

## Selective Reaction Based on the Linked Diamido Ligands of Dinuclear Lanthanide Complexes

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The dinuclear ytterbium pyridyl diamido complexes [Cp<sub>2</sub>Yb(THF)]<sub>2</sub>[μ-η<sup>1</sup>:η<sup>2</sup>-(NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,6)] (**1a**) and [Cp<sub>2</sub>Yb(THF)]<sub>2</sub>[μ-η<sup>1</sup>:η<sup>2</sup>-(NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,3)] (**1b**) are easily prepared by protonolysis of Cp<sub>3</sub>Yb with 0.5 equiv of the corresponding diaminopyridine in accepted yields, respectively. Treatment of **1a** with 2 equiv of dicyclohexylcarbodiimide (CyN=C=NCy) in THF at low temperature leads to the isolation of the formal double N–H addition product (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-(CyN(CyNH)CN)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,6)] (**2**) in 42% yield. Compound **2** is unstable to heat and slowly isomerized to the mixed neutral/dianionic diguanidinate complex (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-(CyNH)<sub>2</sub>CN(C<sub>5</sub>H<sub>3</sub>N-2,6)-NC(NCy)<sub>2</sub>](THF) (**3**) at room temperature. Similarly, treatment of **1b** with 2 equiv of CyN=C=NCy gives the addition/isomerization product (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>:η<sup>1</sup>-(CyNH)<sub>2</sub>CN(C<sub>5</sub>H<sub>3</sub>N-2,3)NC(NCy)<sub>2</sub>] (**4**). Moreover, the reaction of various ytterbium aryl diamido complexes (prepared in situ from [Cp<sub>2</sub>YbMe]<sub>2</sub> and aryl diamine, respectively) with CyN=C=NCy affords the corresponding addition products (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-1,4)] (**5**), (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-1,3)] (**6**), and (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>(C<sub>13</sub>H<sub>8</sub>-2,7)] (**7**), respectively. In contrast to pyridyl-bridged bis(guanidinate monoanion) complexes, aryl-bridged bis(guanidinate monoanion) complexes **5–7** are stable even with prolonged heating at 110 °C. All the results not only demonstrate that the presence of the pyridyl bridge can impart the diamido complexes with a unique reactivity and initiate the unexpected reaction sequence but also indicate evidently that the number and distribution of negative charges of the diguanidinate ligand is tunable from double monoanionic units to mixed neutral/dianionic isomers. All the complexes are characterized by elemental analysis and IR spectroscopies. The structures of complexes **1a**, **3**, **5**, **6**, and **7** are also determined through X-ray single-crystal diffraction analysis.

### Introduction

Guanidinate anions comprise a class of ligand currently finding many applications in coordination and organometallic chemistry<sup>1</sup> and more recently as ancillary ligands<sup>2</sup> or as intermediates<sup>3</sup> in catalytic cycles. Desirable properties of these ligands include their compatibility with a remarkably

wide range of metal-ion requirements from all parts of the periodic table and a tunable stereo profile through directed

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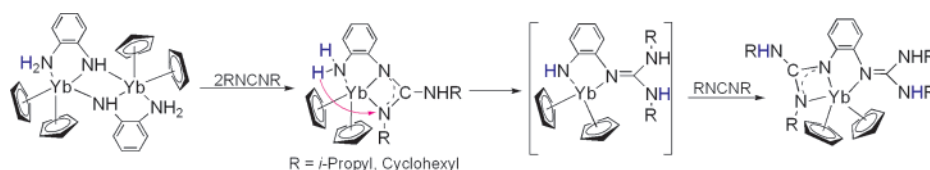
<sup>‡</sup> State Key Laboratory of Organometallic Chemistry.

(1) See, for example: (a) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91. (b) Kenney, A. P.; Yap, G. P. A.; Richeson, D. S.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 2926. (c) Said, F. F.; Ong, T. G.; Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *Cryst. Growth Des.* **2006**, *6*, 1848. (d) Mansfield, N. E.; Coles, M. P.; Avent, A. G.; Hitchcock, P. B. *Organometallics* **2006**, *25*, 2470. (e) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978. (f) Jones, C.; Junk, P. C.; Platts, J. A.; Stasch, A. *J. Am. Chem. Soc.* **2006**, *128*, 2206 and references therein.

(2) (a) Yao, Y. M.; Luo, Y. J.; Chen, J. L.; Zhang, Z. Q.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2003**, *679*, 229. (b) Trifonov, A. A.; Skvortsov, G. G.; Lyubov, D. M.; Skorodumova, N. A.; Fukin, G. K.; Baranov, E. V.; Glushakova, V. N. *Chem.—Eur. J.* **2006**, *12*, 5320. (c) Heitmann, D.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Dalton Trans.* **2007**, 187. (d) Milanov, A.; Bhakta, R.; Baunemann, A.; Becker, H.-W.; Thomas, R.; Ehrhart, P.; Winter, M.; Devi, A. *Inorg. Chem.* **2006**, *45*, 11008.

(3) (a) Zhang, W. X.; Nishiura, M.; Hou, Z. M. *Chem. Commun.* **2006**, 3812. (b) Zhang, W. X.; Nishiura, M.; Hou, Z. M. *Synlett.* **2006**, 1213. (c) Montilla, F.; del Río, D.; Pastor, A.; Galindo, A. *Organometallics* **2006**, *25*, 4996. (d) Shen, H.; Chan, H. S.; Xie, Z. *Organometallics* **2006**, *25*, 5515. (e) Ong, T. G.; O'Brien, J. S.; Korobkov, I.; Richeson, D. S. *Organometallics* **2006**, *25*, 4728. (f) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 8100. (g) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Chem. Commun.* **2003**, 2612. (h) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2001**, *20*, 1792. (i) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795. (j) Birdwhistell, K. R.; Lanza, J.; Pasos, J. J. *Organomet. Chem.* **1999**, *584*, 200.

Scheme 1



variation of the substituents on the nitrogen atoms as well as their ability to function as spectator ligands in analogy with well-precedented ligands such as cyclopentadienyl. Controlling metal coordination environment and reactivity through modification of supporting ligation is an important strategy in organometallic chemistry. Considerable interest has focused on the tailoring of two independent monoanion ligands to a defining and constraining linked dianion ligand for further perfecting the versatility of these ligands.<sup>4–7</sup> Such concepts have been elegantly applied to *ansa*-metallocene complexes<sup>4</sup> and other anionic functionalities including aryl-oxides,<sup>5</sup> amidinates,<sup>6</sup> and amidates.<sup>7</sup> However, there are few reports employing linked diguanidinate dianion analogues. Recent pioneering works show that the linked diguanidinate ligand,  $[\text{CH}_2\text{NC}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})_2]^{2-}$ , provides a more open metal coordination sphere than the unlinked analogues do, which offer a scaffold for interesting metal-centered reactivity.<sup>8</sup> Despite this potential, the synthetic chemistry of complexes possessing these ligands is still relatively unde-

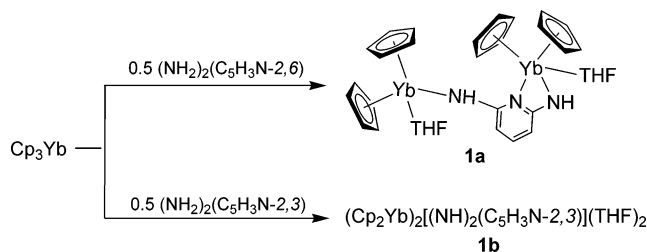
veloped. Therefore, it is highly desirable to develop new routes to novel linked diguanidinate complexes.

