

## 茂基稀土邻氨基苯甲酰胺基双负离子配合物的合成 及其环胺羰化反应和脒基化反应

孙 燕<sup>1</sup> 刘瑞婷<sup>1</sup> 翁林红<sup>1</sup> 周锡庚<sup>\*,1,2</sup>

(<sup>1</sup> 复旦大学化学系, 上海市分子催化与功能材料重点实验室, 上海 200433)

(<sup>2</sup> 金属有机化学国家重点实验室, 上海 200032)

**摘要:**  $\text{Cp}_3\text{Ln}$  与邻氨基苯甲酰胺在甲苯中反应, 之后在 HMPA 和甲苯中结晶, 以中等到高收率得到四核稀土有机配合物  $[\text{Cp}_3\text{Ln}(\mu\text{-}\eta^2\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})(\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})\text{LnCp}(\text{HMPA})]_2$  ( $\text{Ln}=\text{Yb}$ , **1a**;  $\text{Er}$ , **1b**;  $\text{Y}$ , **1c**)。化合物 **1** 与 4 倍物质的量的  $\text{PhNCO}$  在甲苯中反应形成 1,3-喹唑啉二氧基(Quo)双负离子稀土配合物  $[\text{Cp}_2\text{Ln}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^1\text{-Quo})]_3\text{Ln}(\text{HMPA})_2$  ( $\text{Ln}=\text{Yb}$ , **2a**;  $\text{Er}$ , **2b**;  $\text{Y}$ , **2c**), 表明化合物 **1** 中的  $\text{Ln-NHAr}$  键和  $\text{ArCONH-Ln}$  键能与异氰酸酯分子发生连续加成/胺消除反应, 形成 1,3-喹唑啉二氧基骨架。但化合物 **1a~1c** 与  $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  反应, 仅得到  $\text{ArNH}$  基单加成产物  $[\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}^i\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{CONH}]]_3\text{Ln}(\text{HMPA})_3$  ( $\text{Ln}=\text{Yb}$ , **3a**;  $\text{Er}$ , **3b**;  $\text{Y}$ , **3c**)。而  $\text{Cp}_3\text{Ln}$  与邻氨基苯甲酰胺和  $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  在甲苯中进行“一锅”反应, 则形成双核配合物  $[\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-NHCOC}_6\text{H}_4\text{NC}(\text{NH}^i\text{Pr})\text{N}^i\text{Pr}]]_2$  ( $\text{Ln}=\text{Yb}$ , **4a**;  $\text{Er}$ , **4b**;  $\text{Y}$ , **4c**)。值得注意的是, HMPA 能够诱导配合物 **4** 发生配体重排反应, 转化成化合物 **3**。

**关键词:** 稀土配合物; 环胺羰化反应; 异氰酸酯; 邻氨基苯甲酰胺; 加成反应

中图分类号: O614.346; O614.344; O614.32\*2 文献标识码: A 文章编号: 1001-4861(2017)11-2124-15

DOI: 10.11862/CJIC.2017.255

## Syntheses, Cycloaminocarbonylation and Amidination of Rare Earth *o*-Aminobenzamido Dianion Complexes Bearing Cyclopentadienyl Co-ligand

SUN Yan<sup>1</sup> LIU Rui-Ting<sup>1</sup> WENG Lin-Hong<sup>1</sup> ZHOU Xi-Geng<sup>\*,1,2</sup>

(<sup>1</sup>Department of Chemistry, Shanghai Key Laboratory of Molecular  
Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China)

(<sup>2</sup>State Key Laboratory of Organometallic Chemistry, Shanghai 200032, China)

**Abstract:** Treatment of  $\text{Cp}_3\text{Ln}$  with *o*-aminobenzamide followed by crystallization in a HMPA and toluene mixture affords the tetranuclear organolanthanide complexes  $[\text{Cp}_3\text{Ln}(\mu\text{-}\eta^2\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})(\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})\text{LnCp}(\text{HMPA})]_2$  ( $\text{Ln}=\text{Yb}$ , **1a**;  $\text{Er}$ , **1b**;  $\text{Y}$ , **1c**). Reaction of **1** with  $\text{PhNCO}$  ( $n_{\text{PhNCO}}/n_1=4$ ) in toluene gives the dianionic quinazolyldiolate (Quo) complexes  $[\text{Cp}_2\text{Ln}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^1\text{-Quo})]_3\text{Ln}(\text{HMPA})_2$  ( $\text{Ln}=\text{Yb}$ , **2a**;  $\text{Er}$ , **2b**;  $\text{Y}$ , **2c**), indicating that one isocyanate molecule can undergo the tandem reaction with both NH and CONH of **1** to construct a quinazolyldiolate skeleton, accompanying with the elimination of  $\text{PhNH}_2$ . However, **1a~1c** react with  $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  under the same conditions to give only the single  $\text{ArNH}$  addition products  $[\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}^i\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{CONH}]]_3\text{Ln}(\text{HMPA})_3$  ( $\text{Ln}=\text{Yb}$ , **3a**;  $\text{Er}$ , **3b**;  $\text{Y}$ , **3c**). Furthermore, treatment of  $\text{Cp}_3\text{Ln}$  with *o*-aminobenzamide followed by reacting with  $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  gave  $[\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-NHCOC}_6\text{H}_4\text{NC}(\text{NH}^i\text{Pr})\text{N}^i\text{Pr}]]_2$  ( $\text{Ln}=\text{Yb}$ , **4a**;  $\text{Er}$ , **4b**;  $\text{Y}$ , **4c**). Noticeably, HMPA could induce the transformation of **4** into **3** by a ligand redistribution. CCDC: 951003, **1a**; 951104, **1b**; 951102, **2a**; 951004, **3a**; 951106, **3b**; 951005, **3c**; 951103, **4a**; 951107, **4b**; 951105, **4c**.

**Keywords:** lanthanide complexes; cycloaminocarbonylation; isocyanate; *o*-aminobenzamide; addition

收稿日期: 2017-09-01。收修改稿日期: 2017-09-22。

国家自然科学基金(No.21372047, 21572034)资助项目。

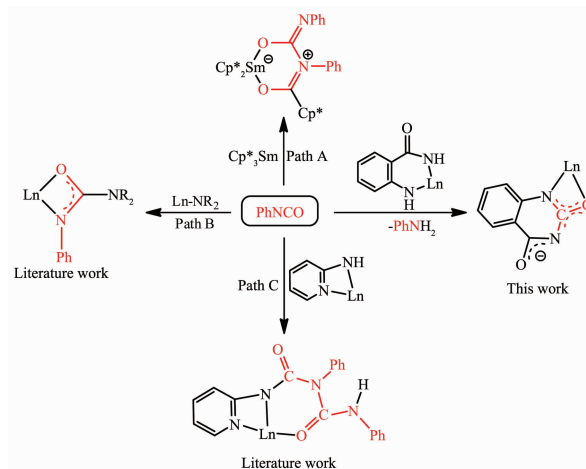
\*通信联系人。E-mail: xgzhou@fudan.edu.cn

## 0 Introduction

There is currently a fundamental interest in the reactivity of organolanthanide complexes toward unsaturated small molecules, because this is the source for design of new catalytic reactions and catalysts<sup>[1-6]</sup>. The selective insertion of an organic functional group into a lanthanide-ligand bond has proved to be a successful and pervasive method for the formation of carbon-carbon and carbon-heteroatom bonds in synthesis of organolanthanide derivatives and organic compounds<sup>[6-13]</sup>. For example, by applying this type of insertions as the key step, many organolanthanide-catalyzed reactions such as hydrosilylation<sup>[7]</sup>, hydroamination<sup>[2b,8]</sup>, hydroalkoxylation<sup>[9]</sup>, hydrothiolation<sup>[10]</sup>, hydrophosphination<sup>[11]</sup>, hydroboration<sup>[12]</sup>, and C-H bond addition<sup>[2c,13]</sup> of diverse C-C unsaturated substrates have been developed. In contrast, the development of metathesis reactions of trivalent organolanthanide complexes with unsaturated substrates leading to the complete cleavage of the unsaturated chemical bond, lags far behind, despite their fundamental scientific interest and the potential utility in organic synthesis. The major reason might be attributed to the absence of conventional oxidative-addition/reductive-elimination processes and the difficulties encountered in the formation of rare earth metal-carbon and rare earth metal-heteroatom multiply-bonded intermediates, which often involve in transition metal-catalyzed metathesis reactions of unsaturated substrates<sup>[14]</sup>. Recent pioneering works show that reaction of tetranuclear rare earth metal polyhydrido complexes with CO yielded ethylene and the corresponding tetraoxo cubane complexes<sup>[15a]</sup>. Chen and coworkers reported that yttrium dihydride reacted with  $\text{Ph}_3\text{P}=\text{Se}$  to give an yttrium selenide complex in the company of the liberation of  $\text{Ph}_3\text{P}$  and  $\text{H}_2$ <sup>[15b]</sup>. Furthermore, methylenide complexes of rare earth metals have proven their ability to cleave the  $\text{C}=\text{O}$ ,  $\text{N}=\text{N}$  and  $\text{C}=\text{N}$  double bonds<sup>[16]</sup>. Despite these achievements, the use of trivalent organolanthanide complexes as reagents for the transformation of an unsaturated functional group into

another unsaturated one in the context of metathesis reactions remains underutilized. The question of whether or not rare earth metal amido complexes can promote formation and transformation of unsaturated carbon-heteroatom bonds as readily as rare earth metal polyhydrido and methylenide complexes mediate  $\text{C}=\text{O}$  bond metathesis reaction is still an open issue.

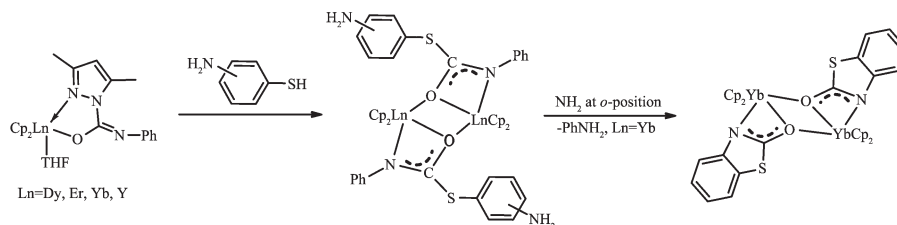
The chemical nature of isocyanates, with an electrophilic center at carbon and nucleophilic centers at oxygen and nitrogen, allows a diverse variety of reactions to occur, thus leading to a great potential for constructing higher organic structures<sup>[17]</sup>. The selectivity of isocyanate transformations has been profitably controlled by metal species, since their participation allows the fine-tuning of bond forming processes and reactivity of isocyanates<sup>[18]</sup>. In attempts to establish more selective catalyst systems and to have a better understanding of the mechanistic aspects as well as to develop new reactions, extensive studies on the reaction of organometallic complexes with isocyanates have been carried out. Noticeably, in contrast to transition metals, selective  $\text{C}=\text{N}$  or  $\text{C}=\text{O}$  bond cleavage of isocyanates mediated by rare earth metals remains a significant challenge, mainly due to the instability of the resulting nitrene and carbonyl complexes and to the facile  $\text{C}=\text{O}$  addition pathways available<sup>[18]</sup>. The stoichiometric reaction of trivalent organolanthanide compounds with isocyanates gives generally the addition products (Scheme 1)<sup>[19]</sup>.



