

Highly Efficient Hydrophosphonylation of Aldehydes and Unactivated Ketones Catalyzed by Methylene-Linked Pyrrolyl Rare Earth Metal Amido Complexes

Shuangliu Zhou,^[a] Zhangshuan Wu,^[a] Jiewei Rong,^[a] Shaowu Wang,^{*,[a, b]}
Gaosheng Yang,^[a] Xiancui Zhu,^[a] and Lijun Zhang^[a]

Dedicated to Professor Christian Bruneau on the occasion of his 60th birthday.

Abstract: A series of rare earth metal amido complexes bearing methylene-linked pyrrolyl-amido ligands were prepared through silylamine elimination reactions and displayed high catalytic activities in hydrophosphonylations of aldehydes and unactivated ketones under solvent-free conditions for liquid substrates. Treatment of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with 2-(2,6-Me₂C₆H₃NHCH₂)C₄H₃NH (**1**, 1 equiv) in toluene afforded the corresponding trivalent rare earth metal amides of formula $\{(\mu\text{-}\eta^5\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2](\text{C}_4\text{H}_3\text{N})\text{LnN}(\text{SiMe}_3)_2)_2$ [**Ln** = Y (**2**), Nd (**3**), Sm (**4**), Dy (**5**), Yb (**6**)] in moderate to good yields. All compounds were fully characterized by spectroscopic methods and elemental

analyses. The yttrium complex was also characterized by ¹H NMR spectroscopic analyses. The structures of complexes **2**, **3**, **4**, and **6** were determined by single-crystal X-ray analyses. Study of the catalytic activities of the complexes showed that these rare earth metal amido complexes were excellent catalysts for hydrophosphonylations of aldehydes and unactivated ketones. The catalyzed reactions between diethyl phosphite and aldehydes in the presence of the rare earth metal amido

Keywords: carbonyl compounds • homogeneous catalysis • hydrophosphonylation • organometallic compounds • rare earths

complexes (0.1 mol %) afforded the products in high yields (up to 99 %) at room temperature in short times of 5 to 10 min. Furthermore, the catalytic addition of diethyl phosphite to unactivated ketones also afforded the products in high yields of up to 99 % with employment of low loadings (0.1 to 0.5 mol %) of the rare earth metal amido complexes at room temperature in short times of 20 min. The system works well for a wide range of unactivated aliphatic, aromatic or heteroaromatic ketones, especially for substituted benzophenones, giving the corresponding α -hydroxy diaryl phosphonates in moderate to high yields.

Introduction

α -Hydroxy phosphonates have attracted significant attention, owing to their biological activities.^[1] The addition of dialkyl phosphites to carbonyl compounds (Pudovik reaction) is a direct and atom-economical method for the synthesis of

α -hydroxyphosphonates and for C–P bond formation.^[2] Various metal complexes, including aluminum,^[3] titanium,^[4] lanthanide,^[5] niobium,^[6] and molybdenum complexes,^[7] have been used as effective catalysts for additions of phosphites to aldehydes. In sharp contrast to hydrophosphonylations of aldehydes, efficient catalysts for hydrophosphonylation of unactivated ketones remain hardly developed, due to their low reactivities.^[8] Moreover, quaternary α -hydroxyphosphonates are of considerable value because they can potentially increase rigidity and resistance to protease enzymes and enhance bioactivity.^[9] Strong bases have until now been the most general reagents for the synthesis of quaternary α -hydroxy phosphonates. However, the yields were not always good and mixtures of products were sometimes obtained, due to side reactions.^[10] Recently, Feng and co-workers reported the first highly efficient Lewis-acid-catalyzed hydrophosphonylations of acetophenones and trifluoromethyl ketones in the presence of $\text{Ti}(\text{O}i\text{Pr})_4$ ^[11] or Et_2AlCl ^[12] as catalysts. It was found that $\text{Ln}(\text{OTf})_3$ species ($\text{Ln} = \text{Sc}, \text{La}, \text{Yb}$) exhibited poor catalytic activities for hydrophosphonylations of acetophenones.^[11] Development of high catalytic activities of lanthanide complexes as catalysts for hydrophosphonyla-

[a] Dr. S. Zhou, Z. Wu, J. Rong, Prof. Dr. S. Wang, Prof. Dr. G. Yang, X. Zhu, Dr. L. Zhang
Laboratory of Functionalized Molecular Solids
Ministry of Education, Anhui Laboratory of Molecule-Based Materials
College of Chemistry and Materials Science
Anhui Normal University
Wuhu, Anhui 241000 (P.R. China)
Fax: (+86) 553-3883517
E-mail: swwang@mail.ahnu.edu.cn

