



Synthesis and characterization of homoleptic imidazolin-2-iminato rare earth metal complexes

Tarun K. Panda^a, Cristian G. Hrib^b, Peter G. Jones^b, Matthias Tamm^{b,*}

^aIndian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram 502205, Andhra Pradesh, India

^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

ARTICLE INFO

Article history:

Received 4 May 2010

Received in revised form

21 June 2010

Accepted 25 June 2010

Available online 3 July 2010

Dedicated, in memoriam, to Prof. Dr. Herbert Schumann.

Keywords:

Rare earth metals

Imines

Homoleptic complexes

Nitrogen ligands

Cp-analogous ligands

ABSTRACT

The reactions of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine ($\text{Im}^{\text{ipr}}\text{NH}$) with the trimethylsilylmethyl (neosilyl) complexes $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ ($\text{M} = \text{Sc}, \text{Y}, \text{Lu}$) in a 3:1 ratio afforded tetramethylsilane (TMS) and the dinuclear imidazolin-2-iminato complexes $[\text{M}_2(\text{Im}^{\text{ipr}}\text{N})_6(\text{THF})_n]$ (**1a**, $\text{M} = \text{Sc}$, $n = 0$; **1b**, $\text{M} = \text{Y}$, $n = 1$; **1c**, $\text{M} = \text{Lu}$, $n = 1$), in which the metal atoms are bridged by two μ_2 - $\text{Im}^{\text{ipr}}\text{N}$ ligands. **1a** crystallized from THF/pentane solution to afford a solvent-free, centrosymmetric, dimeric complex, in which both scandium atoms attain a coordination number of four; three uncoordinated THF per dimer are observed. In contrast, the X-ray crystal structures of **1b**·2THF and **1c**·2THF reveal the formation of unsymmetric THF solvate complexes that contain one THF ligand and therefore both four- and five-coordinated rare earth metal atoms; other THF molecules are non-coordinating. The reaction of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ with three equivalents of the sterically more demanding 1,3-di-*tert*-butylimidazolin-2-imine ($\text{Im}^{\text{tBu}}\text{NH}$) afforded the mononuclear complex $[\text{Y}(\text{Im}^{\text{tBu}}\text{N})_3(\text{THF})_2]$ (**2**) with a five-coordinated yttrium atom, as indicated by X-ray diffraction analysis of **2**·2THF.

© 2010 Elsevier B.V. All rights reserved.

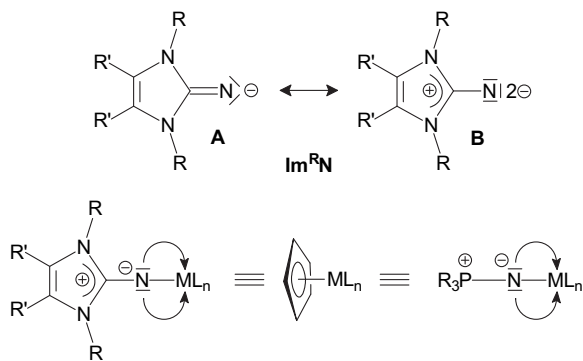
1. Introduction

Ever since the preparation of the first tris(cyclopentadienyl) rare earth metal complexes, $[(\eta\text{-C}_5\text{H}_5)_3\text{M}]$, by Wilkinson and Birmingham in 1954 [1], the organometallic chemistry of the rare earth elements has been dominated by cyclopentadienyl ligands (Cp) or related aromatic ligands [2]. In recent years, however, cyclopentadienyl-free complexes have been playing an increasingly important role in organolanthanide and organo rare earth metal chemistry [3], and a number of monodentate and monoanionic ancillary ligands such as alkoxides, siloxides, aryloxides [4], amides [5], and phosphoraneiminates [6] have been used to replace of the Cp ligand and to prepare homoleptic complexes of the type ML_3 ($\text{L} = \text{OR}, \text{OSiR}_3, \text{NR}_2, \text{NPR}_3$). For the latter ligands, *Dehnicke* has proposed a pseudo-isolobal relationship with the cyclopentadienyl system because of their ability to act as $2\sigma, 4\pi$ -electron donors [6–9]. Similar considerations apply to related imidazolin-2-iminato ligands ($\text{Im}^{\text{R}}\text{N}$) [10,11], which can be described by the two limiting resonance structures **A** and **B** (Scheme 1), indicating that the ability of the imidazolium ring to efficiently stabilize a positive charge

affords highly basic ligands with a strong electron-donating capacity toward early transition metals or metals in a higher oxidation state [12,13]. In our hands, these ligands proved to be viable systems for the preparation of catalytically active transition metal complexes [14] and also for the stabilization of mononuclear rare earth metal complexes, in which the terminal imidazolin-2-iminato ligands exhibit exceptionally short metal–nitrogen bonds [15].

