Inorganic Chemistry

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Lanthanide Amido Complexes Incorporating Amino-Coordinate-Lithium Bridged Bis(indolyl) Ligands: Synthesis, Characterization, and Catalysis for Hydrophosphonylation of Aldehydes and Aldimines

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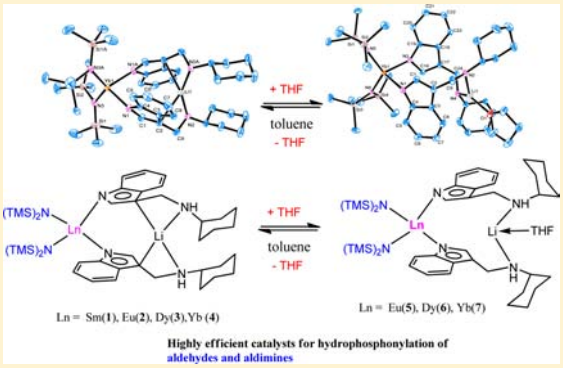
Supporting Information

ABSTRACT: Two series of new lanthanide amido complexes supported by bis(indolyl) ligands with amino-coordinate-lithium as a bridge were synthesized and characterized. The interactions of $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of 3-$(CyNHCH_2)$-C_8H_5NH in toluene produced the amino-coordinate-lithium bridged bis(indolyl) lanthanide amides $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)\text{-}Ind]_2Li\}Ln[N(SiMe_3)_2]_2]$ (Cy = cyclohexyl, Ind = Indolyl, Ln = Sm (**1**), Eu (**2**), Dy (**3**), Yb (**4**)) in good yields. Treatment of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Ln[N(SiMe_3)_2]_2]$ with THF gave new lanthanide amido complexes $[\mu\text{-}\{[\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\text{-}(THF)\}Ln[N(SiMe_3)_2]_2]$ (Ln = Eu (**5**), Dy (**6**), Yb (**7**)), which can be transferred to amido complexes **2**, **3**, and **4** by reflux the corresponding complexes in toluene. Thus, two series of rare-earth-metal amides could be reciprocally transformed easily by merely changing the solvent in the reactions. All new complexes **1**–**7** are fully characterized including X-ray structural determination. The catalytic activities of these new lanthanide amido complexes for hydrophosphonylation of both aromatic and aliphatic aldehydes and various substituted aldimines were explored. The results indicated that these complexes displayed a high catalytic activity for the C–P bond formation with employment of low catalyst loadings (0.1 mol % for aldehydes and 1 mol % for aldimines) under mild conditions. Thus, it provides a convenient way to prepare both α-hydroxy and α-amino phosphonates.



INTRODUCTION

Structurally well-defined cyclopentadienyl-free rare-earth-metal complexes bearing nitrogen-based supporting ligands have been a continuous interest, due to easy tailorability of substituents on the nitrogen atom in consideration of steric demand and electronic properties in the development of activity controllable new metal catalysts.[1] In view of this point, many nitrogen-based monodentate or polydentate ligands, such as various modified amido ligands,[2] β-diketiminates,[3] amidinates or guanidinates,[4] cyclic pyrrolyl,[5] aromatic indolyl,[6] and carbazolyl[7] ligands, as alternatives to the cyclopentadienyl, have been developed. Indole or its derivatives are widely distributed in biological systems as an important constituent of biomolecules and natural products.[8] Indole is an electron-rich aromatic compound with characteristic properties due to the presence of an electron-rich pyrrole moiety,[9] which makes the indolyl ligands having plentiful applications in transition-metal chemistry: (1) Research focused on the syntheses and the bonding modes of indolyl or substituted indolyl ligands with transition metals such as palladium,[10] molybdenum,[11] manganese,[12] platinum,[13] copper,[14] and lanthanide,[15] etc., has been documented; (2) catalytic activities for the olefins polymerization in the presence of transition-metal complexes bearing indolide-imine ligands have been reported in the references. For example, nickel[16] and titanium dichloride[17] complexes bearing unsymmetrical bidentate indolide-imine ligands are reported to display high activities toward ethylene polymerization, and rare-earth-metal alkyl complexes[18] incorporating indolide-imine ligands in combination with aluminum alkyls and borate generated efficient homogeneous catalysts for the polymerization of isoprene. However, the syntheses and catalytic activities for transformation of small molecules in the presence of lanthanide amido complexes bearing amino-functionalized indolyl ligands remain to be less investigated.

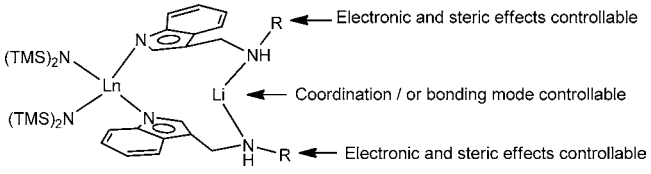
Received: January 18, 2012
Published: June 19, 2012

   dx.doi.org/10.1021/ic300137r | *Inorg. Chem.* 2012, 51, 7134–7143

The α-hydroxy or α-amino phosphonic acids and their derivatives have been recognized as a class of important bioactive compounds, which have been widely used as pesticides, antibiotics, anticancer drugs, antiviral agents, enzyme inhibitors, and HIV protease.[19] The addition of dialkyl phosphites to carbonyl compounds (Pudovik or Abramov reaction) has been regarded as the most straightforward and atom-economical pathway for the C−P bond formation in syntheses of α-hydroxyphosphonates or α-hydroxyphosphonic acids, and this reaction should be promoted by a base, however, side reaction, byproduct and harsh reaction conditions cannot be avoided. In the process of developing a more-convenient way to synthesize α-hydroxyphosphonates and α-hydroxyphosphonic acids, some organic base,[20] metal compounds including rare-earth-metal complexes[21−24] as catalysts for promoting the reaction efficiently were found, but, the drawbacks such as harsh reaction conditions, high catalyst loading, long reaction time, and narrow scope of the substrates in most cases remain to be solved. To meet the growing demands for enantiomerically pure materials, the synthesis of α-amino phosphonates asymmetrically has been developed. The first example was reported by Shibasaki and co-workers[25] using the heterometallic lanthanide-potassium-binaphthol complexes for the preparation of acyclic and cyclic α-amino phosphonates in the presence of a large catalyst loading (5−20 mol %). The Al(salalen)[26] catalyst and some organocatalysts, such as chiral thiourea,[27] quinine,[28] and phosphoric acid[29] have been found to be active in catalyzing the hydrophosphonylation of imines, but 10 mol % catalyst loading and excess dialkyl phosphonates (1.5−2.0 equiv) were required. Therefore, the development of a more-efficient catalyst with regard to reducing the catalyst loading and the amount of phosphonates for the synthesis of α-amino phosphonate is still strongly required.

