Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 5078–5089
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Bis(phosphinimino)methanides as ligands in divalent lanthanide and alkaline earth chemistry – synthesis, structure, and catalysis

Tarun K. Panda, Agustino Zulys, Michael T. Gamer, Peter W. Roesky *

Institut für Chemie, Freie Universität Berlin Fabeckstrasse 34-36, 14195 Berlin, Germany

Received 21 January 2005; received in revised form 16 March 2005; accepted 16 March 2005
Available online 5 May 2005

Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

Abstract

Divalent bis(phosphinimino)methanide lanthanide complexes of composition $[\{(Me_3SiNPPh_2)_2CH\}EuI(THF)]_2$ and $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ have been prepared by a salt metathesis reactions of $K\{CH(PPh_2NSiMe_3)_2\}$ and LnI_2. Further reactions of these complexes with $[K(THF)_nN(PPh_2)_2]$ led selectively to the heteroleptic amido complexes $[\{(Me_3SiNPPh_2)_2CH\}Ln\{(Ph_2P)_2N\}(THF)]$ (Ln = Eu, Yb). The ytterbium complex can also be obtained by reduction of $[\{CH(PPh_2NSiMe_3)_2\}Yb\{(Ph_2P)_2N\}Cl]$ with elemental potassium. The single crystals of $[\{(Me_3SiNPPh_2)_2CH\}Ln\{(Ph_2P)_2N\}(THF)]$ contain enantiomerically pure complexes. As a result of the similar ionic radii of the divalent lanthanides and the heavier alkaline earth metals some similarities in coordination chemistry of the bis(phosphinimino)methanide ligand were anticipated. Therefore, MI_2 (M = Ca, Sr, Ba) was reacted with $K\{CH(PPh_2NSiMe_3)_2\}$ to give $[\{(Me_3SiNPPh_2)_2CH\}CaI(THF)_2]$, $[\{(Me_3SiNPPh_2)_2CH\}SrI(THF)]_2$, and $[\{(Me_3SiNPPh_2)_2CH\}BaI(THF)_2]_2$, respectively. As expected the Sr and Eu complexes and the Ca and Yb complexes are very similar, whereas for the Ba compound, as a result of the large ion radius, a different coordination sphere is observed. For all new complexes the solid-state structures were established by single crystal X-ray diffraction. In the solid-state the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand acts as tridentate donor forming a long methanide carbon metal bond. Thus, all complexes presented can be considered as organometallic compounds. $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ was also used as precatalyst for the intramolecular hydroamination/cyclization reaction of different aminoalkynes and aminoolefines. Good yields but moderate activities were observed.

Keywords: Alkaline earth metals; Bis(phosphinimino)methanides; Catalysis; Hydroamination; Lanthanides; P,N ligands

1. Introduction

In the last 15 years, enormous progress has been observed in the design and application of amido-metal chemistry of the early transition metals. In the early stages of this area cyclopentadienyl-analogous amido ligands were studied for comparison with and for further investigations of the well-known cyclopentadienyl moiety. Today, the stable amido-metal bond is utilized in amido-metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be specifically tailored to allow applications in areas such as the activation of small poorly reactive molecules, homogeneous catalysis, or organic synthesis [1,2]. One synthetic approach among others is the use of P–N ligands such as phosphoraneiminate, phosphinimines, and phosphinimides in main group and transition metal chemistry [3–8]. Recently, the deprotonated derivatives of the well-known bis(phosphinimine), $CH_2(PPh_2NSiMe_3)_2$ [9] have drawn the attention of a number of research groups. It was shown that a monoanionic

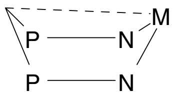
---

* Corresponding author. Tel.: +49 (0) 308 385 4004; fax: +49 (0) 308 385 2440.
E-mail address: roesky@chemie.fu-berlin.de (P.W. Roesky).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.03.023

