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Journal of Organometallic Chemistry 628 (2001) 271–274

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Iodo bis bistrimethylsilylamido lanthanides

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Received 5 February 2001; accepted 29 March 2001

Abstract

Reactions of lanthanide triiodides with potassium bistrimethylsilyl amide have been investigated. For lanthanum, recrystallisation from THF–toluene led to monocrystals of the dimeric bisamide $[La(\mu\text{-}I)\{N(TMS)_2\}_2(THF)]_2$. We have shown that samarium diiodide and lanthanide triiodides are efficient for lanthanum and samarium reactions, a mixture of tris amides and iodo bisamides is obtained, while only the latter compound is obtained for ytterbium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanides; Amides

1. Introduction

In the course of our previous investigations we had shown samarium diiodide and lanthanide triiodides as efficient Lewis acid catalysts for a wide range of reactions [1–3]. These findings led us to synthesise new iodo lanthanide complexes coordinated with asymmetric cyclopentadienyl [4–6] or binaphthol [7] ligands, for their evaluation as enantioselective catalysts. Iodobinaphthoxide lanthanide compounds are active and enantioselective catalysts for Diels–Alder reactions. Replacing the binaphthol ligand by bis-3,3′-*o*-anisyl-binaphthol led to an improvement of enantiomeric excesses and to variations of the sense of induction with temperature [8,9]. For the preparation of the catalysts we used mainly metathesis reactions starting with lanthanide triiodides and the potassium salts of the ligands. However, in lanthanide chemistry, the reaction of alcohols with trivalent homoleptic trisamides $[R_2N]_3Ln$, specially bistrimethylsilylamides [10–13], is a well-known clean and practical method for the preparation of alkoxides. Thus, we thought that lanthanide iodo amides could be convenient starting materials allowing a ready access to lanthanide iodo binaphthoxides, avoiding the preparation of the instable binaphthoxide potassium salts. Some heteroleptic amido lanthanide derivatives have been isolated [10], but lanthanide amido halide complexes are scarce. Bistrimethylsilylamido lanthanide chlorides have been prepared with several lanthanides but the corresponding bromide only with samarium [13,14]. The biscyclohexyl amido chloro samarium has also been characterised [15]. To the best of our knowledge, the only iodo heteroleptic amido lanthanide described is the divalent iodo bistrimethylsilyl amido samarium [16].

In this paper, we report the characterisation of iodo bis bistrimethylsilyl amides of lanthanum, samarium and ytterbium.

2. Results

With the aim of preparing heteroleptic lanthanides, we studied the reaction of $LaI_3(DME)_2$ (**1a**) with two equivalents of potassium bistrimethylsilylamide, $KN(TMS)_2$ (**2**), in THF. We observed a change of colour of the reaction mixture from beige to off-white and precipitation of a white powder of potassium iodide. After filtration and evaporation of THF, we obtained a powder that has been analysed. The ^1H-NMR spectrum of this powder in $CDCl_3$ showed two resonances at 0.16 and 0.13 ppm. The resonance at 0.13

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PII: S0022-328X(01)00793-8

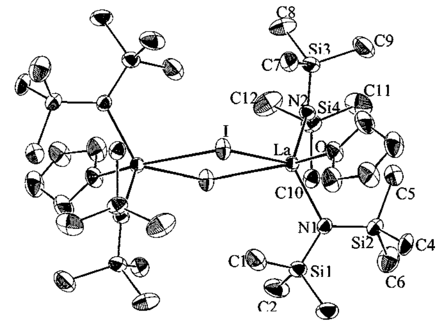

Fig. 1. Structure of iodo bis bistrimethylsilyl lanthanum amide **3a**.