We herein report the synthesis and structural characterization of two series of new lanthanide amides supported by bis(indolyl) ligands with amino-coordinate-lithium as a bridge, this kind of complex would possess different sites to be modified, with regard to an electronic, steric, and even lithium coordination environment (see Chart 1). The catalytic activity

Chart 1

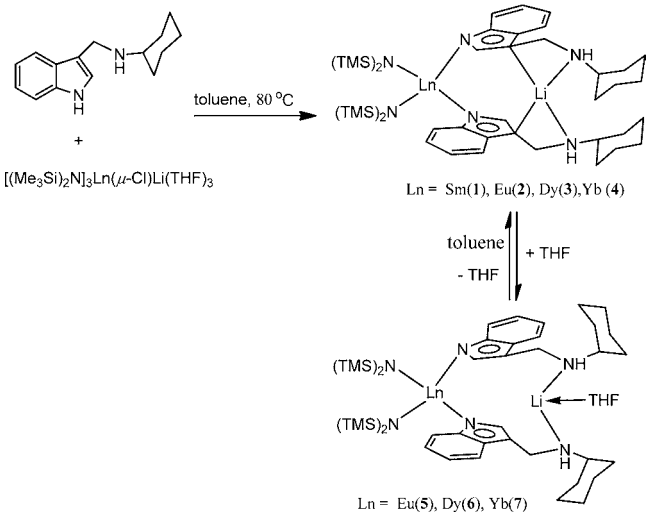


of these new lanthanide amido complexes on the hydrophosphonylation of both aromatic and aliphatic aldehydes and substituted imines under mild conditions will be for the first time reported.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Rare-Earth-Metal Complexes. Treatment of $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-Cl})Li(THF)_3$ with 2 equiv of 3-$(CyNHCH_2)C_8H_5NH$ in toluene, after workup, produced the lanthanide complexes $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Ln[N(SiMe_3)_2]_2]$ (Cy = cyclohexyl, Ind = indolyl, Ln = Sm (**1**), Eu (**2**), Dy (**3**), Yb (**4**)) in good isolated yields. The addition of THF to the toluene solution of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Ln[N(SiMe_3)_2]_2]$ at room temperature, after workup, gave the corresponding new amino and THF-coordinate-lithium bridged bis(indolyl) lanthanide amido complexes $[\mu\text{-}\{[\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li(THF)\}Ln[N(SiMe_3)_2]_2]$ (Ln = Eu (**5**), Dy (**6**), Yb (**7**)) in good yields, which can be transferred to the amido complexes **2**, **3**, and **4** by reflux the corresponding complexes in toluene (Scheme 1). Thus, two series of rare-

Scheme 1. Preparation of Complexes



earth-metal amides could be reciprocally transformed by merely changing the solvents in the reactions. The complexes are sensitive to air and moisture, and they are soluble in solvents such as tetrahydrofuran (THF), toluene, CH_2Cl_2, and even *n*-hexane. All complexes were fully characterized by spectroscopic methods and elemental analyses. The structures of the complexes **1**−**7** were additionally determined by single-crystal X-ray diffraction (XRD) study.

X-ray analyses revealed that complexes **1**−**4** were centrosymmetrical mononuclear structures crystallized in the tetragonal system with space group $P\bar{4}2_1c$. They are neutral compounds composed of bis(indolyl) ligands with amino-coordinate-lithium as a bridge, the lanthanide metal is coordinated by two amino-functionalized indolyl monoanions in an η^1 mode through indolyl nitrogen atom, two amido ligands $N(SiMe_3)_2$ (the representative structure of the complexes is shown in Figure 1 and Scheme 1; figures for complexes **2**, **3**, and **4** are given in the Supporting Information). The lithium ion is

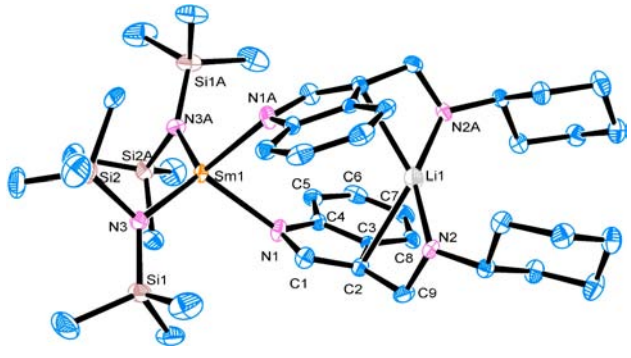


Figure 1. ORTEP diagram of the molecular structure of complex **1**. All hydrogen atoms are omitted for clarity.

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

Table 1. Selected Bond Length (Å) and Bond Angle (deg) of Complexes 1−7

	1	2	3	4	5	6	7
				Bond Distance (Å)			
Ln(1)−N(1)	2.381(2)	2.372(5)	2.328(6)	2.266(4)	2.424(6)	2.322(2)	2.264(4)
Ln(1)−N(3)	2.294(2)	2.283(5)	2.234(6)	2.197(4)	2.376(7)	2.301(2)	2.246(3)
Ln(1)−N(5)					2.301(6)	2.253(2)	2.212(3)
Ln(1)−N(6)					2.278(5)	2.241(2)	2.204(3)
Ln−$N_{av.}$	2.338(2)	2.328(5)	2.281(6)	2.232(4)	2.345(7)	2.279(2)	2.232(4)
Li(1)−N(2)	2.027(3)	2.029(6)	2.023(7)	2.018(5)	2.065(15)	2.094(4)	2.080(9)
Li(1)−N(4)					2.042(15)	2.074(4)	2.087(9)
Li(1)−C(2)	2.531(4)	2.522(9)	2.534(11)	2.528(8)			
Li(1)−O(1)					1.932(15)	1.968(4)	1.970(9)
				Bond Angle (deg)			
N(3)−Ln(1)−N(1A)	111.99(7)	109.54(17)	110.3(2)	110.34(16)			
N(3)−Ln(1)−N(1)	109.24(7)	110.84(16)	109.5(2)	109.05(17)			
N(1)−Ln(1)−N(1A)	82.39(11)	82.5(3)	83.1(3)	84.5(2)			
N(3)−Ln(1)−N(3A)	124.21(12)	125.4(3)	125.9(3)	125.8(2)			
N(6)−Ln(1)−N(5)					113.9(2)	122.97(6)	121.70(12)
N(6)−Ln(1)−N(3)					117.5(2)	112.07(6)	112.14(13)
N(5)−Ln(1)−N(3)					101.4(2)	108.29(6)	109.18(12)
N(6)−Ln(1)−N(1)					103.6(2)	105.92(6)	107.49(12)
N(5)−Ln(1)−N(1)					131.0(2)	116.16(6)	114.74(13)
N(3)−Ln(1)−N(1)					87.1(2)	85.15(6)	85.99(13)
N(2)−Li(1)−N(2A)	147.2(3)	146.7(8)	147.4(10)	148.0(7)			
N(2)−Li(1)−N(4)					126.4(7)	118.19(19)	117.0(4)
N(2)−Li(1)−O(1)					120.0(7)	111.9(2)	113.5(5)
N(4)−Li(1)−O(1)					110.2(7)	127.2(2)	127.5(5)

coordinated by a carbon atom of *β*-position of the indolyl ligands as compared Li−C distances (2.531(4) Å in **1**, 2.522(9) Å in **2**, 2.534(11) Å in **3**, 2.528(8) Å in **4**) with those of Li−C_5 ring distances found in CpLi(solvent)$_x$ and IndLi(solvent)$_x$ (here, Ind = indenyl),[30] and amino nitrogen atoms, thus formed the amino-coordinate-lithium bridged bis(indolyl) ligands. It is found that the protons on nitrogen atoms of the substituent amino groups have not been removed. Comparison of the Ln−N bond distances of the same molecule indicated that they are not identical, and also N(1)−Ln−N(1A), N(3)−Ln−N(3A) are far from the ideal tetrahedral angles (see Table 1), so the coordination geometry of the central metal can be described as distorted tetrahedral. The geometry of central lanthanide metals in complexes **1**−**4** is very similar to the *racemic*-bis(indenyl) group IV metal complexes.[31] From Figure 2 and Table 1, we could see that the coordinate mode of

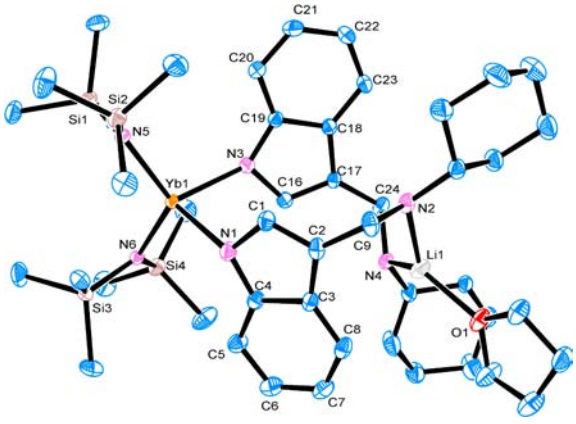


Figure 2. ORTEP diagram of the molecular structure of complex **7**. All hydrogen atoms are omitted for clarity.

lithium ion was changed from coordinated by carbon atom of indolyl ligand and the amino nitrogen atoms to coordinated by the amino nitrogen atoms and THF molecule, and the molecular symmetry found in complexes **1**−**4** was also completely changed (the representative structure of the complex **7** is shown in Figure 2 and Scheme 1; figures for complexes **5** and **6** are shown in the Supporting Information).