Scheme 1

On the other hand, using isocyanates as CO precursors in organic synthesis remains little explored<sup>[20]</sup>. Hou and coworkers reported in 2004 that yttrocene tetrahydrido complex  $[(C_5Me_4SiMe_3)Y(\mu-H)]_4(L)$  ( $L = Me_3SiCCHCHCSiMe_3$ ) could abstract the oxygen from aryl isocyanate to form the corresponding  $\mu_3$ -oxo complex  $[(C_5Me_4SiMe_3)Y]_4(\mu_3-O)(\mu-H)_2(L)$  or  $[(C_5Me_4SiMe_3)Y]_4(\mu_3-O)_2(L)$ , depending on the substrate ratio<sup>[21]</sup>. In the course of our ongoing studies involving the reaction of organolanthanide complexes with isocyanates, we found that the further interaction of the neighboring  $NH_2$  group with an isocyanate unit inserted into the lanthanide-sulfur bond could lead to unique reactivity and selectivity trends, allowing a

mild and efficient construction of the coordinated benzothiazole 2-oxide ligand<sup>[20a]</sup> (Scheme 2). So far, no general method for rare earth metal-based carbonylation has been reported. Given that the above reaction provides an alternative route to carbonylation of organic substrates, we were interested in broadening the reaction. Herein, we report the synthesis and structure of lanthanocene complexes containing *o*-aminobenzamido dianion ligand, and a new reactivity pattern of amido complexes toward isocyanates: carbonylative coupling/cyclization, which provides a new method for the construction of a coordinated quinazolyldiolate ring skeleton.



Scheme 2

## 1 Experimental

### 1.1 General remarks

All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. All organic solvents such as THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under  $N_2$  prior to use. *o*-Aminobenzamide, HMPA (hexamethylphosphorictriamide), *N,N'*-diisopropyl carbodiimide (DIC) and phenyl isocyanate (PhNCO) were purchased from commercial sources and were used without further purification. Elemental analyses for C, H, and N were carried out by using a Rapid CHN-O analyzer. Metal analyses were accomplished using the literature method<sup>[22]</sup>. Infrared spectra for air- and moisture-sensitive compounds were obtained on a Nicolet FTIR 360 spectrometer with samples prepared as Nujol mulls.  $^1H$  NMR data were obtained on a Bruker DMX-400 NMR spectrometer.

### 1.2 Preparation

#### 1.2.1 Synthesis of $[CpYb(\mu-\eta^2:\eta^2-NHC_6H_4CONH)(\mu_3-\eta^1:\eta^1:\eta^2-NHC_6H_4CONH)YbCp(HMPA)]_2$ (**1a**)

To a toluene solution (20 mL) of  $Cp_3Yb$  (0.331 g, 0.898 mmol) was added *o*-aminobenzamide (0.122 g, 0.898 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. Then, HMPA (0.161 g, 0.898 mmol) was added to the resulting yellow turbid solution. After stirring for 2 h, the reaction mixture was changed to a clear solution. The solution was then cooled at  $-10\text{ }^\circ\text{C}$  overnight to give **1a** as orange crystals. Yield: 0.388 g (94%). Anal. Calcd. for  $C_{60}H_{80}N_{14}O_6P_2Yb_4$ (%): C, 39.01; H, 4.36; N, 10.61; Yb, 37.47. Found(%): C, 39.12; H, 4.41; N, 10.53; Yb, 37.33. IR (Nujol,  $cm^{-1}$ ): 3 365 m, 3 309 w, 1 601 m, 1 526 m, 1 457 vs, 1 378 m, 1 327 m, 1 145 s, 990 s, 873 w, 758 s.

#### 1.2.2 Synthesis of $[CpEr(\mu-\eta^2:\eta^2-NHC_6H_4CONH)(\mu_3-\eta^1:\eta^1:\eta^2-NHC_6H_4CONH)ErCp(HMPA)]_2$ (**1b**)

Following the described method for synthesis of

**1a**, using  $\text{Cp}_3\text{Er}$  (0.496 g, 1.37 mmol), *o*-aminobenzamide (0.187 g, 1.37 mmol) and HMPA (0.246 g, 1.37 mmol) afforded **1b** as light pink crystals. Yield: 0.534 g (86%). Anal. Calcd. for  $\text{C}_{60}\text{H}_{80}\text{N}_{14}\text{O}_6\text{P}_2\text{Er}_4$ (%): C, 39.50; H, 4.42; N, 10.75; Er, 36.67. Found(%): C, 39.55; H, 4.43; N, 10.69; Er, 36.58. IR (Nujol,  $\text{cm}^{-1}$ ): 3 365 m, 3 310 w, 1 600 m, 1 525 m, 1 457 vs, 1 379 m, 1 327 m, 1 144 s, 989 s, 872 w, 757 s.

### 1.2.3 Synthesis of $[\text{CpY}(\mu\text{-}\eta^2\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})(\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})\text{YCp}(\text{HMPA})_2$ (**1c**)

Following the described method for synthesis of **1a**, using  $\text{Cp}_3\text{Y}$  (0.86 g, 1.01 mmol), *o*-aminobenzamide (0.137 g, 1.01 mmol) and HMPA (0.181 g, 1.01 mmol) afforded **1c** as a light yellow crystalline powder. Yield: 0.281 g (74%). Anal. Calcd. for  $\text{C}_{60}\text{H}_{80}\text{N}_{14}\text{O}_6\text{P}_2\text{Y}_4$ (%): C, 47.69; H, 5.34; N, 12.98; Y, 23.54. Found(%): C, 47.74; H, 5.37; N, 12.90; Y, 23.52. IR (Nujol,  $\text{cm}^{-1}$ ): 3 364 m, 3 309 w, 1 600 m, 1 524 m, 1 458 vs, 1 378 m, 1 327 m, 1 143 s, 988 s, 758 s.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 25  $^\circ\text{C}$ ):  $\delta$  7.92 (s, NH, 2H), 7.90 (s, NH, 2H), 7.08 ~6.43 (m,  $\text{C}_6\text{H}_4$ , 16H), 6.29 (s,  $\text{C}_5\text{H}_5$ , 20H), 3.71 (s, NH, 2H), 3.56 (s, NH, 2H), 2.28 (d,  $J=8.0$  Hz,  $\text{N}(\text{CH}_3)_2$ , 36H).

### 1.2.4 Synthesis of $[\text{Cp}_2\text{Yb}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-Quo})_3]\text{Yb}(\text{HMPA})_2$ (**2a**)

To a toluene solution (20 mL) of **1a** (0.412 g, 0.225 mmol) was added PhNCO (0.107 g, 0.901 mmol) at 0  $^\circ\text{C}$ . The reaction mixture was stirred at room temperature overnight. The solution was concentrated and cooled at  $-15$   $^\circ\text{C}$  for several days to give **2a** as a yellow powder. Crystals of **2a** suitable for X-ray analysis were obtained by recrystallization in a mixed solvent of toluene and THF. Yield: 0.230 g (53%). Anal. Calcd. for  $\text{C}_{66}\text{H}_{78}\text{N}_{12}\text{O}_8\text{P}_3\text{Yb}_4$ (%): C, 41.25; H, 4.09; N, 8.75; Yb, 36.02. Found(%): C, 41.29; H, 4.14; N, 8.69; Yb, 35.96. IR(Nujol,  $\text{cm}^{-1}$ ): 3 411 w, 3 339 s, 2 192 m, 1 598 m, 1 537 s, 1 465 s, 1 373 s, 1 300 m, 1 149 m, 991 s, 751 s.

### 1.2.5 Synthesis of $[\text{Cp}_2\text{Er}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^1\text{-Quo})_3]\text{Er}(\text{HMPA})_2$ (**2b**)

Following the method described for synthesis of **2a**, using **1b** (0.552 g, 0.30 mmol) and PhNCO (0.144 g, 1.21 mmol) afforded **2b** as a pink powder. Yield: 0.268 g (46%). Anal. Calcd. For  $\text{C}_{66}\text{H}_{78}\text{N}_{12}\text{O}_8\text{P}_2\text{Er}_4$ (%): C, 41.76; H, 4.14; N, 8.85; Er, 35.24. Found(%): C,

41.47; H, 4.04; N, 8.69; Er, 35.16. IR (Nujol,  $\text{cm}^{-1}$ ): 3 410 w, 3 339 s, 2 191 m, 1 597 m, 1 537s, 1 463 s, 1 373 s, 1 300 m, 1 149 m, 991 s, 753 s.

### 1.2.6 Synthesis of $[\text{Cp}_2\text{Y}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^1\text{-Quo})_3]\text{Y}(\text{HMPA})_2$ (**2c**)

Following the method described for synthesis of **2a**, using **1c** (0.408 g, 0.27 mmol) and PhNCO (0.128 g, 1.08 mmol) afforded **2c** as a light yellow powder. Yield: 0.214 g (50%). Anal. Calcd. for  $\text{C}_{66}\text{H}_{78}\text{N}_{12}\text{O}_8\text{P}_2\text{Y}_4$ (%): C, 50.01; H, 4.96; N, 10.60; Y, 22.44. Found: C, 49.96; H, 4.91; N, 10.49; Y, 22.39. IR (Nujol,  $\text{cm}^{-1}$ ): 3 407 w, 3 337 s, 2 192 m, 1 597 m, 1 536s, 1 463 s, 1 373 s, 1 301 m, 1 240 w, 1 147 m, 990 s, 756 s.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 25  $^\circ\text{C}$ ):  $\delta$  7.34~7.08 (m,  $\text{C}_6\text{H}_4$ , 12H), 6.15 (s,  $\text{C}_5\text{H}_5$ , 30H), 2.12 (s,  $\text{NMe}_2$ , 36H).