On the other hand, there is currently considerable interest in studying the reactivities of lanthanide amides due to their applications in organic synthesis and catalysis.<sup>9</sup> Nonetheless, research efforts are primarily focused on nonlinked lanthanide amido complexes.<sup>10</sup> Surprisingly, the regioselective reaction involving the linked diamido ligand in organolanthanide chemistry has remained unexplored to date, although it would be expected to have synthetic potential because the presence of an unique reaction system in which the two amido groups can react with two separate reagents bearing the same or different functionality. In most cases, the linked diamido ligands are only typically ancillary ligands which stabilize coordination and construct framework but do not participate in organometallic reactions.<sup>7</sup> The long-term goal of our research program over the years has been the development of insertion chemistry of organolanthanide complexes.<sup>11</sup> The catalytic transformation of amines by organometallic complexes is currently an active research area.<sup>1</sup> To elucidate the mechanism of metal-promoted guanylation of primary amines and thereby design a more ideal catalyst, we recently initiated an examination of chemical behavior of bifunctional amido lanthanide complexes toward carbodiimides and have determined that the hybrid amino/amido ligands bound to lanthanides can undergo a clean tandem guanylation with carbodiimides to afford new linked guanidine/guanidinate monoanion complexes.<sup>12</sup> Evidence suggests that this reaction maybe proceed via a sequential addition/protonation/addition pathway (Scheme 1). These observations prompted us to

- (4) (a) Qian, C. T.; Nie, W. L.; Sun, J. *J. Organomet. Chem.* **2001**, 626, 171. (b) Qian, C. T.; Nie, W. L.; Chen, Y. F.; Sun, J. *J. Organomet. Chem.* **2002**, 645, 82. (c) Nie, W. L.; Qian, C. T.; Chen, Y. F.; Sun, J. *J. Organomet. Chem.* **2002**, 647, 114. (d) Qian, C. T.; Zou, G.; Gao, L. *J. Organomet. Chem.* **1996**, 525, 23.
- (5) (a) Wang, Z. G.; Sun, H. M.; Yao, H. S.; Yao, Y. M.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, 691, 3383. (b) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124. (c) Yao, Y. M.; Xu, X. P.; Liu, B.; Zhang, Y.; Shen, Q.; Wong, W. T. *Inorg. Chem.* **2005**, 44, 5133. (d) Deng, M. Y.; Yao, Y. M.; Shen, Q.; Zhang, Y.; Sun, J. *Dalton Trans.* **2004**, 944.
- (6) (a) McNevin, M. J.; Hagadorn, J. R. *Inorg. Chem.* **2004**, 43, 8547. (b) Clare, B.; Sarker, N.; Shoemaker, R.; Hagadorn, J. R. *Inorg. Chem.* **2004**, 43, 1159. (c) Hagadorn, J. R.; McNevin, M. J. *Organometallics* **2003**, 22, 609. (d) Hagadorn, J. R.; McNevin, M. J.; Wiedenfeld, G.; Shoemaker, R. *Organometallics* **2003**, 22, 4818. (e) Chen, C.-T.; Huang, C.-A.; Tzeng, Y.-R.; Huang, B.-H. *Dalton Trans.* **2003**, 2585. (f) Grundy, J.; Coles, M. P.; Hitchcock, P. B. *J. Organomet. Chem.* **2002**, 662, 178.
- (7) (a) Garner, L. E.; Zhu, H. P.; Hlavinka, M. L.; Hagadorn, J. R.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2006**, 128, 14822. (b) Hlavinka, M. L.; McNevin, M. J.; Shoemaker, R.; Hagadorn, J. R. *Inorg. Chem.* **2006**, 45, 1815. (c) Zhao, B.; Li, H. X.; Shen, Q.; Zhang, Y.; Yao, Y. M.; Lu, C. R. *Organometallics* **2006**, 25, 1824. (d) Zhou, L. Y.; Yao, Y. M.; Li, C.; Zhang, Y.; Shen, Q. *Organometallics* **2006**, 25, 2886. (e) Antiñolo, A.; Dorado, I.; Fajardo, M.; Garcés, A.; López-Solera, I.; López-Mardomingo, C.; Kubicki, M. M.; Otero, A.; Prashar, S. *Eur. J. Inorg. Chem.* **2004**, 1299. (f) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, 22, 1212. (g) Skinner, M. E. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 1694. (h) Cloke, F. G. N.; Elvidge, B. R.; Hitchcock, P. B.; Lamarche, V. M. E. *J. Chem. Soc., Dalton Trans.* **2002**, 2413. (i) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, 20, 1387. (j) Dorado, I.; Garcés, A.; López-Mardomingo, C.; Fajardo, M.; Rodríguez, A.; Antiñolo, A.; Otero, A. *J. Chem. Soc., Dalton Trans.* **2000**, 2375. (k) Hogarth, G.; Humphrey, D. G.; Kaltsayannis, N.; Kim, W. S.; Lee, M. Y.; Norman, T.; Redmond, S. P. *J. Chem. Soc., Dalton Trans.* **1999**, 2705. (l) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, 18, 2896. (m) Graf, D. D.; Davis, W. M.; Schrock, R. R. *Organometallics* **1998**, 17, 5820. (n) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1997**, 119, 9071. (o) Shah, S. A. A.; Dorn, H.; Roesky, H. W.; Lubini, P.; Schmidt, H.-G. *Inorg. Chem.* **1997**, 36, 1102. (p) Lee, L.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, 33, 5302.

- (8) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2003**, 22, 387.
- (9) (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, 37, 673. (b) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, 102, 1953.
- (10) (a) Evans, W. J.; Rego, D. B.; Ziller, J. W. *Inorg. Chem.* **2006**, 45, 3437. (b) Layfield, R. A.; Bashall, A.; McPartlin, M.; Rawson, J. M.; Wright, D. S. *Dalton Trans.* **2006**, 1660. (c) Cui, C.; Shafir, A.; Schmidt, J. A. R.; Oliver, A. G.; Arnold, J. *Dalton Trans.* **2005**, 1387. (d) Evans, W. J.; Lee, D. S.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, 126, 454. (e) Giesbrecht, G. R.; Gordon, J. C.; Clark, D. L.; Hay, P. J.; Scott, B. L.; Tait, C. D. *J. Am. Chem. Soc.* **2004**, 126, 6387. (f) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, 126, 14574. (g) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; Parvez, M.; McDonald, R. *Organometallics* **2004**, 23, 2087. (h) Hou, Z. M.; Yoda, C.; Koizumi, T.-A.; Nishiura, M.; Wakatsuki, Y.; Fukuzawa, S.-I.; Takats, J. *Organometallics* **2003**, 22, 3586. (i) Chan, H. S.; Li, H. W.; Xie, Z. *Chem. Commun.* **2002**, 652. (j) Gordon, J. C.; Giesbrecht, G. R.; Clark, D. L.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G. *Organometallics* **2002**, 21, 4726. (k) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1996**, 35, 5435.
- (11) (a) Liu, R. T.; Zhang, C. M.; Zhu, Z. Y.; Luo, J.; Zhou, X. G.; Weng, L. H. *Chem.—Eur. J.* **2006**, 12, 6940. (b) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. G. *Organometallics* **2004**, 23, 3303. (c) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. G. *J. Organomet. Chem.* **2003**, 672, 94.
- (12) Pi, C. F.; Zhang, Z. X.; Pang, Z.; Zhang, J.; Luo, J.; Chen, Z. X.; Weng, L. H.; Zhou, X. G. *Organometallics* **2007**, 26, 1934.

Scheme 2



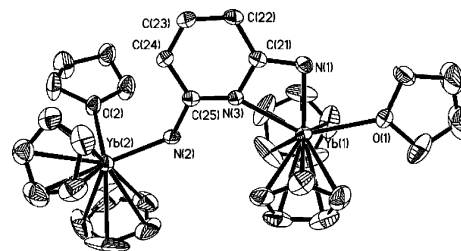
explore the selective linked bis(amido)-centered reactivity of lanthanide complexes.