From Table 1, we can see that the usual consequences of the contraction of the ionic radius of the Ln^{3+} ions when moving from Sm^{3+} to Yb^{3+} are clearly reflected by the average Ln−N distances of 2.338(2) Å in **1**, 2.328(5) Å in **2**, 2.281(6) Å in **3**, and 2.232(4) Å in **4**. The similar results can be found in the average Ln−N distances of complexes **5**−**7**. From Table 1, we can also find that the Ln−N bond distances from the metal to the indolyl ligand are generally longer than those from the metal to the $N(SiMe_3)_2$. For example, the Sm(1)−N(1) distances are 2.381(2) Å in **1**, which are longer than the Sm(1)−N(3) distances of 2.294(2) Å. The similar results can also be found in other lanthanide metal complexes **2** to **4**. This may be attributable to the steric effect of indolyl ligands. From Table 1, we can find that the average Eu−N bond distance of 2.345(7) Å found in **5** is a slightly longer than that of 2.328(5) Å found in **2**. But, the average Dy−N and Yb−N distances found in **3** or **6**, and **4** or **7** are almost identical regardless of a THF molecule coordinated to a lithium ion. The average Sm−N bond distance found in **1** (2.338(2) Å), and the average Yb−N bond distance found in **4** and **7** (2.232(4) Å), are longer than the corresponding Ln−N distances of 2.268(3) Å found in the mononuclear complex $\{(Me_2Si)[(2,6\text{-}^{i}Pr_2C_6H_3)N]_2\}SmN(SiMe_3)_2(THF)$[2e] and 2.181(4) Å found in $\{(Me_2Si)[(2,6\text{-}^{i}Pr_2C_6H_3)N]_2\}YbN(SiMe_3)_2(THF)$,[2e] probably due to the steric effect of indolyl ligands. The average Sm−N bond distance of 2.338(2) Å found in **1** is comparable to the Sm−N distance of 2.399(4) Å found in the samarium(III) complex

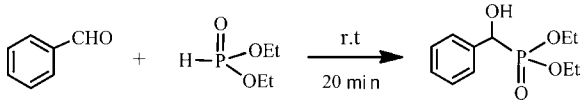
dx.doi.org/10.1021/ic300137r | *Inorg. Chem.* 2012, 51, 7134−7143

$(C_5Me_5)_2Sm(DMI)$ (DMI = $Me_2C_8H_4N$),[32] but the average Sm−N distance in **1** is shorter than those of 2.610(4) Å and 2.601(4) Å in $(DMI)_2Sm(THF)_4$.[32] The Eu−N bond distance for the metal to the indolyl nitrogen atom of 2.372(5) Å in complex **2** is also shorter than that of 2.633(7) Å in the binuclear complex $[Eu_2(Ind)_4(NH_3)_6]$ (Ind = Indolyl).[33] The Yb−N bond distance of 2.266(4) Å in **4** is comparable with 2.262(2) Å found in $L^1Lu(CH_2SiMe_3)_2(THF)$ (L^1 = 7-(2,6-$Me_2C_6H_3NCH$)Ind), and 2.274(3) Å found in $L^2{}_2Lu[^iPr_2NC(CH_2SiMe_3)N^iPr_2]$ (L^2 = 7-(2,6-$^iPr_2C_6H_3NCH$)Ind) (Ind = Indolyl),[18] even if the ionic radii differences between these types of complexes were taken into account.[34] The average Dy−N bond distance of 2.281(6) Å found in **3**, 2.279(2) Å in **6**, is longer than the average Dy−N bond distance of 2.219(3) Å found in the complex $\{(CH_2SiMe_2)[(2,6\text{-}^iPr_2C_6H_3)N]_2\}DyN(SiMe_3)_2(THF)$.[2d] The corresponding average Yb−N distances of 2.232(4) Å found in **4** and **7**, are longer than that of 2.181(4) Å found in $\{(CH_2SiMe_2)[(2,6\text{-}^iPr_2C_6H_3)N]_2\}YbN(SiMe_3)_2(THF)$.[2d]

Catalytic Activities of the Complexes on Hydrophosphonylation of Aldehydes. During the study of the catalytic reactivity of the above complexes, it is found that the above complexes can function as efficient catalysts for hydrophosphonylation of aldehydes with a high activity and compatibility with a wide range of substrates under an environmentally benign solvent-free conditions.

Ytterbium complex **4** was employed as a catalyst for selecting the favorable catalytic reaction conditions for hydrophosphonylation of aldehydes, and the results are listed in Table 2.

Table 2. Catalytic Reaction of Benzaldehyde with Diethyl Phosphite



entry	cat	loading (mol %)	solvent	yield (%)[a]
1	complex **4**	1	toluene	99
2	complex **4**	0.5	toluene	98
3	complex **4**	0.1	toluene	98
4	complex **4**	0.05	toluene	51
5	complex **4**	0.1	solvent-free	99
6	none		solvent-free	0
7	complex **1**	0.1	solvent-free	97
8	complex **2**	0.1	solvent-free	98
9	complex **3**	0.1	solvent-free	99
10	complex **5**	0.1	solvent-free	97
11	complex **6**	0.1	solvent-free	98
12	complex **7**	0.1	solvent-free	97

[a]Benzaldehyde and diethyl phosphite (1:1 equiv).

From the table (entry 1), it is found that the hydrophosphonylation of benzaldehyde could be accomplished in toluene at room temperature within 20 min, producing the product in 99% yield in the presence of 1 mol % of catalyst. It is found that the outputs of the catalytic reactions were not affected by the catalyst loadings when the catalyst loadings were changed from 1 mol % to 0.5 mol % and to 0.1 mol % (entries 1−3), but further decreasing the catalyst loadings to 0.05 mol % led to a dramatically low yield of product (entry 4). When the reaction was carried out under solvent-free conditions, it was surprising to find that the output of the product remained high (99% yield, entry 5). However, no product was observed when the reaction was carried out in the absence of catalyst under the same conditions (entry 6). Then, the reaction conditions were selected as 0.1 mol % of rare-earth-metal complexes at room temperature under solvent-free conditions for 20 min for the following studies. Examinations of the catalytic activity of other amino-coordinate-lithium bridged bis(indolyl) rare-earth-metal amides under the selected conditions also provided high isolated yields of products. The result indicated that the ionic radii of the rare-earth metals or solvated lanthanide amido complexes have little influence on the catalytic activity of those catalysts (entries 7−12).

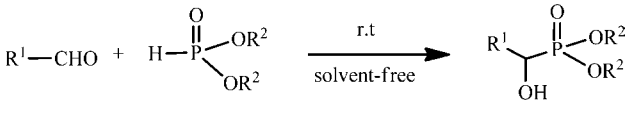
With the optimized reaction conditions in hand, all the complexes exhibited similar catalytic activity. So, the ytterbium complex **4** was selected as the catalyst for the following experiments to study the electronic effects and steric effects of the substrates and the scope of the hydrophosphonylation reaction. A variety of aromatic and aliphatic aldehydes were evaluated under the optimized reaction conditions, and the results are presented in Table 3.