[b] Prof. Dr. S. Wang
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Shanghai 200032 (P.R. China)

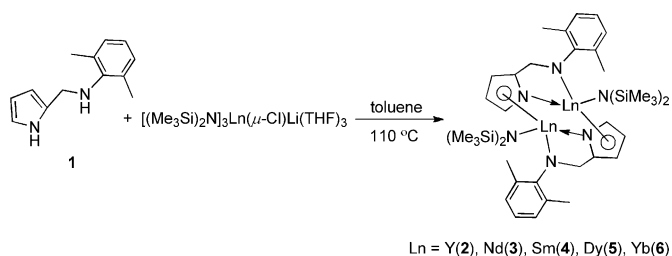
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tion of unactivated ketones such as acetophenones still remains to be reported.

Pyrrolyl derivatives have recently been attracting particular research interest in lanthanide chemistry because they can act as versatile ligands, due to their η^5/η^1 bonding capability, and are anticipated to be alternatives to cyclopentadiene.^[13] It has been demonstrated that lanthanide complexes containing pyrrolide ligands produced unexpected structures and displayed various reactivities with regard to polymerization, reduction of N_2 , and reversible fixation of ethylene.^[14] We have reported that methylene-linked pyrrolyl lanthanide amido complexes were able to catalyze additions of the N–H bond of the amines to carbodiimides.^[15] Here we report the synthesis and characterization of rare earth metal amides with methylene-linked pyrrolyl-amido ligands exhibiting η^1 and η^5 bonding modes, together with their first applications as catalysts for hydrophosphonylations of aldehydes and unactivated ketones.

Results and Discussion

Synthesis and characterization of rare earth metal amides with methylene-linked pyrrolyl-amido ligands: Treatment of $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ with 2-[(2,6- $Me_2C_6H_3$)- $NHCH_2$](C_4H_3NH) (**1**, Scheme 1, 1 equiv) in toluene at



Scheme 1. Synthesis of rare earth metal amides with methylene-linked pyrrolyl-amido ligands.

100 °C afforded the dinuclear rare earth metal amido complexes $\{(\mu-\eta^5:\eta^1):\eta^1-2-[(2,6-Me_2C_6H_3)NCH_2](C_4H_3N)LnN(SiMe_3)_2\}_2$ [$Ln = Y$ (**2**), Nd (**3**), Sm (**4**), Dy(**5**), Yb(**6**)]. The complexes are sensitive to air and moisture and have good solubilities either in polar solvents or in nonpolar solvents. All complexes were fully characterized by IR and elemental analyses. The complex **2** was additionally characterized by 1H NMR spectroscopic analyses. The structures of the complexes **2**, **3**, **4**, and **6** were further determined by single-crystal X-ray analyses.

X-ray analyses revealed that complexes **2**, **3**, **4**, and **6** are isostructural centrosymmetric dinuclear structures. A representative structure diagram of complex **2** is shown in Figure 1. Each of the rare earth metals adopts a distorted tetrahedral geometry, and the two metals in each complex are bridged by the dianion ligand with the pyrrolyl ring coordinated to one rare earth metal in an η^5 mode, whereas

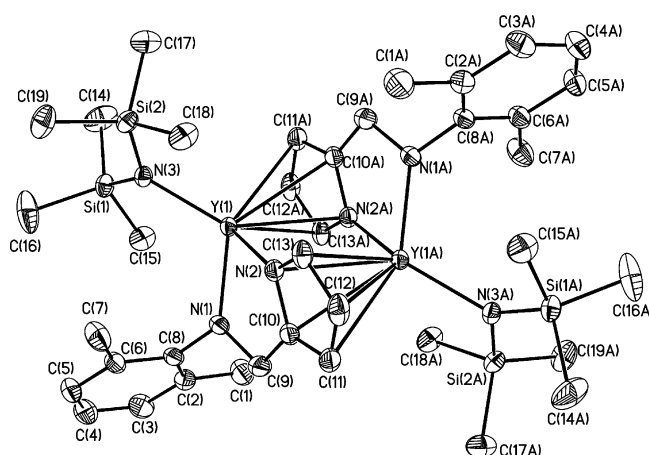


Figure 1. Representative molecular structure of complex **2**. Hydrogen atoms are omitted for clarity.

the tethered nitrogen anion and the nitrogen atom of the pyrrolyl ring coordinate to another rare earth metal in the η^1 modes. The bridged bonding mode of a pyrrolyl ligand of this type is different to those of the so-called constrained geometry ligands of the cyclopentadienyl-based ligands in which the dianion ligand bonds to one metal.^[16] Selected interatomic distances and angles are listed in Table 1.