In this paper, we describe the reaction of various linked lanthanide diamido complexes with carbodiimides, leading to a series of novel dianionic diguanidinate binuclear and polynuclear lanthanide complexes. The results provide a convenient and efficient method for synthesis of linked diguanidinate complexes. Furthermore, it is found that the binding modes of the pyridyldiamido ligand, from double monoanionic units to mixed neutral/dianionic isomer, is tunable, which is impossible for linked bis(cyclopentadienyl) and other linked dianionic functionalities including diamidinate, diamidates, and diaryloxide analogues.

## Results and Discussion

**Synthesis and Reactivity of Lanthanocene Pyridyldiamido Complexes toward Carbodiimide.** The chemistry of lanthanide amido complexes has received a great deal of attention in recent years,<sup>9,10</sup> due to its fundamental scientific interest and potential utility in organic synthesis. Nonetheless, well-defined bridged diamido complexes are rare relative to their nonbridged counterparts. To our knowledge, the regioselective reaction involving the bridged diamido ligand in organolanthanide chemistry has remained unexplored to date, probably due to the lack of suitable complexes. Given that pyridyl substituent on the nitrogen atom can help to stabilize the coordination of amido ligands and initiates the unexpected reaction sequence,<sup>12</sup> we prepared  $[\text{Cp}_2\text{Yb}(\text{THF})_2][\mu\text{-(HN)}_2(\text{C}_5\text{H}_3\text{N-2,6})]$  (**1a**) and  $[\text{Cp}_2\text{Yb}(\text{THF})_2][\mu\text{-(HN)}_2(\text{C}_5\text{H}_3\text{N-2,3})]$  (**1b**) by the protonolysis of  $\text{Cp}_3\text{Yb}$  with 0.5 equiv of 2,6-diaminopyridine  $[(\text{H}_2\text{N})_2(\text{C}_5\text{H}_3\text{N-2,6})]$  and 2,3-diaminopyridine  $[(\text{H}_2\text{N})_2(\text{C}_5\text{H}_3\text{N-2,3})]$  in THF at room temperature, respectively (Scheme 2). Then, **1a** reacted with 2 equiv of dicyclohexylcarbodiimide ( $\text{CyN}=\text{C}=\text{NCy}$ ) in THF at 0 °C to give  $(\text{Cp}_2\text{Yb})_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-(CyN(CyNH)CN)}_2(\text{C}_5\text{H}_3\text{N-2,6})]$  (**2**), indicating that carbodiimide inserted into each the N–H bond of two amido groups of **1a** (Scheme 3),<sup>12,13</sup> although it is likely the result of rearrangement following initial insertion into the Ln–N bond.

It is interesting to note that compound **2** was unstable to heat and spontaneously transformed to the unusual neutral



**Figure 1.** Thermal ellipsoid (30%) plot of complex **1a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)–N(1) 2.291(6), Yb(1)–N(3) 2.392(5), Yb(1)–O(1) 2.454(5), Yb(2)–N(2) 2.194(6), Yb(2)–O(2) 2.272(5), N(2)–C(25) 1.362(9), N(1)–C(21) 1.360(8), C(21)–C(22) 1.414(9), C(22)–C(23) 1.379(10), C(23)–C(24) 1.344(11), C(24)–C(25) 1.407(9), N(3)–C(25) 1.334(8), N(3)–C(21) 1.354(9); N(1)–Yb(1)–N(3) 57.7(2), N(3)–C(21)–N(1) 112.8(6), N(3)–C(25)–N(2) 119.0(6).

guanidine-containing dianionic guanidinate complex  $(\text{Cp}_2\text{Yb})_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-(CyNH)}_2\text{CN(CyNH)CN(Cy)}_2](\text{THF})$  (**3**) at room temperature slowly via the unprecedented disproportionation reaction of diguanidinate ligands (Scheme 3). To our knowledge, although the linked dianion ligands bearing the same functionality have been investigated extensively in organometallic chemistry, no example of isomerization concentrating two individual negative charges on one functional group is reported so far.

The formation of **2** and **3** represents a good example that the binding mode of the functional ligand from double monoanionic units to mixed neutral/dianionic isomers is tunable and highlights distinctive fluxional structures of linked diguanidinate complexes beyond that possible with the traditional linked dicyclopentadienyl, diamidinate, diamido, and diaryloxide analogues, owing to the presence of reactive NH groups. The protonation of guanidinate ligands is an important step in metal-mediated guanylation of amines,<sup>3</sup> while the deprotonation of anionic guanidinate/neutral guanidine ligands plays a key role in the metal-mediated functionalization of guanidines.<sup>15</sup> Therefore, the transformation of **2** to **3** should provide a new understanding of the nature and chemical behavior of guanidinate complexes and thereby demonstrate that a more diverse selection of ancillary stabilizing ligand environments is important in the design of new catalysts for guanylation of amines.

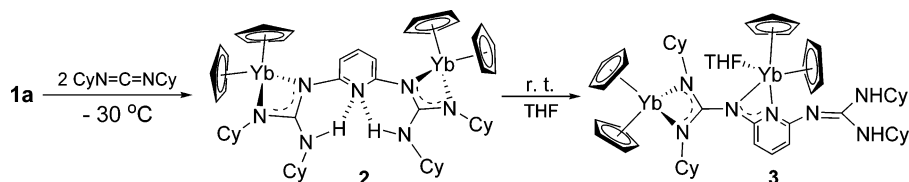
Complexes **1a–3** were characterized by elemental analysis and spectroscopic properties, which were in good agreement with the proposed structures. In the IR spectral data, all complexes show the sharp N–H stretching vibrations of coordinated amido groups in the range 3200–3600  $\text{cm}^{-1}$ . These complexes were further confirmed by the X-ray single-crystal structural determination. Although the quality of the structural determination of **2** was sufficient to unequivocally define the overall connectivity of the atoms (Figure 2), the data were not good enough to allow a detailed discussion of bond distances and angles.<sup>14</sup> Structures of **1a** and **3** are shown in Figures 1 and 3, with selected bond lengths and angles, respectively. In addition, the crystal data are summarized in Table 1. Unfortunately, little information concerning the

(13) (a) Holland, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 14684. (b) Rais, D.; Bergman, R. G. *Chem.–Eur. J.* **2004**, *10*, 3970. (c) Zhang, J. B.; Gunnoe, T. B.; Petersen, J. L. *Inorg. Chem.* **2005**, *44*, 2895. (d) Vicente, J.; Abad, J. A.; López-Sáez, M. J. *Organometallics* **2006**, *25*, 1851.

(14) Data for **2**:  $\text{C}_{51}\text{H}_{69}\text{N}_7\text{Yb}_2$ , fw = 1126.21;  $T = 293.2$  K;  $\lambda = 0.710$  73 Å; crystal color orange; space group  $P2_1/c$ ;  $a = 15.827(5)$ ,  $b = 34.658(12)$ ,  $c = 9.038(3)$  Å;  $\alpha = 90$ ,  $\beta = 103.207(5)$ ,  $\gamma = 90$  deg;  $V = 4826(3)$  Å<sup>3</sup>;  $Z = 4$ ;  $D_c = 1.550$   $\text{g}\cdot\text{cm}^{-3}$ ;  $\mu = 3.893$   $\text{mm}^{-1}$ ;  $R_1 = 0.1018$  [ $I > 2\sigma(I)$ ],  $R_2 = 0.2195$  [ $I > 2\sigma(I)$ ].

(15) Zhang, J.; Zhou, X. G.; Cai, R. F.; Weng, L. H. *Inorg. Chem.* **2005**, *44*, 716.