As shown in Table 3, a wide range of substituted aromatic aldehydes are suitable for the catalytic addition of diethyl or diphenyl phosphite. The substituents on the phenyl ring of aldehydes could be either electron-donating groups, such as CH_3, CH_3O, and $(CH_3)_2N$, or electron-withdrawing groups, such as Cl, Br, and NO_2, and excellent yields (97−99%) of the products can be isolated (entries 1−9). Next, the scope of the substrates were expanded to various aliphatic aldehydes. The results showed that the steric effects of aldehydes have little influence on the outputs of the reaction (entries 10−14). For example, when the more sterically hindered aldehydes such as 2,2-dimethyl-propionaldehyde or the less bulky propionaldehyde was employed in the reactions, the outputs of the reaction still remained at 96%−97% yields (entries 10−14). Comparison the results of hydrophosphonylation of aldehydes with diethyl phosphite, hydrophosphonylation of aldehydes with dipheyl phosphite also gave excellent results, regardless of the electronic effects of the substituents, but the reaction required for 12 h for completion (entries 15−19). These results further suggested that these lanthanide complexes supported by amino-coordinate-lithium bridged bis(indolyl) ligands exhibited a high catalytic activity for the C−P bond formation than the prevous lanthanide amides $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$[24a] and $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,6\text{-}Me_2C_6H_3)NCH_2](C_4H_3N)SmN(SiMe_3)_2\}_2$,[24c] including the scope of the substituents both aldehydes and phosphites, the ratio of aldehydes to phosphites, and the solvent in the reaction.

Catalytic Activities of the Complexes on Hydrophosphonylation of Aldimines. Given the proven bioactivity of the α-amino phosphonates, we try to explore the application of the above complexes in the synthesis of α-amino phosphonates via catalytic additions of diethyl phosphite to aldimines. Ytterbium complex **4** was employed as a catalyst for selecting the optimized reaction conditions for hydrophosphonylation of aldimines. An excellent yield of product (99%) could be isolated for the catalytic addition of diethyl phosphite to benzylideneaniline in the presence of 3 mol % of the ytterbium complex **4** as a catalyst in THF at 40 °C for 6 h (Table 4, entry 1). Decreasing catalyst loading from 3 mol % to 2 mol % and then to 1 mol % did not affect the yields of the product (Table 4, entries 2 and 3). While the catalyst loading was reduced from 1 mol % to 0.5 mol %, the yield of the product decreased dramatically from 99% to 64% (entry 4). A

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

Table 3. Results of Phosphonylation Reaction of Aldehydes with Diethyl Phosphites[a] or Diphenyl Phosphites[b] Catalyzed by Complex 4



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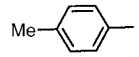
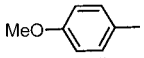
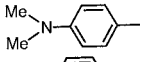
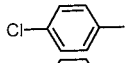
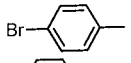
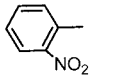
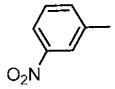
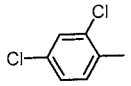
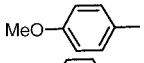
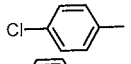
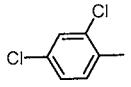
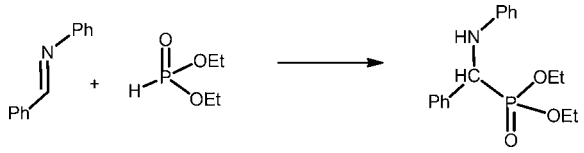
entry	R^1	R^2	product	yield (%)
1		Et	**10a**	98
2		Et	**10b**	99
3		Et	**10c**	97
4		Et	**10d**	98
5		Et	**10e**	99
6		Et	**10f**	99
7		Et	**10g**	98
8		Et	**10h**	98
9		Et	**10i**	99
10		Et	**10j**	97
11		Et	**10k**	97
12		Et	**10l**	97
13		Et	**10m**	98
14		Et	**10n**	96
15		Ph	**10o**	94
16		Ph	**10p**	94
17		Ph	**10q**	92
18		Ph	**10r**	90
19		Ph	**10s**	91

[a]Aldehyde and diethyl phosphite (1:1 equiv) for 20 min. [b]Aldehyde and diphenyl phosphite (1:1 equiv) for 12 h.

survey of the solvents indicated that the catalysts were compatible with a variety of solvents with isolation of excellent yields of product (entries 5−8). When the reaction was carried out at room temperature for 6 h in the presence of 1 mol % of complex **4** as a catalyst, a 76% yield of product was obtained; by prolonging the reaction time to 12 h, a 99% yield of product could be obtained (entries 9 and 10). A 98% yield of product could be obtained when the catalytic addition of diethyl phosphite to benzylideneaniline was carried out at 80 °C in toluene for 2 h (entry 11). However, the results were still dissatisfactory when the catalytic reaction was carried out at 80 °C in the presence of 0.5 mol % of the catalyst, even the reaction time was prolonged to 12 h (entries 12 and 13).

Table 4. Catalytic Reaction of Benzylideneaniline with Diethyl Phosphite



entry	cat (mol %)	solvent	temp (°C)	time (h)	yield (%)[a]
1	**4** (3)	THF	40	6	99
2	**4** (2)	THF	40	6	99
3	**4** (1)	THF	40	6	99
4	**4** (0.5)	THF	40	6	64
5	**4** (1)	toluene	40	6	98
6	**4** (1)	*n*-hexane	40	6	97
7	**4** (1)	Et_2O	40	6	98
8	**4** (1)	CH_2Cl_2	40	6	99
9	**4** (1)	THF	rt	6	76
10	**4** (1)	THF	rt	12	99
11	**4** (1)	toluene	80	2	98
12	**4** (0.5)	toluene	80	6	65
13	**4** (0.5)	toluene	80	12	65
14	**1** (1)	THF	40	6	97
15	**2** (1)	THF	40	6	99
16	**3** (1)	THF	40	6	98
17	**5** (1)	THF	40	6	98
18	**6** (1)	THF	40	6	97
19	**7** (1)	THF	40	6	98
20	**8** (1)	THF	40	6	70
21	**9** (1)	THF	40	6	72
22	**10** (1)	THF	40	6	80
23	**11** (1)	THF	40	6	82

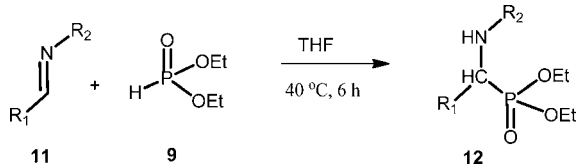
[a]Aldimine and diethyl phosphite (1:1.2 equiv); **8** = $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$;[35] **9** = $[(Me_3Si)_2N]_3Sm(\mu\text{-}Cl)Li(THF)_3$;[35] **10** = $\{(\mu\text{-}\eta^5{:}\eta^1)\text{-}2\text{-}[(2,6\text{-}Me_2C_6H_3)NCH_2](C_4H_3N)SmN(SiMe_3)_2\}_2$;[24d] **11** = $(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8\text{-calix}[4]\text{-pyrrolyl})\{SmN(SiMe_3)_2\}_2$.[24c]

Examination of the catalytic activity of the different lanthanide amides on hydrophosphonylation of benzylideneaniline also produced high yields of product, indicating that the ionic radii of the rare-earth metals or coordination on the lithium of the complexes have little influence on the catalytic activities on the hydrophosphonylation of benzylideneaniline (entries 14−19). Notably, other lanthanide complexes only displayed moderate activities of hydrophosphonylation of benzylideneaniline in comparative experiments on catalytic activity of different lanthanide complexes,[24] suggesting the ligands' effect on the catalytic activity for hydrophosphonylation of benzylideneaniline and the advantages of the present catalysts (entries 20−23).