Table 1. Selected interatomic distances (Å) and angles (°).

	2	3	4	6
Ln(1)–N(1)	2.184(3)	2.255(2)	2.230(3)	2.146(10)
Ln(1)–N(2)	2.406(2)	2.513(3)	2.483(3)	2.358(10)
Ln(1)–N(3)	2.212(2)	2.292(2)	2.269(3)	2.164(10)
Ln(1)–N(2A)	2.687(2)	2.775(3)	2.749(3)	2.653(9)
Ln(1)–C(10A)	2.800(3)	2.889(3)	2.864(4)	2.769(12)
Ln(1)–C(11A)	2.812(3)	2.913(3)	2.884(4)	2.758(12)
Ln(1)–C(12A)	2.714(3)	2.823(3)	2.789(4)	2.656(13)
Ln(1)–C(13A)	2.634(3)	2.735(3)	2.702(4)	2.609(13)
Ln(1)–C _{av}	2.740(3)	2.840(3)	2.810(4)	2.698(13)
N(1)–Ln(1)–N(2)	73.34(9)	70.41(9)	71.05(11)	74.1(4)
N(2)–Ln(1)–N(3)	130.27(9)	129.21(8)	129.63(10)	129.3(3)
N(1)–Ln(1)–N(3)	114.14(10)	117.35(9)	116.91(11)	113.3(4)

The interatomic distances between lanthanide ions and the pyrrolyl carbon in **2**, Y– η^5 –C(pyr ring) range from 2.634(3) to 2.812(3) Å, with an average of 2.740(3) Å (Table 1), which is comparable to those of 2.729(4) Å in $\{2-[(2,4,6-Me_3C_6H_2)NCH_2](C_4H_3N)Y(N(SiMe_3)_2)_2\}_2$,^[15] 2.763(6) Å in $\{[2-(2,6-iPr_2C_6H_3)NC(H)(CH_2SiMe_3)]-(C_4H_3N)Y(CH_2SiMe_3)(THF)_2\}_2$,^[13d] and 2.735(3) Å in $\{[2-(Me_2NCH_2)(C_4H_3N)Y(CH_2SiMe_3)_2]\}_2$.^[13e] The average Sm– η^5 –C(pyr ring) distance of 2.810(3) Å in complex **4** is comparable to that of 2.796(4) Å in $\{2-[(2,4,6-Me_3C_6H_2)NCH_2](C_4H_3N)SmN(SiMe_3)_2\}_2$.^[15] The average Nd– η^5 –C(pyr ring) distance of 2.840(3) Å in complex **3** is comparable to the average Sm– η^5 –C(pyr ring) distance of 2.810(3) Å in complex **4**, and these are slightly longer than those of 2.740(3) Å

and 2.698(13) Å in **2** and **6**, respectively, indicating the effects of the lanthanide ionic radii. The Ln(1)–N(2) and Ln(1)–N(2A) interatomic distances in each of the complexes **2–4** and in **6** are much longer than their Ln(1)–N(1A) counterparts, highly consistently with the $\eta^5/\eta^1:\eta^1$ -coordination mode of the pyrrolide ligand, which is also found in $\eta^5/\eta^1:\eta^1$ -pyrrolyl rare earth metal amido complexes $\{2-[(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\text{NCH}_2](\text{C}_4\text{H}_3\text{N})\text{LnN}(\text{SiMe}_3)_2\}_2$ (Ln = Y, Nd, Sm, Dy, Er)^[15] and in an $\eta^5/\eta^1:\eta^1$ -pyrrolyl yttrium alkyl complex $[(2-(\text{Me}_2\text{NCH}_2)(\text{C}_4\text{H}_3\text{N})\text{Y}(\text{CH}_2\text{SiMe}_3)_2)]_2$.^[13e]

Catalytic additions of diethyl phosphite to aldehydes catalyzed by the methylene-linked pyrrolyl rare earth metal amides: The additions of diethyl phosphite to benzaldehyde were first optimized in the presence of the pyrrolyl rare earth metal amido complexes **2–6** (0.1 mol %), and the results are summarized in Table 2. From the table we can see

Table 2. Optimization of hydrophosphonylation of benzaldehyde catalyzed by the methylene-linked pyrrolyl rare earth metal amides.^[a]

Entry	Cat.	Solvent	Yield [%] ^[b]
1	4 (Ln = Sm)	THF	96
2	4 (Ln = Sm)	toluene	99
3	4 (Ln = Sm)	Et ₂ O	98
4	4 (Ln = Sm)	solvent-free	99
5	2 (Ln = Y)	solvent-free	98
6	3 (Ln = Nd)	solvent-free	96
7	5 (Ln = Dy)	solvent-free	99
8	6 (Ln = Yb)	solvent-free	99