[10–13], and a dianionic species [14,15] ($\{CH(PPh_2NSiMe_3)_2\}^-$ and $\{C(PPh_2NSiMe_3)_2\}^{2-}$, respectively) can be generated by deprotonation of the precursor $CH_2(PPh_2NSiMe_3)_2$. The monoanionic species was used as a ligand in main group and transition metal chemistry, [16–19], whereas the dianionic ligand was reported by Cavell and co-workers [17,20] to form carbene like complexes with a series of transition metals and samarium. Recently, we introduced the monoanionic phosphinimine $\{CH(PPh_2NSiMe_3)_2\}^-$, into yttrium and lanthanide chemistry. We have previously reported the synthesis of a series of lanthanide bis(phosphinimino)methanide dichloride complexes including yttrium, $[\{CH(PPh_2NSiMe_3)_2LnCl_2]_2$ (Ln = Y, Sm, Dy, Er, Yb, Lu) [21]. These compounds were obtained by the reaction of $K\{CH(PPh_2NSiMe_3)_2\}$ [12], with the corresponding yttrium or lanthanide trichlorides. Furthermore, reactions with the $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ compounds have led to the corresponding amido complexes, $[\{CH(PPh_2NSiMe_3)_2\}Ln(NPh_2)_2]$ (Ln = Y, Sm) [21], diphosphinoamido complexes, $[\{CH(PPh_2NSiMe_3)_2\}Ln\{(Ph_2P)_2N\}Cl]$ (Ln = Y, La, Nd, Yb) [22], cyclopentadienyl complexes, $[\{CH(PPh_2NSiMe_3)_2\}Ln(\eta^5\text{-}C_5H_5)_2]$ (Ln = Y, Sm, Er) [23], and cyclooctatetraene bis(phosphinimino) methanide complexes, $[\{CH(PPh_2NSiMe_3)_2\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y, Sm, Er, Yb, Lu) [24], which have been reported by us. These derivatives were used as homogenous catalysts for a number of different catalytic applications. Thus, $[\{CH(PPh_2NSiMe_3)_2\}Ln\{(Ph_2P)_2N\}Cl]$ are active catalysts for the ring-opening polymerization of ε-caprolactone and the polymerization of methyl methacrylate, whereas $[\{CH(PPh_2NSiMe_3)_2\}Ln(\eta^8\text{-}C_8H_8)]$ was used as catalysts for the hydroamination/cyclization reaction.

In all lanthanide compounds we reported so far with, $\{CH(PPh_2NSiMe_3)_2\}^-$ tends to show an uncommon coordination mode. In the solid-state structures the methine carbon atom coordinates via a long interaction on to the metal atom. Thus, the six membered metallacycle (N1–P1–C1–P2–N2–Ln), which is formed by chelation of the two trimethlysilylimine groups to the metal center, adopts a pseudo-boat conformation (Scheme 1). In one case the interaction between the methine carbon atom and the metal atom was also observed in solution. By using yttrium as metal center, $^1J(C,Y)$ and a $^2J(H,Y)$ coupling was reported. These observations were also supported by DFT calculations [21]. Thus, this class of compounds can be considered as organometallic compounds. Motivated by these results we were interested to extend our studies on to the divalent lanthanides and to the heavier alkaline earth metals. It is well known that the divalent lanthanides and the heavier alkaline earth metals exhibit similar ion radii, thus comparable coordination chemistry can be applied. Currently in this field, there are limited related complexes containing the mesityl substituted bis(phosphinimino)methanide, $\{CH(PPh_2N\text{-}Mes)_2\}^-$ ligand in the coordination sphere, which have been reported by Hill et al. [25]. Best to our knowledge in this area one Sm(II) complex, $[Sm\{CH(PPh_2N\text{-}Mes)_2\}_2]$, the related Ba compound $[Ba\{CH(PPh_2N\text{-}Mes)_2\}_2]$, and the amido compounds $[\{CH(PPh_2N\text{-}Mes)_2\}_2MN(SiMe_3)_2]$ (M = Ca, Sr) are the only known compounds.



Scheme 1.

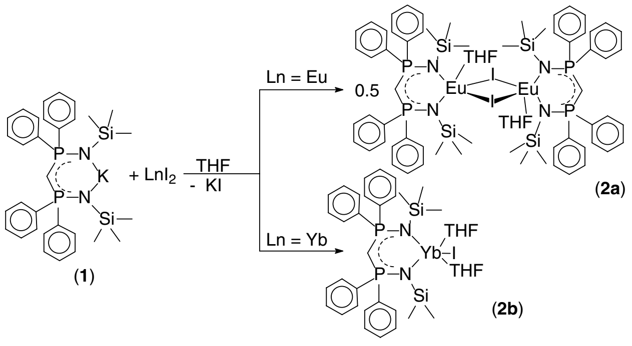
In this contribution, we present a full account of the reaction of LnI_2 (Ln = Eu, Yb) and MI_2 (M = Ca, Sr, Ba) with $K\{CH(PPh_2NSiMe_3)_2\}$ as well as some further reactions of the obtained mono iodine compounds. Additionally the application of the ytterbium iodine complex as a catalyst in the hydroamination/cyclization is reported.

2. Results and discussion

2.1. Lanthanide iodine complexes

Reaction of $K\{CH(PPh_2NSiMe_3)_2\}$ (**1**) with ytterbium and europium diiodide in a 1:1 molar ratio in THF afforded the corresponding divalent lanthanide complexes $[\{(Me_3SiNPPh_2)_2CH\}EuI(THF)]_2$ (**2a**) and $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ (**2b**) as crystals in good yields (Scheme 2) [26]. The potassium reagent **1**, which was described earlier [12] was used as starting material to avoid coordination of lighter alkali halides such as lithium chloride. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of both compounds were established by single crystal X-ray diffraction.

The signal of the methine proton (δ 1.91) in ^1H NMR spectrum of the diamagnetic ytterbium compound (**2b**) is in the range of comparable trivalent lanthanide complexes ($[\{CH(PPh_2NSiMe_3)_2\}YCl_2]_2$ (δ 1.93)) but shows



Scheme 2.