ppm was identified as $\mathrm{La[N(TMS)_2]_3}$ (**4a**) by comparison with a real sample prepared by reacting $\mathrm{LaI_3(DME)_2}$ with $\mathrm{KN(TMS)_2}$ in THF in the molar ratio 1:3. The identification of the other species was made by X-ray crystallographic analysis together with NMR spectroscopy. In fact recrystallisation from toluene–THF of the crude product obtained in the reaction of **1** with **2** in the molar ratio 1:2 allowed us to obtain two different types of single crystals. Some of them, yellow needle shaped crystals, were analysed as being $\mathrm{La[N(TMS)_2]_3}$ (**4a**), by comparison of their cell parameters with the cell parameters of $\mathrm{Nd[N(TMS)_2]_3}$ [17], they were found to be isomorphous. The second type of crystals were light yellow and by X-ray diffraction analysis were identified as iodo bis(bistrimethylsilyl) amide **3a** with the dimeric structure $\mathrm{[La(\mu\text{-}I)\{N(TMS)_2\}_2(THF)]_2}$. The structure of **3a** is a centrosymmetric dimer with asymmetrically bridging iodide ligands (3.3096(11) and 3.3051(11) Å), as shown in Fig. 1. Selected bond distances and angles are given in Table 1. The planar $\mathrm{La_2I_2}$ ring presents angles at the La atom noticeably smaller than at the I atom (I–La–I′ 76.05(3)°, La–I–La′ 103.95(3)°), with a La···La′ separation of 5.210 Å. The coordination at the La atom is five-coordinate with a geometry described as distorted trigonal bipyramidal, with the THF oxygen and one bridging iodide in axial positions, O–La–I′ 153.6(2)°, far from 180° for the regular geometry. The equatorial plane is defined by the two amide nitrogen atoms and by the other bridging iodide (N(1)–La–N(2), 120.8(3); I–La–N(1), 119.4(2); I–La–N(2), 119.7(2)°). The La–N bond lengths are identical within experimental error (La–N(1), 2.352(9); La–N(2), 2.331(8) Å), with an average of 2.342(9) Å. The La–O(THF) bond distance is 2.561(8) Å. A comparison of La–I and the La–O(THF) bond distances (average 3.3074(11) and 2.561(8) Å, respectively) can also be made with the corresponding distances in the seven-coordinate pentagonal bipyramidal $\mathrm{LaI_3(THF)_4}$ structure (average 3.154(4) and 2.554(8) Å) [2]. The La–I distance in **3a** is longer as expected for a bridging La–μI distance even though it is in a lower coordinate complex. The La–O(THF) distance in **3a** is in the range 2.535(8)–2.576(8) Å observed in $\mathrm{LaI_3(THF)_4}$. No unusually short intra- and intermolecular contacts are observed. The structure of **3a** is very similar to the reported structures of $\mathrm{[Sm(\mu\text{-}X)\{N(TMS)_2\}_2(THF)]_2}$ (X = Cl, Br) [14].

Table 1
Selected bond lengths (Å) and angles (°) for **3a**

La–N(1)	2.352(9)	La–I	3.3096(11)
La–N(2)	2.331(8)	La–I [a]	3.3051(11)
La–O	2.561(8)	Si(3)–N(2)	1.718(9)
Si(1)–N(1)	1.716(9)	Si(4)–N(2)	1.711(10)
Si(2)–N(1)	1.715(9)		
N(1)–La–N(2)	120.8(3)	N(2)–La–I	119.7(2)
N(1)–La–O	85.4(3)	N(2)–La–I [a]	90.6(2)
N(2)–La–O	106.2(3)	O(1)–La–I	77.9(2)
I–La–I [a]	76.05(3)	O(1)–La–I [a]	153.6(2)
N(1)–La–I	119.4(2)	La–I–La [a]	103.95(3)
N(1)–La–I [a]	103.6(2)		

[a] Atoms related by the symmetry operation: $-x, -y+1, -z+1$.

We then studied reactions of $\mathrm{SmI_3(THF)_3}$ (**1b**) or $\mathrm{YbI_3(THF)_3}$ (**1c**) with two equivalents of potassium bistrimethylsilylamide **2** in THF and also observed by NMR the formation of two species in the case of Sm. The ^{1}H-NMR spectra of the crude product obtained in the reaction with samarium presented one resonance at -1.58 and another at -1.68 ppm. The presence of tris bistrimethylsilyl amide **4b** (samarium) was established by comparison with the reported shifts [11] and with the NMR of a real sample prepared by reacting the corresponding triiodide with three equivalents of **2**. By extraction of the crude product obtained in the reaction with hexane, the insoluble samarium triiodide was separated from the samarium bis and tris bistrimethylsilyl amides. Then the trisamide **4b** (white powder) was sublimed and separated from the pure bisamide **3b** isolated as a yellow powder. Only one peak ($\mathrm{C_6D_6}$, $\delta = -1.68$ ppm) was observed in the ^{1}H-NMR spectrum of the non-sublimed product, and elemental analysis of the yellow powder was consistent with $\mathrm{[SmI[N(TMS)_2]_2]_2}$ (**3b**). The ratios of bis and tris amides **3** and **4** were measured by integration of ^{1}H-NMR spectra of crude products: for lanthanum **3a**/**4a**, 86:14; for samarium **3b**/**4b**, 70:30. By NMR spectroscopy and, in the case of **3a**, by X-ray analysis we concluded that both iodoamides **3a** (La) and **3b** (Sm) have one molecule of THF coordinated. Heteroleptic chloro bis trimethylsilylamido europium [18] and divalent iodo bistrimethylsilyl amido samarium [16] have been prepared by disproportionation reactions. Similarly, we observed that a mixture of lanthanum triiodide **1a** and lanthanum tris bistrimethylsilyl amide **4a** in THF, at room temperature, yielded lanthanum iodo bisamide **3a**, as indicated by ^{1}H-NMR spectroscopy.