### 1.2.7 Synthesis of $\{\text{Cp}_2\text{Yb}[\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^3\text{-}i\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{-CONH}]\}_3\text{Yb}(\text{HMPA})_3$ (**3a**)

To a toluene solution (20 mL) of **1a** (0.412 g, 0.225 mmol) was added DIC (0.141 g, 1.12 mmol) at 0  $^\circ\text{C}$ . The reaction mixture was stirred at room temperature overnight. The solution was concentrated and cooled at  $-15$   $^\circ\text{C}$  for several days to give **3a** as a yellow powder. The yellow crystals of **3a**·THF suitable for X-ray analysis were obtained by recrystallization in a mixed solvent of toluene and THF. Yield: 0.389 g (70%). Anal. Calcd. for  $\text{C}_{90}\text{H}_{144}\text{N}_{21}\text{O}_6\text{P}_3\text{Yb}_4$ (%): C, 45.01; H, 6.04; N, 12.25; Yb, 28.82. Found(%): C, 45.14; H, 6.07; N, 12.17; Yb, 28.75. IR (Nujol,  $\text{cm}^{-1}$ ): 3 410 m, 3 381 w, 3 280 w, 1 600 w, 1 522 w, 1 460 vs, 1 377 s, 1 127 m, 837 w, 727 s.

### 1.2.8 Synthesis of $\{\text{Cp}_2\text{Er}[\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^3\text{-}i\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{-CONH}]\}_3\text{Er}(\text{HMPA})_3$ (**3b**)

Following the described method for synthesis of **3a**, using **1b** (0.552 g, 0.30 mmol) and DIC (0.152 g, 1.20 mmol) afforded **3b**·THF as light pink crystals. Yield: 0.375 g (50%). Anal. Calcd. for  $\text{C}_{90}\text{H}_{144}\text{N}_{21}\text{O}_6\text{P}_3\text{Er}_4$ (%): C, 45.45; H, 6.10; N, 12.37; Er, 28.13. Found(%): C, 45.44; H, 6.13; N, 12.31; Er, 28.05. IR(Nujol,  $\text{cm}^{-1}$ ): 3 409 m, 3 381 w, 3 279 w, 1 599 w, 1 556 w, 1 459 vs, 1 379 s, 1 158 w, 1 126 m, 988 w, 729 s.

### 1.2.9 Synthesis of $\{\text{Cp}_2\text{Y}[\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^3\text{-}i\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{-CONH}]\}_3\text{Y}(\text{HMPA})_3$ (**3c**)

Following the described method for synthesis of **3a**, using **1c** (0.468 g, 0.31 mmol) and DIC (0.154 g,

1.22 mmol) afforded **3c** as light yellow crystalline solid. Yield: 0.285 g (43%). Anal. Calcd. for  $C_{90}H_{144}N_{21}O_6P_3Y_4$  (%): C, 52.35; H, 7.03; N, 14.25; Y, 17.22. Found(%): C, 52.39; H, 7.09; N, 14.23; Er, 17.20. IR (Nujol,  $cm^{-1}$ ): 3 406 m, 3 380 w, 3 280 w, 1 598 w, 1 554 w, 1 460 vs, 1 377 s, 1 155 w, 1 128 m, 993 w, 726 w.  $^1H$  NMR ( $C_6D_6$ , 400 MHz, 25  $^{\circ}C$ ):  $\delta$  8.31 (s, NH, 3H), 7.23~6.99 (m,  $C_6H_4$ , 12H), 6.09 (s,  $C_5H_5$ , 30H), 3.75 (m,  $CH(CH_3)_2$ , 3H), 3.55 (s, NH, 3H), 3.33 (m,  $CH(CH_3)_2$ , 3H), 2.49(d,  $J=8.0$  Hz,  $N(CH_3)_2$ , 54H), 1.34 (d,  $J=6.4$  Hz,  $CH(CH_3)_2$ , 18H), 0.93 (d,  $J=6.4$  Hz,  $CH(CH_3)_2$ , 18H). Crystals of **3c**·THF suitable for X-ray analysis were obtained by layering *n*-hexane to its concentrated toluene/THF solution.

#### 1.2.10 Synthesis of $\{CpYb[\mu-\eta^1:\eta^2:\eta^2-PrNC(NH^iPr)NC_6H_4-CONH]\}_2$ (**4a**)

To a toluene solution (20 mL) of  $Cp_3Yb$  (0.238 g, 0.646 mmol) was added *o*-aminobenzamide (0.088 g, 0.646 mmol) at room temperature. After stirred at room temperature overnight, DIC (0.082 g, 0.646 mmol) was added to the resulting yellow turbid solution at 0  $^{\circ}C$ . Then, the reaction mixture was heated at 110  $^{\circ}C$  for 12 h. The hot clear solution was slowly cooled to room temperature, affording **4a** as yellow crystals. Yield: 0.300 g (93%). Anal. Calcd. for  $C_{38}H_{50}N_8O_2Yb_2$  (%): C, 45.78; H, 5.06; N, 11.24; Yb, 34.71. Found (%): C, 45.84; H, 5.02; N, 11.20; Yb, 34.65. IR (Nujol,  $cm^{-1}$ ): 3 396 m, 3 381 w, 1 598 w, 1 463 vs, 1 377 s, 1 327 m, 1 170 m, 1 124 w, 875 w, 763 s.

#### 1.2.11 Synthesis of $\{CpEr[\mu-\eta^1:\eta^2:\eta^2-PrNC(NH^iPr)NC_6H_4-CONH]\}_2$ (**4b**)

Following the method described for synthesis of **4a**, using  $Cp_3Er$  (0.326 g, 0.898 mmol), *o*-aminobenzamide (0.123 g, 0.898 mmol) and DIC (0.113 g, 0.898 mmol) afforded **4b** as light pink crystals. Yield: 0.400 g (91%). Anal. Calcd. for  $C_{38}H_{50}N_8O_2Er_2$  (%): C, 46.32; H, 5.11; N, 11.37; Er, 33.95. Found (%) C, 46.39; H, 5.15; N, 11.28; Er, 33.82. IR (Nujol,  $cm^{-1}$ ): 3 399 m, 3 379 w, 1 598 w, 1 548 w, 1 459 vs, 1 377 s, 1 172 m, 1 124 m, 874 w, 764 s.

#### 1.2.12 Synthesis of $\{CpY[\mu-\eta^1:\eta^2:\eta^2-PrNC(NH^iPr)NC_6H_4CO-NH]\}_2$ (**4c**)

Following the method described for synthesis of **4a**, using  $Cp_3Y$  (0.317 g, 1.11 mmol), *o*-aminobenzamide

(0.152 g, 1.11 mmol) and DIC (0.140 g, 1.11 mmol) afforded **4c** as light yellow crystals. Yield: 0.321 g (70%). Anal. Calcd. for  $C_{38}H_{50}N_8O_2Y_2$  (%): C, 55.08; H, 6.08; N, 13.52; Y, 21.46. Found(%): C, 55.09; H, 6.12; N, 13.50; Y, 21.45. IR (Nujol,  $cm^{-1}$ ): 3 399 m, 3 375 w, 1 741 w, 1 598 w, 1 547 w, 1 460 vs, 1 377 s, 1 171 m, 1 124 m, 763 s.  $^1H$  NMR ( $C_6D_6$ , 400 MHz, 25  $^{\circ}C$ ):  $\delta$  7.28~7.11 (m,  $C_6H_4$ , 8H), 6.94 (s, NH, 2H), 6.45 (s,  $C_5H_5$ , 10H), 6.12 (s, NH, 2H), 3.35~3.22 (m,  $CH(CH_3)_2$ , 4H), 1.28 (d,  $J=6.4$  Hz,  $CH_3$ , 6H), 0.86 (d,  $J=6.4$  Hz,  $CH_3$ , 6H).

#### 1.2.13 Transformation from **4a** to **3a**

To a toluene solution (20 mL) of **4a** (0.254 g, 0.255 mmol) was added HMPA (0.091 g, 0.510 mmol) at room temperature. After stirring for 12 h, the solution was concentrated and cooled at -15  $^{\circ}C$  for several days to give **3a** as yellow crystals. Yield: 0.165 g (54%).

#### 1.3 X-ray data collection, structure determination and refinement

Suitable single crystals were sealed under  $N_2$  in thin-walled glass capillaries for X-ray structural analysis. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo  $K\alpha$  radiation,  $\varphi$ - $\omega$  scan technique,  $\lambda=0.071\ 073$  nm). The intensity data were integrated by means of the SAINT program<sup>[23]</sup>. SADABS<sup>[24]</sup> was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against  $F^2$  using all reflections with the aid of the SHELXTL package<sup>[25]</sup>. All non-hydrogen atoms were found from the difference Fourier syntheses and refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Details of this SQUEEZE are given in the cif files. Crystal data, data collection, and processing parameters for the complexes are summarized in Table 1~2.

CCDC: 951003, **1a**; 951104, **1b**; 951102, **2a**; 951004, **3a**; 951106, **3b**; 951005, **3c**; 951103, **4a**; 951107, **4b**; 951105, **4c**.