The scope of substrates for the catalytic hydrophosphonylations of aldimines was then investigated using 1 mol % of complex **4** as a catalyst in THF at 40 °C for 6 h. The results are presented in Table 5. It is found that the electronic nature of the substituents on C-terminal of the imines had little effect on the activity of hydrophosphonylation of aldimines (except for $-NO_2$, only 42% yield, entry 7), regardless of the electron-donating groups or electron-withdrawing groups (entries 1−6). When the electron-donating substituents were used, such as Me, OMe, on N-terminal of the imines, good to high yields of products **12h** and **12i** were isolated (entries 8 and 9). It was also found that the electronic and steric nature have some effects on the activities of the hydrophosphonylation of

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

Table 5. Results of Hydrophosphonylation Reaction of Aldimines with Diethyl Phosphite Catalyzed by Complex 4



11 9 12

entry	R_1	R_2	product	yield (%)[a]
1	C_6H_5	C_6H_5	**12a**	99
2	4-MeC_6H_4	C_6H_5	**12b**	98
3	4-$MeOC_6H_4$	C_6H_5	**12c**	97
4	2-$MeOC_6H_4$	C_6H_5	**12d**	96
5	4-ClC_6H_4	C_6H_5	**12e**	96
6	4-BrC_6H_4	C_6H_5	**12f**	95
7	4-$O_2NC_6H_4$	C_6H_5	**12g**	42
8	C_6H_5	4-MeC_6H_4	**12h**	90
9	C_6H_5	4-$MeOC_6H_4$	**12i**	83
10	4-$MeOC_6H_4$	4-MeC_6H_4	**12j**	84
11	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**12k**	80
12	4-ClC_6H_4	4-MeC_6H_4	**12l**	92
13	4-ClC_6H_4	4-$MeOC_6H_4$	**12m**	89
14	4-BrC_6H_4	4-$MeOC_6H_4$	**12n**	84
15	2-pyrrolyl	^{t}Bu	**12o**	97
16	2-pyrrolyl	C_6H_5	**12p**	98
17	3-indolyl	^{t}Bu	**12q**	81
18	3-indolyl	4-^{t}BuC_6H_4	**12r**	90
19	3-indolyl	cyclohexyl	**12s**	78
20	C_6H_5	4-$MeC_6H_4SO_2$	**12t**	92

[a]Aldimine and diethyl phosphite (1:1.2 equiv); complex **4** as a catalyst.

aldimines when the substituents existed on both the N-terminal and the C-terminal (entries 10−14). Heteroaromatic aldimines, such as 2-(^{t}BuN═CH)C_4H_3NH, 2-(PhN═CH)C_4H_3NH, also worked well, and 97% and 98% yields of products could be isolated, respectively (entries 15 and 16). When the indolyl imines were used in the reaction, product yields of 78%−90% could be obtained, depending on the electronic and steric nature of the substrates (entries 17−19). The *N*-benzylidenebenzenesulfonamide can also be hydrophosphonylated under the same conditions, using complex **4** as a catalyst (entry 20).

In order to understand the mechanism of the catalytic reaction, several experiments were probed by the NMR technique, and the catalytic reaction was probed stepwise with ^{1}H NMR spectra. First, the stoichiometric reaction of complex **1** with diethyl phosphite was monitored by ^{1}H NMR spectrum. ^{1}H NMR spectra clearly indicated the equilibium process of $HP(O)(OCH_2CH_3)_2$ and $HOP(OCH_2CH_3)_2$, and the resonances of the protons of the $HP(O)(OCH_2CH_3)_2$ and $HOP(OCH_2CH_3)_2$ at 7.81 ppm, 5.53 ppm. These resonances disappeared when the diethyl phosphite was treated with complex **1**; instead, the protons of the OCH_2CH_3 of the diethyl phosphite appeared in the ^{1}H NMR spectrum (see page 54 of the Supporting Information), suggesting the reaction of complex **1** with diethyl phosphite produced the active species of **A** (as indicated in Scheme 2). The solid state of the suggested **A** exihited a catalytic activity on reaction of C_6H_5CH═NC_6H_5 with diethyl phophite, producing the hydrophosphonylation product **12a** with 90% isolated yield, almost a similar catalytic activity to that of complex **1**. Then, the interaction of the intermediate **A** with C_6H_5CH═NC_6H_5 was probed by ^{1}H NMR spectrum. The resonance of imine proton of C_6H_5CH═NC_6H_5 at 8.50 ppm with the addition of C_6H_5CH═NC_6H_5 to the mixture of intermediate **A** within 10 min can be observed. This imine proton disappeared upon heating the reaction mixture at 40 °C for 6 h in THF-d_8; instead, the characteristic resonances at 4.88 and 4.80 ppm for the $(EtO)_2P(O)-PhCH-NHPh$, which was formed via the addition of a phosphorus atom to the imine carbon appeared, suggesting that the intermediate **C** produced. The intermediate **C** was also obtained through the reaction of **12a** with complex **1**, and was characterized by ^{1}H NMR, infrared (IR), and elemental analyses. ^{1}H NMR spectrum of the intermediate **C** shown identical resonances as those obtained by reaction of intermediate **A** with the imine C_6H_5CH═NC_6H_5 in NMR probing process (see page 54 of the Supporting Information). Several attempts to grow crystals of **A** and **C** failed, but intermediates **A** and **C** were fully characterized. On the basis of these experimental results, the catalytic mechanism is proposed as follows (Scheme 2): interaction of catalyst with diethyl phosphite produced the intermediate **A**, which coordinates with aldehydes or aldimines to afford intermediate **B** of which O or N atom may have a weak coordination with lithium, resulting in greater electron deficiency on the carbon atom of aldehydes or aldimines. The addition of the phosphorous atom of the diethyl phosphite to the carbon atom of aldehydes or aldimines gave intermediate **C**, which then interacted with diethyl phosphite to produce the final products.