In the course of these studies, a number of mono- and bis(imidazolin-2-iminato) scandium, yttrium, gadolinium and lutetium complexes of the types $[(\text{Im}^{\text{Dipp}}\text{N})\text{MCl}_2(\text{THF})_3]$ [15] and $[(\text{Im}^{\text{Dipp}}\text{N})_2\text{MCl}(\text{THF})_2]$ [16] containing the $\text{Im}^{\text{Dipp}}\text{N}$ ligand ($\text{R} = \text{Dipp} = 1,3$ -diisopropylphenyl, $\text{R}' = \text{H}$, Scheme 1) were prepared, which proved to be versatile starting materials for the preparation of cyclooctatetraenyl, cyclopentadienyl, amido and alkyl complexes by chloride substitution [15]. In continuation of this work, we aimed at the synthesis of tris(imidazolin-2-iminato) rare earth metal complexes, which might be regarded as isolobal to tris(cyclopentadienyl) complexes $[(\text{Cp})_3\text{M}]$ [2] and to homoleptic tris(phosphoraneiminato) complexes $[\text{M}(\text{NPR}_3)_3]$ [6]. For the latter, however, only dinuclear species such as $[\text{M}(\text{NPPH}_3)_3]_2$ ($\text{M} = \text{Y}, \text{La}$) were reported, which can be used as initiators for the ring-opening polymerization of lactones [9]. Herein, we wish to present the preparation and structural characterization of analogous homoleptic imidazolin-2-iminato complexes containing the

* Corresponding author. Tel.: +49 531 391 5309; fax: +49 531 391 5387.
E-mail address: matthias.tamm@tu-bs.de (M. Tamm).



Scheme 1. Mesomeric structures for imidazolin-2-iminato complexes and isobal relationship between imidazolin-2-iminato, cyclopentadienyl and phosphoraneiminato complexes.

ligands 1,3-diisopropyl-4,5-dimethylimidazolin-2-imide ($Im^{iPr}NH$, $R = iPr$, $R' = Me$) and 1,3-di-*tert*-butylimidazolin-2-imide ($Im^{tBu}NH$, $R = tBu$, $R' = H$), which have a different steric demand and might therefore lead to rare earth metal complexes of variable nuclearity.

2. Experimental

2.1. General information

All air-sensitive materials were manipulated with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled glove box (MBraun 200B). All solvents were purified using an MBraun system and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all ≥ 99 atom % D) and were degassed, dried, and stored in the argon-filled glove box. NMR spectra were recorded on a Bruker DPX 200 spectrometer. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard. Elemental analyses (C, H, N) were carried out by combustion and gas chromatographical analysis with an Elementar vario MICRO. 1,3-Diisopropyl-

4,5-dimethylimidazolin-2-imine ($Im^{iPr}NH$) [11], 1,3-di-*tert*-butylimidazolin-2-imine ($Im^{tBu}NH$) [11], and $[Ln(CH_2SiMe_3)_3(THF)_2]$ ($Ln = Sc, Y, Lu$) [17] were prepared according to literature procedures.

2.2. General procedure for the preparation of $[M_2(Im^{iPr}N)_6(THF)_n]$ (**1a**, $M = Sc$, $n = 0$; **1b**, $M = Y$, $n = 1$; **1c**, $M = Lu$, $n = 1$) and $[Y(Im^{tBu}N)_3(THF)_2]$ (**2**)

100 mg of $[M(CH_2SiMe_3)_3(THF)_2]$ were dissolved in hexane (5 mL) and added dropwise to a hexane solution (5 mL) containing three equivalents of $Im^{iPr}NH$ or $Im^{tBu}NH$, respectively. In all cases, a white suspension formed instantaneously, which gradually re-dissolved. After stirring the reaction mixture for 12 h at room temperature, the solvent was evaporated. The yellowish residues were re-crystallized from THF/pentane solutions to isolate the complexes **1** and **2** as a colourless crystalline materials.

