopentadienyl)lanthanides(III) although an excess of vinylcyclopentadienyl lithium had been used. So, tris(vinylcyclopentadienyl)dysprosium(III) was prepared in good yield and purity by the reaction of bis(vinylcyclopentadienyl)mercury(II) with metallic dysprosium.

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Table 1
Infrared frequencies (cm^{-1}) of compounds[a]

La[b]	Nd[c]	Sm[b]	Eu[b]	Gd[b]	Tb[c]	Dy[b]	Er[b]	Assignment
3069 w	3076 w	3075 w	3058 w	3070 w	3068 w	3075 w	3077 w	ν_{as}(C–H)
2940 vs	2945 vs	2943 vs	2950 vs	2948 vs	2850 vs	2952 vs	2955 vs	ν_s(C–H)
2841 s	2843 s	2850 s	2849 s	2852 s	2849 s	2855 s	2861 s	δ(C–H)
2332 w	2327 w	2332 w	2326 w	2348 w	–	2332 w	2340 w	δ(C–H)
1672 w	1671 w	1674 w	1673 w	1671 w	1675 w	1673 w	1675 w	ν(C=CH_2) (vinyl)
1569 vs	1571 vs	1575 vs	1578 vs	1570 vs	1572 vs	1576 vs	1576 vs	ν(C=C) (Cp)
1440 s	1443 s	1449 s	1441 s	1440 s	1438 s	1447 s	1442 s	ω(C–C)
1302 w	–	1305 w	–	1300 w	–	1305 w	1301 w	δ(CH_3)
1125 w	1124 w	1118 w	1121 w	1125 w	1129 w	1118 w	1121 w	ν_{as}(C–C)
1040 vs	1042 vs	1048 vs	1039 vs	1038 vs	1040 vs	1040 vs	1043 vs	γ(CH)
843 vs	845 vs	847 vs	849 vs	850 vs	840 vs	847 vs	853 vs	δ (=CH_2)
807 s	803 s	807 s	805 s	795 s	800 s	801 s	805 s	ν_{as}(C–H) (vinyl)
720 vs	722 vs	720 vs	723 vs	725 vs	729 vs	730 vs	733 vs	γ(C–H)

[a] v, very; s, strong; m, medium; w, weak; sh, shoulder.

[b] [Ln($C_5H_4CH{=}CH_2$)$_2$Cl].

[c] [Ln($C_5H_4CH{=}CH_2$)Cl_2].

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