■ CONCLUSION

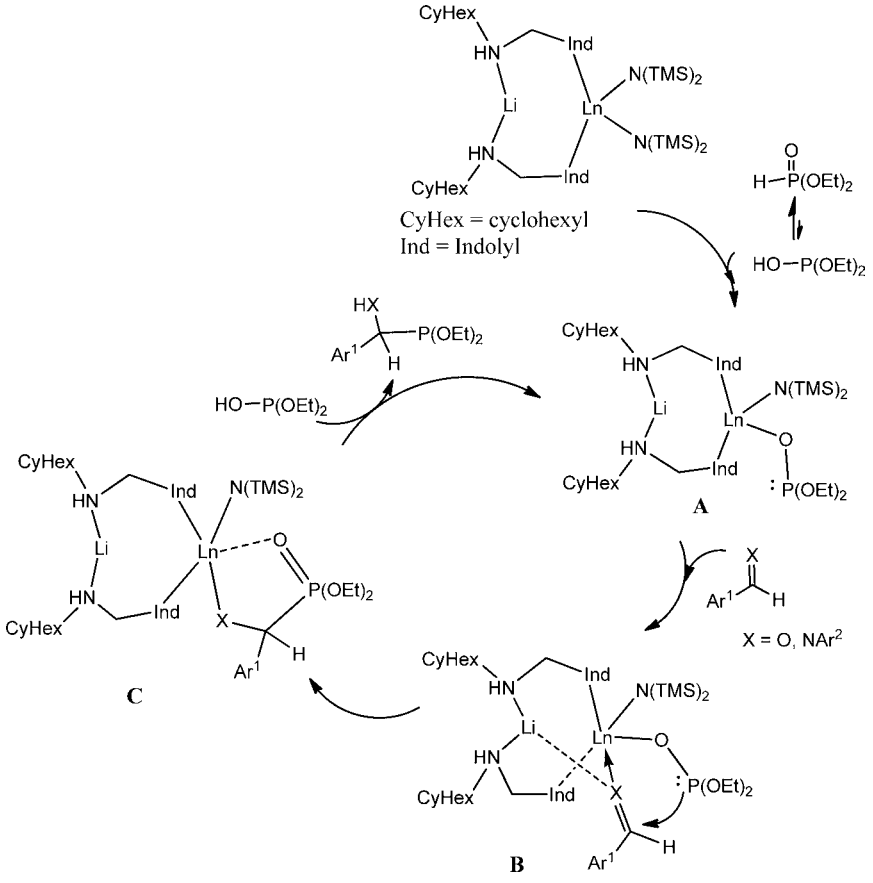
New lanthanide amides [μ-{[η^1:η^1:η^1:η^1-3-($CyNHCH_2$)-Ind]$_2$Li}Ln[N($SiMe_3$)$_2$]$_2$] bearing amino-coordinate-lithium bridged bis(indolyl) ligands were synthesized in good isolated yields via reactions of [$(Me_3Si)_2N]_3Ln^{III}(\mu$-Cl)Li(THF)$_3$ (Ln = Sm, Eu, Dy, Yb) with the amino-substituted indolyl ligand 3-($CyNHCH_2$)C_8H_5NH. These complexes can be transferred to [μ-{[η^1:η^1-3-($CyNHCH_2$)Ind]$_2$Li(THF)}Ln[N($SiMe_3$)$_2$]$_2$] (Ln = Eu, Dy, Yb) via the addition of THF to [μ-{[η^1:η^1:η^1:η^1-3-($CyNHCH_2$)Ind]$_2$Li}Ln[N($SiMe_3$)$_2$]$_2$] at room temperature. Reflux complexes [μ-{[η^1:η^1-3-($CyNHCH_2$)Ind]$_2$Li(THF)}Ln-[N($SiMe_3$)$_2$]$_2$] in toluene resulted in the isolation of [μ-{[η^1:η^1:η^1:η^1-3-($CyNHCH_2$)Ind]$_2$Li}Ln[N($SiMe_3$)$_2$]$_2$]. Thus, two different rare-earth-metal amides could be reciprocally transferred easily by merely changing the solvents. These new lanthanide complexes were found to exhibit an excellent catalytic activity on the hydrophosphonylation of aldehydes and aldimines. These catalysts have the advantages of easy preparation, compatibility with a wide range of substrates (aldehydes and aldimines) and solvents, high yield of products, and proceeding under an environmentally benign condition for aldehydes. High catalytic activity catalysts with a low catalyst loading (1 mol %) for hydrophosphonylation of aldimines are for the first time to be reported in this field. These advantages of these complexes imply the potential applications of other rare-earth metal amides in this field. Using NMR technique, the intermediates of the catalytic reaction can be observed, thus, the mechanism of the catalytic reaction was proposed. Further works on this field are now under investigation in our laboratory.

■ EXPERIMENTAL SECTION

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere, using standard Schlenk techniques or a glovebox. All solvents were refluxed and distilled over sodium

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

Scheme 2. Proposed Mechanism for the Catalytic Reactions



benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-Cl})Li(THF)_3$ (Ln = Sm, Eu, Dy, and Yb),[35] 3-$(CyNHCH_2)C_8H_5NH$,[36] aldimines were prepared according to literature methods.[37] Elemental analyses data were obtained on a Perkin−Elmer Model 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker Model AV-300 NMR spectrometer (300 MHz for ^1H; 75.0 MHz for ^{13}C) in C_6D_6 for lanthanide complexes and in $CDCl_3$ for organic compounds. Chemical shifts (δ) were reported in ppm. J values are reported in Hz. IR spectra were recorded on a Shimadzu Model FTIR-8400s spectrometer (KBr pellet). HRMS measurements were conducted with an Agilent Model 6220 ESI-TOF mass spectrometer.

Preparation of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Sm[N(SiMe_3)_2]_2]$ (1). To a toluene (10.0 mL) solution of 3-$(CyNHCH_2)$-C_8H_5NH (0.63 g, 2.76 mmol) was added a toluene (20.0 mL) solution of $[(Me_3Si)_2N]_3Sm^{III}(\mu\text{-Cl})Li(THF)_3$ (1.23 g, 1.38 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then heated at 80 °C for 24 h and the color of the solution was gradually changed from colorless to yellow. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 10 mL). The combined extractions were concentrated to ∼10.0 mL. The yellow crystals were obtained at 0 °C for several days (0.75 g, 58% yield). ^1H NMR (300 MHz, C_6D_6, ppm): δ 13.02 (d, 2H, J = 7.50 Hz, C_8H_5), 8.56 (s, 2H, C_8H_5), 7.89−7.77 (m, 6H, C_8H_5), 3.60 (d, 4H, J = 8.40 Hz, $-CH_2$), 2.46−1.66 (m, 22H, C_6H_{11}), −1.34 (s, 36H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6, ppm): δ 150.4 (C_8H_5), 135.9 (C_8H_5), 125.3 (C_8H_5), 122.6 (C_8H_5), 122.3 (C_8H_5), 119.9 (C_8H_5), 115.8 (C_8H_5), 106.1 (C_8H_5), 57.7 ($-CH_2$), 40.6 (C_6H_{11}), 34.0 (C_6H_{11}), 26.1 (C_6H_{11}), 25.4 (C_6H_{11}), 2.9 ($Si(CH_3)_3$). IR (KBr pellet, cm^{-1}): ν 2941 (w), 2846 (m), 1618 (m), 1552 (m), 1498 (m), 1450 (s), 1357 (s), 1338 (w), 1265 (m), 1207 (m), 1180 (s), 1134 (m), 1031 (m), 966 (m), 918 (w), 889 (m), 846 (w), 788 (w), 648 (w). Anal. Calc. for $C_{42}H_{74}LiN_6Si_4Sm$: C, 54.08; H, 8.00; N, 9.01. Found: C, 54.32; H, 8.23; N, 8.82.

Preparation of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Eu[N(SiMe_3)_2]_2]$ (2). This compound was isolated as red crystals in 60% yield by treatment of $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-Cl})Li(THF)_3$ (1.01 g, 1.13 mmol) with 3-$(CyNHCH_2)C_8H_5NH$ (0.51 g, 2.26 mmol) following the procedures similar to those used for the preparation of **1**. Because of significant paramagnetic shifts and broadening effects, the ^1H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2926 (s), 2850 (m), 1635 (s), 1577 (w), 1533 (w), 1454 (s), 1357 (m), 1350 (w), 1217 (m), 1184 (m), 1095 (w), 1010 (w), 964 (m), 891 (m), 837 (w), 740 (m). Anal. Calc. for $C_{42}H_{74}LiN_6Si_4Eu$: C, 53.99; H, 7.98; N, 8.99. Found: C, 53.76; H, 8.02; N, 8.65.

Preparation of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Dy[N(SiMe_3)_2]_2]$ (3). This compound was isolated as colorless crystals in 64% yield by treatment of $[(Me_3Si)_2N]_3Dy^{III}(\mu\text{-Cl})Li(THF)_3$ (0.99 g, 1.10 mmol) with 3-$(CyNHCH_2)C_8H_5NH$ (0.50 g, 2.20 mmol) following the procedures similar to those used for the preparation of **1**. Because of significant paramagnetic shifts and broadening effects, the ^1H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2922 (s), 2848 (m), 1618 (w), 1552 (w), 1498 (w), 1450 (s), 1357 (m), 1338 (w), 1261 (m), 1238 (m), 1207 (m), 1180 (m), 1134 (m), 1031 (w), 966 (m), 889 (m), 846 (w), 829 (m), 779 (w). Anal. Calc. for $C_{42}H_{74}LiN_6Si_4Dy$: C, 53.39; H, 7.89; N, 8.89. Found: C, 53.54; H, 7.81; N, 8.69.