[a] Reaction conditions: benzaldehyde (20.0 mmol), diethyl phosphite (24.0 mmol), catalyst (0.1 mol %), solvent (2 mL), room temperature. [b] Isolated yields.

that the additions of diethyl phosphite to benzaldehyde afforded the product **8a** in high yields ($\geq 96\%$) with use of the samarium amide **4** as a catalyst in all solvents or under solvent-free conditions (Table 2, entries 1–4) in 5 min. It was found that the Ln^{III} ionic radii in the complexes had little influence on the hydrophosphonylation of benzaldehyde (Table 2, entries 5–8).

We next examined hydrophosphonylations of a wide variety of aldehydes in the presence of the samarium amide **4** (0.1 mol %) as a catalyst under solvent-free conditions or in toluene (2 mL, to increase the solubility for solid aldehydes). The results are listed in Table 3. The results showed that the additions of diethyl phosphite to the aromatic aldehydes afforded the corresponding α -hydroxy phosphonates in excellent yields of $\geq 90\%$, regardless of the electronic natures or the steric effects of the substituents on the aryl groups except for the substrates 2-chlorobenzaldehyde (80 % yield, Table 3, entry 6), 2,4-dichlorobenzaldehyde (60 % yield, entry 8), and 4-(dimethylamino)benzaldehyde

Table 3. Hydrophosphonylations of aldehydes catalyzed by catalyst **4**.^[a]

Entry	R	Solvent	t [min]	Product	Yield [%] ^[b]
1	Ph	none	5	8a	99
2	2-O ₂ NC ₆ H ₄	toluene (2 mL)	10	8b	97
3	3-O ₂ NC ₆ H ₄	toluene (2 mL)	10	8c	98
4	4-O ₂ NC ₆ H ₄	toluene (2 mL)	10	8d	99
5	3-F ₃ CC ₆ H ₄	none	5	8e	96
6	2-ClC ₆ H ₄	none	5	8f	80
7	4-ClC ₆ H ₄	toluene (2 mL)	10	8g	98
8	2,4-Cl ₂ C ₆ H ₃	toluene (2 mL)	10	8h	60
9	2-BrC ₆ H ₄	toluene (2 mL)	10	8i	97
10	4-BrC ₆ H ₄	toluene (2 mL)	10	8j	98
11	4-MeC ₆ H ₄	none	5	8k	99
12	2-MeOC ₆ H ₄	toluene (2 mL)	0	8l	98
13	3-MeOC ₆ H ₄	none	5	8m	99
14	4-MeOC ₆ H ₄	none	5	8n	99
15	4-Me ₂ NC ₆ H ₄	toluene (2 mL)	10	8o	83
16	1-naphthyl	none	5	8p	96
17	<i>n</i> Bu	none	5	8q	87 ^[c]
18	<i>i</i> Pr	none	5	8r	90 ^[c]

[a] Reaction conditions: aldehyde (20.0 mmol), diethyl phosphite (24.0 mmol), catalyst (0.1 mol %), solvent (2 mL), room temperature. [b] Isolated product yields. [c] Aldehyde (1.2 equiv) and diethyl phosphite (1.0 equiv) were used.

(83 % yield, entry 15). The low yields of **8f** and **8h** are probably due to the steric effects of the *ortho*-Cl atom(s), hindering the coordination of the carbonyl group to the lanthanide metal center. The low yield of **8o** may be attributed to the strong coordination effect of the nitrogen atom of the substrate, slowing down or hindering the coordination of the carbonyl group to the active metal center. The catalyst **4** also works equally well for both linear and branched aliphatic aldehydes, affording the corresponding α -hydroxy phosphonates in high yields (Table 3, entries 17 and 18).

Catalytic additions of diethyl phosphite to unactivated ketones catalyzed by rare earth metal amides with methylene-linked pyrrolyl-amido ligands: Inspired by the highly efficient hydrophosphonylations of aldehydes, we examined catalytic additions of diethyl phosphite to unactivated ketones. The addition of diethyl phosphite to acetophenone in the presence of the dinuclear rare earth metal amido complexes (0.1 mol %) was optimized and the results are summarized in Table 4. It was exciting to find that the hydrophosphonylation of acetophenone could afford the products in high yields of $\geq 90\%$ with employment of the rare earth metal amides (0.1 mol %) at room temperature in a short time of 20 min, in contrast to Lewis-acid-catalyzed hydrophosphonylations of ketones in the presence of Ti(O*i*Pr)₄ (5 mol %) as a catalyst.^[11] From Table 4 it can be seen that the Ln^{III} ionic radii in the complexes had little influence on the reaction and that high yields of $\geq 90\%$ were obtained (Table 4, entries 1–5). Next, investigations directed towards the choice of solvent (Table 4, entries 1, 6–8) found that THF (Table 4,