For ytterbium after the metathesis reaction we tried to separate ytterbium tris bistrimethylsilyl amide **4c** from the crude product by sublimation under vacuum. A prolonged heating at 125°C under 1×10^{-4} Torr [11] did not allow the sublimation of **4c**. Elemental analysis of the off-white powder was consistent with the structure $[YbI[N(TMS)_2]_2]_2$ (**3c**). The bis bistrimethylsilyl amido ytterbium is obtained readily as a pure compound without contamination by ytterbium tris bistrimethylsilylamide. This behaviour, in comparison with the results observed for lanthanum and samarium, can be explained by the smaller size of the metal. The heteroleptic chloro bistrimethylsilyl amido lanthanides are stable only for the smaller metals due to steric insaturation for the other [13].

The X-ray diffraction study of the iodo bis amide lanthanum **3a** indicates a dimeric structure. We have no information concerning the monomeric or dimeric structures of the samarium and ytterbium derivatives **3b** and **3c**. The structure of the trivalent bis bistrimethylsilylamido bromo samarium and chloro samarium [14], or chloro ytterbium [13] are reported to be dimeric. Thus, in spite of the differences of size of iodine with respect with bromine and chlorine, we believe that samarium and ytterbium amides **3b** and **3c** are dimers.

3. Conclusions

We have characterised heteroleptic iodo bis amido complexes of lanthanum, samarium and ytterbium stabilised with bistrimethylsilylamide ligands. For lanthanum and samarium the complexes are contaminated with small quantities of the corresponding tris amides. X-ray crystallographic analysis for La bisamide has shown a dimeric structure for the complex, with one molecule of THF coordinated to each lanthanum atom. The ytterbium complex is isolated as a pure compound and the first exchange reactions with binaphthol or bis 3,3′-*o*-anisylbinapthol have been realised. The complexes obtained give similar results in Diels–Alder reactions as the previously prepared ytterbium iodo binaphthoxide [9]. This seems to indicate that ytterbium bis amide is a good precursor for the preparation of a variety of ytterbium based catalysts.

4. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove-box techniques. THF and hexane were distilled from sodium benzophenone ketyl and degassed immediately prior to use. $CDCl_3$ and C_6D_6 were distilled from CaH_2 and degassed immediately prior to use. SmI_2 and YbI_2 were prepared according to published methods [19]. $SmI_3(THF)_3$ and $YbI_3(THF)_3$ were, respectively, obtained by reacting SmI_2 and YbI_2 with I_2 in THF in the molar ratio 1:0.5 at room temperature (r.t.). $LaI_3(DME)_2$ was prepared from La powder and iodine [20]. Bruker AM 200 and Varian Unity 300 spectrometers, operating at 200 and 300 MHz, were used for the NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from Me_4Si for spectra in $CDCl_3$. Infrared spectra were recorded as Nujol mulls using NaCl plates on a Perkin–Elmer 1000 FTIR spectrometer and are reported in cm^{-1}. Carbon, hydrogen and nitrogen elemental analyses were performed on a Perkin–Elmer automatic analyser.

4.1. Reactions of lanthanum triiodide **1a** and samarium triiodide **1b** with potassium amide

To a suspension of $LaI_3(DME)_2$ (**1a**) (0.350 g, 0.50 mmol) or $SmI_3(THF)_3$ (**1b**) (0.373 g, 0.50 mmol) in 10 ml THF was added under magnetic stirring a solution of potassium bistrimethylsilyl amide **2** (0.199 g, 1.0 mmol) in 10 ml THF within 15 min. A change of colour of the reaction mixture from beige (lanthanum) or yellow (samarium) to off-white was observed, together with formation of a white precipitate. After 18 h the KI was filtrated and the supernatant solution was evaporated under vacuum yielding an off-white powder of **3** + **4**. Two peaks are observed in the ^{1}H-NMR spectra of the crude product.