Scheme 3



structures of the complex **1b** could be gained due to its paramagnetic nature and low solubility even in polar organic solvents such as THF.

Crystals of **1a** suitable for a single-crystal X-ray study were grown from a cold, concentrated THF solution. As shown in Figure 1, **1a** is a dinuclear structure possessing one bridging pyridyldiamido ligand. The two Yb centers possess different coordination environments with Yb(1) being nine-coordinated to two  $\eta^5$ -cyclopentadienyl groups, one THF oxygen, and two nitrogen atoms from pyridyl and amido, respectively, to give a pseudo-trigonal-bipyramid geometry, while Yb(2) atom is coordinated by two  $\eta^5$ -cyclopentadienyl groups, one THF O atom, and one amido N atom and its formal coordination number is 8. The Yb(1)–N(1)/Yb(2)–N(2) bond length [2.291(6)/2.194(6) Å] is slightly shorter than that of the Yb(1)–N(3) bonds [2.392(5) Å]. Formally these bonds can be considered to be of the  $\sigma$ - and donor–acceptor-type, respectively.<sup>16</sup>

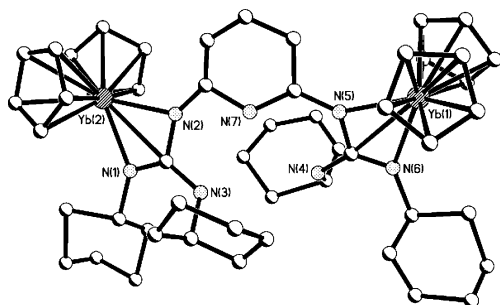


Figure 2. Ball and stick of **2**. Hydrogen atoms are omitted for clarity.

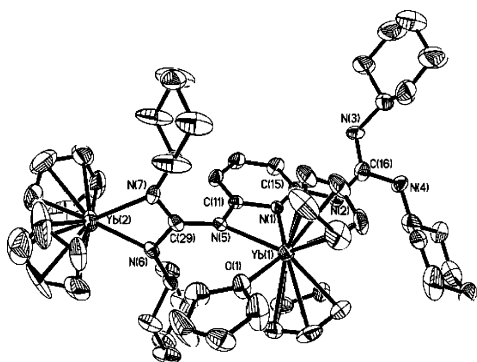


Figure 3. Thermal ellipsoid (30%) plot of complex **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)–N(1) 2.379(7), Yb(1)–N(5) 2.393(6), Yb(1)–O(1) 2.429(7), N(5)–C(29) 1.419(10), N(6)–C(29) 1.349(10), N(7)–C(29) 1.329(10), Yb(2)–N(6) 2.239(7), Yb(2)–N(7) 2.267(7), N(1)–C(11) 1.369(9), N(5)–C(11) 1.345(10), N(2)–C(16) 1.299(11), N(2)–C(15) 1.402(11), N(3)–C(16) 1.339(11), N(4)–C(16) 1.379(11); N(1)–Yb(1)–N(5) 55.8(2), N(6)–Yb(2)–N(7) 58.9(2), N(7)–C(29)–N(6) 111.7(8), N(7)–C(29)–N(5) 125.4(8), N(6)–C(29)–N(5) 122.9(9), N(2)–C(16)–N(3) 127.5(9), N(2)–C(16)–N(4) 117.6(10), N(3)–C(16)–N(4) 114.9(9), N(1)–C(15)–N(2) 113.7(8), N(5)–C(11)–N(1) 110.7(7).

Table 1. Crystal and Data Collection Parameters of Complexes **1a**, **3**, and **5**

param	<b>1a</b>	<b>3</b>	<b>5</b> ·2THF
Formula	C <sub>33</sub> H <sub>41</sub> N <sub>3</sub> O <sub>2</sub> Yb <sub>2</sub>	C <sub>55</sub> H <sub>77</sub> N <sub>7</sub> OYb <sub>2</sub>	C <sub>60</sub> H <sub>86</sub> N <sub>6</sub> O <sub>2</sub> Yb <sub>2</sub>
Fw	<b>857.77</b>	<b>1198.32</b>	<b>1269.43</b>
temp (K)	293.2	293.2	293.2
$\lambda$ (Å)	0.710 73	0.710 73	0.710 73
cryst color	black-red	orange-red	purple-red
space group	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>Pbcn</i>	<i>I4</i> <sub>1</sub> / <i>a</i>
<i>a</i> (Å)	15.286(5)	39.077(10)	28.357(8)
<i>b</i> (Å)	13.357(4)	9.963(3)	28.357(8)
<i>c</i> (Å)	5.847(5)	27.155(7)	14.586(6)
$\beta$ (deg)	100.134(4)	90	90
<i>V</i> (Å <sup>3</sup> )	3185.2(16)	10572(5)	11729(6)
<i>Z</i>	4	8	8
<i>D</i> <sub>c</sub> (g·cm <sup>-3</sup> )	1.89	1.506	1.438
$\mu$ (mm <sup>-1</sup> )	5.868	3.560	3.214
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0374	0.0620	0.0708
<i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0732	0.1086	0.1451

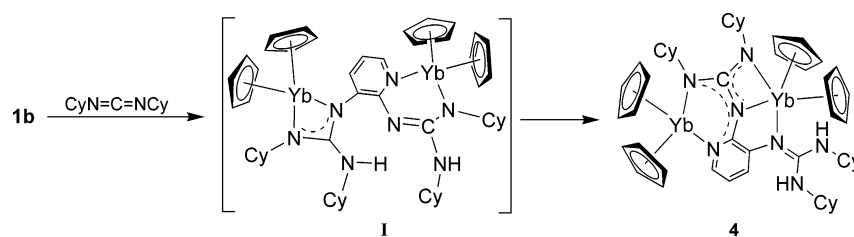
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_2 = \frac{(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}}{}$$

The intra-ring bond lengths of the pyridine ligands of **1a** are significantly different from those of unligated 2,6-diaminopyridine. The C<sub>aromatic</sub>–C<sub>aromatic</sub> distances are 1.414(9), 1.379(10), 1.344(11), and 1.407(9), for C(21)–C(22), C(22)–C(23), C(23)–C(24), and C(24)–C(25), respectively, and suggestive of double bond localization. This is significantly different from the observations in free<sup>17</sup> and neutral coordinated<sup>18</sup> 2,6-diaminopyridine, where all C<sub>aromatic</sub>–C<sub>aromatic</sub> bond lengths are nearly equivalent. Presumably, the replacement of the amino H atom by metallic Yb<sup>3+</sup> might be responsible for the observed changes, similar to that found in AlMe[AlMe<sub>2</sub>{(NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,6)}]<sub>2</sub>.<sup>19</sup>

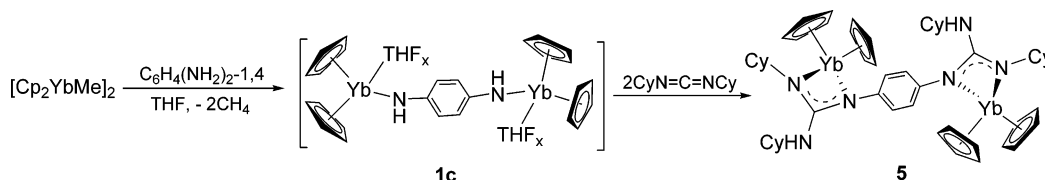
Figure 3 clearly confirms that **3** contains two CyN=C=NCy molecules that have been activated and inserted into two original N–H bond of **1a** followed by the proton transfer between two guanidinate units, in which the newly formed hybrid guanidine–guanidinate dianion ligand acts as a tetradentate bridge to connect the two Cp<sub>2</sub>Yb units through four N atoms. The two Yb centers possess different coordination environments with Yb(1) being nine-coordinated to two  $\eta^5$ -Cp groups, one THF oxygen, and two nitrogen atoms from pyridyl and guanidinate bridge respectively to give a pseudo-trigonal-bipyramid geometry, while Yb(2) atom is coordinated by two  $\eta^5$ -Cp groups and one  $\eta^2$ -guanidinate ligand and its formal coordination number is

