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Synthesis, characterization and catalytic activity in cyclohexene hydrogenation of some organolanthanides

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Abstract

In this work we present the synthesis and characterization of a new class of organolanthanide compounds, based on methanesulfonate and cyclopentadienide anions with the triphenylphosphine ligand. The catalytic activity of these compounds was verified in cyclohexene hydrogenation. Cyclohexane was identified by ^{1}H-NMR analysis of the reaction products. © 1998 Elsevier Science S.A.

Keywords: Cyclopentadienyl; Hydrogenation; Organolanthanides; Triphenylphosphine

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1. Introduction

Organolanthanide chemistry has shown great development in the last 20 years [1]. Several organolanthanide complexes containing π-bonds or σ-bonds have been synthesized. In addition, organolanthanide complexes have also been reported as reagents and catalysts in organic synthesis [2]. In a recent review [3] one can see that most organolanthanide compounds containing the cyclopentadienyl ligand display catalytic activity in interesting reactions, such as olefin polymerization and hydrogenation.

In an attempt to contribute to the applications of organolanthanides, we prepared a novel class of complexes, the cyclopentadienyllanthanidedimethanesulphonates, $[Ln(Cp)(MS)_2]$, and cyclopentadienyllanthanidedimethanesulphonatetriphenyl-phosphine, $[Ln(Cp)(MS)_2PPh_3]$ (Ln=La, Pr, Nd, Eu and Yb).

Our interest in these compounds containing the triphenylphosphine ligand is based on the fact that many of them have been used as catalyst in cyclohexene hydrogenation [4]. Thus, we compare in this work the catalytic activity of these two groups of compounds in the same reaction.

2. Experimental details

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

The compounds were characterized by microanalysis. Lanthanide determination (% Ln) was performed by complexometric titration with EDTA [5] or using ICP-AES (Atomic Emission Spectrometry Laboratory, Chemistry Institute, USP). 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. ^{1}H-NMR spectra were recorded in chloroform-d$_1$ on a Bruker 200 instrument at 200 MHz using $SiMe_4$ as internal standard. Chemical shifts are reported as δ (ppm).

2.1. Synthesis and characterization of compounds

2.1.1. $[Ln(MS)_3]$

Anhydrous lanthanide methanesulphonates were prepared by heating, under vacuum (~10^{-5} mmHg), for 4 h, the hydrated lanthanide methanesulphonates, which were prepared as previously described in the literature [6].

2.1.2. $[LnCp(MS)_2]$

These compounds were obtained by reaction of anhydrous lanthanide (III) methanesulphonates with sodium cyclopentadienide in tetrahydrofuran, using different molar ratios. The mixture was heated under reflux for ca. 6 h, followed by filtration and concentration until dry. Yield 30–40%. Anal. Calc. for $[LaCp(MS)_2\cdot THF]$: C, 28.33; H, 4.11; S, 13.74; La, 29.79. Found: C, 28.42; H, 4.08; S, 13.61; La, 29.58; for $[PrCp(MS)_2\cdot 2THF]$: C, 28.21; H, 4.09; S, 13.68; Pr, 30.09. Found: C, 28.12; H, 3.98; S,

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13.55; Pr, 30.23; for [NdCp(MS)$_2$·2THF]: C, 33.13; H, 5.01; S, 11.78; Nd, 26.53. Found: C, 33.69; H, 5.36; S, 11.67; Nd, 26.76; for [EuCp(MS)$_2$·2THF]: C, 32.67; H, 4.94; S, 11.62; Eu, 27.56. Found: C, 32.82; H, 5.06; S, 11.50; Eu, 27.75 and for [YbCp(MS)$_2$]: C, 19.63; H, 2.59; S, 14.95; Yb, 40.40. Found: C, 19.98; H, 2.74; S, 14.80; Yb, 40.46.