**Table 1 Crystal and data collection parameters of complexes 1a, 1b and 4a~4c**

	1a	1b	4a	4b	4c
Formula	C <sub>60</sub> H <sub>80</sub> N <sub>14</sub> O <sub>6</sub> P <sub>2</sub> Yb <sub>4</sub>	C <sub>60</sub> H <sub>80</sub> N <sub>14</sub> O <sub>6</sub> P <sub>2</sub> Er <sub>4</sub>	C <sub>38</sub> H <sub>50</sub> N <sub>8</sub> O <sub>2</sub> Yb <sub>2</sub>	C <sub>38</sub> H <sub>50</sub> N <sub>8</sub> O <sub>2</sub> Er <sub>2</sub>	C <sub>38</sub> H <sub>50</sub> N <sub>8</sub> O <sub>2</sub> Y <sub>2</sub>
Formula weight	1 847.48	1 824.36	996.94	985.38	828.68
Crystal size/ mm	0.25×0.22×0.14	0.15×0.12×0.10	0.30×0.25×0.15	0.35×0.18×0.08	0.19×0.10×0.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> / nm	2.837 8(9)	3.091 3(10)	1.388 2(5)	1.390 9(3)	1.395 5(4)
<i>b</i> / nm	1.256 2(4)	1.330 0(4)	0.990 0(4)	0.993 2(2)	0.995 5(3)
<i>c</i> / nm	2.539 3(8)	2.466 4(8)	1.474 2(5)	1.477 2(3)	1.481 8(5)
$\beta$ / (°)	106.834(4)	112.082(4)	102.548(5)	102.550(2)	102.724(4)
<i>V</i> / nm <sup>3</sup>	8.664(5)	9.397(5)	1.977 7(12)	1.991 9(7)	2.007 9(10)
<i>Z</i>	4	4	2	2	2
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.416	1.290	1.674	1.643	1.371
$\mu$ / mm <sup>-1</sup>	4.360	3.611	4.742	4.226	2.917
<i>F</i> (000)	3 584	3 552	980	972	856
Reflection measured	19 258	19 109	8 648	8 713	8 896
Unique reflection	8 420 ( <i>R</i> <sub>int</sub> =0.046 0)	8 311 ( <i>R</i> <sub>int</sub> =0.038 5)	3 822 ( <i>R</i> <sub>int</sub> =0.076 8)	3 890 ( <i>R</i> <sub>int</sub> =0.032 1)	2 916( <i>R</i> <sub>int</sub> =0.068 7)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.002	1.006	1.015	0.993	0.997
Final <i>R</i> indices	<i>R</i> <sub>1</sub> =0.040 3,	<i>R</i> <sub>1</sub> =0.039 1,	<i>R</i> <sub>1</sub> =0.051 3,	<i>R</i> <sub>1</sub> =0.033 3,	<i>R</i> <sub>1</sub> =0.038 6,
[ <i>I</i> >2σ( <i>I</i> )]	<i>wR</i> <sub>2</sub> =0.079 0	<i>wR</i> <sub>2</sub> =0.105 6	<i>wR</i> <sub>2</sub> =0.134 4	<i>wR</i> <sub>2</sub> =0.088 2	<i>wR</i> <sub>2</sub> =0.055 7
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.074 0,	<i>R</i> <sub>1</sub> =0.062 0,	<i>R</i> <sub>1</sub> =0.061 4,	<i>R</i> <sub>1</sub> =0.040 2,	<i>R</i> <sub>1</sub> =0.083 2,
	<i>wR</i> <sub>2</sub> =0.082 7	<i>wR</i> <sub>2</sub> =0.111 2	<i>wR</i> <sub>2</sub> =0.140 7	<i>wR</i> <sub>2</sub> =0.093 1	<i>wR</i> <sub>2</sub> =0.059 3

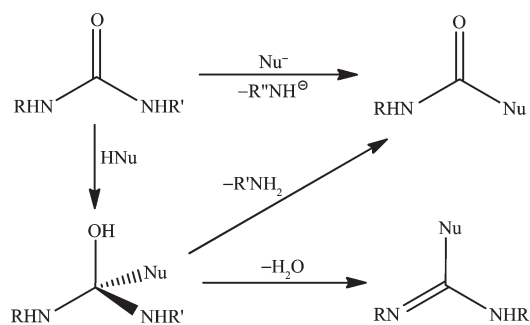
**Table 2 Crystal and data collection parameters of complexes 2a and 3·THF**

	2a	3a·THF	3b·THF	3c·THF
Formula	C <sub>66</sub> H <sub>78</sub> N <sub>12</sub> O <sub>8</sub> P <sub>2</sub> Yb <sub>4</sub>	C <sub>94</sub> H <sub>152</sub> N <sub>21</sub> O <sub>7</sub> P <sub>3</sub> Yb <sub>4</sub>	C <sub>94</sub> H <sub>152</sub> Er <sub>4</sub> N <sub>21</sub> O <sub>7</sub> P <sub>3</sub>	C <sub>94</sub> H <sub>152</sub> N <sub>21</sub> O <sub>7</sub> P <sub>3</sub> Y <sub>4</sub>
Formula weight	1 921.50	2 473.44	2 450.32	2 136.92
Crystal size/ mm	0.30×0.20×0.15	0.15×0.06×0.05	0.40×0.15×0.10	0.20×0.12×0.12
Crystal system	Trigonal	Triclinic	Triclinic	Triclinic
Space group	<i>P6<sub>3</sub>/m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / nm	1.563 4(4)	1.579 2(5)	1.586 9(4)	1.590 4(11)
<i>b</i> / nm	1.563 4(4)	1.858 6(6)	1.806 1(4)	1.869 4(13)
<i>c</i> / nm	2.074 7(8)	2.461 4(7)	2.494 5(6)	2.471 2(16)
$\alpha$ / (°)	90	77.664(5)	77.505(3)	77.669(11)
$\beta$ / (°)	90	78.642(5)	77.840(3)	78.692(10)
$\gamma$ / (°)	120	66.029(4)	66.919(3)	65.831(10)
<i>V</i> / nm <sup>3</sup>	4.392(2)	6.400(3)	6.358(3)	6.500(8)
<i>Z</i>	2	2	2	2
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.453	1.284	1.242	1.092
$\mu$ / mm <sup>-1</sup>	4.305	2.983	2.698	1.854
<i>F</i> (000)	1 864	2 488	2 390	2 240
Reflection measured	18 196	26 698	25 656	27 071
Unique reflection	2 661 ( <i>R</i> <sub>int</sub> =0.067 8)	22 124 ( <i>R</i> <sub>int</sub> =0.057 8)	21 540 ( <i>R</i> <sub>int</sub> =0.063 1)	22 493 ( <i>R</i> <sub>int</sub> =0.063 2)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.002	1.016	1.052	1.204
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.051 6, <i>wR</i> <sub>2</sub> =0.150 8	<i>R</i> <sub>1</sub> =0.059 8, <i>wR</i> <sub>2</sub> =0.140 1	<i>R</i> <sub>1</sub> =0.076 3, <i>wR</i> <sub>2</sub> =0.145 5	<i>R</i> <sub>1</sub> =0.072 4, <i>wR</i> <sub>2</sub> =0.155 0
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.067 3, <i>wR</i> <sub>2</sub> =0.159 7	<i>R</i> <sub>1</sub> =0.116 1, <i>wR</i> <sub>2</sub> =0.150 0	<i>R</i> <sub>1</sub> =0.185 8, <i>wR</i> <sub>2</sub> =0.162 7	<i>R</i> <sub>1</sub> =0.175 5, <i>wR</i> <sub>2</sub> =0.165 6

## 2 Results and discussion

### 2.1 Syntheses and characterization of lanthanocene derivatives with the *o*-aminobenzamido dianion ligand

Considering that the ureido resulting from addition of amine to isocyanate might potentially undergo the nucleophilic substitution or addition<sup>[26-27]</sup> (Scheme 3), our interest in the rare earth metal-mediated C=N bond cleavage of isocyanates prompted us to explore the possibility of reacting two coordinated NH anions with one isocyanate molecule.



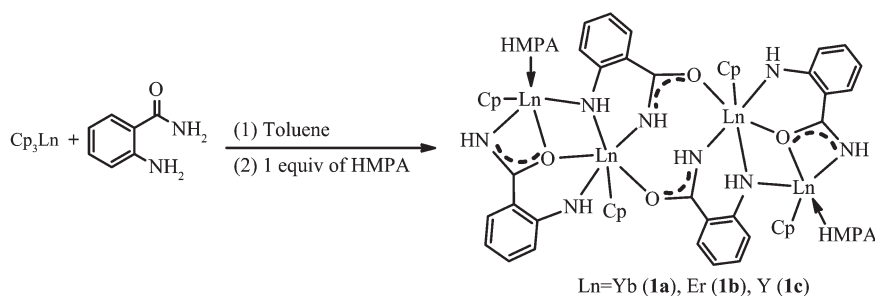
Scheme 3

On the basis of this idea, we focused our attention on using the linked NH/CONH dianion lanthanide complexes as the template of the target reaction as the anionic NH and CONH groups offer a degree of selectivity, in which the two NH groups can react either with a reagent having two functionalities or with two separate reagents bearing the same or different functionality. Thus, it may be expected that the different reactivity between coordinated NH and CONH anions toward the same functionality would control reaction degree of advancement, for less reactive substrates only the NH addition takes place, whereas the more reactive ones lead to the occurrence

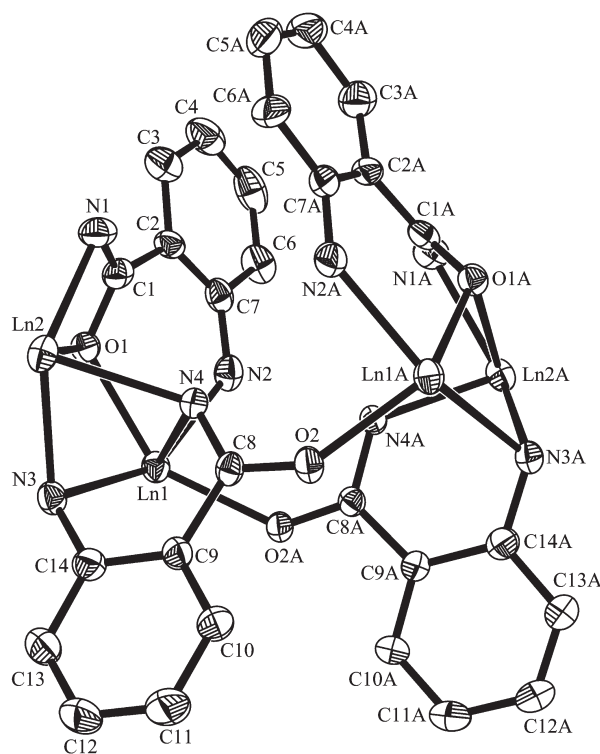
of a tandem reaction involved the two kinds of amido groups. Three *o*-aminobenzamido dianion lanthanide complexes  $[\text{CpLn}(\mu\text{-}\eta^2\text{:}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})\text{LnCp}(\text{HMPA})]_2$  ( $\text{Ln}=\text{Yb}$ , **1a**;  $\text{Er}$ , **1b**;  $\text{Y}$ , **1c**) as the designed starting materials were synthesized in good yields by protonolysis of  $\text{Cp}_3\text{Ln}$  with *o*-aminobenzamide followed by crystallization in a HMPA and toluene mixture (Scheme 4).