Preparation of $[\mu\text{-}\{[\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}Yb[N(SiMe_3)_2]_2]$ (4). This compound was isolated as yellow crystals in 60% yield by treatment of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-Cl})Li(THF)_3$ (1.29 g, 1.41 mmol) with 3-$(CyNHCH_2)C_8H_5NH$ (0.64 g, 2.82 mmol) following the procedures similar to those used for the preparation of **1**. Because of significant paramagnetic shifts and broadening effects, the ^1H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2922 (s), 2846 (w), 2360 (s), 2341 (m), 1577 (w), 1550 (w), 1498 (w), 1373 (m), 1357 (m), 1238 (m), 1207 (w), 1180 (m), 1031 (m),

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

Table 6. Crystallographic Data for Complexes 1−7

	1	2	3	4	5	6	7
formula	$C_{42}H_{74}SmLiN_6Si_4$	$C_{42}H_{74}EuLiN_6Si_4$	$C_{42}H_{74}DyLiN_6Si_4$	$C_{42}H_{74}YbLiN_6Si_4$	$C_{46}H_{82}EuLiN_6OSi_4$	$C_{46}H_{82}DyLiN_6OSi_4$	$C_{46}H_{82}YbLiN_6OSi_4$
mol wt	932.72	934.33	944.87	955.41	1006.44	1016.98	1027.52
T (K)	113(2)	293(2)	113(2)	113(2)	113(2)	113(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	tetragonal	tetragonal	tetragonal	tetragonal	monoclinic	triclinic	triclinic
space group	$P\bar{4}2_1c$	$P\bar{4}2_1c$	$P\bar{4}2_1c$	$P\bar{4}2_1c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.050(4)	12.1994(7)	12.1877(7)	12.2057(3)	18.343(5)	11.7126(13)	11.7254(7)
b (Å)	12.050(4)	12.1994(7)	12.1877(7)	12.2057(3)	17.565(4)	15.2595(19)	15.3734(9)
c (Å)	34.797(12)	34.813(3)	34.665(2)	34.5086(18)	17.537(4)	15.9326(19)	16.1586(9)
α (deg)	90	90	90	90	90	81.424(7)	81.8810(10)
β (deg)	90	90	90	90	97.687(5)	70.535(5)	70.4730(10)
χ (deg)	90	90	90	90	90	81.591(7)	81.5320(10)
V (Å^3)	5053(3)	5181.1(6)	5149.1(5)	5141.1(3)	5600(2)	2640.6(5)	2702.0(3)
Z (Å^3)	4	4	4	4	4	2	2
D_{calcd} (g cm^{-3})	1.226	1.198	1.219	1.234	1.194	1.279	1.263
μ (mm^{-1})	1.290	1.335	1.576	1.944	1.241	1.543	1.856
F (000)	1956	1960	1972	1988	2120	1066	1074
θ range (deg)	1.79−27.87	1.77−27.72	1.77−27.52	1.77−27.54	1.61−26.00	1.36−27.84	1.34−27.58
reflcns collcd/ unique	32477/6032	43489/6045	42058/5934,	43498/5930	49680/11011	33526/12491	23610/12178
R_{int}	0.0400	0.0297	0.0510	0.0678	0.0610	0.0345	0.0298
GOF	1.075	1.094	1.189	1.016	1.337	1.020	1.018
R_1, wR_2 ($I > 2\sigma(I)$)	0.0288, 0.0545	0.0477, 0.1213	0.0471, 0.0693	0.0376, 0.0626	0.0833, 0.1597	0.0259, 0.0608	0.0399, 0.0777
R_1, wR_2 (all data)	0.0319, 0.0559	0.0573, 0.1272	0.0813, 0.0781	0.0898, 0.0743	0.0904, 0.1627	0.0288, 0.0617	0.0645, 0.0879
largest diff peak/hole (e Å^{-3})	0.315 and −0.739	0.574 and −0.554	0.809 and −1.104	0.648 and −0.516	1.116 and −1.301	1.266 and −0.723	0.867 and −0.862

966 (m), 933 (m), 889 (w), 869 (w), 738 (m). Anal. Calc. for $C_{42}H_{74}LiN_6Si_4Yb$: C, 52.80; H, 7.81; N, 8.80. Found: C, 53.17; H, 7.79; N, 8.48.

Preparation of [μ-{[η^1:η^1-3-(CyNHCH$_2$)Ind]$_2$Li(THF)}Eu[N(SiMe$_3$)$_2$]$_2$] (5). A toluene solution of [μ-{[η^1:η^1:η^1-3-(CyNHCH$_2$)-Ind]$_2$Li}Eu[N(SiMe$_3$)$_2$]$_2$] (**2**) (0.51 g, 0.55 mmol) was treated with 10 mL of THF at room temperature (rt) for 5 h. The solvent was evaporated under reduced pressure, and the residue was extracted with 10 mL of *n*-hexane. Red rectangular crystals were obtained upon allowing the extraction to stand at room temperature for several days (0.26 g, 53% yield). Because of significant paramagnetic shifts and broadening effects, the ^{1}H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2922 (s), 2848 (m), 1637 (s), 1581 (w), 1500 (w), 1448 (s), 1390 (w), 1357 (m), 1232 (s), 1207 (m), 1182 (m), 1134 (w), 1056 (w), 968 (m), 889 (m), 846 (w), 738 (m). Anal. Calc. for $C_{46}H_{82}LiN_6OSi_4Eu$·THF: C, 55.73; H, 8.33; N, 7.80. Found: C, 55.65; H, 8.12; N, 7.85. A toluene (10 mL) solution of complex **5** (0.22 g, 0.22 mmol) was refluxed at 100 °C temperature for 5 h. The solvent was evaporated under reduced pressure and the residue was extracted with 10 mL *n*-hexane. Complex **2** was obtained again upon allowing the extraction at room temperature (0.13 g, 61% yield).

Preparation of [μ-{[η^1:η^1-3-(CyNHCH$_2$)Ind]$_2$Li(THF)}Dy[N(SiMe$_3$)$_2$]$_2$] (6). This compound was isolated as colorless crystals in 45% yield by treatment of [μ-{[η^1:η^1:η^1-3-(CyNHCH$_2$)Ind]$_2$Li}-Dy[N(SiMe$_3$)$_2$]$_2$] (**3**) (0.42 g, 0.44 mmol) with 10 mL THF following the procedures similar to those used for the preparation of **5**. Because of significant paramagnetic shifts and broadening effects, the ^{1}H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2922 (s), 2846 (w), 1658 (w), 1618 (w), 1450 (s), 1373 (m), 1238 (m), 1180 (s), 1131 (m), 1111 (w), 1008 (s), 966 (m), 829 (w), 738 (m), 586 (w). Anal. Calc. for $C_{46}H_{82}LiN_6OSi_4Dy$·0.5THF: C, 54.75; H, 8.23; N, 7.98. Found: C, 54.97; H, 7.78; N, 7.78. Complex **3** was obtained again in 50% yield by refluxing **6** in toluene, following the procedures similar to those described above for transferring **5** to **2**.

Preparation of [μ-{[η^1:η^1-3-(CyNHCH$_2$)Ind]$_2$Li(THF)}Yb[N(SiMe$_3$)$_2$]$_2$] (7). This compound was isolated as yellow crystals in 39% yield by treatment of [μ-{[η^1:η^1:η^1:η^1-3-(CyNHCH$_2$)Ind]$_2$Li}-Yb[N(SiMe$_3$)$_2$]$_2$] (**4**) (0.63 g, 0.66 mmol) with 10 mL THF following the procedures similar to those used for the preparation of **5**. Because of significant paramagnetic shifts and broadening effects, the ^{1}H and ^{13}C NMR spectra are not informative. IR (KBr pellet, cm^{-1}): ν 2922 (m), 2848 (w), 1917 (w), 1880 (w), 1620 (w), 1452 (s), 1357 (m), 1238 (m), 1180 (m), 1031 (m), 1008 (m), 933 (m), 829 (w), 738 (m), 586 (w). Anal. Calc. for $C_{46}H_{82}LiN_6OSi_4Yb$·THF: C, 54.61; H, 8.25; N, 7.64. Found: C, 54.85; H, 7.74; N, 7.89. Complex **4** was obtained again in 47% yield by refluxing **7** in toluene, following the procedures similar to those described above for transferring **5** to **2**.