- (16) (a) Ma, L. P.; Zhang, J.; Zhang, Z. X.; Cai, R. F.; Chen, Z. X.; Zhou, X. G. *Organometallics* **2006**, *25*, 4571. (b) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. G. *Dalton Trans.* **2006**, 1168. (c) Zhang, J.; Ma, L.; Cai, R. F.; Weng, L. H.; Zhou, X. G. *Organometallics* **2005**, *24*, 738.  
 (17) Schwalbe, C. H.; Williams, G. J. B.; Koetzle, T. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 2191.  
 (18) Kristiansson, O. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 165.  
 (19) Shukla, P.; Gordon, J. C.; Cowley, A. H.; Jones, J. N. *Inorg. Chim. Acta* **2005**, *358*, 4407.

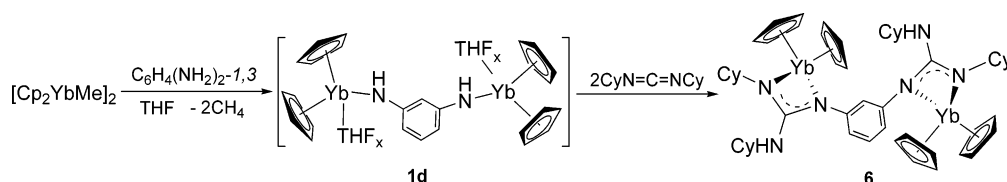
Scheme 4



Scheme 5



Scheme 6



8. The C(11)–N(1) distance (1.369(9) Å) is comparable to the C(11)–N(5) length, 1.345(10) Å, and shorter than the value of C(29)–N(5), 1.419(10) Å, but slightly longer than the C(29)–N(6) and C(29)–N(7) distances [1.349(10) and 1.329(10) Å, respectively]. These features are consistent with negative charges of the ligand delocalized on the two amidinate units bonded to Yb<sup>3+</sup> due to the conjugation effect of the pyridyl substituent, which is different from the observations in other known dianionic guanidinate complexes.<sup>3f–j</sup> The average Yb(1)–N distance of 2.386(6) Å is longer than the average Yb(2)–N distance of 2.253(7) Å due to the higher coordination number. All these findings are indicative that a delocalization of ytterbium–nitrogen bonds as in case of the guanidinate part does take place for the pyridylamido fragment. Complex **3** has no unusual distances and angles in the uncoordinated guanidine unit.

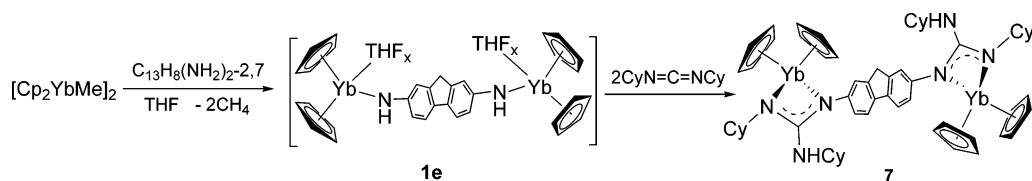
The selective protonation and deprotonation of ligands for organometallic complexes is a challenge to address in their preparation and in their potential competence as intermediates in catalytic cycles. To explore the generality of isomerization of pyridyldiguanidinate ligands, we then examined the reaction of related (pyridyldiamido-2,3)ytterbium complex **1b** with CyN=C=NCy. In contrast to the observation for **1a**, treatment of **1b** with CyN=C=NCy gave only the addition/isomerization product (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>:η<sup>1</sup>-(CyNH)<sub>2</sub>-CN(C<sub>5</sub>H<sub>3</sub>N-2,3)NC(NCy)<sub>2</sub>] (**4**) (Scheme 4). Attempts to isolate the intermediate **I** similar to **2** at low temperature were unsuccessful. These differences may be attributed to the weaker acidity of the guanidine group at the 3-position as compared with that at the 6-position, which enhances the tendency of the proton transfer from guanidinate at the 2-position to guanidinate at 3-position. These observations imply subtle differences in the position of guanidinate groups on the pyridyl ring brought about differences in their reactivity.

Complex **4** dissolves readily in THF and only sparingly soluble in toluene and *n*-hexane. Complex **4** was characterized by microanalysis and X-ray diffraction analysis, which were in good agreement with the results in the literature.<sup>12</sup>

**Synthesis and Reactivity of Compounds 1c–e toward Carbodiimide.** The formation and the release of guanidinate ligands are important steps in metal-mediated guanylation of amines. Although a wide variety of metal-promoted transformation reactions of carbodiimides have been studied,<sup>3</sup> few tandem reactions have been observed in literatures. After having established that pyridyldiguanidinate ligands bound to the lanthanide center can undergo self-protonation, we were interested to find out the factors that affect the proton transfer. To that purpose, several novel aryl diamido complexes, [Cp<sub>2</sub>Yb(THF)<sub>x</sub>]<sub>2</sub>[μ-(NH)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-1,4)] (**1c**), [Cp<sub>2</sub>Yb(THF)<sub>x</sub>]<sub>2</sub>[μ-(NH)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-1,3)] (**1d**), and [Cp<sub>2</sub>Yb(THF)<sub>x</sub>]<sub>2</sub>[μ-(NH)<sub>2</sub>(C<sub>13</sub>H<sub>8</sub>-2,7)] (**1e**), were synthesized in situ by treatment of [Cp<sub>2</sub>YbMe]<sub>2</sub> with the corresponding aryl diamine, and their doubly N–H activation properties were probed by exploring their reactivity toward carbodiimides. The results similar to those of Schemes 3 and 4 would be expected for the insertion of carbodiimide into the N–H bond of **1c–e**.<sup>13</sup> However, treatment of complexes **1c–e** with 2 equiv of CyN=C=NCy, even prolonged heating at 110 °C, afforded only the products of formal double CyN=C=NCy insertion into the N–H bond of the Yb-bonded NHAr group, to yield complexes (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>-1,4)] (**5**), (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>-1,3)] (**6**), and (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-{CyN(CyNH)CN}<sub>2</sub>-(C<sub>13</sub>H<sub>8</sub>-2,7)] (**7**), respectively (Schemes 5–7). These results indeed demonstrate that the chelating effect of pyridyl rings can impart the amido complexes a unique reactivity and initiates the unexpected reaction sequence.

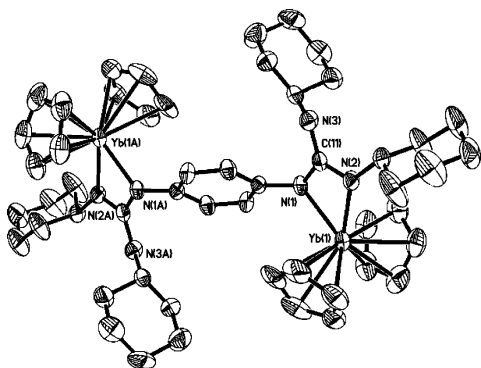
Complexes **5–7** were characterized by elemental analysis and spectroscopic properties, which were in good agreement

## Scheme 7

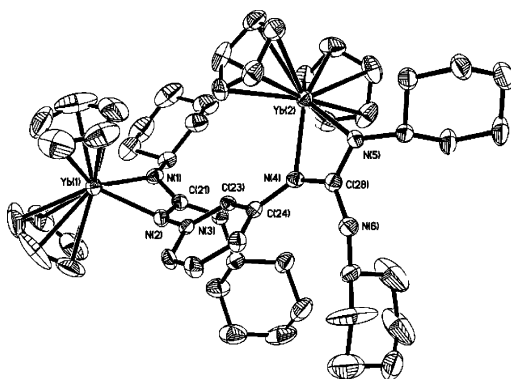


with the proposed structures. The molecular structures of complexes **5–7** were further confirmed using the X-ray crystallography (Figures 4–6). The crystal details of **5** are given in Table 1, while details of **6** and **7** are given in Table 2.