Complexes **1a**~**1c** are air- and moisture-sensitive, and readily dissolved in toluene and THF. They are thermally stable at room temperature. Complexes **1a**~**1c** were characterized by elemental analysis and spectroscopic methods. In the IR spectra, all of them show two sharp N-H stretching vibration peaks at about 3 310 and 3 365  $\text{cm}^{-1}$  attributable to the different chemical environments of NH groups.  $^1\text{H}$  NMR spectra of complex **1c** show four NH resonance peaks at 7.92, 7.90 3.71, and 3.56, respectively. The solid-state structures of **1a** and **1b** were determined by X-ray analysis.

As shown in Fig.1, X-ray analysis results show that **1a** and **1b** are isostructural, four *o*-aminobenzamido dianion ligands connect with two  $\text{CpLn}$  and two  $\text{CpLn}(\text{HMPA})$  fragments via two different  $\mu\text{-}\eta^2\text{:}\eta^2\text{-}$  and  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}$  bonding modes, respectively. These bond parameters indicate that the amido moiety acts as both a bridging and side-on chelating group, in which the negative charge is delocalized over the OCN unit. Characteristically, both of bridging O and N atoms have two distinctive metal-oxygen (nitrogen) distances. One is between those expected for an  $\text{Ln}^{3+}\text{-O(N)}$  single bond and an  $\text{Ln}^{3+}\leftarrow\text{O(N)}$  donor bond, while another falls in the range of the  $\text{Ln}^{3+}\leftarrow\text{O(N)}$  donating bond lengths for neutral oxygen or nitrogen donor ligands<sup>[28]</sup>.



Scheme 4



Hydrogen atoms, Cp rings and HMPA ligands are omitted for clarity; Selected bond lengths (nm) and angles ( $^{\circ}$ ): for **1a**: Yb(1)-N(2) 0.228 5(6), Yb(1)-O(1) 0.226 0(5), Yb(1)-O(2A) 0.226 0(4), Yb(1)-N(3) 0.247 0(6), Yb(1)-N(4) 0.255 7(5), Yb(2)-N(1) 0.232 7(6), Yb(2)-O(1) 0.238 2(5), Yb(2)-O(3) 0.220 6(4), Yb(2)-N(3) 0.231 2(6), N(2)-Yb(1)-O(1) 74.6(2), N(3)-Yb(2)-N(4) 68.1(2); For **1b**: Er(1)-N(2) 0.231 3(6), Er(1)-O(1) 0.226 9(5), Er(1)-O(2A) 0.227 9(5), Er(1)-N(3) 0.249 1(5), Er(1)-N(4) 0.253 8(6), Er(2)-N(1) 0.236 0(6), Er(2)-O(1) 0.241 5(5), Er(2)-O(3) 0.219 3(5), Er(2)-N(3) 0.234 3(6), N(1)-C(1) 0.128 1(9), O(1)-C(1) 0.130 6(8), N(4)-C(8) 0.134 5(9), O(2)-C(8) 0.126 4(8), N(2)-Er(1)-O(1) 74.4(2), N(3)-Er(2)-N(4) 67.4(2), N(1)-C(1)-O(1) 115.3(6), N(4)-C(8)-O(2) 123.8(6); Symmetry codes: A:  $-x, y, 0.5-z$

Fig.1 Thermal ellipsoid (30%) plot of complexes  $\{CpLn(\mu-\eta^2:\eta^2-NHC_6H_4CONH)[\mu_3-\eta^1:\eta^1:\eta^2-NHC_6H_4CONH]LnCp-(HMPA)\}_2$  (Ln=Yb, **1a**; Er, **1b**)

This difference may be attributed to the chelating coordination effect caused by the amido ligand.

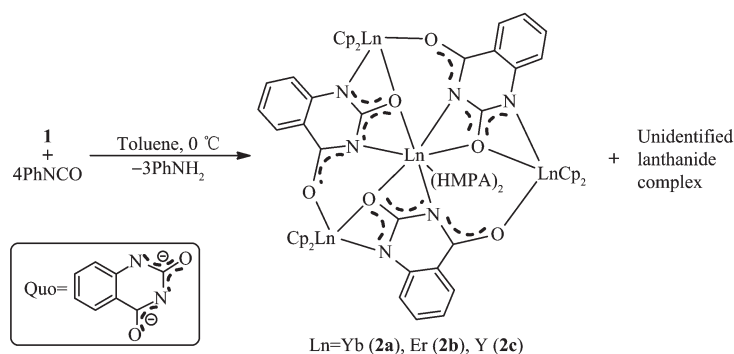
## 2.2 Reaction of **1** with phenyl isocyanate

With dianionic *o*-aminobenzamido organolanthanides **1** in hand, we next explored their reactivity toward phenyl isocyanate. As expected, treatment of **1** with PhNCO ( $n_{PhNCO}/n_1=4$ ) in toluene led to the occurrence of an unusual tandem addition/cyclization/amine elimination/ligand redistribution reaction, giving the dianionic quinazolyldiolate lanthanide complexes  $\{Cp_2Ln[\mu_3-\eta^2:\eta^2:\eta^1-Quo]\}_3Ln(HMPA)_2$  (Ln=Yb, **2a**; Er, **2b**; Y, **2c**) in moderate isolated yields (Scheme 5). The elimination product PhNH<sub>2</sub> was unambiguously identified by GC-MS, but attempts to isolate another metal-containing product were unsuccessful. The metathesis reactions of isocyanates with organolanthanide complexes are rarely observed<sup>[20-21]</sup>. This is the

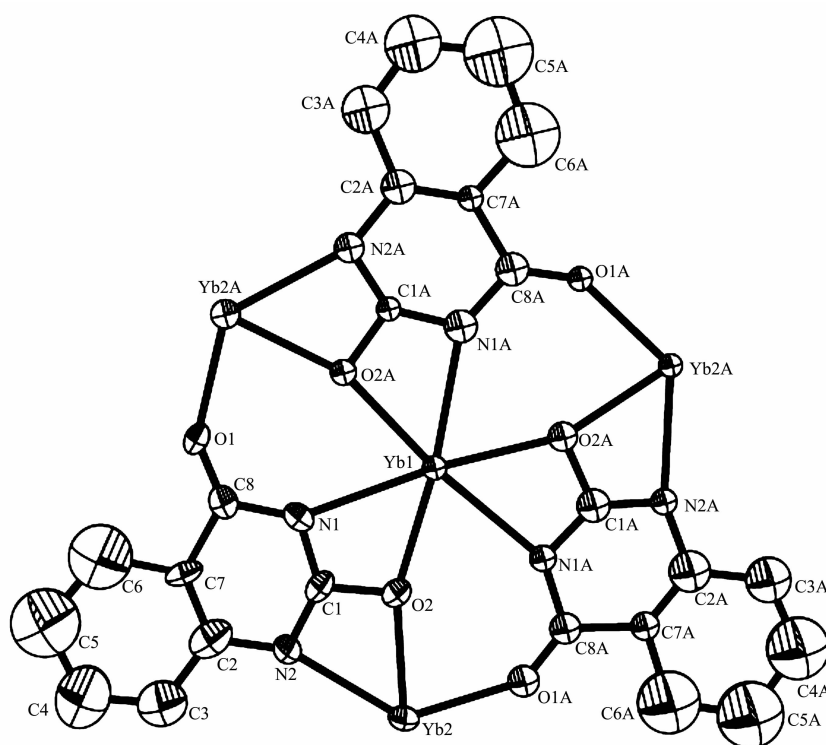
first example of the amido complex-mediated C=N bond cleavage of isocyanates, and provides an effective method for the construction of quinazolyldiol skeleton<sup>[29]</sup>.

Complexes **2a~2c** are readily dissolved in THF but slightly soluble in toluene. They were characterized by elemental analysis and IR spectroscopy. The <sup>1</sup>H NMR spectra of **2c** was also determined and showed that there is no N-H resonance absorption peak. The structure of **2a** was identified by X-ray single-crystal diffraction analysis. As shown in Fig.2, **2a** is a tetranuclear structure possessing three bridging dianionic quinazolyldione ligands. **2a** has a three-fold rotation axis on the O-O alignment, and the three ytterbium and two HMPA oxygen atoms occupy an equatorial plane and an apical position of the hexahedral skeletal structure, respectively (Fig.2). The





Scheme 5



Hydrogen atoms, Cp rings and HMPA ligands are omitted for clarity; Selected bond lengths (nm) and angles (°): Yb(1)-N(1) 0.254(1), Yb(1)-O(2) 0.234(1), Yb(1)-O(3) 0.217(1), Yb(2)-N(2) 0.244(1), Yb(2)-O(2) 0.228(1), Yb(2)-O(1B) 0.224(1), C(2)-N(2) 0.136(2), C(1)-N(2) 0.127(2), C(1)-N(1) 0.130(2), C(1)-O(2) 0.136(2), C(8)-N(1) 0.134(2), C(8)-O(1) 0.121(2), N(1)-C(1)-N(2) 136(1), C(1)-N(1)-C(8) 118(1), N(1)-C(8)-C(7) 107(1); Symmetry codes: A:  $-x+y, -x+1, -z+1.5$ ; B:  $-y+1, x-y+1, z$

Fig.2 Thermal ellipsoid (30%) plot of complex  $[\text{Cp}_2\text{Yb}[\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-Quo}]]_3\text{Yb}(\text{HMPA})_2$  (**2a**)

four Yb atoms locate in two different coordinate environments. Atoms Yb(2), Yb(2A) and Yb(2B) are coordinated by one chelating  $\eta^2\text{-N,O}$  unit, one non-bridging oxygen atom and two  $\eta^5\text{-Cp}$  groups, respectively, to form a distorted trigonal-bipyramidal geometry, while the central Yb(1) is coordinated by three  $\eta^2\text{-N,O}$  units from different quinazolyldiolate ligands and two HMPA oxygen atoms to form a hexagonal bipyramidal geometry. The bond parameters

indicate that the  $\pi$ -electrons of  $\text{C}=\text{O}$  and  $\text{C}=\text{N}$  double bonds are delocalized over the pyrimidinyldionate skeleton. The Yb-O distances are in normal range<sup>[5c]</sup>. The rather long distances between ytterbium and N atoms may be attributed to both the rigidity of the quinazolyldiolate ring and the steric crowding<sup>[30]</sup>.