Table 4. Optimization of hydrophosphonylation of acetophenone catalyzed by the methylene-linked pyrrolyl rare earth metal amides.^[a]

Entry	Cat.	Solvent	Yield [%] ^[b]
1	2 (Ln = Y)	THF	94
2	3 (Ln = Nd)	THF	91
3	4 (Ln = Sm)	THF	90
4	5 (Ln = Dy)	THF	90
5	6 (Ln = Yb)	THF	94
6	2 (Ln = Y)	toluene	87
7	2 (Ln = Y)	Et ₂ O	85
8	2 (Ln = Y)	CH ₂ Cl ₂	60
9	2 (Ln = Y)	solvent-free	94
10	[(Me ₃ Si) ₂ N] ₃ Y(μ-Cl)Li(THF) ₃	solvent-free	73 ^[c]
11	[(Me ₃ Si) ₂ N] ₃ La(μ-Cl)Li(THF) ₃	solvent-free	77 ^[c]
12	[(Me ₃ Si) ₂ N] ₃ Nd(μ-Cl)Li(THF) ₃	solvent-free	73 ^[c]
13	[(Me ₃ Si) ₂ N] ₃ Sm(μ-Cl)Li(THF) ₃	solvent-free	70 ^[c]
14	Y(OiPr) ₃	solvent-free	NR ^[d]
15	Sm(OiPr) ₃	solvent-free	NR ^[d]

[a] Reaction conditions: acetophenone (20.0 mmol), diethyl phosphite (24.0 mmol), catalyst (0.1 mol %), solvent (2 mL), room temperature.

[b] Isolated product yields. [c] With 1 mol % catalyst. [d] No reaction occurred.

entry 1) was the best. Furthermore, we found that the hydrophosphonylation of acetophenone also worked well under solvent-free conditions (Table 4, entry 9). In order to assess the practical applicability, we examined the activities of the “ate-” tris amido rare earth metal complexes [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ and of the commercially available homoleptic lanthanide alkoxides as catalysts for hydrophosphonylation of the ketone (Table 4, entries 10–15). In contrast with the lack of reactivity of the rare earth metal alkoxides, the rare earth metal amides [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ could catalyze hydrophosphonylation of the ketone with moderate activities [in the presence of [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (1 mol %)], indicating that modification of the ligand greatly influenced the catalytic activities of the catalysts for hydrophosphonylation of the ketone.

The substrate scope of catalytic hydrophosphonylations of ketones was then investigated with the yttrium amide **2** as a catalyst either under solvent-free conditions or in THF (2 mL, in order to increase solubilities for solid ketones). The results are presented in Table 5 and show that the optimized catalytic system worked excellently for a wide range of aromatic ketones regardless of the electronic natures of the substituents on the aryl groups. It was also found that the steric hindrance of the substrates had an effect on the reactivities of hydrophosphonylation of ketones, with the corresponding products being obtained in moderate yields, except in the case of 2'-methoxyacetophenone. The addition of diethyl phosphite to 2'-bromoacetophenone, for example, afforded the product **10f** in a 50% yield (Table 5, entry 6), the addition to 2'-chloroacetophenone gave **10h** in

a 69% yield (Table 5, entry 8), and the addition to 2'-nitroacetophenone gave **10j** in a 65% yield (Table 5, entry 10). However, the addition to 2'-methoxyacetophenone afforded **10b** in an excellent yield of 93% (Table 5, entry 2), which can be attributed to the *ortho*-chelate effect of the substrate, which presumably facilitated the coordination of 2'-methoxyacetophenone to the active metal center. For heteroaromatic ketones, the α-hydroxy phosphonates **10n–10r** were also obtained in good yields (Table 5, entries 14–18). It is worth noting that a series of α-hydroxy diaryl phosphonates could also be obtained in high yields through additions of diethyl phosphite to substituted benzophenones in the presence of the yttrium amide **2** as a catalyst (Table 5, entries 19–24), except in the case of 2,4'-difluorobenzophenone (51% yield, entry 23), probably due to steric hindrance of the substrate. Catalyst **2** also works well for both linear and branched aliphatic ketones, affording the quaternary α-hydroxy phosphonates in high yields (Table 5, entries 25 and 26).