Complexes **5–7** adopt a similar overall dinuclear structure with a different bridge-length linked bis(guanidinate) ligand, indicating that the addition of each N–H bond to a carbodiimide has led to the formation of a coordinated diguanidinate ligand. As expected, the coordinated guanidinate group forms essentially a planar four-membered ring with the each Yb atom within experimental errors. The sums of the angles around central C of the guanidinate core N<sub>3</sub>C in **5–7** [360.0(11)° (**5**), 360.0(5)° (**6**), and 360.0(8)° (**7**),



**Figure 4.** Thermal ellipsoid (30%) plot of complex **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)–N(1) 2.268(9), Yb(1)–N(2) 2.293(9), N(1)–C(11) 1.348(13), N(2)–C(11) 1.332(13), N(3)–C(11) 1.359(14); N(1)–Yb(1)–N(2) 58.7(3), N(2)–C(11)–N(1) 113.1(10), N(2)–C(11)–N(3) 123.5(11), N(1)–C(11)–N(3) 123.4(10). Letter A indicates the following symmetry transformation:  $-x + 3/2, -y + 3/2, -z + 5/2$ .

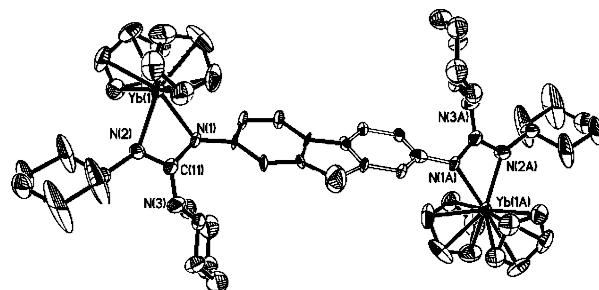


**Figure 5.** Thermal ellipsoid (30%) plot of complex **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)–N(2) 2.271(5), Yb(1)–N(1) 2.301(5), Yb(2)–N(4) 2.280(4), Yb(2)–N(5) 2.286(4), N(1)–C(21) 1.318(7), N(2)–C(21) 1.356(7), N(3)–C(21) 1.371(7), N(4)–C(28) 1.362(6), N(5)–C(28) 1.312(7), N(6)–C(28) 1.363(7); N(2)–Yb(1)–N(1) 59.01(16), N(4)–Yb(2)–N(5) 58.56(15), N(1)–C(21)–N(2) 114.8(5), N(1)–C(21)–N(3) 123.5(5), N(2)–C(21)–N(3) 121.7(5), N(5)–C(28)–N(4) 113.2(5), N(5)–C(28)–N(6) 124.1(5), N(4)–C(28)–N(6) 122.7(5).

**Table 2.** Crystal and Data Collection Parameters of Complexes **6** and **7**

param	<b>6</b>	<b>7</b>
formula	C <sub>52</sub> H <sub>70</sub> N <sub>6</sub> Yb <sub>2</sub>	C <sub>59</sub> H <sub>74</sub> N <sub>6</sub> Yb <sub>2</sub>
fw	<b>1125.22</b>	<b>1213.32</b>
temp (K)	293.2	293.2
λ (Å)	0.710 73	0.710 73
cryst color	red	red
space group	P1	P2 <sub>1</sub> /c
a (Å)	13.573(4)	9.453(3)
b (Å)	13.804(5)	35.987(10)
c (Å)	16.113(5)	8.267(2)
α (deg)	104.092(4)	90
β (deg)	113.479(4)	103.094(4)
γ (deg)	103.867(5)	90
V (Å <sup>3</sup> )	2486.0(14)	2739.2(14)
Z	2	2
D <sub>c</sub> (g·cm <sup>-3</sup> )	1.503	1.471
μ (mm <sup>-1</sup> )	3.778	3.435
R <sub>1</sub> [I > 2σ(I)] <sup>a</sup>	0.0356	0.0532
R <sub>2</sub> [I > 2σ(I)] <sup>b</sup>	0.0820	0.1272

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$



**Figure 6.** Thermal ellipsoid (30%) plot of complex **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)–N(1) 2.277(7), Yb(1)–N(2) 2.277(7), N(1)–C(11) 1.336(11), N(2)–C(11) 1.344(11), N(3)–C(11) 1.346(12); N(1)–Yb(1)–N(2) 58.6(3), N(1)–C(11)–N(3) 124.4(8), N(1)–C(11)–N(2) 112.6(8), N(3)–C(11)–N(2) 123.0(8). Letter A indicates the following symmetry transformation:  $-x + 1, -y + 1, -z + 1$ .

respectively] are consistent with sp<sup>2</sup>-hybridization. The bond distances within the N<sub>coord</sub>CN<sub>coord</sub> moiety ( $\Delta\text{CN}_{\text{coord}} = 0.016$ –(13) Å (**5**),  $\Delta\text{CN}_{\text{coord}} = 0.038$ (7) Å (**6**),  $\Delta\text{CN}_{\text{coord}} = 0.008$ –(11) Å (**7**)) are in agreement with an extensive delocalized  $\pi$  interaction.<sup>20</sup> Consistent with this case, the average Yb–N bond distances in **5–7** (2.281(9)–2.277(7) Å) are intermediate between the values observed for the Yb–N single bond distance and the Yb–N donor bond distances (2.19–2.69 Å)<sup>21</sup> and are comparable to the corresponding values found in [(C<sub>5</sub>H<sub>4</sub>Me)Yb(PzMe<sub>2</sub>)(OSiMe<sub>2</sub>PzMe<sub>2</sub>)]<sub>2</sub> (average 2.293–(6) Å)<sup>22</sup> and {CyNC[N(SiMe<sub>3</sub>)<sub>2</sub>]NCy}<sub>2</sub>YbN(SiMe<sub>3</sub>)<sub>2</sub> (average 2.317(13) Å).<sup>23</sup>

(20) (a) Luo, Y. J.; Yao, Y. M.; Shen, Q.; Yu, K. B.; Weng, L. H. *Eur. J. Inorg. Chem.* **2003**, 318. (b) Lu, Z. P.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (c) Trifonov, A. A.; Lyubov, D. M.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. A. *Organometallics* **2006**, *25*, 3935.

