Pergamon

PII: S0277-5387(96)00517-7

Polyhedron Vol. 16, No. 12, pp. 2013–2020, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277-5387/97 $17.00+0.00

Effects of metal-size and auxiliary ligand on the alkylation of lanthanide–halide with Li[$(CH_2)(CH_2)PPh_2$]. X-ray crystal structures of [Me_2PPh_2][$Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl$] and [$Li(C_4H_8O)_4$][$Er(NPh_2)_4$]

Wai-Kwok Wong,[a]* Lilu Zhang,[a] Feng Xue[b] and Thomas C. W. Mak[b]

[a]Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon, Hong Kong;
[b]Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

(Received 4 September 1996; accepted 21 October 1996)

Abstract—The interaction of Li[$(CH_2)(CH_2)PPh_2$] in tetrahydrofuran with one equivalent of [$(\eta^5\text{-}C_5H_4Bu^t)_2LnCl \cdot LiCl$] (Ln = Sm, Yb) gave the anionic lanthanide *ate* complex [Me_2PPh_2][$Ln(\eta^5\text{-}C_5H_4Bu^t)_3Cl$] (**1**, Sm) or the neutral lanthanide-ylide complex [$(\eta^5\text{-}C_5H_4Bu^t)_2Ln(Cl)CH_2P(Me)Ph_2$] (**3**, Yb). The interaction of $LnCl_3$ (Ln = Er, Yb) in tetrahydrofuran with two equivalents of $NaNPh_2$ followed by one equivalent of Li[$(CH_2)(CH_2)PPh_2$] gave the unexpected anionic homoleptic tetra-coordinate lanthanide–amide *ate* complex, [$Li(C_4H_8O)_4$][$Ln(NPh_2)_4$] (**4**, Er; **5**, Yb). All of these complexes have been characterized by analytical and spectroscopic methods. The structures of **1** and **4** have been established by X-ray diffraction. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: samarium; erbium; ytterbium; lanthanide-amide *ate* complexes; ylide; structure.

Phosphorus ylides have been shown to possess an extensive coordination chemistry with main group, *d*-block and *f*-block metal atoms and to form metal–carbon σ-bonds of unusual stability [1–3]. With actinide metals, depending on the reaction conditions, phosphorus ylidic ligand can act either as a monodentate or a bidentate ligand, as shown below [3].

We are interested in examining the factors that affect the mode of coordination of phosphorus ylidic ligands, particularly the steric and electronic effects of substituents of the cyclopentadienyl rings. Recently, we have shown that the interaction of $Cp'_2LnCl \cdot LiCl$ (Ln = Nd, Sm) with Li[$(CH_2)(CH_2)PPh_2$] gives the cyclic ylidic complex when Cp′ is the sterically bulky C_5Me_5 ring [4] and the ylide complex when Cp′ is the sterically less demanding C_5H_5 and $C_5H_4Bu^t$ rings [5]. We have examined the effect of the size of lanthanide metals and the nature of the auxiliary ligands of the lanthanide complexes on the mode of coordination of the phosphorus ylidic ligand. Herein we report the results of the interaction of [$(\eta^5\text{-}C_5H_4Bu^t)_2LnCl \cdot LiCl$] (Ln = Sm, Yb) and $Ln(NPh_2)_2Cl$ (Ln = Er, Yb) with the ylidic ligand Li[$(CH_2)(CH_2)PPh_2$].