2.3. Characterization of $[Sc_2(Im^{iPr}N)_6]$ (**1a**)

From $[Sc(CH_2SiMe_3)_3(THF)_2]$ (100.0 mg, 0.22 mmol) and $Im^{iPr}NH$ (130.1 mg, 0.66 mmol), 115 mg of **1a** were obtained. Yield: 83%. 1H NMR (C_6D_6 , 200 MHz, 25 °C): δ 5.83 (sept., 4H, CH, $^3J_{H,H}$ 6.8 Hz), 5.21 (sept., 8H, CH, $^3J_{H,H}$ 6.8 Hz), 1.92 (s, 24H, CH_3), 1.86 (s, 12H, CH_3), 1.52 (d, 24H, CH_3 , $^3J_{H,H}$ 7.2 Hz), 1.32 (d, 48H, CH_3 , $^3J_{H,H}$ 7.2 Hz). $^{13}C\{H\}$ NMR (C_6D_6 , 50.32 MHz, 25 °C): δ 113.3 (NCMe), 44.7 (CHMe), 22.9 (CHCH₃), 10.6 (NCCH₃); the resonance for the CN carbon atom was not observed. Anal. Calc. for $C_{66}H_{120}N_{18}Sc_2$ (1255.72): C, 63.13; H, 9.63; N, 20.07. Found: C, 62.94; H 9.28; N, 19.89.

2.4. Characterization of $[Y_2(Im^{iPr}N)_6(THF)]$ (**1b**)

From $[Y(CH_2SiMe_3)_3(THF)_2]$ (100 mg, 0.20 mmol) and $Im^{iPr}NH$ (119 mg, 0.60 mmol) 140 mg of **1b** were obtained. Yield: 91%. 1H NMR (C_6D_6 , 200 MHz, 25 °C): δ 5.18 (br, 12H, CH), 3.56–3.50 (br, 4H, THF), 1.86 (s, 36H, CH_3) 1.67–1.42 (m, 4H, THF), 1.33 (d, 72H, CH_3 , $^3J_{H,H}$ 5.8 Hz). $^{13}C\{H\}$ NMR (C_6D_6 , 50.32 MHz, 25 °C): δ 113.1 (NCMe), 44.3 (CHMe), 22.5 (CHCH₃), 10.5 (NCCH₃); the resonance for the CN carbon atom was not observed. 1H NMR (THF-*d*₈, 300 MHz,

Table 1
Crystallographic data for complexes **1a**·3THF, **1c**·2THF, and **2**·2THF.

	1a ·3THF	1b ·2THF	1c ·2THF	2 ·2THF
Empirical formula	$C_{78}H_{144}N_{18}O_3Sc_2$	$C_{78}H_{144}N_{18}O_3Y_2$	$C_{78}H_{144}Lu_2N_{18}O_3$	$C_{49}H_{92}N_9O_4Y$
M_r [$g\ mol^{-1}$]	1472.03	1559.93	1732.05	960.23
T [K]	133(2)	133(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P2 ₁ /c	P2 ₁ /c
a [Å]	20.9793(15)	13.0964(14)	13.0315(8)	24.2650(7)
b [Å]	13.9545(10)	14.3019(14)	25.9173(15)	9.5954(3)
c [Å]	28.989(2)	24.788(2)	25.3648(15)	23.2667(7)
α , °	90	80.713(3)	90	90
β , °	98.109(2)	84.841(3)	91.442(3)	105.1140(1)
γ , °	90	72.241(3)	90	90
V [Å ³]	8401.8(10)	4359.6(8)	8564.0(9)	5229.9(3)
Z	4	2	4	4
$\rho_{calcd.}$ [Mg/m^{-3}]	1.164	1.188	1.343	1.220
μ [mm^{-1}]	0.217	1.378	2.346	1.165
$F(000)$	3216	1680	3616	2080
Reflections collected	66,574	66,129	282,997	116,189
Independent reflections	8599	17,784	32,619	13,052
$R(int)$	0.0853	0.0856	0.0455	0.0952
GOF	1.136	1.011	1.062	1.023
$R1$ [$I > 2\sigma(I)$]	0.0610	0.0545	0.0278	0.0441
wR2	0.1880	0.1496	0.0585	0.0932

Download English Version:

<https://daneshyari.com/en/article/1325539>

Download Persian Version:

<https://daneshyari.com/article/1325539>

[Daneshyari.com](https://daneshyari.com)