2.1.3. [LnCp(MS)$_2$PPh$_3$]

These compounds were obtained by the reaction of [LnCp(MS)$_2$·xTHF] with triphenylphosphine (PPh$_3$) in toluene, using a molar ratio [LnCp(MS)$_2$·xTHF]/[PPh$_3$] of 1:1. The mixture was refluxed for ca. 12 h, followed by filtration, addition of pentane and stirring for ca. 4 h followed by concentration until dry. Yield 10–20%. Anal. Calc. for [LaCp(MS)$_2$PPh$_3$]: C, 45.63; H, 4.00; S, 9.76; La, 21.17. Found: C, 46.64; H, 4.60; S, 9.56; La, 20.89; for [PrCp(MS)$_2$PPh$_3$]: C, 45.59; H, 3.99, S, 9.72; Pr, 21.41. Found: C, 46.50, H, 4.06, S, 990; Pr, 21.04; for [NdCp(MS)$_2$PPh$_3$]: C, 45.36; H, 3.97; S, 9.68; Nd, 21.81. Found: C, 46.27; H, 4.05; S, 9.48; Nd, 21.29; for [EuCp(MS)$_2$PPh$_3$]: C, 44.84; H, 3.92; S, 9.56; Eu, 22.71. Found: C, 45,74; H, 4.00; S, 9.75; Eu, 21.95; for [YbCp(MS)$_2$PPh$_3$]: C, 43.47; H, 3.80; S, 9.27; Yb, 25.07. Found: C, 44.34; H, 3.87; S, 9.08; Yb, 24.73.

2.2. Catalytic hydrogenation of cyclohexene

Cyclohexene hydrogenation was performed under atmospheric pressure in a reactor consisting of a flask attached to a burette filled with water and provided with stopcocks. This permitted air evacuation of the system before hydrogen introduction; agitation was provided by a magnetic stirrer and the temperature was controlled using a water-bath. The catalytic activities for all compounds were studied at 40°C and 1 atm. The quantities used in the experiments were 1 ml of cyclohexene and 0.02 g of the organolanthanide compound.

3. Results and discussion

The analytical data (presented in the Experimental section) allow the compounds to be expressed as [LaCp(MS)$_2$·THF], [YbCp(MS)$_2$], [LnCp(MS)$_2$·2THF] (Ln=Pr, Nd, Eu) and [LnCp(MS)$_2$PPh$_3$] (Ln=La, Pr, Nd, Eu, Yb). The salts [LnCp(MS)$_2$·xTHF] are soluble in toluene and benzene, less soluble in chloroform and acetone and practically insoluble in tetrahydrofuran. The compounds containing triphenylphosphine ligand are practically insoluble in acetone, ethanol, chloroform, toluene and benzene.

Infrared spectra of the compounds [LnCp(MS)$_2$·2THF] (Ln=Pr, Nd, Eu), [LaCp(MS)$_2$·THF], [YbCp(MS)$_2$] (Table 1) and [LaCp(MS)$_2$·PPh$_3$] (Ln=La, Pr, Nd, Eu, Yb) (Table 2) are typical of pentahaptocyclopentadienyl organometallic structures [7–12]. They exhibit characteristic absorption at the following frequencies: 780 (s), 1015 (m), 1120 (m) and 3080 (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.

The MS$^-$ anion has a C_{3v} point group symmetry and may act as a non-coordinating or as a mono-, bi- or tridentate ligand. The $H_3CSO_3^-$ group shows strong bands, which have been assigned [13] and calculated [14–16] as antisymmetric and symmetric SO_3^- modes in the spectrum region between 1300 and 1050 cm^{-1}. The coordination to the anion (mono-, bi- or tridentate) distorts and reduces the C_{3v} symmetry [14]. The splitting (ca. 100 cm^{-1}) observed in vibrations attributed to ν_{as}(SO) of the MS$^-$ anion (1270–1160 cm^{-1}) were interpreted in terms of a lowering of its C_{3v} symmetry [10] and that the MS$^-$ anions were coordinated to the tripositive lanthanide through the oxygen atoms. This behavior has also been observed in other compounds containing methanesulfonate ions [17–20]. The infrared spectra of the compounds [LaCp(MS)$_2$·THF] and [LnCp(MS)$_2$·2THF] (Ln=Pr, Nd, Eu) also show weak