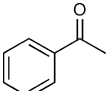
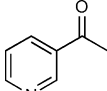
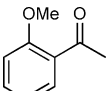
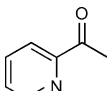
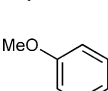
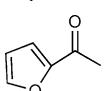
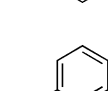
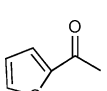
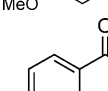
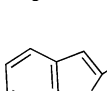
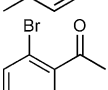
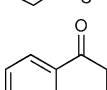
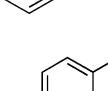
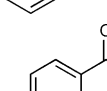
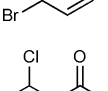
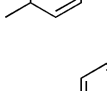
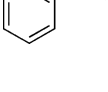
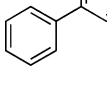
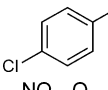
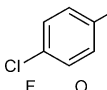
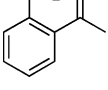
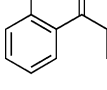
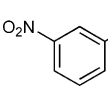
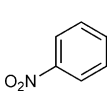
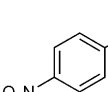
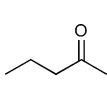
Conclusion

A series of dinuclear rare earth metal amido complexes {(μ-η⁵:η¹):η¹-2-[(2,6-Me₂C₆H₃)NCH₂](C₄H₃N)LnN(SiMe₃)₂]₂ [Ln = Y (**2**), Nd (**3**), Sm (**4**), Dy(**5**), Yb(**6**)] containing a methylene-linked pyrrolyl-amido ligand were synthesized and characterized. The X-ray diffraction analyses of the complexes indicated that the complexes were centrosymmetric dinuclear complexes and that the pyrrolyl ligands coordinated to one rare earth metal in an η⁵ mode whereas the tethered nitrogen anion and nitrogen atom of the pyrrolyl ring coordinated to another rare earth metal in η¹ modes. All of the rare earth metal amido complexes displayed high catalytic activities for hydrophosphonylations of aldehydes and unactivated ketones. The results represent the first examples of such lanthanide complexes as catalysts for hydrophosphonylations of unactivated ketones. The catalyst systems have the advantages of high atom efficiency and high yields of products (up to 99%), low catalyst loadings (0.1 to 0.5 mol %), mild conditions (room temperature, solvent-free for liquid substrates), and short reaction times (within 20 min). The systems work well for a wide range of aliphatic, aromatic, and heteroaromatic ketones, and even for substituted benzophenones. Further investigations into asymmetric hydrophosphonylations of ketones catalyzed by chiral organo rare earth metal complexes are in progress.

Experimental Section

General Remarks: All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon by standard Schlenk techniques or in a glovebox. All solvents were heated at reflux and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Solvents were heated at reflux and distilled over sodium/benzophenone (THF, Et₂O, *n*-hexane, and toluene) or P₂O₅ (CH₂Cl₂) under argon prior to use. Solid aldehydes or ketones were used

Table 5. Hydrophosphonylations of ketones catalyzed by the yttrium amide **2**.^[a]

$ \begin{array}{c} \text{R}-\text{C}(=\text{O})-\text{R}' + \text{H}-\text{P}(\text{O})(\text{OEt})_2 \xrightarrow[\text{RT, 20 min}]{0.1-0.5 \text{ mol\% } \mathbf{2}} \text{R}-\text{C}(\text{OH})(\text{R}')-\text{P}(\text{O})(\text{OEt})_2 \\ \mathbf{9} \qquad \qquad \qquad \mathbf{10} \end{array} $											
Entry	Ketone	Solvent	Cat. [mol %]	Product	Yield [%] ^[b]	Entry	Ketone	Solvent	Cat. [mol %]	Product	Yield [%] ^[b]
1	9a 	solvent-free	0.1	10a	94	14	9n 	solvent-free	0.1	10n	99
2	9b 	solvent-free	0.1	10b	93	15	9o 	solvent-free	0.1	10o	91
3	9c 	solvent-free	0.1	10c	95	16	9p 	solvent-free	0.1	10p	73
4	9d 	THF (2.0 mL)	0.1	10d	96	17	9q 	solvent-free	0.1	10q	70
5	9e 	solvent-free	0.1	10e	89	18	9r 	THF (2.0 mL)	0.5	10r	97
6	9f 	solvent-free	0.1	10f	50 (60) ^[c]	19	9s 	THF (2.0 mL)	0.1	10s	85
7	9g 	THF (2.0 mL)	0.1	10g	85	20	9t 	THF (2.0 mL)	0.1	10t	89
8	9h 	solvent-free	0.1	10h	69	21	9u 	THF (2.0 mL)	0.1	10u	79
9	9i 	solvent-free	0.1	10i	93	22	9v 	THF (2.0 mL)	0.1	10v	94
10	9j 	solvent-free	0.5	10j	65 (71) ^[c]	23	9w 	solvent-free	0.5	10w	51
11	9k 	THF (2.0 mL)	0.1	10k	89	24	9x 	THF (2.0 mL)	0.5	10x	91
12	9l 	THF (2.0 mL)	0.1	10l	99	25	9y 	solvent-free	0.1	10y	88 ^[d]
13	9m 	solvent-free	0.1	10m	95	26	9z 	solvent-free	0.1	10z	84 ^[d]