### 2.3 Reactivity of **1** toward diisopropylcarbodiimide

To obtain additional insight into the mechanism

and scope of the reaction, we further examined the behavior of **1** toward carbodiimide. In markedly contrast to isocyanate, treatment of **1** with  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  ( $n_{\text{ligand}}/n_1=4$ ) provided  $\{\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{:}\eta^2\text{-}\eta^2\text{-}\text{PrNC}(\text{NH}^i\text{Pr})\text{NC}_6\text{H}_4\text{CONH}]\}_3\text{Ln}(\text{HMPA})_3$  ( $\text{Ln}=\text{Yb}$ , **3a**; Er, **3b**; Y, **3c**) as the main metal-containing products, even with a prolonged heating at 110 °C (Scheme 6). In addition, **3a**~**3c** are inactive to excess  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ . These results indicate that  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  is preferentially added to NH rather than CONH group. The coordinated CONH group is inert, and undergoes neither addition to  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  nor nucleophilic attack to the newly formed guanidinate ligand under the conditions involved. This difference might be attributed to the strong chelating interaction between CONH and metal, leading to the lower nucleophilicity compared with the NH group.

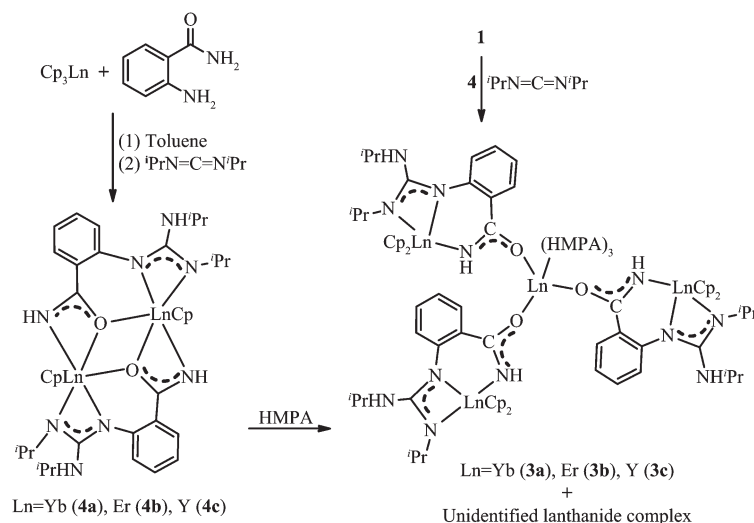
Crystallographic data for **3** show that there are two independent molecules (Fig.3), crystallizing in one asymmetrical unit. It is noteworthy that the  $\pi$ -electrons of the C=N double bond of two guanidinate groups are delocalized over the N-C-N unit (N(2)-C(1) and N(4)-C(1), 0.135(2) and 0.134(2) nm; C(49)-N(10) and C(49)-N(12), 0.136(2) and 0.135(2) nm), whereas the bond parameters (N(6)-C(25) and N(8)-C(25)) of a third guaninate group suggest a tendency toward CN double and single bonds (cf. mean values of 0.136 nm for  $\text{C}(\text{sp}^2)\text{-N}$  and 0.129 nm for  $\text{C}(\text{sp}^2)=\text{N}$ )<sup>[31]</sup>.

In order to exclude the effect of HMPA, the

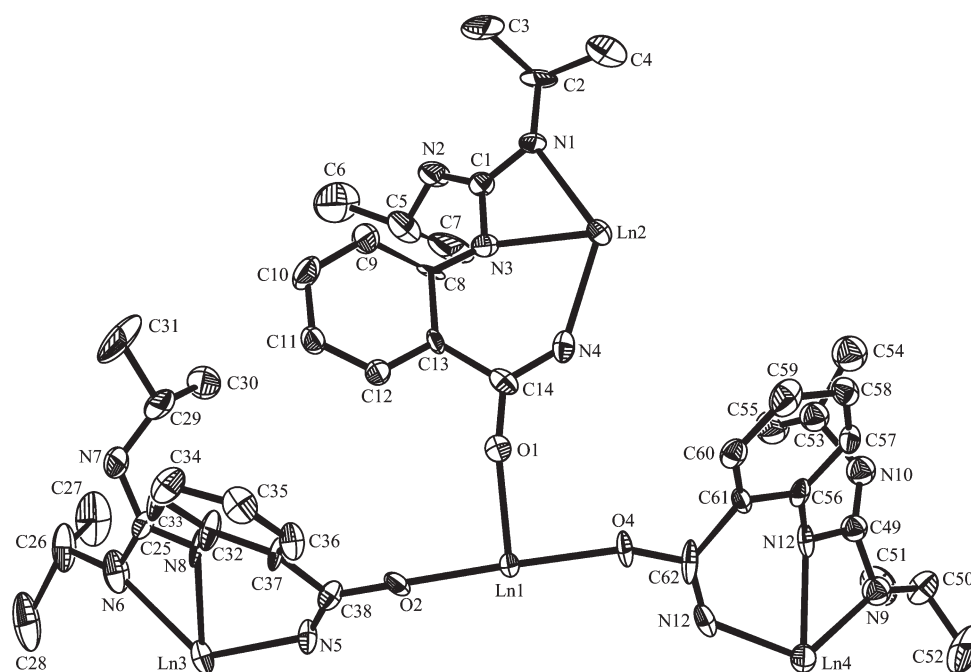
HMPA-free reaction was examined. As shown in Scheme 6, the treatment of  $\text{Cp}_3\text{Ln}$  with *o*-aminobenzamide followed by reacting with  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$  gave  $\{\text{CpLn}[\mu\text{-}\eta^1\text{:}\eta^2\text{-}\eta^2\text{-}\text{NHCOC}_6\text{H}_4\text{NC}(\text{NH}^i\text{Pr})\text{N}^i\text{Pr}]\}_2$  ( $\text{Ln}=\text{Yb}$ , **4a**; Er, **4b**; Y, **4c**), indicating that the CONH group in **4** is also inert. Interestingly, **4** can be transformed into **3** in the presence of HMPA, revealing an unusual HMPA-induced ligand redistribution of organolanthanides.

Crystals suitable for a single-crystal X-ray study were grown by slow cooling a hot toluene solution of **4**. As shown in Fig.4, compounds **4a**, **4b** and **4c** are isostructural, and each of the lanthanide atoms is coordinated by one  $\eta^5\text{-C}_5\text{H}_5$  ligand, one chelating  $\eta^2\text{-CONH}$  with side donating coordination, one chelating guanidinate group and one bridging oxygen atom, indicating that only NHAr groups have combined with  ${}^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ . There are no informal bond lengths and angles compared to other guanidinate lanthanide complexes<sup>[27]</sup>.

Based on these experimental results, a possible reaction pathway for the formation of **2** is proposed in Scheme 7. Coordination insertion of  $\text{PhNCO}$  into the  $\text{Ln-NHAr}$  bond followed by a ligand redistribution give the intermediate **II**, which places the CONH group and the resulting ureido into close proximity, as observed in the formation of **3**. A sequential addition of the activated N-H to the C=N double bond leads to the occurrence of the cyclization<sup>[13]</sup>. Reductive

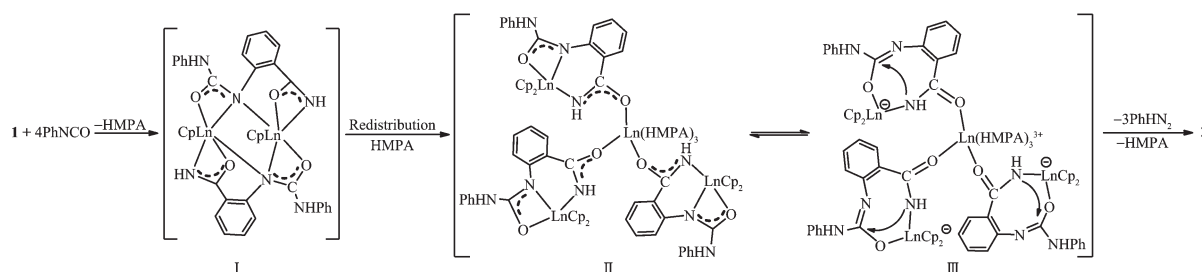


Scheme 6



Hydrogen atoms and HMPA ligands are omitted for clarity; Selected bond lengths (nm) and angles ( $^{\circ}$ ) for **3a**: Yb(1)-O(1) 0.214(1), Yb(1)-O(4) 0.222(1), Yb(2)-N(2) 0.241(1), Yb(2)-N(4) 0.231(1), Yb(2)-N(1) 0.242(1), C(1)-N(2) 0.131(2), C(1)-N(4) 0.133(2), Yb(3)-N(6) 0.241(1), Yb(3)-N(8) 0.228(1), Yb(3)-N(5) 0.234(1), C(25)-N(6) 0.132(1), C(25)-N(8) 0.141(2), Yb(4)-N(10) 0.246(1), Yb(4)-N(12) 0.232(1), Yb(4)-N(9) 0.235(1), C(49)-N(10) 0.131(2), C(49)-N(12) 0.134(1), N(2)-C(1)-N(4) 112(1); For **3b**: Er(1)-O(1) 0.222(1), Er(1)-O(4) 0.218(1), Er(2)-N(3) 0.230(1), Er(2)-N(4) 0.233(1), Er(2)-N(1) 0.241(1), C(1)-N(2) 0.126(2), C(1)-N(4) 0.142(2), Er(3)-N(6) 0.242(2), Er(3)-N(8) 0.233(1), Er(3)-N(5) 0.235(1), C(25)-N(6) 0.136(2), C(25)-N(8) 0.135(2), C(25)-N(7) 0.135(2), Er(4)-N(10) 0.240(1), Er(4)-N(12) 0.228(1), Er(4)-N(9) 0.238(1), C(49)-N(10) 0.139(2), C(49)-N(12) 0.148(2), N(2)-C(1)-N(4) 112(1); For **3c**: Y(1)-O(1) 0.216(1), Y(1)-O(4) 0.228(1), Y(2)-N(2) 0.247(1), Y(2)-N(4) 0.233(1), Y(2)-N(1) 0.238(1), C(1)-N(2) 0.131(1), C(1)-N(4) 0.141(1), Y(3)-N(6) 0.246(1), Y(3)-N(8) 0.2339(8), Y(3)-N(5) 0.2414(7), C(25)-N(6) 0.132(1), C(25)-N(8) 0.138(1), C(25)-N(7) 0.136(1), Y(4)-N(10) 0.244(1), Y(4)-N(12) 0.235(1), Y(4)-N(9) 0.235(1), C(49)-N(10) 0.130(1), C(49)-N(12) 0.138(1), C(49)-N(11) 0.138(1), N(2)-C(1)-N(4) 115 (1)