Table 1
Infrared Frequencies (cm^{-1}) of compounds [LnCp(MS)$_2$·xTHF]

LaCp(MS)$_2$·THF[a]	PrCp(MS)$_2$·2THF[a]	NdCp(MS)$_2$·2THF[a]	EuCp(MS)$_2$·2THF[a]	YbCp(MS)$_2^{a}$	Assignment
3090 (w)	3100 (w)	3100 (w)	3166 (w)	3080 (w)	ν_{as}(CH) (Cp)
2967 (w)	2960 (w)–2920 (w)	2960 (sh)–2920 (sh)	3018 (w)–2933 (w)	2960 (sh)–2920 (sh)	ν_s(CH$_3$) (MS)+ν_s(CH) (Cp)
2942 (w)	2850 (sh)	2850 (sh)		2850 (sh)	ν_s(CH) (Cp)
1411 (vw)	1410(vw)	1410 (w)	1411 (w)	1410 (w)	ω(C–C) (Cp)
1338 (w)	1335 (sh)	1343 (w)	1349 (w)	1341 (w)	δ_s(CH$_3$) (Cp)
1262 (w)–1249(s)	1245 (w)	1261 (s)–1160 (s)	1269 (s)–1159 (m)	1271 (s)–1159 (s)	ν_{as}(SO) (MS)
1116 (w)	1112 (w)	1099 (w)	1118 (w)	1119 (w)	γ_s(CH) (Cp)
1063 (s)	1070 (s)–1060 (sh)	1070 (s)–1060 (s)	1066 (s)	1070 (s)–1058 (s)	ν_s(SO) (MS)+ν(CO) (THF)
1015 (w)	1015 (w)	1016 (m)	1013 (m)	1012 (m)	δ(CH) (Cp)
968 (w)	978 (w)	970 (w)	969 (w)	977 (w)	ρ_r(CH) (Cp)
789 (s)	780 (s)	782 (s,br)	798 (s)	790 (s)–778 (w)	ν_{as}(CH) (CP)+ν(CS) (MS)
722 (m)	720 (w)	725 (w)	724 (w)	726 (w)	δ(CH) (THF)