[a] Reaction conditions: ketone (20.0 mmol), diethyl phosphite (24.0 mmol), room temperature. [b] Isolated yields. [c] Values in parentheses obtained with 1 mol % catalyst. [d] Ketone (1.2 equiv) and diethyl phosphate (1.0 equiv) were used.

directly, and liquid aldehydes or ketones were distilled before use. $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ^[17] and $2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NHCH}_2\text{-(C}_4\text{H}_3\text{NH)}]^{12\text{g}}$ were prepared by literature methods. IR spectra were recorded with a SHIMADZU FTIR-8400S spectrometer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded with a Bruker AV 300 NMR spectrometer in C_6D_6 for lanthanide complexes and in CDCl_3 for organic compounds.

Synthesis of $\{(\mu\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{-(C}_4\text{H}_3\text{N)}\text{YN}(\text{SiMe}_3)_2]_2\}$ (2): A toluene (10.0 mL) solution of $2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NHCH}_2\text{-(C}_4\text{H}_3\text{NH)}]$ (**1**, 0.40 g, 2.00 mmol) was added at room temperature to a toluene (30.0 mL) solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.66 g, 2.00 mmol). After the reaction mixture had been stirred at room temperature for 6 h, the mixture was stirred for 24 h at 100 °C. The solvent was evaporated under reduced pressure and the residue was extracted with *n*-hexane (2 × 10.0 mL). The extracts were combined and concentrated to about 10.0 mL. Products were obtained by recrystallization from the concentrated hexane solution at 0 °C for several days. Colorless crystals, 79 % yield. M.p. 289–291 °C; ^1H NMR (300 Hz, C_6D_6 , 25 °C): δ = 7.21–7.02 (m, 3H), 6.67–5.25 (m, 3H), 3.85 (d, 2H), 2.43 (s, 6H), 0.34–0.14 ppm (d, 18H); IR (KBr pellet): $\tilde{\nu}$ = 3587 (w), 3564 (w), 3387 (s), 1558 (w), 1539 (w), 1474 (s), 1435 (w), 1258 (w), 1196 (w), 1096 (s), 1026 (s), 976 (w), 953 (w), 910 (w), 883 (w), 768 (s), 721 (s), 644 (w), 544 cm^{-1} (w); elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{72}\text{ON}_6\text{Si}_4\text{Y}_2$: C 52.21, H 7.41, N 8.70; found: C 52.28, H 7.36, N 9.02.

Synthesis of $\{(\mu\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{-(C}_4\text{H}_3\text{N)}\text{NdN}(\text{SiMe}_3)_2]_2\}$ (3): Complex **3** was prepared as pale blue crystals in 71 % yield from the reaction between compound **1** (0.40 g, 2.00 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Nd}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.77 g, 2.00 mmol) by procedures similar to those used for the preparation of **2**. M.p. 283–285 °C; IR (KBr pellet): $\tilde{\nu}$ = 3352 (m), 3291 (s), 3125 (w), 2943 (m), 1508 (m), 1474 (s), 1447 (m), 1424 (m), 1377 (w), 1339 (m), 1257 (m), 1234 (m), 1196 (s), 1126 (s), 1096 (vs), 1026 (s), 945 (m), 826 (m), 783 (s), 729 (s), 648 (m), 606 (w), 548 cm^{-1} (w); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{64}\text{N}_6\text{Si}_4\text{Nd}_2$: C 45.38, H 6.41, N 8.36; found: C 45.65, H 6.31, N 8.42.

Synthesis of $\{(\mu\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{-(C}_4\text{H}_3\text{N)}\text{SmN}(\text{SiMe}_3)_2]_2\}$ (4): Complex **4** was prepared as yellow crystals in 83 % yield from the reaction between compound **1** (0.40 g, 2.00 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Sm}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.78 g, 2.00 mmol) by procedures similar to those used for the preparation of **2**. M.p. 280–282 °C; IR (KBr pellet): $\tilde{\nu}$ = 3565 (w), 3403 (s), 3102 (w), 3044 (w), 2944 (m), 2855 (w), 1509 (m), 1474 (s), 1435 (w), 1397 (w), 1377 (w), 1339 (w), 1258 (m), 1196 (m), 1096 (s), 1026 (s), 989 (w), 945 (w), 910 (w), 883 (w), 768 (s), 721 (s), 652 (w), 544 cm^{-1} (m); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{64}\text{N}_6\text{Si}_4\text{Sm}_2$: C 44.83, H 6.34, N 8.26; found: C 44.86, H 6.16, N 8.12.