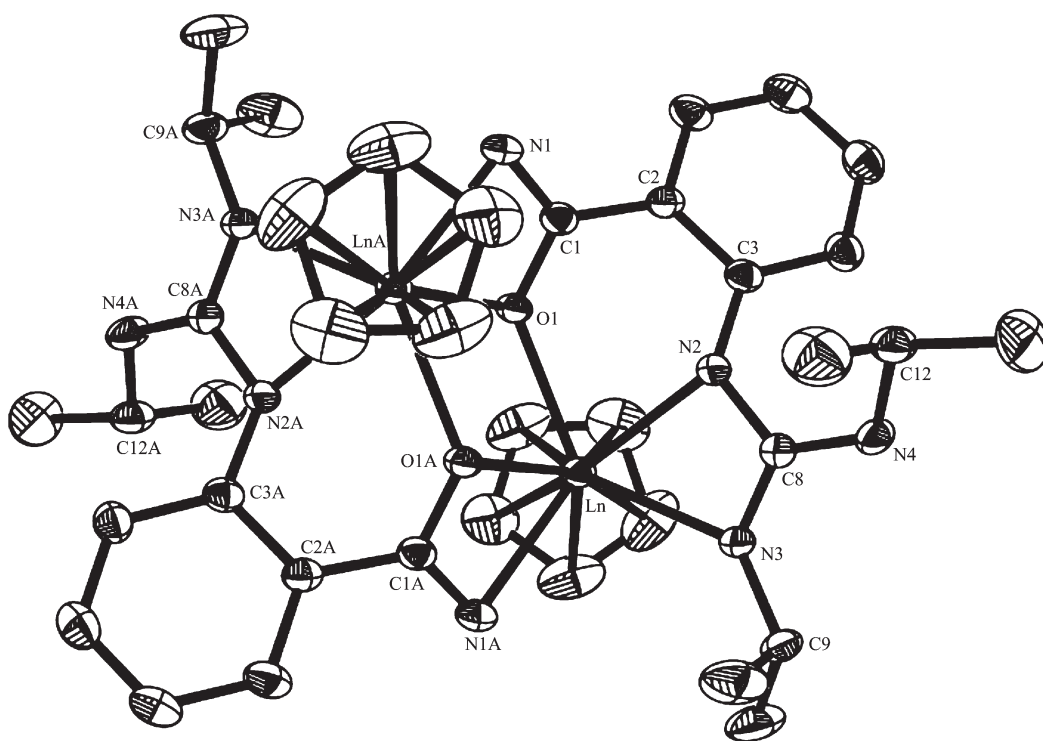
Fig.3 Thermal ellipsoid (30%) plot of complex  $\{\text{Cp}_2\text{Ln}[\mu\text{-}\eta^1\text{:}\eta^2\text{-}\eta^2\text{-PrNC(NH'Pr)NC}_6\text{H}_4\text{CONH}]\}_3\text{Ln}(\text{HMPA})_3$  (Ln=Yb, **3a**; Er, **3b**; Y, **3c**)



Scheme 7

elimination of  $\text{PhNH}_2$  generates the quinazolyldiolate ring. Obviously, the formation of a more stable aromatic quinazolyldiolate skeleton might contribute to the occurrence of the cyclization/amine-elimination reaction of the putative amido intermediate (II). But

attempts to isolate the intermediates I and II have been unsuccessful due to their thermodynamic instability. A tandem addition/cyclization/elimination reaction is observed in the treatment of **1** with  $\text{PhNCO}$ , whereas for **3** no subsequent reactions are



Hydrogen atoms are omitted for clarity; Selected bond lengths (nm) and angles ( $^{\circ}$ ) for **4a**: Yb-N(3) 0.233(1), C(3)-N(2) 0.137(1), N(2)-Yb-N(3) 57(2), N(1)-C(1)-O(1) 114(1), Yb-O(1)-Yb(A) 112(2), N(2)-C(8)-N(3) 114(1); For **4b**: Er-N(3) 0.234(1), C(3)-N(2) 0.138(1), N(2)-Er-N(3) 57(2), N(1)-C(1)-O(1) 115(1), Er-O(1)-Er(A) 111(2), N(2)-C(8)-N(3) 112(1); For **4c**: Y-N(3) 0.235(1), C(3)-N(2) 0.138(1), O(1)-Y-O(1A) 69(1), N(1)-C(1)-O(1) 114(1), N(1)-C(1)-C(2) 125(1), Y-O(1)-Y(A) 111(1), N(2)-C(8)-N(3) 112(1); Symmetry codes: A: 0.5-x, 0.5+y, 0.5-z

Fig.4 Thermal ellipsoid (30%) plot of complex  $[\text{CpLn}(\mu\text{-}\eta^1\text{:}\eta^2\text{-OCNHC}_6\text{H}_4\text{NC}(\text{NHPr})\text{NPr})]_2$  (Ln=Yb, **4a**; Er, **4b**; Y, **4c**)

observed even with a longer reaction time and higher temperature. It is possible that both the larger steric hindrance and the weaker electrophilic reactivity of guanidinate compared to ureido prevent the subsequent cyclization.

### 3 Conclusions

In conclusion, three new tetranuclear lanthanocene derivatives incorporating the *o*-aminobenzamido dianion ligand,  $[\text{CpLn}(\mu\text{-}\eta^1\text{:}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-NHC}_6\text{H}_4\text{CONH})\text{LnCp}(\text{HMPA})]_2$  (Ln=Yb, Er, Y), have been synthesized by reaction of  $\text{Cp}_3\text{Ln}$  with *o*-aminobenzamide followed by crystallization in a mixed HMPA and toluene solvent. The first example of tandem reaction of two coordinated NH moieties with an isocyanate molecule resulting in the formation of a dianionic quinazolyldiolate fragment is described. Furthermore, these *o*-aminobenzamido complexes can

also undergo the single NH addition to carbodiimide selectively. In addition, an unusual HMPA-induced ligand redistribution of organolanthanides is observed in these processes. The present results demonstrate that *o*-aminobenzamido organolanthanide complexes can be expected to have synthetic potential because they provide a reaction system in which the two coordinated NH moieties show different reactivity toward the same functionality. In this case, after the first reaction one surviving NH group could undergo cyclization across the first reaction product. On the other hand, this work provides an alternative route to carbonylation of organic substrates, which is very difficult to achieve by rare earth metal system due to the mismatch in the orbital energy of the hard rare earth metal ion and the soft CO ligand. The catalytic synthesis of heterocycles, which is based on such reactions, is undergoing.

## References:

- [1] (a) Molander G A, Romero J A C. *Chem. Rev.*, **2002**, **102**(6): 2161-2185  
(b) Muller T E, Hultsch K C, Yus M. *Chem. Rev.*, **2008**, **108**(9):3795-3892  
(c) Bartoli G, Marcantoni E, Marcolini M, et al. *Chem. Rev.*, **2010**, **110**(10):6104-6143  
(d) Zeng X M. *Chem. Rev.*, **2013**, **113**(8):6864-6900
- [2] (a) Evans W J, Davis B L. *Chem. Rev.*, **2002**, **102**(6):2119-2136  
(b) Zhou X G, Zhu M. *J. Organomet. Chem.*, **2002**, **647**(1/2): 28-49  
(c) Hong S, Marks T J. *Acc. Chem. Res.*, **2004**, **37**(9):673-686  
(d) Zhang J, Zhou X G. *Dalton Trans.*, **2011**, **40**(38):9637-9648  
(e) Liu R T, Zhou X G. *Chem. Commun.*, **2013**, **49**(31):3171-3187
- [3] (a) Jeske G, Lauke H, Mauermann H, et al. *J. Am. Chem. Soc.*, **1985**, **107**(26):8091-8103  
(b) Cui D M, Nishiura M, Hou Z M. *Angew. Chem. Int. Ed.*, **2005**, **44**(6):959-962  
(c) Wang B L, Wang D, Cui D M, et al. *Organometallics*, **2007**, **26**(13):3167-3172  
(d) Kaneko H, Nagae H, Tsurugi H, et al. *J. Am. Chem. Soc.*, **2011**, **133**(49):19626-19629  
(e) Zhou S L, Wang H Y, Ping J, et al. *Organometallics*, **2012**, **31**(5):1696-1702  
(f) Hong L C, Lin W J, Zhou X G, et al. *Chem. Commun.*, **2013**, **49**(49):5589-5591
- [4] (a) Li W B, Xue M Q, Xu F, et al. *Dalton Trans.*, **2012**, **41**(27): 8252-8260  
(b) Basalov I V, Lyubov D M, Fukin G K, et al. *Angew. Chem. Int. Ed.*, **2012**, **51**(14):3444-3447  
(c) Sun J L, Berg D J, Twamley B. *Organometallics*, **2008**, **27**(4):683-690  
(d) Yang Y, Cui D M, Chen X S. *Dalton Trans.*, **2010**, **39**(16): 3959-3967  
(e) Li X Q, Hong J Q, Zhou X G, et al. *Organometallics*, **2010**, **29**(20):4606-4610  
(f) Pi C F, Li X Q, Zhang L L, et al. *Inorg. Chem.*, **2010**, **49**(17):7632-7634  
(g) Zhang Z X, Bu X L, Zhang J, et al. *Organometallics*, **2010**, **29**(9):2111-2117  
(h) Lu E L, Chen Y F, Leng X B. *Organometallics*, **2011**, **30**(20):5433-5441  
(i) Casely I J, Ziller J W, Evans W J. *Organometallics*, **2011**, **30**(18):4873-4881
- [5] (a) Liu R T, Zhang C M, Zhu Z Y, et al. *Chem. Eur. J.*, **2006**, **12**(26):6940-6952  
(b) Li X Q, Liu R T, Zhang Z X, et al. *Organometallics*, **2010**, **29**(15):3298-3302  
(c) Chu J X, Lu E L, Liu Z X, et al. *Angew. Chem. Int. Ed.*, **2011**, **50**(33):7677-7680  
(d) Shao Y L, Zhang F J, Zhang J, et al. *Angew. Chem. Int. Ed.*, **2016**, **55**(38):11485-11489  
(e) Hong J Q, Li Z H, Chen Z N, et al. *Dalton Trans.*, **2016**, **45**(15):6641-6649  
(f) Huang S J, Shao Y L, Zhang L X, et al. *Angew. Chem. Int. Ed.*, **2015**, **54**(48):14452-14456  
(g) Luo Y, Teng H L, Nishiura M, et al. *Angew. Chem. Int. Ed.*, **2017**, **56**(31):9207-9210
- [6] (a) Yasuda H, Yamamoto H, Yokota K, et al. *J. Am. Chem. Soc.*, **1992**, **114**(12):4908-4910  
(b) Giardello M A, Yamamoto Y, Brard L, et al. *J. Am. Chem. Soc.*, **1995**, **117**(11):3276-3277  
(c) Zhang W X, Nishiura M, Hou Z M. *Angew. Chem. Int. Ed.*, **2008**, **47**(50):9700-9703  
(d) Yang J Y, Shen H, Xie Z W. *J. Organomet. Chem.*, **2015**, **798**:204-208  
(e) Xu L, Zhai M K, Wang F, et al. *Dalton Trans.*, **2016**, **45**(43):17108-17112  
(f) Song G Y, Wang B L, Nishiura M, et al. *Chem. Eur. J.*, **2015**, **21**(23):8394-8398  
(g) Xu P F, Yao Y M, Xu X. *Chem. Eur. J.*, **2017**, **23**(6):1263-1267
- [7] (a) Molander G A, Romero J A C. *Chem. Rev.*, **2002**, **102**(6): 2161-2185  
(b) Konkol M, Kondracka M, Voth P, et al. *Organometallics*, **2008**, **27**(15):3774-3784  
(c) Ohashi M, Konkol M, Rosal D, et al. *J. Am. Chem. Soc.*, **2008**, **130**(22):6920-6921  
(d) Barros N, Eisenstein O, Maron L. *Dalton Trans.*, **2010**, **39**(44):10757-10767  
(e) Abinet E, Spaniol T P, Okuda J. *Chem. Asian J.*, **2011**, **6**(2):389-391
- [8] (a) Lauterwasser F, Hayes P G, Piers W E, et al. *Adv. Synth. Catal.*, **2011**, **353**(8):1384-1390  
(b) Zhang Y Y, Yao W, Li H, et al. *Organometallics*, **2012**, **31**(13):4670-4679  
(c) Trambitas A G, Melcher D, Hartenstein L, et al. *Inorg. Chem.*, **2012**, **51**(12):6753-6761  
(d) Reznichenko A L, Hultsch K C. *Organometallics*, **2013**, **32**(5):1394-1408  
(e) Huang S J, Shao Y L, Zhang L X, et al. *Angew. Chem. Int. Ed.*, **2015**, **54**(48):14452-14456  
(f) Hong S, Marks T J. *Acc. Chem. Res.*, **2004**, **37**(9):673-686
- [9] (a) Yu X H, Seo S Y, Marks T J. *J. Am. Chem. Soc.*, **2007**,