(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

The coordinated guanidinate arms show structural effects resulting from their steric requirements. Because of the steric crowding of the substituents, the guanidinate arms in compounds **5–7** are positioned away from each other on each side of the phenyl and fluorenyl bridges, where the guanidinate arms are positioned along the benzene ring toward a single direction, similar to residue of the azaallyl group in the *meta*-substituted complex  $\{m\text{-}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Bu}^t)\text{C}(\text{H})\}_2\text{C}_6\text{H}_4\}\{\text{Li}_2(\text{TMEDA})_2\}$ .<sup>24</sup>

## Conclusion

In summary, we have reported the insertion of dicyclohexylcarbodiimide into the N–H bond of the heteroaryldiamido and aryldiamido ligands bonded to the center metal ion Yb<sup>3+</sup>. The results indicate that the reactivity behavior of the linked diamido ligand strongly depends on the nature of the bridge system. The pyridyldiamido ligand bonded to the lanthanide metal can undergo a clean tandem diguanylation/isomerization to afford a variety of rare mixed neutral guanidine/dianionic guanidinate complexes, while the resultant aryldiguanidinate ligands are stable under the same conditions. These results provide a clear insight into the role of the flexibility and remarkable reactivity of linked diguanidinate ligands and demonstrate that the diguanidinate dianion ligands can undergo the intraligand proton transfer which is impossible for other homotopic linked bifunctional ligands R<sup>−</sup>–Z–R<sup>−</sup> (R<sup>−</sup> = cyclopentadienyl, aryloxy, amidinate, amidate, and amido). Furthermore, our results provide a new route for preparation of linked diguanidinate complexes directly under mild conditions and represent a good example that can map out the versatility of the guanidinate system. The formation and the release of guanidinate ligands are important steps in metal-mediated guanylation of amines. Thus, the results obtained in this work should provide useful data for the design of new catalytic guanylation. On the other hand, these findings would be expected to be useful for synthesis of new asymmetry dianionic ligand-bridged complexes because of the possibility for two separate additions of different functionality at two amido groups. Further development on this methodology is currently under way in our laboratory.

## Experimental Section

**General Procedure.** All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen gas using standard Schlenk techniques. The solvents THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen gas prior to use. Elemental analyses for C, H, and N were carried out by using a Rapid CHN-O analyzer. Infrared spectra were obtained on a Nicolet FTIR 360 spectrometer with samples prepared as Nujol mulls. Solution-phase <sup>1</sup>H NMR spectra were obtained on a Bruker DPX 400 NMR spectrometer at 400 MHz. The complexes [Cp<sub>2</sub>YbMe]<sub>2</sub><sup>25</sup>

and Cp<sub>3</sub>Yb<sup>26</sup> were prepared according to the procedures described in the literatures. 2,6-Diaminopyridine, 2,3-diaminopyridine, 1,4-diaminobenzene, 1,3-diaminobenzene, 2,7-diaminofluorene, and dicyclohexylcarbodiimide were purchased from commercial sources and were used without further purification.

**Preparation of [Cp<sub>2</sub>Yb(THF)]<sub>2</sub>[μ-η<sup>1</sup>:η<sup>2</sup>-(NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,6)] (1a).** To a 50 mL THF solution of Cp<sub>3</sub>Yb (1.656 g, 4.496 mmol) was added (NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,6) (0.246 g, 2.25 mmol) at room temperature. After being stirred for 15 h, the solution was concentrated and cooled at −15 °C for several days to give **1a** as black-red crystals. Yield: 1.293 g (67.06%, based on Yb). Anal. Calcd for C<sub>33</sub>H<sub>41</sub>N<sub>3</sub>O<sub>2</sub>Yb<sub>2</sub>: C, 46.21; H, 4.82; N, 4.90. Found: C, 46.10; H, 4.79; N, 4.86. <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>): δ 28.78 (s, NH), 3.35 (s, THF), 1.26 (s, THF), −10.73 (s, Cp), −15.39 (s, Cp). IR (Nujol, cm<sup>−1</sup>): 3561 (m), 3507 (m), 3388 (m), 3333 (m), 3071 (m), 1612 (m), 1578 (vs), 1344 (w), 1285 (m), 1243 (s), 1177 (m), 1121 (w), 1069 (m), 1010 (s), 920 (m), 861(s), 773 (s), 724 (s), 699 (w), 670 (w).

**Preparation of (Cp<sub>2</sub>Yb)<sub>2</sub>[(NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,3)](THF)<sub>2</sub> (1b).** To a 40 mL THF solution of Cp<sub>3</sub>Yb (0.869 g, 2.36 mmol) was added (NH)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N-2,3) (0.129 g, 1.18 mmol) at room temperature, and the solution was stirred for 15 h. A lot of orange precipitate came into being. After filtration, the residue was dried under reduced pressure to give **1b** as orange solid. Yield: 0.516 g (51.0%). Anal. Calcd for C<sub>33</sub>H<sub>41</sub>N<sub>3</sub>O<sub>2</sub>Yb<sub>2</sub>: C, 46.21; H, 4.82; N, 4.90. Found: C, 46.17; H, 4.78; N, 4.88. IR (Nujol, cm<sup>−1</sup>): 3540 (m), 3486 (m), 3372 (m), 3330 (m), 3069 (m), 1612 (m), 1567 (vs), 1341 (w), 1280 (m), 1232 (s), 1173 (m), 1121 (w), 1069 (m), 1010 (s), 920 (m), 860 (s), 770 (s), 724 (s), 690 (w).

**Preparation of (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-CyN(CyNH)CN(C<sub>5</sub>H<sub>3</sub>N-2,6)-NC(NHCy)NCy] (2).** To a 30 mL THF solution of **1a** (0.386 g, 0.450 mmol) was added *N,N'*-dicyclohexylcarbodiimide (0.186 g, 0.901 mmol) at −30 °C. After being stirred for 30 min, the mixture solution was warmed up to room temperature and stirred for another 8 h. Then, the solution was concentrated and subsequently cooled to −15 °C for several days to give **2** (0.213 g, 42.0%) as orange crystals. Anal. Calcd For C<sub>51</sub>H<sub>69</sub>N<sub>7</sub>Yb<sub>2</sub>: C, 54.39; H, 6.18; N, 8.71. Found: C, 54.32; H, 6.16; N, 8.66. <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>): δ 3.77 (s, NH), 2.62–1.02 (m, Cy) (many broad, unresolved peaks). IR (Nujol, cm<sup>−1</sup>): 3209 (m), 3089 (m), 3060 (m), 1568 (vs), 1492 (s), 1433 (vs), 1388 (m), 1335 (s), 1265 (m), 1239 (w), 1190 (m), 1156 (s), 1010 (s), 883 (w), 863 (s), 775 (s), 725 (m), 668 (w).

**Preparation of (Cp<sub>2</sub>Yb)<sub>2</sub>[μ-η<sup>2</sup>:η<sup>2</sup>-(CyNH)<sub>2</sub>C=N(C<sub>5</sub>H<sub>3</sub>N-2,6)-NC(NCy)<sub>2</sub>](THF) (3).** To the 30 mL THF solution of **1a** (0.609 g, 0.710 mmol) was added *N,N'*-dicyclohexylcarbodiimide (0.293 g, 1.42 mmol) at −30 °C. After being stirred for 30 min, the mixture solution was slowly warmed to room temperature. After being stirring for 48 h, the solution was concentrated under vacuum and several drops of *n*-hexane were added. Cooling at −15 °C for 2 weeks gave **3** as red crystals. Yield: 0.536 g (63.0%). Anal. Calcd for C<sub>55</sub>H<sub>77</sub>N<sub>7</sub>OYb<sub>2</sub>: C, 55.13; H, 6.48; N, 8.18. Found: C, 55.07; H, 6.45; N, 8.15. <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>): δ 6.35 (s, Cp), 6.19 (s, Cp), 3.76 (s, NH), 3.42 (m, THF), 2.64 (br, Cy), 1.84 (s, THF), 1.37–0.65 (m, Cy). IR (Nujol, cm<sup>−1</sup>): 3444 (m), 3387 (w), 3095 (w), 3065 (w), 1616 (m), 1571 (s), 1550 (m), 1525 (m), 1357 (s), 1308 (m), 1259 (w), 1212 (m), 1082 (s), 1014 (s), 866(m), 769 (s), 720 (m).

**Preparation of (Cp<sub>2</sub>Yb)<sub>2</sub>[η<sup>2</sup>:η<sup>2</sup>:η<sup>1</sup>-(NCy)<sub>2</sub>CN(C<sub>5</sub>H<sub>3</sub>N-2,3)NC(NHCy)<sub>2</sub>] (4).** To a solution of **1b** (0.437 g, 0.510 mmol) was added *N,N'*-dicyclohexylcarbodiimide (0.210 g, 1.02 mmol) at −30 °C.