Experiments for Tracking the Intermediates with ^{1}H NMR. All manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere in a glovebox or under argon with exclusion of air and moisture. The catalytic reaction was probed by NMR stepwise. Diethyl phosphite (2.0 mg, 14.5 μmol) was dissolved in THF-d_8, which was characterized by ^{1}H NMR. First, the addition of complex **1** (13.5 mg, 14.5 μmol) to the mixture of diethyl phosphite and THF-d_8; the mixture was monitored by ^{1}H NMR. The disappearance of resonances of the protons of the *H*P(O)(OCH$_2$CH$_3$)$_2$ and *H*OP(OCH$_2$CH$_3$)$_2$ at 7.81 ppm, 5.53 ppm, and appearance of protons of ethyl suggested the formation of intermediate **A**. Then, to the above solution was added C$_6$H$_5$CH═NC$_6$H$_5$ (2.6 mg, 14.5 μmol) at rt, and the reaction mixture was probed by ^{1}H NMR. The disappearance of resonance of the imines proton C$_6$H$_5$C*H*═NC$_6$H$_5$, and appearance of the resonance of the −C*H*N− proton at 4.88 and 4.80 ppm suggested the formation of intermediate **C**.

Experiments for Identification of the Intermediates A and C. A mixture of complex **1** with dialkyl phosphite in a 1:1 molar ratio was stirred in 10 mL of THF at room temperature for 30 min. The solvent was evaporated under reduced pressure and the residues were washed

dx.doi.org/10.1021/ic300137r | Inorg. Chem. 2012, 51, 7134−7143

with 5 mL of *n*-hexane. The volatiles were removed under reduced pressure. The isolated white solid was characterized as intermediate **A**. IR (KBr pellet, cm^{-1}): ν 2927 (m), 2854 (m), 2393 (m), 1454 (s), 1352 (w), 1261 (s), 1101 (w), 1051 (w), 802 (s), 740 (s), 424 (w). Anal. Calc. for $C_{40}H_{66}LiN_5O_3PSi_2Sm$: C, 52.83; H, 7.31; N, 7.70. Found: C, 52.79; H, 7.78; N, 7.77.

A mixture of the intermediate **A** with 1 equiv of PhN=CHPh was heated to 40 °C for 6 h in 10 mL of THF. The solvent was evaporated under reduced pressure, and the residues were washed with 5 mL of *n*-hexane. The volatiles were removed under reduced pressure. The isolated solid material was characterized as intermediate **C**.

Alternative route to intermediate **C**: Reaction of the complex **1** with **12a** in a 1:1 molar ratio, after workup using the procedures similar to those for reaction of intermediate **A** with imine PhN=CHPh. The isolated solid material was characterized as intermediate **C**. IR (KBr pellet, cm^{-1}): ν 2922 (s), 2848 (m), 2384 (w), 1498 (m), 1452 (s), 1357 (m), 1238 (m), 1207 (w), 1116 (w), 1058 (w), 829 (m), 738 (s), 428 (w). ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 8.13 (1H), 7.92−7.80 (m, 2H), 7.54 (s, 3H), 7.18−7.00 (m, 10H), 6.64 (s, 4H), 5.67 (s, 1H), 4.91 (d, 1H, J = 20.6 Hz), 4.06 (d, 4H, J = 6.4 Hz), 3.57 (s, 4H), 2.52−0.82 (m, 28H), 0.09 (s, 18H). Anal. Calc. for $C_{53}H_{77}LiN_6O_3PSi_2Sm$: C, 58.37; H, 7.12; N, 7.71. Found: C, 58.43; H, 7.65; N, 7.28.

Crystal Structure Determinations. A suitable crystal of complexes **1**−**7** was each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[38] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[39] All hydrogen atoms were refined using a riding model. Crystal data and details of the data collection are given in Table 6. Further details are included in the Supporting Information.

General Experimental Procedure for Hydrophosphonylation of Aldehydes. A mixture of complex **4** (9.55 mg, 0.01 mmol) and dialkyl phosphite (10 mmol) was stirred for 5 min. Benzaldehyde (10 mmol) was then added, and the resulting mixture was stirred under solvent-free conditions for 20 min. After 20 min, the temperature of the exothermic reaction returned to room temperature. Water was added, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, after filtration, the solvent was evaporated under reduced pressure. Recrystallization of the crude product from hexane and diethyl ether gave the desired product **10a** (2.41 g, 99% yield) as white crystals.

Diethyl(hydroxy(phenyl)methyl)phosphonate (10a). Melting point (mp) 81−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.42−7.40 (d, 2H, J = 6.0 Hz, Ar*H*), 7.30−7.28 (d, 3H, J = 7.8 Hz, Ar*H*), 4.98 (d, J = 10.5 Hz, 1H, C*H*), 4.00−3.93 (m, 4H, CH_2), 2.72 (s, 1H, O*H*), 1.22−1.13 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 136.6, 128.2, 128.0, 127.1 (d, J = 5.7 Hz), 71.8 (d, J = 157.9 Hz), 63.3 (d, J = 6.9 Hz), 63.0 (d, J = 7.4 Hz), 16.3. HRMS (ESI) m/z: calcd for $C_{11}H_{17}O_4P$ $[M+H]^+$: 245.0943; Found: 245.0941.

General Experimental Procedure for Hydrophosphonylation of Aldimines. A mixture of complex **4** (9.55 mg, 0.01 mmol), aldimines (10 mmol) and dialkyl phosphite (12 mmol) was stirred in 2 mL of THF. The resulting mixture was heated to 40 °C for 6 h. After the reaction was completed, water was added, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and filtered, the solvent was evaporated under reduced pressure. Recrystallization of the crude product from hexane and ethyl acetate gave the desired product.

Diethyl (*N*-phenylamino)(phenyl)methylphosphonate (12a). Melting point (mp) 86−87 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.48 (d, J = 7.2 Hz, 2H), 7.35−7.28 (m, 3H), 7.13−7.08 (m, 2H), 6.71−6.67 (m, 1H), 6.60 (d, J = 7.9 Hz, 2H), 4.84 (d, J = 12.8 Hz, 1H), 4.73 (d, J = 7.6 Hz, 1H), 4.14−4.05 (m, 2H), 3.97−3.86 (m, 1H), 3.72−3.61 (m, 1H), 1.31−1.26 (m, 3H), 1.13−1.08 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 146.8 (d, J = 14.7 Hz), 136.3, 129.4, 128.8, 128.3, 128.2, 118.5, 114.1, 63.5 (d, J = 6.7 Hz), 57.2 (d, J = 149.7 Hz), 16.8 (d, J = 5.7 Hz), 16.5 (d, J = 5.6 Hz). HRMS (ESI) m/z: calcd for $C_{17}H_{22}NO_3P$ $[M+H]^+$: 320.1416; Found: 320.1416.

The solid of the suggested active species **A** was isolated and was used for the catalytic reaction of $C_6H_5CH{=}NC_6H_5$ with diethyl phosphite with isolation of product **12a** in 90% yield under the reaction conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data and spectra for compounds, and figures for **1**−**7** with bond distances and angles. X-ray crystallographic files, in CIF format, for structure determination of complexes **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (Nos. 20832001, 20802001, 21072004), the National Basic Research Program of China (No. 2012CB821604), the grant from the Ministry of Education (No. 20103424110001), and Anhui Province (Nos. 2007Z016, KJ2012A138). The help for this work from Prof. Dr. Hai-bin Song from Nankai University is acknowledged.

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