- 129**(23):7244-7245
- (b)Seo S Y, Yu X H, Marks T J. *J. Am. Chem. Soc.*, **2009**, **131**(1):263-276
- [10](a)Weiss C J, Marks T J. *Dalton Trans.*, **2010**,**39**:6576-6588  
(b)Weiss C J, Wobser S D, Marks T J. *Organometallics*, **2010**,**29**(23):6308-6320
- [11](a)Douglass M R, Stern C L, Marks T J. *J. Am. Chem. Soc.*, **2001**,**123**(42):10221-10238  
(b)Takaki K, Koshiji G, Komeyama K, et al. *J. Org. Chem.*, **2003**,**68**(17):6554-6565  
(c)Kawaoka A M, Marks T J. *J. Am. Chem. Soc.*, **2004**,**126**(40):12764-12765  
(d)Hu H F, Cui C M. *Organometallics*, **2012**,**31**(3):1208-1211  
(e)Behrle A C, Schmidt J A R. *Organometallics*, **2013**,**32**(5):1141-1149
- [12](a)Hung S C, Wen Y F, Chang J W, et al. *J. Org. Chem.*, **2002**,**67**(4):1308-1313  
(b)Schumann H, Heim A, Demtschuk J, et al. *Organometallics*, **2003**,**22**(1):118-128  
(c)Yuan Y Y, Wang X F, Li Y X, et al. *Organometallics*, **2011**,**30**(16):4330-4341
- [13](a)Guan B T, Hou Z M. *J. Am. Chem. Soc.*, **2011**,**133**(45):18086-18089  
(b)Oyamada J, Hou Z M. *Angew. Chem. Int. Ed.*, **2012**,**51**:12828-12832  
(c)Guan B T, Wang B L, Nishiura M, et al. *Angew. Chem. Int. Ed.*, **2013**,**52**:4418-4421  
(d)Shi X C, Nishiura M, Hou Z M. *J. Am. Chem. Soc.*, **2016**, **138**:61476150  
(e)Arnold P L, McMullon M W, Rieb J, et al. *Angew. Chem. Int. Ed.*, **2015**,**55**:82-100
- [14](a)Monsaert S, Vila A L, Drozdak R, et al. *Chem. Soc. Rev.*, **2009**,**38**:3360-3372  
(b)Leitao E M, van der Eide E F, Romero P E, et al. *J. Am. Chem. Soc.*, **2010**,**132**(8):2784-2794  
(c)Woodward C P, Spiccia N D, Jackson W R, et al. *Chem. Commun.*, **2011**,**47**:779-781
- [15](a)Shima T, Hou Z M. *J. Am. Chem. Soc.*, **2006**,**128**(25):8124-8125  
(b)Zhou J L, Chu J X, Zhang Y Y, et al. *Angew. Chem. Int. Ed.*, **2013**,**52**(15):4243-4246
- [16](a)Zhang W X, Wang Z, Nishiura M, et al. *J. Am. Chem. Soc.*, **2011**,**133**(15):5712-5715  
(b)Hong J Q, Zhang L X, Yu X Y, et al. *Chem. Eur. J.*, **2011**,**17**(7):2130-2137  
(c)Hong J Q, Zhang L X, Wang K, et al. *Chem. Eur. J.*, **2013**,**19**(24):7865-7873
- [17](a)Masui H, Fuse S, Takahashi T. *Org. Lett.*, **2012**,**14**(16):4090-4093  
(b)Campbell M J, Toste F D. *Chem. Sci.*, **2011**,**2**(7):1369-1378  
(c)Attanasi O A, de Crescentini L, Favi G S. et al. *Org. Lett.*, **2011**,**13**(3):353-355  
(d)Groenendaal B, Vugts D J, Schmitz R F, et al. *J. Org. Chem.*, **2008**,**73**(2):719-722  
(e)Church T L, Byrne C M, Lobkovsky E B, et al. *J. Am. Chem. Soc.*, **2007**,**129**(26):8156-8162
- [18](a)Braunstein P, Nobel D. *Chem. Rev.*, **1989**,**89**(8):1927-1945  
(b)Kuninobu Y, Tokunaga Y, Kawata A, et al. *J. Am. Chem. Soc.*, **2006**,**128**(1):202-209  
(c)Paul F, Moulin S, Piechaczyk O, et al. *J. Am. Chem. Soc.*, **2007**,**129**(23):7294-7304  
(d)Zhu X C, Fan J X, Wu Y J, et al. *Organometallics*, **2009**,**28**(13):3882-3888  
(e)Sharpe H R, Geer A M, Williams H E L, et al. *Chem. Commun.*, **2017**,**53**(5):937-940
- [19](a)Evans W J, Forrestal K J, Ziller J W. *J. Am. Chem. Soc.*, **1998**,**120**(36):9273-9282  
(b)Shen Q, Li H R, Yao C S, et al. *Organometallics*, **2001**, **20**(14):3070-3073  
(c)Shen Q, Yao Y M. *J. Organomet. Chem.*, **2002**,**647**(1/2):180-189  
(d)Han Y N, Zhang J, Han F Y, et al. *Organometallics*, **2009**, **28**(13):3916-3921  
(e)Yi W Y, Zhang J, Li M, et al. *Inorg. Chem.*, **2011**,**50**(22):11813-11824
- [20](a)Zhang J, Ma L P, Cai R F, et al. *Organometallics*, **2005**, **24**(4):738-742  
(b)Du Z, Zhou H, Yao H, et al. *Chem. Commun.*, **2011**,**47**(12):3595-3597
- [21]Tardif O, Hashizume D, Hou Z M. *J. Am. Chem. Soc.*, **2004**, **126**(26):8080-8081
- [22]Qian C T, Ye C Q, Lu H Z, et al. *J. Organomet. Chem.*, **1983**,**247**(2):161-170
- [23]SAINTPlus, *Data Reduction and Correction Program Ver. 6.02a*, Bruker AXS, Madison, WI, **2000**.
- [24]Sheldrick G M. *SADABS, A Program for Empirical Absorption Correction*, University of Göttingen, Germany, **1998**.
- [25]Sheldrick G M. *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [26](a)Sun Y, Zhang Z X, Wang X, et al. *Organometallics*, **2009**, **28**(21):6320-6330  
(b)Sun Y, Zhang Z X, Wang X, et al. *Dalton Trans.*, **2010**, **39**(1):221-226  
(c)Zhang J, Han Y N, Han F Y, et al. *Inorg. Chem.*, **2008**, **47**(13):5552-5554

- [27](a)Pi C F, Liu R T, Zheng P Z, et al. *Inorg. Chem.*, **2007**,**46** (13):5252-5259  
(b)Pi C F, Zhu Z Y, Weng L H, et al. *Chem. Commun.*, **2007** (21):2190-2192  
(c)Pi C F, Zhang Z X, Pang Z, et al. *Organometallics*, **2007**, **26**(8):1934-1946
- [28](a)Evans W J, Ulibarri T A, Chamberlain L R, et al. *Organometallics*, **1990**,**9**(7):2124-2130  
(b)Evans W J, Foster S E. *J. Organomet. Chem.*, **1992**,**433** (1/2):79-94  
(c)Venugopal A, Kamps I, Bojer D, et al. *Dalton Trans.*, **2009**(29):5755-5765
- [29](a)Willis M C, Snell R H, Fletcher A J, et al. *Org. Lett.*, **2006**,**8**(22):5089-5091  
(b)Vorbruegggen H, Krolikiewicz K. *Tetrahedron*, **1994**,**50** (22):6549-6558  
(c)Li J R, Chen X A, Shi D X, et al. *Org. Lett.*, **2009**,**11**(6): 1193-1196  
(d)Patil Y P, Tambade P J, Deshmukh K M, et al. *Catal. Today*, **2009**,**148**(3/4):355-360
- [30]Zhou X G, Huang Z E, Cai R F, et al. *J. Organomet. Chem.*, **1998**,**563**(1/2):101-112
- [31]Allen F H, Kennard O, Watson D G, et al. *J. Chem. Soc., Perkin Trans.*, **1987**(12):S1-S19