3a + **4a**: [$CDCl_3$, 200 MHz, δ ppm: 0.13 (14%) **4a**, 0.16 (86%) **3a**].

3b + **4b**: [C_6D_6, 300 MHz, δ ppm: −1.58 (30%) **4b**, −1.68 (70%) **3b**].

For **3b** + **4b** the crude product was extracted with hexane to separate the insoluble samarium triiodide. After evaporation the residue was heated at 120°C under 10^{-4} Torr, **4b** was sublimed. The non-sublimed product is a yellow powder of **3b**. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): −1.68 (s). IR (ν, cm^{-1}): 1250, 1160, 1090, 1010, 950, 860, 835, 800, 650. Anal. Found: C 22.97; H 7.27; N 4.16. Calc. for $C_{12}H_{36}IN_2Si_4Sm$: C 24.10; H 6.03; N 4.69%.

4.2. Preparation of tris bistrimethylsilyl amido lanthanum **4a** and samarium **4b**

To a suspension of $LaI_3(DME)_2$ (**1a**) (0.350 g, 0.5 mmol) in 10 ml THF or $SmI_3(THF)_3$ (**1b**) (0.373 g, 1 mmol) was added under magnetic stirring a solution of potassium bistrimethylsilyl amide **2** (0.300 g, 1.5 mmol) in 10 ml THF. After 18 h the KI was filtered and the supernatant solution was evaporated under vacuum yielding an off-white powder. Heating the residue under 10^{-4} Torr at 140°C for lanthanum, and 120°C for samarium, allowed to sublime, respectively, **4a** and **4b** as white powders. **4a**: ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm) 0.13. **4b:** ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm) −1.58.

Table 2
Crystallographic data for **3a**

Formula	$C_{16}H_{44}ILaN_2OSi_4$
Formula weight	658.70
Crystal system	Triclinic
Space group	P
Unit cell dimensions	
a (Å)	10.6124(10)
b (Å)	11.9212(7)
c (Å)	14.127(2)
α (°)	71.933(8)
β (°)	74.201(9)
γ (°)	63.482(7)
V (Å^3)	1501.4(3)
Z	2
D_{calc} (g cm^{-3})	1.457
μ (mm^{-1})	2.618
R_1 [a]	0.0640
wR_2 [b]	0.0953

[a] $R_1 = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$.

[b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The values were calculated for data with $I > 2\sigma(I)$.

X-ray crystallographic analysis. An irregular slightly yellow crystal of **3a** of approximate dimensions 0.31 × 0.23 × 0.16 mm^3 was mounted in a thin-walled glass capillary in a nitrogen-filled glove-box. Data were collected at r.t. on an Enraf–Nonius CAD4-diffractometer with graphite-monochromatised Mo–K$_\alpha$ radiation, using a ω–2θ scan mode. A summary of the crystallographic data is given in Table 2. Data were corrected [21] for Lorentz and polarisation effects, for linear decay and for absorption by empirical corrections based on ψ scans. The structures were solved by Patterson methods [22] and refined by full-matrix least-squares on F^2 using SHELXL-93 [23]. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters and the contributions of the hydrogen atoms were included in calculated positions. Atomic scattering factors and anomalous dispersion terms were taken as in Ref. [23]. The drawings were made with ORTEPII [24] and all the calculations were performed on a Dec α 3000 computer.

4.3. *Iodo bis bistrimethylsilyl amido ytterbium* **3c**

To a suspension of $YbI_3(THF)_3$ (**1c**) (0.447 g, 0.58 mmol) in 10 ml THF was added under magnetic stirring a solution of potassium bistrimethylsilyl amide (0.231 g, 1.16 mmol) in 10 ml THF within 15 min. A change of colour of the reaction mixture from orange to off-white was observed, together with formation of a white precipitate. After 18 h the KI was filtered (0.172 g, 89%) and the supernatant solution was evaporated under vacuum yielding an off-white powder of **3c** (0.350 g, 97% yield). IR (ν, cm^{-1}): 1255, 1245, 1175, 1090, 1010, 970, 835, 770, 650, 610. Anal. Found: C 22.92; H 6.00; N 3.56. Calc. for $C_{12}H_{36}IN_2Si_4Yb$: C 23.2; H 5.81; N 4.50%.

Acknowledgements

We thank CNRS for financial support and MENRES for a fellowship for N. Giuseppone. The work at ITN and at Orsay was partially supported by ICCTI/MENRES through a French–Portuguese research network.

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