Synthesis of $\{(\mu\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{-(C}_4\text{H}_3\text{N)}\text{DyN}(\text{SiMe}_3)_2]_2\}$ (5): Complex **5** was prepared as a colorless crystalline solid in 81 % yield from the reaction between compound **1** (0.40 g, 2.00 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Dy}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.80 g, 2.00 mmol) by procedures similar to those used for preparation of **2**. M.p. 287–289 °C; IR (KBr pellet): $\tilde{\nu}$ = 3352 (m), 2967 (w), 1626 (w), 1591 (w), 1476 (s), 1445 (m), 1422 (m), 1098 (m), 1026 (s), 824 (m), 797 (s), 783 (m), 737 (m), 727 (m), 650 (m), 606 cm^{-1} (m); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{64}\text{N}_6\text{Si}_4\text{Dy}_2$: C 43.79, H 6.19, N 8.06; found: C 43.98, H 6.04, N 7.63.

Synthesis of $\{(\mu\text{-}\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2\text{-(C}_4\text{H}_3\text{N)}\text{YbN}(\text{SiMe}_3)_2]_2\}$ (6): Complex **6** was prepared as red crystals in 75 % yield from the reaction between compound **1** (0.40 g, 2.00 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.83 g, 2.00 mmol) by procedures similar to those used for preparation of **2**. M.p. 290–292 °C; IR (KBr pellet): $\tilde{\nu}$ = 3408 (m), 3217 (m), 2972 (w), 1628 (s), 1591 (m), 1474 (s), 1440 (s), 1416 (m), 1377 (m), 1337 (w), 1254 (s), 1191 (m), 1096 (m), 1034 (m), 860 (s), 792 (s), 768 (s), 731 (s), 606 cm^{-1} (m); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{64}\text{N}_6\text{Si}_4\text{Yb}_2$: C 42.92, H 6.07, N 7.90; found: C 43.38, H 5.83, N 7.88.

Crystal structure determinations: Suitable crystals of complexes **2**, **3**, **4**, and **6** were each mounted in a sealed capillary. Diffraction was performed with a Bruker SMART CCD area detector diffractometer and use of graphite-monochromated *Mo*- K_α radiation (λ = 0.71073 Å); an empirical absorption correction was applied by use of the SADABS program.^[18] All structures were solved by direct methods, completed by sub-

sequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix, least-squares calculations on F^2 by use of the SHELXTL program package.^[19] All hydrogen atoms were refined with use of a riding model.

CCDC-791771 (**2**), CCDC-791772 (**3**), CCDC-791773 (**4**), and CCDC-791774 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedures for hydrophosphonylations of aldehydes: A 30.0 mL Schlenk tube was charged under dried argon with the dinuclear rare earth metal amido complex **4** (20.0 mg, 0.02 mmol) and diethyl phosphite (3.32 g, 24 mmol), either under solvent-free conditions or in toluene (2.0 mL), and the relevant aldehyde (20.0 mmol) was then added to the mixture. The resulting mixture was allowed to stir at RT for 5 min. After the reaction was complete, the reaction mixture was hydrolyzed with water (3 mL), extracted with ethyl acetate (3 × 10 mL), dried over anhydrous Na_2SO_4 , and filtered. After the solvent had been removed under reduced pressure, the final products were further purified by washing with hexane. The full characterization data for the resulting products can be found in the Supporting Information.

General Procedures for hydrophosphonylations of ketones: A 30.0 mL Schlenk tube was charged under dried argon with the dinuclear rare earth metal amido complex **2** (17.9 mg, 0.02 mmol) and diethyl phosphite (3.32 g, 24 mmol), either under solvent-free conditions or in THF (2.0 mL), and the relevant ketone (20.0 mmol) was then added to the mixture. The resulting mixture was allowed to stir at RT for 20 min. After the reaction was complete, the mixture was hydrolyzed with water (3 mL), extracted with ethyl acetate (3 × 10 mL), dried over anhydrous Na_2SO_4 , and filtered. After the solvent had been removed under reduced pressure, the final products were further purified by washing with hexane. The full characterization data for the resulting products can be found in the Supporting Information.

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