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

Table 2
Infrared frequencies (cm^{-1}) of compounds $[LnCp(MS)_2PPh_3]$

PPh_3^a	La^a	Pr^a	Nd^a	Eu^a	Yb^a	Assignment
1582 (m)	1583 (m)	1580 (m)	1580 (m-w)	1580 (m-w)	1584 (m)	$k\upsilon$(C–C) (a_1)
1569 (w)	1562 (m)	1560 (w)	1567 (w)	1560 (w)	1560 (w)	$l\upsilon$(C–C) (b_2)
1566 (w)	1537 (w)	1541 (w)		1545 (w)	1542 (vw)	
1482 (s)	1480 (m)	1479 (m-w)	1480 (m)	1480 (w)	1482 (w)	$m\upsilon$(C–C) (a_1)
1435(s)–1429(s)	1461 (s)	1462 (s)	1458 (m)	1457 (w)	1461 (s)	$n\upsilon$(C–C) (b_2)+ω(C–C) (Cp)
1307(w)	1312 (w)	1315 (w)	1314 (w)	1315 (w)	1318 (w)	$\omega+i$(B2)
1268(w)–1260(w)	1260 (m)	1265 (m)	1270 (m)	1268 (m)	1254 (w)	$e\beta$(C–H) (b_2)+ν_{as}(SO) (MS)
1179(w)	1182 (w)	1183 (w)	1185 (sh)	1186 (w)	1187 (w)	$a\beta$(C–H) (a_1)
1157(w)–1152(w)	1156 (w)	1154 (w)	1153 (w-m)	1152 (w)	1157 (w)	$c\beta$(C–H) (b_2)+γ_s(C–H) (Cp)+ν_{as}(SO) (MS)
1089 (m)	1093 (m)	1092 (m)	1093 (m)	1092 (m)	1095 (m-w)	qX-sens. (a_1)
1068 (w)	1067 (w)	1069 (w)	1068 (w)	1068 (vw)	1069 (w)	$d\beta$(C–H) (b_2)+ν_s(SO) (MS)
1028 (m)	1027 (m-w)	1026 (m)	1025 (m)	1028 (m)	1026 (w)	$b\beta$(C–H) (a_1)+δ(C–H) (Cp)
997 (m)	1001 (m)	1002 (m-w)	999(m-w)	998 (w)	997 (w)	p ring (a_1)
970(w)	965 (w)	966 (w)	967 (w)	967 (m-w)	975 (s)	h(C–H) (a_2)
754(m)–746(w)	745 (s)	742 (s)	745 (s)	754 (w)	770 (m)	$f\gamma$(C–H) (b_1)+ν(CS) (MS)
	728 (s)	722 (s)	728 (vs)	721 (s)	719 (s)	rX-sens. (a_1)+γ(C–H) (Cp)
692(vs)	696 (s)	696 (m-s)	695 (s)	698 (s)	696 (m-s)	νPh(C–C) (b_2)
512(w)–489(m)	530(w)–497(s)	535(w)–495(m)	525(sh)–498(s)	525(w)–498(m)	528(w)–497(m)	yX-sens. (b_1)
433(w)	445(w)– 425(w)	440(w)–425(w)	440(w)–424(w)	442(w)–424(w)	450(w)–423(w)	tX-sens. (a_1)

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

bands at 2960, 1325, 840, 723 and 565 cm^{-1} due to the coordinated tetrahydrofuran [21,22].

The vibrational frequency assignments for the phenyl group in triphenylphosphine compounds $[LnCp(MS)_2PPh_3]$ (Ln=La, Pr, Nd, Eu, Yb) (Table 2) were made by comparison of the spectra of triphenylphosphine and several triphenylphosphine complexes [23,24]. The vibrational frequency notation used here for these compounds is the same as described in Whiffen's work [24], based on monochlorobenzene corresponding assignments, but with the recommended orientation of axes for C_{2v} symmetry. One important result of this approach for triphenylphosphine is that P–C stretching contributes to three X-sensitive modes, q, r and t. These bands are shifted most with coordination of the triphenylphosphine to the metallic ions [23,24]. The X-sensitive modes q and t were shifted to higher wavenumber relative to their position in free triphenylphosphine. Mode r is believed to display the same behavior and probably coincides with the band assignment to the γ(C–H) of the group Cp [6–12].

Cyclohexene hydrogenation presented different results when we compare the organolanthanide compounds containing triphenylphosphine ligand to those where this ligand is absent. No hydrogen consumption was observed for the compounds $[LaCp(MS)_2\cdot THF]$, $[YbCp(MS)_2]$ and $[LnCp(MS)_2\cdot 2THF]$ (Ln=Pr, Nd, Eu). The compounds containing triphenylphosphine ligand showed catalytic activity in cyclohexene hydrogenation. The ^{1}H-NMR spectra of the hydrogenation reaction products showed the presence of a chemical shift characteristic of cyclohexane (1.42 ppm). The experimental turnover numbers (N_t) for compounds $[LnCp(MS)_2\cdot PPh_3]$ (Ln=La, Pr, Nd, Eu and Yb) were around 0.04 TN min^{-1}. Similar results were obtained for alkyne hydrogenation using organolanthanide compounds, as in 3-hexin hydrogenation using ErC_9H_{10} as catalyst [25].

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