(22) Zhou, X. G.; Ma, H. Z.; Huang, X. Y.; You, X. Z. *J. Chem. Soc., Chem. Commun.* **1995**, 2483.

(23) Zhou, Y. L.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1998**, *17*, 4387.

(24) Leung, W. P.; Cheng, H.; Liu, D. S.; Wang, Q. G.; Mak, T. C. W. *Organometallics* **2000**, *19*, 3001.

(25) Ely, N. M.; Tsutsui, M. *Inorg. Chem.* **1975**, *14*, 2680.

(26) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42.

After being stirred for 12 h at ambient temperature, the red solution was concentrated under vacuum. Standing at  $-15\text{ }^{\circ}\text{C}$  for 2 weeks gave **4**·1.5THF (0.447 g, 71.0%) as red crystals. Anal. Calcd for  $\text{C}_{57}\text{H}_{81}\text{N}_7\text{O}_{1.5}\text{Yb}_2$ : C, 55.46; H, 6.61; N, 7.94. Found: C, 55.41; H, 6.55; N, 7.89.  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  6.30 (s, Cp), 3.43 (m, THF), 1.34–2.70 (m, Cy + THF). IR (Nujol,  $\text{cm}^{-1}$ ): 3500 (m), 3380 (s), 3330 (m), 3082 (w), 1610 (m), 1575 (vs), 1520 (s), 1330 (s), 1285 (m), 1251 (s), 1200 (m), 1130 (m), 1070 (m), 1054 (m), 1015 (s), 980 (w), 885 (m), 842 (w), 761 (vs). Its crystal structure had been confirmed by X-ray diffraction analysis and was identical with the results in the literature.<sup>12</sup>

**Preparation of  $(\text{Cp}_2\text{Yb})_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}\{\text{CyN}(\text{CyNH})\text{CN}\}_2(\text{C}_6\text{H}_4\text{-1,4})]$  (**5**).** To a solution of freshly prepared  $[\text{Cp}_2\text{YbMe}]_2$  (0.420 g, 0.660 mmol) in 30 mL of THF was added 1,4-diaminobenzene (0.071 g, 0.66 mmol) at  $-30\text{ }^{\circ}\text{C}$ . After being stirred for 0.5 h at low temperature, the reaction solution was slowly warmed to room temperature and stirred for another 5 h. Then, at  $-30\text{ }^{\circ}\text{C}$ , to the mixture was added  $N,N'$ -dicyclohexylcarbodiimide (0.272 g, 1.32 mmol). After being stirred for 12 h at ambient temperature, the red solution was concentrated under vacuum to give a purple solid. Crystallization from THF afforded pure **5**·2THF as purple-red crystals. Yield: 0.654 g (78.1%). Anal. Calcd For  $\text{C}_{60}\text{H}_{86}\text{N}_6\text{O}_2\text{-Yb}_2$ : C, 56.77; H, 6.83; N, 6.62. Found: C, 56.71; H, 6.80; N, 6.58.  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  6.13 (s, Cp), 5.43 (s, NH), 3.36 (m, THF), 2.57–0.82 (m, Cy + THF). IR (Nujol,  $\text{cm}^{-1}$ ): 3390 (m), 3086 (m), 1639 (w), 1601 (m), 1495 (vs), 1365 (vs), 1342 (s), 1285 (s), 1246 (s), 1187 (m), 1150 (s), 1102 (m), 1071 (m), 1011 (s), 981 (m), 891 (m), 867 (m), 844 (w), 771 (vs), 736 (w), 702 (w).

**Preparation of  $(\text{Cp}_2\text{Yb})_2[\eta^2\text{:}\eta^2\text{-}\{\text{CyN}(\text{CyNH})\text{CN}\}_2(\text{C}_6\text{H}_4\text{-1,3})]$  (**6**).** Compound **6** was prepared according to the procedure described for **5**, using freshly prepared  $[\text{Cp}_2\text{YbMe}]_2$  (0.395 g, 0.621 mmol), 1,3-diaminobenzene (0.067 g, 0.62 mmol), and  $N,N'$ -dicyclohexylcarbodiimide (0.256 g, 1.24 mmol). Crystallization from THF afforded **6** as red crystals (0.495 g, 70.8% yield based on Yb). Anal. Calcd for  $\text{C}_{52}\text{H}_{70}\text{N}_6\text{Yb}_2$ : C, 55.51; H, 6.27; N, 7.47. Found: C, 55.45; H, 6.23; N, 7.41. Only broad peaks were observed in the  $^1\text{H}$  NMR spectrum. IR (Nujol,  $\text{cm}^{-1}$ ): 3466 (m), 3269 (m), 3081 (m), 1644 (w), 1614 (m), 1526 (vs), 1420 (vs), 1365 (s), 1329 (s), 1250 (s), 1178 (s), 1149 (s), 1089 (m), 1011 (s), 985 (m), 905 (m), 868 (m), 839 (m), 769 (vs), 732 (w).

**Preparation of  $(\text{Cp}_2\text{Yb})_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}\{\text{CyN}(\text{CyNH})\text{CN}\}_2(\text{C}_{13}\text{H}_8\text{-2,7})]$  (**7**).** Compound **7** was prepared according to the procedure described for **5**, using freshly prepared  $[\text{Cp}_2\text{YbMe}]_2$  (0.535 g, 0.840 mmol), 2,7-diaminofluorene (0.165 g, 0.841 mmol), and  $N,N'$ -dicyclohexylcarbodiimide (0.347 g, 1.68 mmol). The red crystals of **7** were obtained through layering *n*-hexane to its concentrated THF solution. Yield: 0.764 g (75.0% based on Yb). Anal. Calcd

for  $\text{C}_{50}\text{H}_{74}\text{N}_6\text{Yb}_2$ : C, 58.40; H, 6.15; N, 6.93. Found: C, 58.32; H, 6.11; N, 6.90.  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  6.23 (s, Cp), 2.64–0.91 (m, Cy). IR (Nujol,  $\text{cm}^{-1}$ ): 3404 (m), 3065 (w), 3015 (w), 1634 (m), 1603 (m), 1528 (vs), 1366 (vs), 1342 (s), 1299 (s), 1276 (s), 1258 (s), 1187 (s), 1152 (m), 1117 (m), 1099 (m), 1011 (m), 984 (m), 927 (w), 885 (vs), 856 (m), 823 (w), 768 (m), 721 (m), 663 (w).

**Crystal Structure Determination.** Suitable single crystals were sealed under  $\text{N}_2$  in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo  $\text{K}\alpha$  radiation,  $\phi$ - $\omega$ -scan technique,  $\lambda = 0.71073\text{ \AA}$ ). The intensity data were integrated by means of the SAINT program.<sup>27</sup> SADABS<sup>28</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>29</sup> All non-hydrogen atoms were 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 non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program. There was a cyclohexyl ring disordered in **3**. The fluorenyl ring of the compound **7** is heavily disordered, such that fluorenyl ring atoms have been modeled with 7 anisotropic carbon atoms without hydrogens included. Crystallographic parameters for compounds **1a**, **3**, **5**·2THF, **6**, and **7** along with details of the data collection and refinement are collected in Tables 1 and 2. Selected bond distances and angles for each compound are given in the corresponding figure. Further details are included in the Supporting Information.

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**Supporting Information Available:** Tables of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for all structurally characterized complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC070203P

(27) Bruker SAINTPlus Data Reduction and Correction Program, v. 6.02a; Bruker AXS: Madison, WI, 2000.

(28) Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 1998.

(29) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.