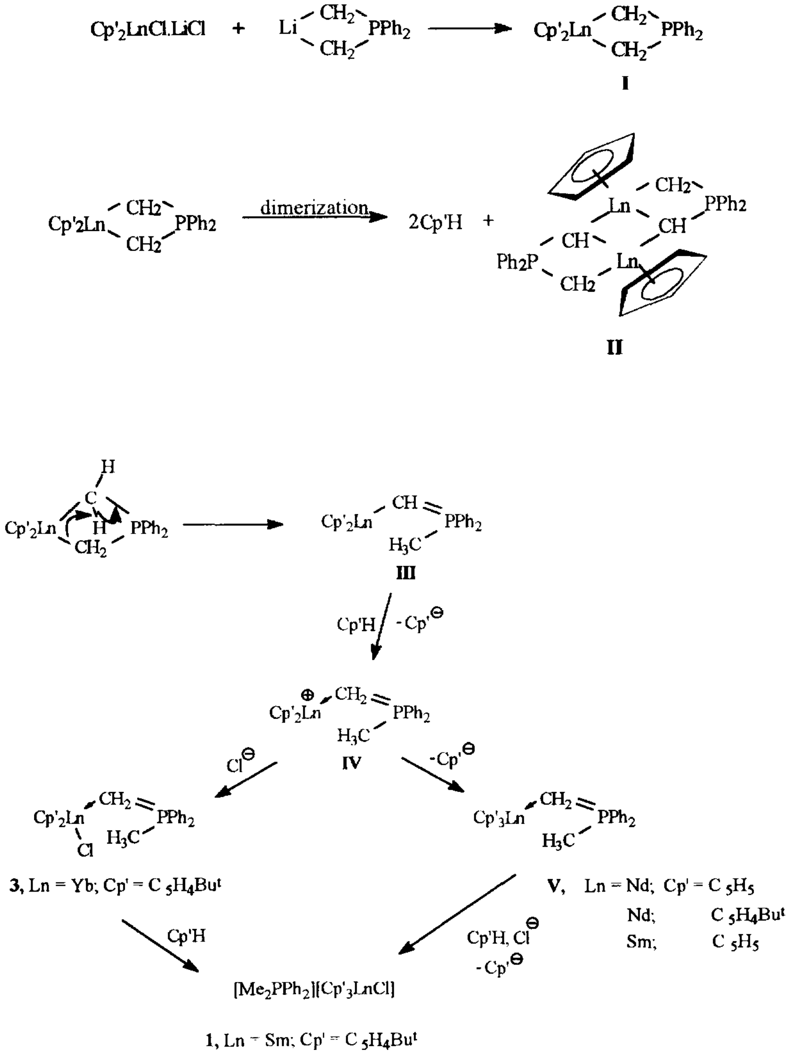
RESULTS AND DISCUSSION

Interaction of [$(\eta^5\text{-}C_5H_4Bu^t)_2LnCl \cdot LiCl$] *with* Li[$(CH_2)(CH_2)PPh_2$]

Ln = Sm. Interaction of [$(\eta^5\text{-}C_5H_4Bu^t)_2SmCl \cdot LiCl$] with one equivalent of Li[$(CH_2)(CH_2)PPh_2$] in tetrahydrofuran at room temperature for 16 h, after work up gave light yellow crystals of stoichiometry [Me_2PPh_2][$Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl$] (**1**) in 20% yield after recrystallization from toluene solution. The structure of **1**

---

*Author to whom correspondence should be addressed.



Scheme 1. A possible mechanism for the formation of **1** and **3**.

was established by X-ray crystallography. Crystals suitable for X-ray diffraction study were grown from a solution in toluene. A perspective drawing of **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1.

The crystal structure analysis revealed that **1** is composed of a discrete cation and a discrete anion. The cation $[Me_2PPh_2]^+$ exists as a discrete moiety with the phosphorus adopting a tetrahedral geometry. The P—C distances and C—P—C angles are normal and range from 1.774(7) to 1.800(7) Å and 106.8(4) to 111.5(4)°, respectively. The anion $[Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]^-$ can be described as a distorted tetrahedron if one considers that the metal is coordinated to the centroid of each cyclopentadienyl ring. The cyclopentadienyl rings are bonded in a η^5-fashion with Sm—C (ring) distances ranging from 2.693(6) to 3.001(7) Å with the longest distances being those carbon atoms bonded to *tert*-butyl groups. Similar observations have been reported for $[(\eta^5\text{-}C_5H_4Bu^t)_3NdCH_2P(Me)Ph_2]$ [5b] and $[(\eta^5\text{-}C_5H_4Bu^t)_2NdMe]_2$ [6]. The mean Sm—C distances for the three cyclopentadienyl rings are 2.82, 2.85 and 2.85 Å which are slightly longer than that of $[(\eta^5\text{-}C_5H_5)_3SmCH_2P(Me)Ph_2]$ [5a] (2.75, 2.78 and 2.79 Å). This is consistent with the fact that *tert*-butyl group is an electron-donating group and in agreement with a negative charge delocalized on to the samarium metal. The Sm—Cl(1) distance of 2.719(2) Å is comparable to that of $[(\eta^5\text{-}C_5Me_5)_2Sm(Cl)(THF)]$ [2.709 (8) Å] [7].

Ln = *Yb*. Interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl \cdot LiCl]$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran at room temperature for 16 h, work up gave white crystals of stoichiometry $[Me_2PPh_2][(\eta^5\text{-}C_5H_4Bu^t)_2Li]$ (**2**) and yellow crystals of stoichiometry $[(\eta^5\text{-}C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**3**) in 10% and 30% yield, respectively, after successive recrystallization from a tetrahydrofuran/toluene mixture. Both structures were established by X-ray diffraction studies [8]. **2** has a sandwich structure for the discrete